

**THE GEOCHEMICAL PALÆO-OCEANOGRAPHY AND
MINERALOGY OF MARINE SEDIMENTS FROM THE
PERUVIAN CONTINENTAL MARGIN**

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DECLARATION

I, Gavin William McNeill, hereby declare that, except where otherwise stated, the work presented in this thesis for the degree of Doctor of Philosophy was carried out by myself.

ABSTRACT

A comprehensive study of marine sediments collected during the *R.R.S. Charles Darwin* Leg 38 cruise from the Peruvian continental margin, has been carried out using a wide range of geochemical analysis techniques. The prime objective of the study has been to determine the strength and down-core variation of many oceanographic processes during the glacial/interglacial stages of the Late Quaternary by means of geochemical palæo-environmental indicators.

Coastal upwelling is a physical movement of cold, nutrient-rich water to replace surface water which has been blown off-shore by Ekman transport, as a result of along-shore winds. This results in high marine productivity levels within the Peruvian coastal upwelling zone, and is recorded by enrichments of organic carbon and other biogenic-remains in the sediments accumulating below. Particular metals, which have a capacity to be scavenged from sea-water as organic matter falls through it, are also enriched in the sedimentary record.

Organic matter and fish-remains supply a continuous source of phosphorus to the surface sediment. Upon bacterial decomposition of this biogenic debris, phosphate can become enriched in the pore-waters until precipitation of carbonate fluorapatite occurs to form the diagenetic mineral known as phosphorite. Within the Peru margin cores, the presence of disseminated phosphorite pellets and zones of nodular hardgrounds has been determined using pore-water modelling and geochemical partitioning equations. Many trace elements can be incorporated into the phosphorite mineral structure. Quantitative analysis of the uranium, strontium and yttrium concentrations within phosphorite zones has allowed for the partitioning of these elements into the organic, carbonate and terrigenous phases respectively. U-series radiochemical age dating of a phosphorite nodule yielded a "maximum" age of about 114,000 years for the phosphatic material. This age corresponds to an initial pellet growth on the continental margin during an interglacial period and supports the hypothesis of nodule diagenesis during the last glacial period as a result of heavy mineral concentration by bottom-water currents during a eustatic drop in sea-level.

The use of statistical and mathematical methods to interpret the large geochemical dataset from the Peru margin sediments has been examined. Both regression analysis and principal component analysis have been used to highlight the existence of strong element-element and element-phase relationships. Multi-component analysis was used to show that the proximity of the South

American continental landmass and the high "coastal upwelling" productivity have produced sediments which are dominated by terrigenous and biogenic phases.

Iodine and bromine, and their ratios to organic carbon, have been used to distinguish between anoxic sediments accumulating within the oxygen minimum zone on the upper shelf and oxic sediments from deeper water sites along the continental margin. The barium profile from a core on the Nazca Ridge displayed remarkable similarity to the foraminifera oxygen isotope record and the flux of biogenic-barium has been used as a proxy for palæo-productivity calculations. The same core showed a strong correlation between strontium and calcium carbonate concentrations, and the Sr/Ca ratio has been examined as an indicator of the dominance of foraminifera in the marine biomass. The ratio of molybdenum to uranium has previously been used as a proxy of palæo-redox conditions at the sediment/water interface. However, in the Peru margin sediments the measured Mo/U ratios contradict the established theory, due to the complex post-depositional behaviour of these two heavy metals.

Many natural processes, including continental erosion, sediment transport patterns, carbonate and silicate dissolution and volcanic activity, and their variation over the Late Quaternary glacial/interglacial stages have been investigated using the concentrations and fluxes of geochemical components contained within the terrigenous and biogenic sedimentary material. Inter-core comparisons are also made in order to interpret these palæo-environmental processes at sites of varying water depth and environment of deposition along the Peruvian continental margin.

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CHAPTER 1

INTRODUCTION

1.1. MARINE SEDIMENT GEOCHEMISTRY

"By the light by which geology now throws, and will continue to throw, on former changes of climate and of the level of the land, we shall surely be enabled to trace in an admirable manner the former migrations of the inhabitants of the whole world."

Charles Darwin (1859)

The Origin of Species

It is less than one hundred and fifty years since Darwin wrote the above comment about the importance of geological studies in the interpretation of climatic and sea-level changes and in the examination of variations in the biomass of the Earth. This thesis is one small addition to the vast amount of scientific research which has followed since the times of Darwin and other pioneers of the science of our natural environment. The marine sediment samples analysed and interpreted in this study were collected from an area of the world's oceans through which Darwin sailed on his historic travels onboard *H.M.S. Beagle*, namely the Peruvian continental margin, and were collected during scientific cruise Leg 38 of the research ship which bears his name, *R.R.S. Charles Darwin*.

The Earth's surface is approximately 70% water and 30% land and therefore marine sediments are quantitatively the most important geological samples available for scientific analysis. However, due to the immense technological difficulty and expense of collecting marine sediments (compared with collecting rock samples from exposed land outcrops) the first collection and study of such sediments began only just over 100 years ago, during the *Challenger* Expedition (1872–1876). With the introduction of improved sample collection and analysis techniques (e.g. mass spectrometry and X-ray fluorescence) marine sediment geochemistry has developed rapidly in the last 20–30 years.

Increased awareness in the importance of the natural environment (and mankind's effect on it) has led to a need for greater understanding of the complex interplay between the atmosphere, hydrosphere and lithosphere (oceanic and continental). Deep-sea sediments are potentially one of the best sources of natural environmental records for two reasons. Firstly, they can contain continuous records of low frequency (in the order of 10^3 years) cycles and events. Fresh sediment is continuously deposited on top of older sediments, thus preserving the environmental

signals on a vertical depth scale, which corresponds to the age of the sediment. Secondly, the sediments are multi-component mixtures which can include terrigenous (land-derived), biogenic, hydrothermal and authigenic (diagenetic) phases; each of which can be used to answer certain environmental questions about the climatic, geological, chemical and biological conditions that existed in the past.

The time scale for such studies depends on both the depth of sediment core collected and the resolution of the sub-sampling of the core. For example, in this study, piston cores (of up to 9m length) were sub-sampled every 10cm resulting in a high resolution record (< 4000 years between samples) of the Late Quaternary. On the other hand, the Ocean Drilling Program regularly collects cores which are over 500m in length and which contain sediment of Eocene age, but usually sub-samples are taken about every 50cm resulting in a lower-resolution record.

It is important in any study of marine sediments that, if possible, the depth component of the core is converted into an accurate age component. This can be attempted either by direct age determination (e.g. ^{14}C -dating or radiochemistry) or more usually by comparison of a particular signal (either geophysical or geochemical) with a previously-dated reference core(s). The most common method of age-dating marine sediments uses stable isotope mass spectrometric analysis of the carbonate microfossils of foraminifera and comparison of their oxygen isotope record with the stacked SPECMAP reference curve (Imbrie *et al.*, 1984). This is the method which is used for age modelling of the piston cores in this study.

For climatic and environmental interpretations, age modelling is important so that geochemical signals can be represented in terms of the glacial/interglacial stages of the Late Quaternary. Global climatic changes are caused by fluctuations in the atmospheric insolation of the Earth, as a result of variations in the Earth's orbit around the Sun. The pioneering work of the Scottish scientist James Croll (1821–1890) linked the timing of past ice ages with a 100,000 year cycle, relating to the eccentricity of the Earth's elliptical orbit, and a 19,000–22,000 year cycle, relating to the precession of the seasonal equinoxes (Croll, 1867A and B). His work was later extended by a Yugoslavian engineer Milutin Milankovitch (1879–1958), whose theory added a 41,000 year cycle to Croll's eccentricity and precession cycles. This third orbital frequency is caused by variation in the tilt of the Earth's axis relative to the Sun (Milankovitch, 1941). Together, the three orbital parameters of the Earth are known as the Milankovitch orbital frequencies (Berger, 1978; Imbrie and Imbrie, 1979).

The Earth's glacial/interglacial periodicity influences many environmental parameters including atmospheric wind strength, ice-volume, sea-level, continental aridity and, perhaps, oceanic biological productivity (Sarnthein *et al.*, 1988; Shimmield, 1992). All of the above parameters can affect the composition of the sediment input to a particular area of the ocean and their variation over time will be contained in the geochemical signature of the down-core sediment record.

Age modelling can also benefit marine sediment geochemical records by allowing for the concentration of a particular component or element, which is analytically measured as a weight percent (wt.%) or part per million (ppm) of the total, to be expressed as a mass accumulation rate (MAR) flux ($\text{g cm}^{-2} \text{ kyr}^{-1}$). This means that the variation of input to the sediment of an individual component or element over time can be calculated. The MAR flux is independent of the variation of all the other components, i.e. dilution effects on the geochemical signal are removed, allowing for the true reasons of input fluctuations (productivity, preservation, diagenesis, weathering/erosion etc.) to be examined.

Although this study is concerned with the geochemical analysis of marine sediments, its interpretations are by no means limited to just geological or chemical processes. As the diagram in Fig. 1.1 indicates, marine sediment geochemistry is an inter-disciplinary science which relies on an understanding of four basic sciences (chemistry, physics, biology and geology) and their influence on oceanography, climatology and mineralogy. Each of the following chapters in this thesis concentrates on a particular environmental aspect (involving one or more of the natural processes shown in Fig. 1.1) which can affect the geochemical signature of the ocean sediments from the Peruvian continental margin.

1.2. PERU CONTINENTAL MARGIN

The following chapters each contain their own introductory explanations about the various environmental features of interest along the Peru continental margin and their particular geochemical signature. Included in these sections are references to relevant studies by previous authors who have used a wide range of analytical methods to study the sediments of the Peru continental margin (and other similar areas of the world's oceans) in order to further our understanding of the geology, oceanography and climatology of the area. There are two particular textbooks from which many references have been taken and two research cruises

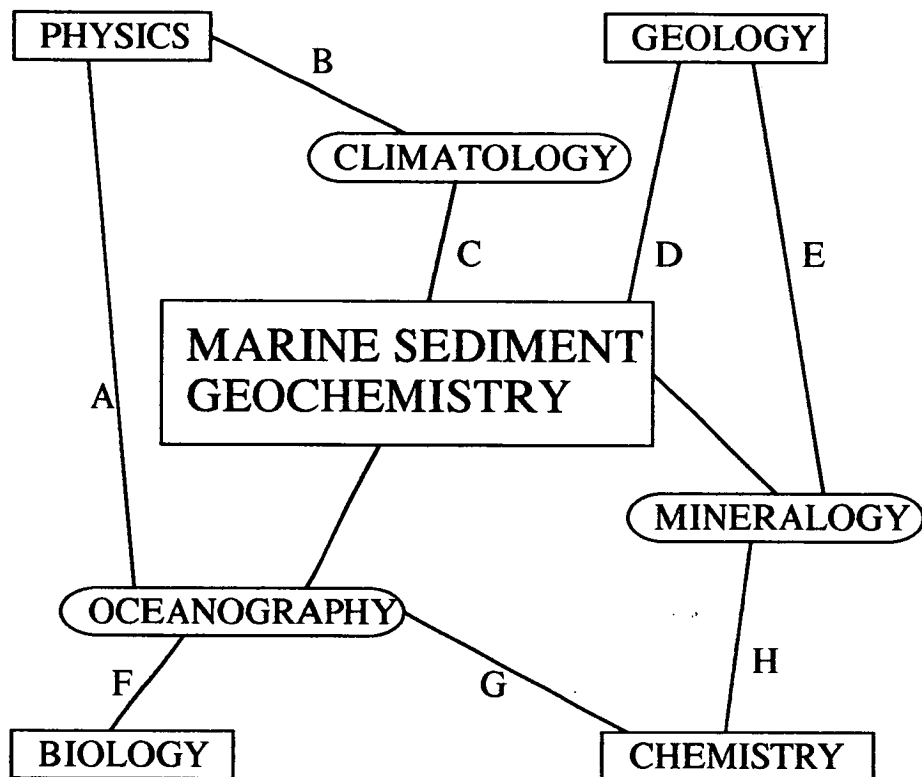


Figure 1.1. Marine sediment geochemistry; an inter-disciplinary science.

- Process:
- A Global wind and water mass circulation,
 - B Milankovitch orbital frequencies,
 - C Glacial/interglacial periodicity,
 - D Ocean tectonics,
 - E Continental erosion and sediment supply,
 - F Marine biomass productivity,
 - G Water chemistry,
 - H Chemical redox reactions.

during which cores were obtained from the Peruvian margin, which deserve to be mentioned here. The books (*Coastal Upwelling*, Volumes A and B, Suess and Thiede, 1983; Thiede and Suess, 1983; *Upwelling Systems*, Summerhayes *et al.*, 1992) contain papers which analyse and interpret all aspects of coastal upwelling (the main oceanographic feature affecting this area; Chapter 3). The cruises were the Ocean Drilling Program (ODP) Leg 112 (Suess *et al.*, 1988) and the *R.V. Robert D. Conrad* cruise 23–06 (Burnett and Froelich, 1988).

The tectonic history and the oceanic setting of the Peru margin are now briefly introduced in order to highlight the global significance of this area in terms of the environmental records that are contained within the marine sediments accumulating on the sea–floor.

1.2.1. Tectonic history

The Andean continental margin, which runs the length of the west coast of South America, is a major boundary in both the global framework of plate tectonics and the global pattern of oceanic circulation. Running parallel to the coastline of Peru, the Peru–Chile Trench (at about 6000m water depth) has been formed by the subduction of the oceanic Nazca plate as it slowly moves south–east (due to sea–floor spreading at the East Pacific Rise) and collides with the continental South American plate. The rate and direction of subduction has been estimated as 7.1cm per year at 102° (Hey *et al.*, 1977). This geological process has produced a complex continental margin, which lacks pervasive compressional deformation and an extensive accretionary complex as seen at other convergent plate margins (Scholl *et al.*, 1970; Rutland, 1971).

The Nazca Plate Project (Kulm *et al.*, 1981) investigated the tectonic history of the margin and observed that the continental crust extended to at least the edge of the shelf and that sediments had accreted along the lower slope. On the continental shelf and upper slope off Peru, a series of elongated, tectonic depressions produced a pattern of off–shore, forearc basins which lie roughly parallel to the coastline, land–ward of the Peru–Chile Trench, and within which marine sediments have slowly accumulated (Thornburg and Kulm, 1981; Suess *et al.*, 1988).

At approximately 15°S, the depth of the Peru–Chile Trench decreases to about 4800m, where it is intersected on the sea–ward side by the Nazca Ridge. The ridge is an aseismic, submarine topographical feature which runs from north east to south west on the Nazca plate and rises over 1200m above the surrounding deep–sea

floor (Couch and Whitsett, 1981; Schweller *et al.*, 1981). The Nazca Ridge has a strong influence on both the water mass circulation and the sedimentation pattern of the Peruvian margin.

1.2.2. Oceanic setting

Although it is the tectonic history of the region that controls the physiographic location of the marine sediments, it is the particular oceanographic setting of the Peruvian continental margin which dominantly influences their geochemical composition. During the Eocene/Miocene period, the initiation of the Eastern Pacific Boundary Current circulation pattern, and its associated wind system, established a coastal upwelling regime along the Peru margin. Coastal upwelling is a physical feature which moves surface-water off-shore, as a result of along-shore wind stress, and therefore deeper-water has to be upwelled to replace it (3.1.1).^{*} Coastal upwelling has dominated the oceanography of the area since the Eocene (Reimers and Suess, 1983A; Suess *et al.*, 1988) and sustained an intense marine biological productivity zone (3.1.2) along the coast.

The level of this productivity has been estimated as being an order of magnitude greater than that of normal ocean surface-waters. In the centre of the Peru upwelling cells, between 1 and 6 g of carbon are fixed by photosynthetic organisms (phytoplankton) every day in an area of just one square metre (Chavez and Barber, 1987). This extreme biological production is the main reason why the Peru margin is an important area for study of the palæo-climate and also for future climate prediction models.

Today, this coastal zone (and other areas such as off south west Africa and California) provides a major sink for organic carbon in the oceans and depletes other carbon reservoirs such as the atmospheric CO₂ levels (Broecker, 1982, 1984). It may be that some of the increase in the CO₂ concentration in the atmosphere over the last 100 years, which has been caused by the anthropogenic burning of fossil fuels, will be compensated for by increased biological production in the oceans, especially at coastal upwelling zones. This may decrease the effects of the global warming scenario as predicted by many climate models.

^{*}Numbers in brackets appear throughout this thesis and are used to refer to another section of the thesis. If the number is not prefixed by Figure, Table or Appendix, then it simply refers to another section or sub-section of the text.

Not only has the high biological production an important role to play in the natural carbon cycle, but it also strongly affects the ocean chemistry and sediment geochemistry. Most of the organic matter produced in the surface-water is decomposed and recycled as it falls through the water column upon death of marine organisms. The high flux of organic matter below a coastal upwelling zone results in extreme levels of microbacterial activity at water depths of between 100 and 500m (Veeh *et al.*, 1973). This decomposition/respiration process uses nearly all of the available dissolved oxygen and creates an oxygen minimum zone (OMZ) between the above depths. The organic matter that avoids decomposition reaches the sea-floor and is incorporated into the sediment column. Under a coastal upwelling zone, organic carbon is found at much higher concentrations than in marine sediments from the deep ocean (Reimers and Suess, 1983A). The degradation of organic matter within the sediment column plays an important role both in the redox environment (oxic, suboxic or anoxic conditions) and in the types of diagenetic processes that occur within the sediment. These two parameters can strongly affect the sediment geochemical composition and any *in situ*, authigenic mineral growth.

1.3. STATION SITES AND CORE DESCRIPTIONS

As previously mentioned, all the sediment cores which were sampled and analysed to provide the geochemical records presented in this thesis, were collected during the scientific cruise Leg 38 of the *R.R.S. Charles Darwin* (core numbers have the prefix CD38). This was an inter-university research cruise which recovered marine sediments using box and piston cores, and also sea-water and pore-water samples, from the Peru margin and the eastern equatorial Pacific during April and May 1989. The cruise report (Price *et al.*, 1989) presents full details of the cores and water samples, and the information contained in Table 1.1 and Fig. 1.2 is taken directly from it. For the cores used in this study, Table 1.1 lists the station site number, its latitudinal and longitudinal position, and the core water-depth, type and length. Figure 1.2 is a simplified map of the Peruvian continental margin and, as well as illustrating the location of each station site, the important topographical features and water circulation patterns of the region are shown.

The cores can be divided into a northerly group and a southerly group (Table 1.1) as follows. The northerly group forms a transect at about 11°S of increasing water depth and includes two shallow-water cores, CD38-09 and CD38-10, located on the continental shelf directly under the coastal upwelling zone, and one deep-water core, CD38-11, located on the continental slope (Fig. 1.2). These three

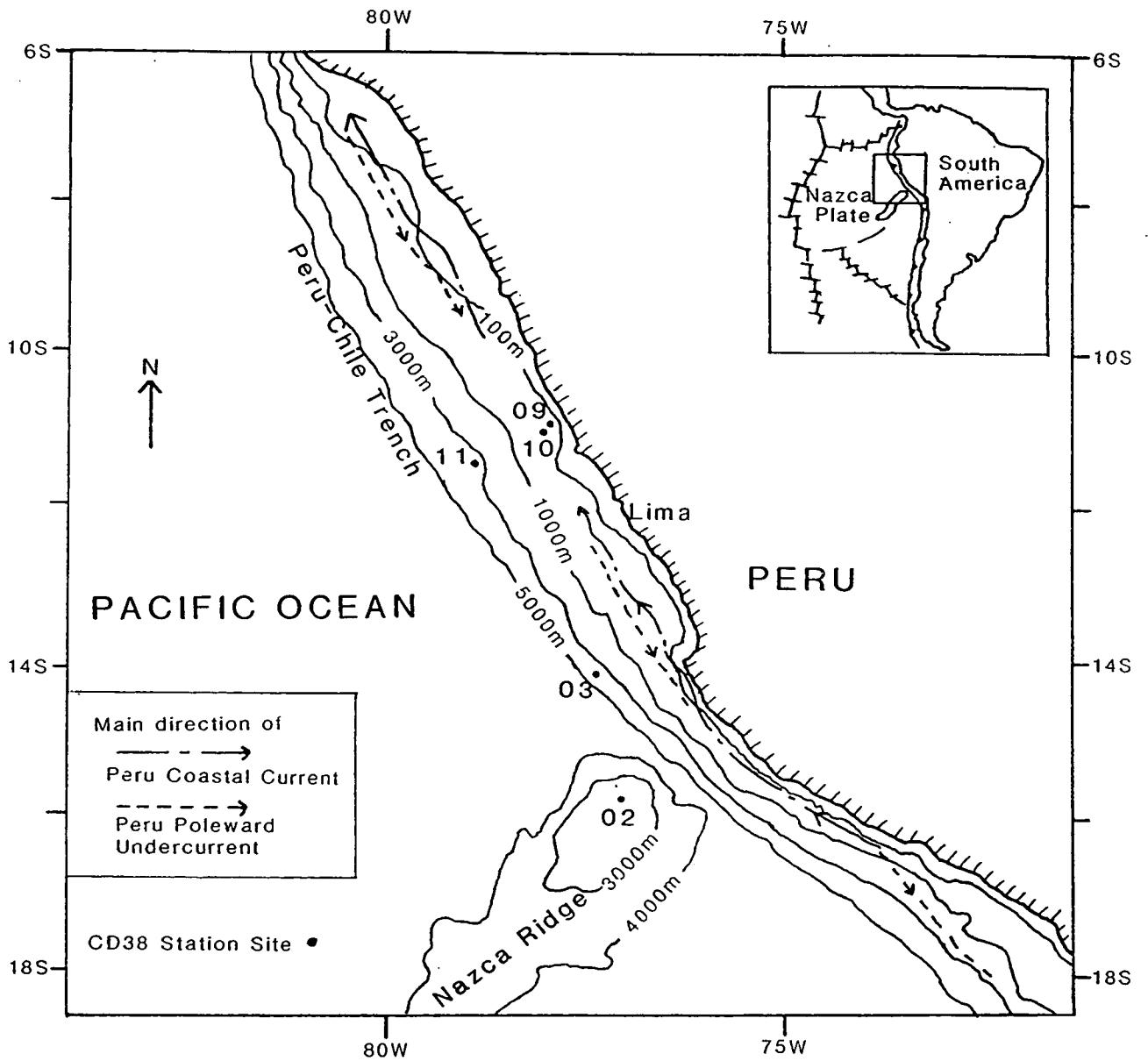


Figure 1.2. Simplified map of the Peru continental margin, indicating the location of the CD38 core sites studied in this thesis, as well as the main topographic and oceanographic features of the area.

cores were drilled at locations close to the ODP Leg 112 sites 681, 680 and 688 respectively to allow for the possibility of inter-core comparisons.

Station	CD38-09	CD38-10	CD38-02	CD38-02	CD38-11	CD38-03
Location	S.Salaverry Basin	S.Salaverry Basin	Nazca Ridge	Nazca Ridge	Lima Basin	Peru Basin
Lat. (S)	10°58'	11°04'	15°56'	15°57'	11°32'	14°36'
Long. (S)	77°57'	78°04'	77°04'	77°04'	78°56'	77°45'
Core Type	Piston	Piston	Piston	Box	Piston	Box
Core Length	895cm	822cm	800cm	57cm	594cm	57cm
Water Depth	148m	257m	2525m	2530m	3835m	4289m

Table 1.1. Core locations

The southerly group (between 14 and 16°S) contains a deep-water box core, CD38-03, from close to the Peru-Chile Trench and intermediate-water box and piston cores, CD38-02, located on the upper slopes of the Nazca Ridge (Fig. 1.2). All the above cores provide a range of water-depth and oceanographic environments from which the geochemical signatures of the marine sediments should contain many contrasting records of the palaeo-oceanography of the Late Quaternary along the Peru margin.

In order to illustrate some of the contrasting ocean water conditions at the core sites, Fig. 1.3 displays the dissolved oxygen, temperature and salinity levels measured at three of the above sites (CD38-03, CD38-10 and CD38-09) during the *R.R.S. Charles Darwin* Leg 38 cruise (Price *et al.*, 1989). The profiles are plotted against water depth and display differences in water chemistry between an area of strong coastal upwelling (CD38-09 and CD38-10) and one which lies at the periphery of such an oceanic phenomena (CD38-03).

It should firstly be noticed that the vertical scales of the profiles in Fig. 1.3 correspond to the station site water depths and therefore vary considerably between the shallow- and deep-water sites. The main points of interest about the water chemistry of the Peru margin that are displayed in Fig. 1.3 are as follows.

1) Although the temperature profile of CD38-03 shows a smooth, exponential decrease with increasing water depth, the salinity and dissolved oxygen profiles both contain a minimum zone at 500-1500m and 200-1000m respectively, which indicates the presence of more than one water mass circulating in this region. The surface-waters, with temperatures above 20°C and salinities close to 35.0‰, are

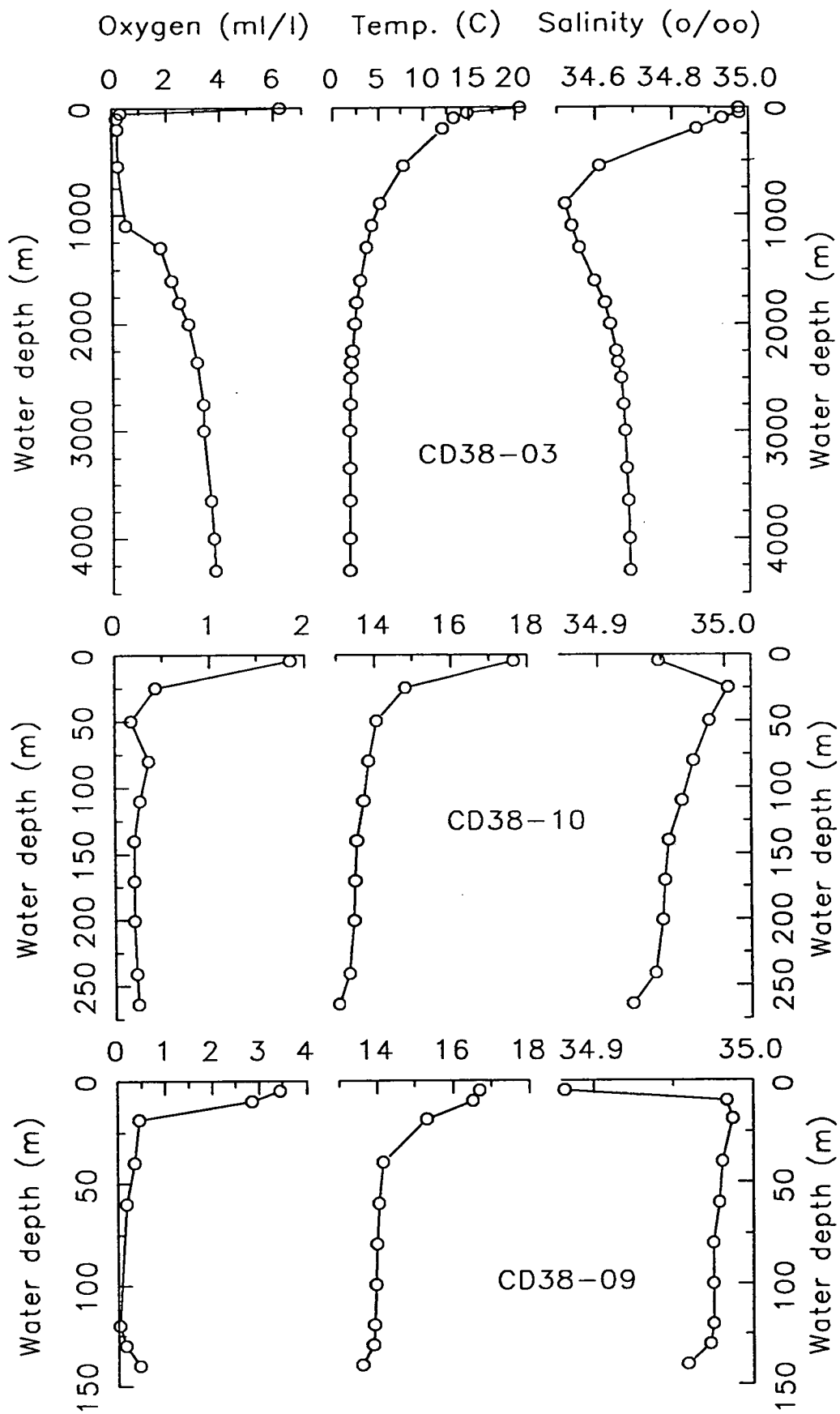


Figure 1.3. Water column profiles of dissolved oxygen content (ml l^{-1}), temperature ($^{\circ}\text{C}$) and salinity ($^{\circ}\text{‰}$) for station sites CD38-03, CD38-10 and CD38-09.

part of the Peru Coastal Current (PCC), underneath which is the Peru Poleward Undercurrent (PPU) between 100 and 500m (Smith, 1983; Huyer *et al.*, 1991; 3.1.1). Below this, lies the Antarctic Intermediate water (AIW); a water mass which flows from the Antarctic Circumpolar Current between 500 and 1000m and is characterised by low salinity and oxygen depletion, resulting respectively from ice melting and high productivity in the polar waters (Lonsdale, 1976). Both the salinity and the dissolved oxygen profiles of CD38-03 increase steadily below 1000m due to the mixing of the AIW with the Pacific Deep Water (PDW). This latter water mass flows southward along the bottom of the continental slope and is more oxygenated with a higher salinity and lower temperature than the AIW due to its relatively older age (Pickard and Emery, 1982).

2) The two shallow-water stations (CD38-09 and CD38-10) display surface-water temperatures which are 2-3°C less than that of the deeper-water site. This is a direct result of the stronger coastal upwelling at the near-shore sites, where colder water (at about 14°C) is upwelled from depths of about 100m (Zuta *et al.*, 1978) to replace the warmer surface-water, which has been moved off-shore by Ekman transport (3.1.1).

3) Stations CD38-09 and CD38-10 show water-depth profiles of dissolved oxygen which drop dramatically in the upper 50m and remain constantly below 0.5ml l⁻¹ down to the sediment/water interface. This graphic representation of the oxygen minimum zone (resulting from the microbacterial utilisation of oxygen for the decomposition of the high organic matter flux) implies that the bottom-water oxygen levels at these two core sites are virtually zero and that the sediment may be accumulating under a suboxic/anoxic environment.

1.4. OBJECTIVES OF GEOCHEMICAL ANALYSES

The prime objective of this study was to obtain as much information as possible about the concentration and variation over time of the principal components of the Peruvian marine sediments, using a wide range of geochemical analyses. The geochemical data from the CD38 cores will provide high-resolution records of the history of sedimentation along the Peru margin and, as well as adding to the geochemical database from previous work on the region's sediments (e.g. Suess *et al.*, 1988), this study will form an integral part of the multi-disciplinary research that is being carried out on these newly-collected cores (1.5). The results and

interpretations presented in the following chapters answer some of the many questions about the oceanographic history of this important area, but lead to many more unanswered ones. By undertaking this geochemical study, both basic, background data and interesting, novel results have been obtained. Implications and suggestions for further research work are discussed in Chapter 8.

Before any geochemical results are discussed, some of the important physical properties of the sediments must be examined. Pore-water dissolved salts are incorporated into the bulk sediment during drying of sub-samples (Appendix A.6) and it is necessary to subtract, from all analytical geochemical concentrations, the effect of the presence of these salts. By measuring the water content of each sample (calculated from the weight lost upon drying) and by assuming a constant salinity of 35‰ in the pore-waters, the salt content is calculated (2.2.1) and thereafter all geochemical data are presented on a salt-free basis. A rough indication of the average grain-size is achieved by measuring the relative weight of the sediment remaining after sieving through a 63 μm mesh (2.2.2). It is then possible to compare this physical measurement with particular element ratios which are thought to act as geochemical indicators of grain-size.

For the interpretation of down-core geochemical signals with respect to glacial/interglacial climate changes, it is useful to be able to convert the depth component of a core into an accurate age component. The oxygen isotopic ratios of benthic foraminifera are presented for each of the four piston cores for comparison with the standard reference SPECMAP curve (Imbrie *et al.*, 1984). The two near-shore cores, CD38-09 and CD38-10, contain non-continuous isotopic records due to either a lack of carbonate microfossils and/or the presence of sediment winnowing and erosion in certain horizons (2.3.2). Therefore, only cores CD38-02 and CD38-11 are used for age modelling and the calculation of sediment accumulation rates, which are seen to vary dramatically over the glacial/interglacial stages of the Late Quaternary (2.4.2 and 2.4.3).

Sediments rich in organic matter and other biogenic-remains, and collected from a continental shelf or slope, provide a good indication of accumulation under a coastal upwelling zone (Diester-Haass, 1978; Calvert, 1987). Cores CD38-09 and CD38-10 are chosen to examine in detail the concentrations of organic carbon, biogenic silica, calcium carbonate and fish-remains found in the sediments accumulating under the Peruvian coastal upwelling zone. These two cores are from relatively shallow water, within the depths at which the OMZ impinges on the

continental shelf (Veeh *et al.*, 1973). Mean organic carbon contents (of 4–5 wt.%) an order of magnitude greater than those of deep-sea sediments give evidence of the importance of coastal upwelling zones in the global carbon cycle as sites for the removal of carbon from the atmosphere and its storage in the sediments below (3.3.1).

Redox-sensitive and/or particle-reactive metals can be scavenged out of sea-water by organic matter as it falls through the water column (Bruland *et al.*, 1974; Francois, 1988) and incorporated into marine sediments. Under a coastal upwelling zone, the high organic matter flux can produce a sediment anomalously enriched in organo-metallic elements, such as Mo, U, Ni, Cr, V and Cu (Calvert and Price, 1970; Shimmield and Pedersen, 1990). Cores CD38-09 and CD38-10 contain enrichments of the above metals which correlate strongly with the levels of organic carbon (3.3.3) and whose mean organo-metallic ratios are representative of accumulation under natural, non-anthropogenic conditions on a continental margin. The metal/organic carbon ratios could possibly be useful in future studies of a polluted, coastal environment as the natural, baseline flux for comparison with any extra, anthropogenic input (3.3.4).

Geochemical analysis of marine sediments can illustrate mineralogical variation contained within a core, especially the presence of any diagenetic minerals. The Peru margin is known to be a site for the authigenic mineral growth of dolomites, cherts and phosphorites (Suess *et al.*, 1988; Burnett and Froelich, 1988). In this study, phosphorites are examined by geochemical partitioning of the total phosphorus content into terrigenous, organic and phosphorite phases in the bulk sediments of the three piston cores at 11°S (4.3.3). Compositional characterisation of nodular hardgrounds found in CD38-09 and CD38-10 (4.3.1) and comparison of the surface-sediment pore-water phosphate profiles of the above cores with those of the *R.V. Robert Conrad* research cruise 23-06 (Froelich *et al.*, 1988; 4.3.2) are also carried out.

The incorporation of certain trace elements into phosphatic minerals is displayed by their down-core enrichment coinciding with zones of phosphorite concentration in the two shallow-water cores. Quantification of the trace element/phosphorite ratios allows for the calculation of the fractions of uranium, strontium and yttrium which are respectively associated with organic matter, calcium carbonate and terrigenous phases (4.3.4).

Diagenetic formation of phosphorite hardgrounds is considered to be linked to eustatic changes of sea-level during the Late Quaternary, as a result of ice-sheet

volume variations during glacial/interglacial periodicity (Baturin, 1982). Evidence for this theory is obtained from U/Th radiochemical age dating of a large phosphorite nodule from core CD38-09, which gives an age representative of initial pelletal growth during an interglacial period (4.3.5). The diagenetic history that the nodule's age, shape and appearance suggests is one of phosphorite pellet growth in an organic-rich sediment, followed by a concentration of these pellets into a hardground caused by a dramatic drop in sea-level during the last glacial event. This eustatic variation brought strong bottom-water currents to this shallow-water site, which winnowed fine-grained clays down-slope to leave behind a concentrated phosphorite deposit along with other coarse-grained, heavy minerals (4.3.6).

Three statistical/mathematical methods of dataset analysis are attempted in order to simplify the large geochemical dataset from the Peru margin piston cores, so that interpretations of element correlations and inter-core/down-core component variations can be presented.

Correlation analysis indicates the presence of many element-element and element-phase relationships (5.2.2) but interpretations are limited if there is a particular phase whose variation of concentration dominates the variation of all the other sediment phases or if a particular element is associated with more than one phase.

Principal component analysis (PCA) avoids the above problems by graphically representing the variation of each element or phase as a factor in relation to the total variation of the dataset. From the PCA diagrams of the piston cores (5.3.2) it is possible to examine which geochemical elements are associated with one (or more than one) of the following; organic matter, biogenic silica, calcium carbonate, phosphorite and/or terrigenous phases.

Heath and Dymond (1977, 1981) and Dymond (1981) proposed multi-component analysis (MCA) models which could define marine sediments in terms of the relative abundance of five components representative of the source of the sedimentary material, i.e. terrigenous, biogenic, authigenic, hydrothermal and residual. Adaption of the algorithms and component geochemical compositions in the MCA models of the above authors allows for the conversion of seven geochemical variables from the Peru margin dataset into the above sediment components. In all the cores, the most abundant component is of terrigenous origin, followed by that from a biogenic source (5.4.2). This is as expected from marine sediments accumulating on a continental margin under the influence of strong coastal upwelling.

The concentration of dissolved oxygen in bottom- and pore-waters and the level of marine productivity in surface-waters are two oceanographic parameters which are of prime importance in controlling many processes within the sediment column. Trace elements are used to act as geochemical proxies of the above parameters, and their down-core profiles as indicators of the palæo-redox and/or palæo-productivity environment of the Peru margin during the Late Quaternary.

The close, but differing, association of the halogens (iodine and bromine) with organic carbon is examined in detail. Due to their diagenetic mobility during organic matter degradation upon burial, the halogens are unreliable palæo-productivity indicators (6.2.3). However, the iodine/organic carbon ratio can be used to distinguish between anoxic (at sites CD38-09 and CD38-10) and oxic (at all other sites) environments of sediment deposition (Price and Calvert, 1977; Shimmield and Pedersen, 1990).

Barium is a trace element which shows a strong relationship to the marine biogeochemical cycle (Church, 1979; Dehairs *et al.*, 1980) and therefore may be useful as a proxy for palæo-productivity (Dymond *et al.*, 1992; Von Breymann *et al.*, 1992). In the anoxic cores of CD38-09 and CD38-10, the barium signal is lost upon burial during barite diagenetic mobilisation (6.3.2). However, in the oxic environment of cores CD38-02 and CD38-11, the barium-productivity signal is preserved as a down-core Ba/Al or biogenic-Ba profile; both of which vary sympathetically with the foraminifera oxygen isotope signal across the glacial/interglacial stages (6.3.3). The model and equations of Dymond *et al.* (1992) for the relationship between the flux of biogenic-Ba to the sediment and the production levels in the surface-waters are critically reviewed, and tested using the barium results from core CD38-02 (6.3.4).

Foraminifera and coccoliths are two important groups of marine plankton, which form carbonate shells and remove strontium from sea-water, as a trace element substitute for calcium (Church, 1970). Core CD38-02 is chosen to observe the close relationship between strontium and calcium carbonate, because of its lack of phosphorite diagenesis, which can also enrich the Sr concentration (6.4.2). The temporal variation of the biogenic-Sr/Ca ratio shows glacial/interglacial fluctuations which possibly relate to changes in the degree of dominance of foraminifera over coccoliths in the marine biomass of the Peru margin (6.4.3).

Molybdenum and uranium are redox-sensitive, trace metals whose ratio has been used as a proxy for palæo-redox conditions at the sediment/water interface (Bertine and Turekian, 1973). The Mo/U ratios measured in the anoxic (CD38-09

and CD38–10) and oxic (CD38–02 and CD38–11) piston cores of the Peru margin contradict the hypothesis of the above authors (6.5.2). The relationship between these two heavy metals is highly complex and depends on their uptake by organic matter in the water column, post-depositional mobility and diagenetic incorporation into ferromanganese and phosphorite minerals (Shimmield and Pedersen, 1990). This renders the Mo/U ratio an unreliable indicator of palæo-redox environment of deposition in continental margin sediments (McNeill and Shimmield, 1991).

There are numerous processes which occur in the natural environment whose relative strengths control the exact sedimentological and therefore geochemical, composition of marine sediments. On the Peru continental margin, it is the proximity to the South American landmass and the presence of persistent coastal upwelling which exert the strongest influences on the process of sediment deposition. The terrigenous (land-derived) and biogenic inputs to the sediment cores, therefore, need to be examined in detail (7.2.1 and 7.3.1).

Questions regarding the composition, source supply and mode of transport of material eroded from the Andes and the Peru coastal plain and deposited on the continental margin, are answered using down-core and inter-core trends of terrigenous geochemical data, e.g. the flux of aluminium and silicon, and Ti/Al, Si/Al, K/Al and Zr/Rb element ratios (7.2.3). By examining the geochemical signature of the terrigenous component over time, environmental factors such as continental volcanic activity and fluctuations in the wind strength and sea-level along the margin are also interpreted (Boyle, 1983).

The concentrations of organic carbon, biogenic silica and calcium carbonate within all the cores, and the fluxes of these biogenic inputs to sites CD38–02 and CD38–11, are presented as indicative of variation in the level of biological productivity and/or preservation in the ocean along the Peru margin (7.3.2).

Decomposition of organic matter, both prior to and after burial in the sediment column, significantly diminishes and distorts the original signal of production (Reimers and Suess, 1983A). This means that accurate interpretations from the organic carbon record are difficult to make. However, the palæo-productivity equation of Müller and Suess (1979) is used (7.3.3) in order to contrast the calculated surface-water biological levels between a site on the Nazca Ridge (CD38–02) and one closer to the main coastal upwelling zone (CD38–11). This also allows for comparison with the productivity calculations from the biogenic-barium flux for core CD38–02 (6.3.4).

Both the biogenic silica and the calcium carbonate shells of marine organisms suffer from dissolution within the water column, thereby distorting the initial productivity signal into a preservation-controlled record within the sediment column (Berger, 1976; Volat *et al.*, 1980). The extent of dissolution varies according to the environment of deposition and fluctuates over time, due to the movement of water masses along the Peru margin (7.3.3). The mechanisms for the dissolution of both silicate and carbonate microfossils are discussed with regards to the water depth and ocean chemistry of each core site.

The above objectives for the analysis and interpretation of the geochemistry of the Peru margin sediments has followed the layout of the chapters which make up the bulk of this thesis. These chapters are presented in such a manner that, although only one particular environmental parameter or process is discussed at a time, each chapter relies on observations and interpretations made in previous chapters. The overall palæo-oceanographic history of the Peru continental margin is brought together in the concluding chapter.

1.5. CO-WORKERS

The sampling of the Peru margin cores was carried out in conjunction with two postgraduate research students from the Department of Oceanography, University of Southampton (who were both under the supervision of Dr A.E.S. Kemp). They are examining various other records and signals contained within the Peruvian marine sediments, as follows.

- 1) S. King – micropalæontological studies, foraminifera abundance, isotopic signatures and pollen analysis (palynology).
- 2) I. Brodie – sedimentological studies, general sediment logging of cores and detailed examination of microscopic laminations.

Two other co-workers involved in analysing some of the sub-samples taken from the cores are Dr T. Clayton (clay mineralogy; Southampton University) and Dr H. Schrader (diatom abundance variations; University of Bergen, Norway).

CHAPTER 2

SEDIMENT PHYSICAL PROPERTIES

2.1. INTRODUCTION

"Time and tide wait for no man, saith the old adage. But all men have to wait for time and tide."

Charles Dickens (1843)

Martin Chuzzlewit

Although the main work in this thesis is based on geochemical analyses, it is necessary to measure some important physical properties of the marine sediments (especially the water content of each sample) before the geochemical data can be correctly interpreted.

The above quote mentions both the physical component of time and the oceanographic parameter which constantly changes with time, the tide. In this palæo-oceanographic study, consideration of the length and period of time over which the marine sediments have accumulated is of prime importance. Taking cores of marine sediments is an ideal method of extracting an historical record of past ocean conditions, in terms of marine biology, chemistry and/or geology. However, no matter what signal is being measured, its down-core interpretation will have much more meaning if the depth component can be converted from a simple measurement in centimetres (cm) to an accurate age in thousands of years before the present (ka). Marine sediments do not accumulate at a constant rate, especially those on a continental margin, because the supply of both the terrigenous and the biogenic components to the sediment can be highly variable with time. Therefore, an accurate age model for each core needs to be constructed so that sediment accumulation rates (SAR, in cm kyr^{-1}) and mass accumulation rates (MAR, in $\text{g cm}^{-2} \text{kyr}^{-1}$) can be calculated and down-core geochemical profiles can be plotted against age (ka) instead of depth (cm).

This chapter will firstly examine the following physical properties of each core; water content, salt content, porosity, dry bulk density and % grain-size $> 63\mu\text{m}$. Then, for the four piston cores, age model construction will be attempted by the measurement of the oxygen (and carbon) isotopic composition of foraminifera shells and the comparison of each isotope record with an internationally-used and dated record (SPECMAP, Imbrie *et al.*, 1984).

2.2. PHYSICAL PROPERTIES OF PERU MARGIN SEDIMENTS

2.2.1. Calculations from the measured water content

The bulk-sediment samples from the six cores used in this study (Table 1.1) were all weighed, both before and after drying at 50°C (Appendix A.1) and this allowed for the calculation of the water content (%) of each sample (Eqn 2.1). This is a measurement of the amount of water, relative to the weight (wt.) of sediment in each sample, which is held as pore-water around each grain of sediment.

Equation 2.1. Water content calculation

$$\text{Water content (\%)} = [(\text{Wet wt.} - \text{Dry wt.}) / \text{Wet wt.}] \times 100$$

Figures 2.1 through to 2.6 illustrate depth profiles of the various physical properties which are discussed in this section for cores CD38-09, CD38-10, CD38-02 (Box), CD38-02, CD38-11 and CD38-03 (Box) respectively and the complete data are tabulated in Appendix C.1.

It may be expected that the water content of any marine sediment core would decrease with (increasing) depth because sediment close to the sediment/water interface will contain more pore-water which will be slowly squeezed out as the sediment is buried and compacted under the pressure of accumulating material. This ideal scenario can, in fact, be seen in both the box cores (Figs 2.3 and 2.6) which show maximum water contents (72% and 82% respectively for CD38-02 and CD38-03) at the sediment/water interface, which exponentially decrease down to relatively constant levels (55% and 62% respectively) within the 55cm sampling depth.

It can be seen from the box cores that within the upper 50cm some pore-water has been squeezed out upon compaction of the sediment but that the buried sediment still contains a high water content (on a wt.% basis) held within its pore spaces. With this knowledge, the water content profiles of the four piston cores can be examined. These longer cores do not display a simple steady-state exponential decrease with depth but show more complex and erratic profiles, related to lithological/sedimentological changes.

The shallow-water cores CD38-09 and CD38-10 (Figs 2.1 and 2.2) have water contents that are generally above 60%. Similar high water contents were measured by Busch and Keller (1981) along the Peruvian continental margin and were attributed to

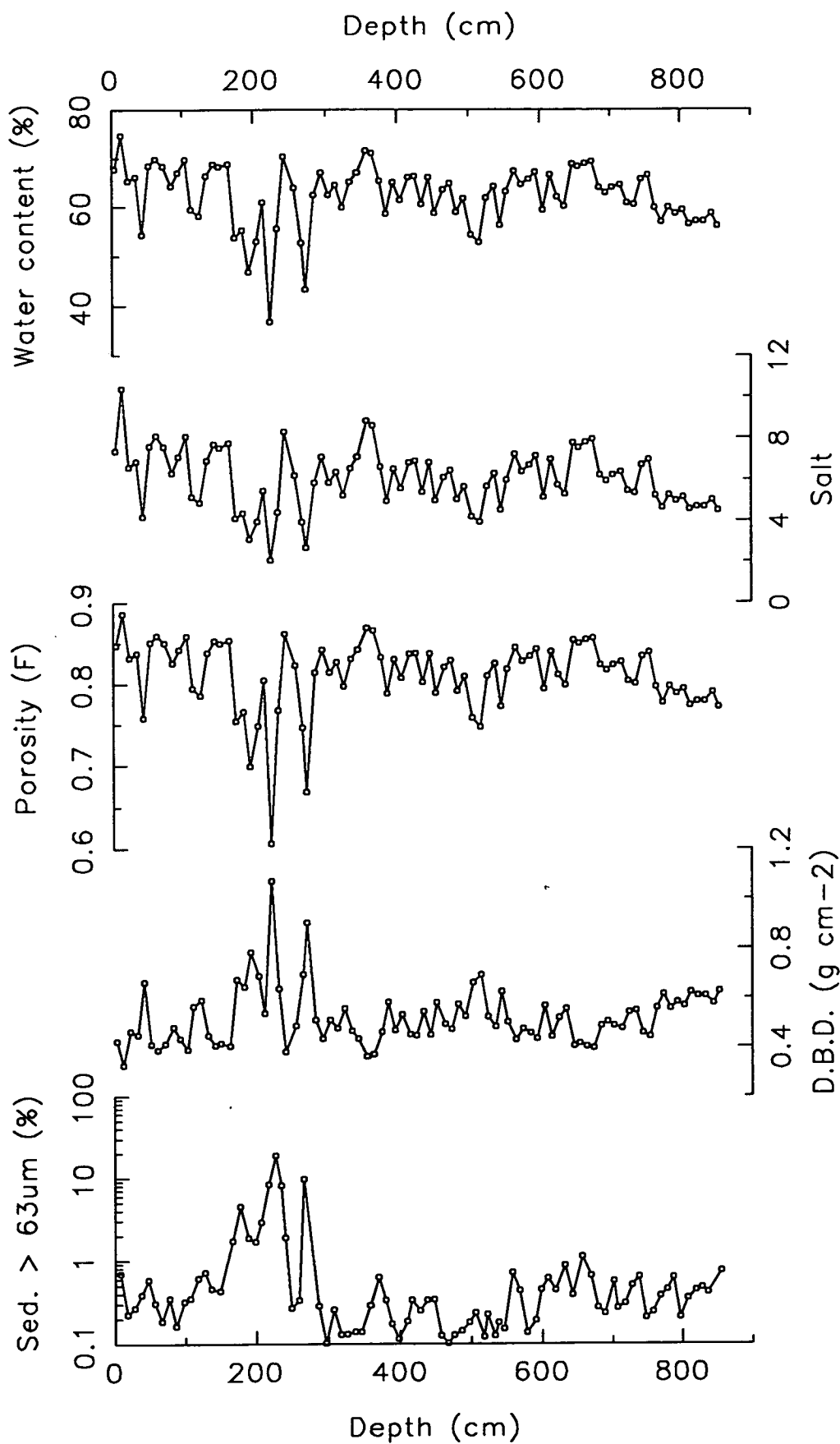


Figure 2.1. Down-core profiles of water content (%), salt content, porosity (F), dry bulk density (g cm^{-2}) and sediment $> 63\mu\text{m}$ (%) against depth (cm) for core CD38-09 (148m).

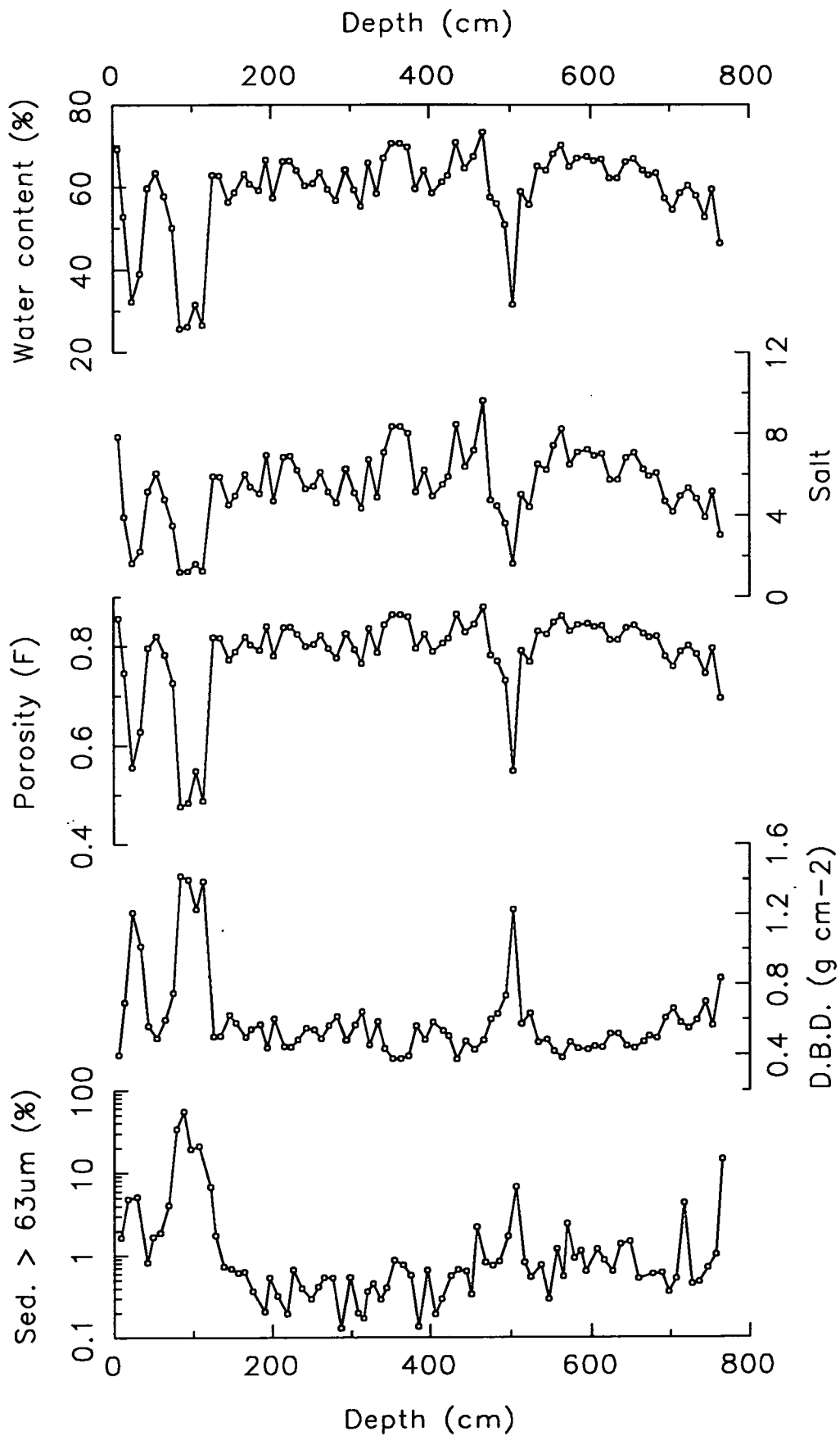


Figure 2.2. Down-core profiles of water content (%), salt content, porosity (F), dry bulk density (g cm⁻²) and sediment > 63µm (%) against depth (cm) for core CD38-10 (257m).

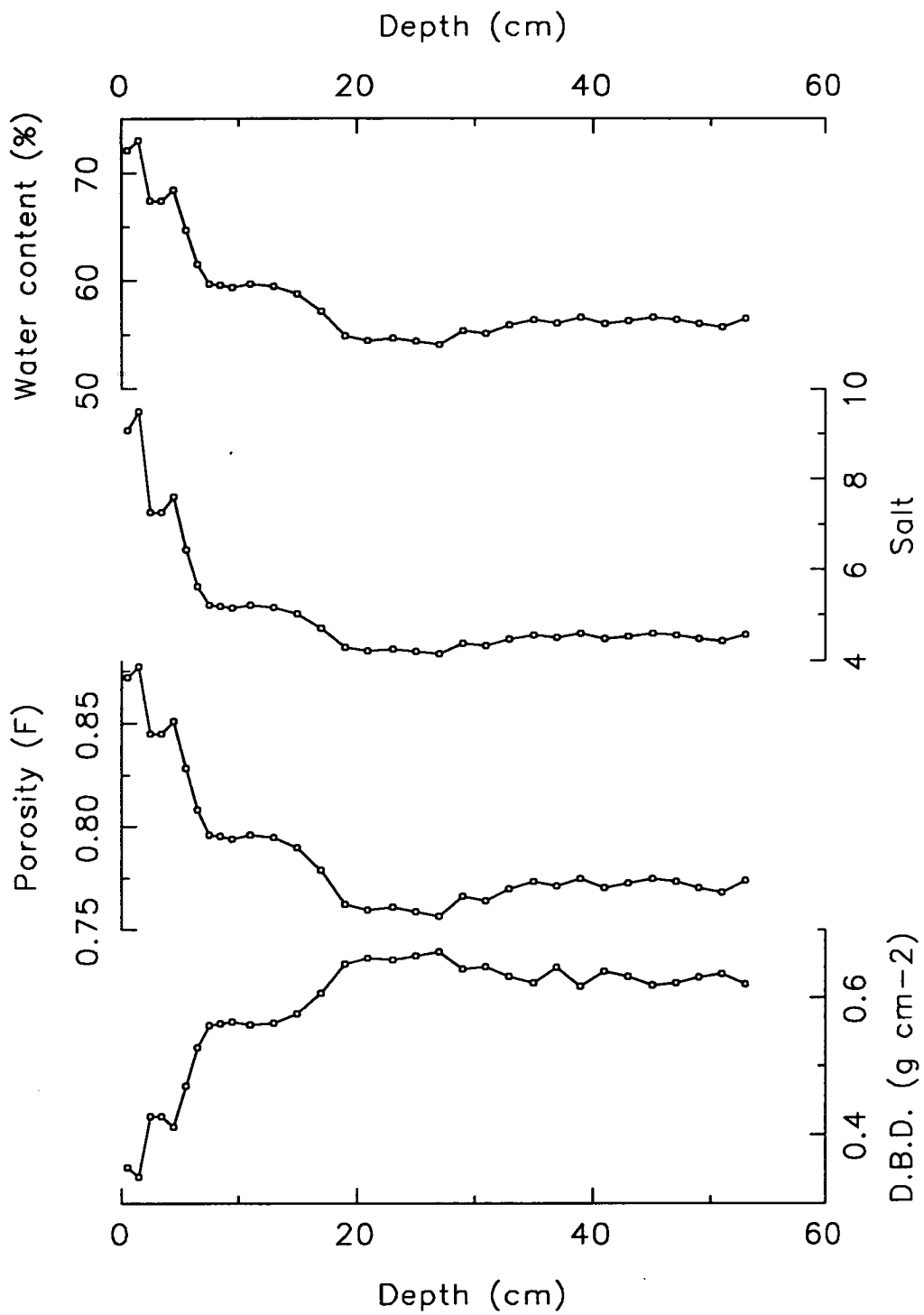


Figure 2.3. Down-core profiles of water content (%), salt content, porosity (F) and dry bulk density (g cm⁻²) against depth (cm) for box core CD38-02 (2530m).

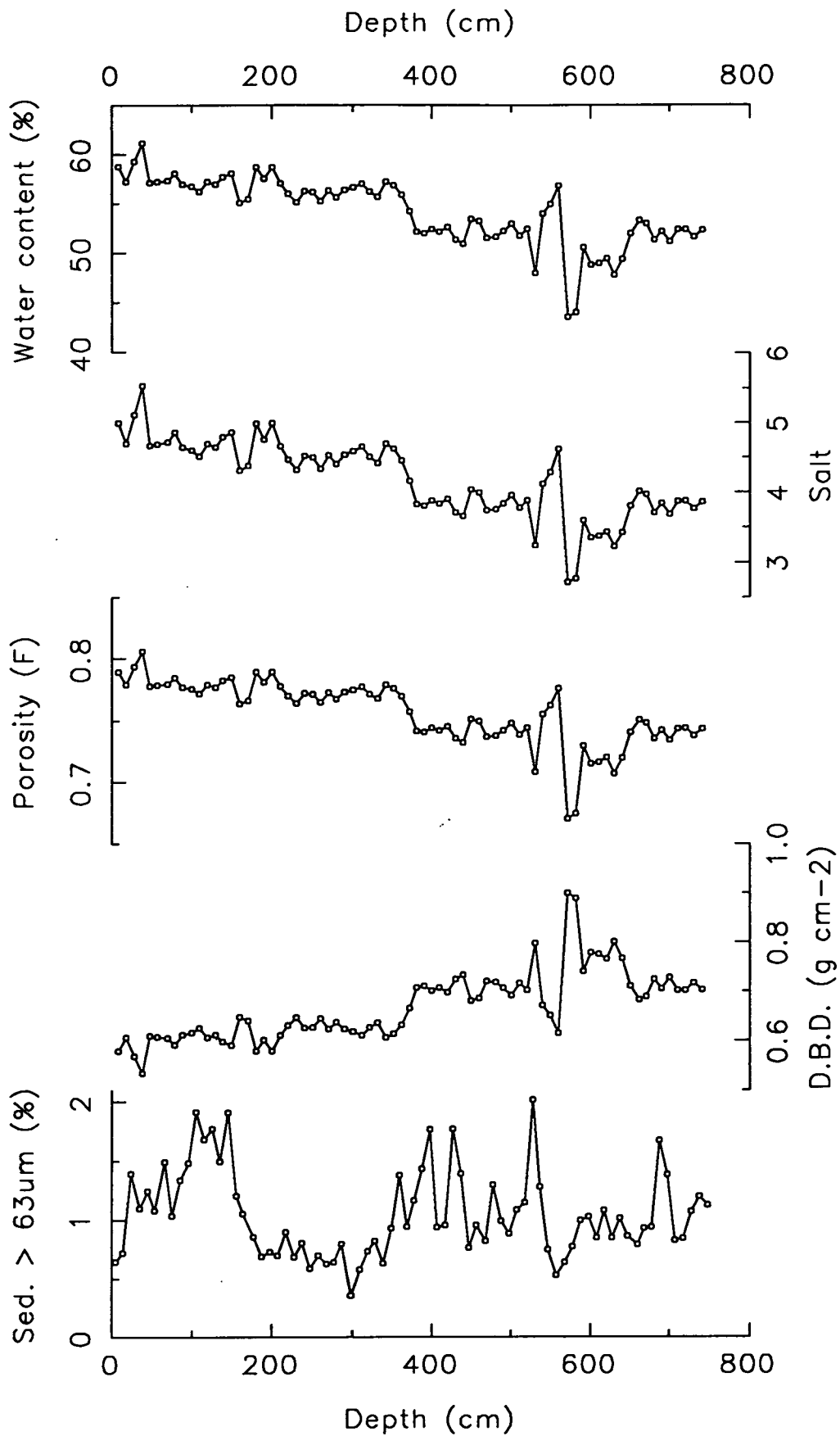


Figure 2.4. Down-core profiles of water content (%), salt content, porosity (F), dry bulk density (g cm^{-2}) and sediment $> 63\mu\text{m}$ (%) against depth (cm) for piston core CD38-02 (2525m).

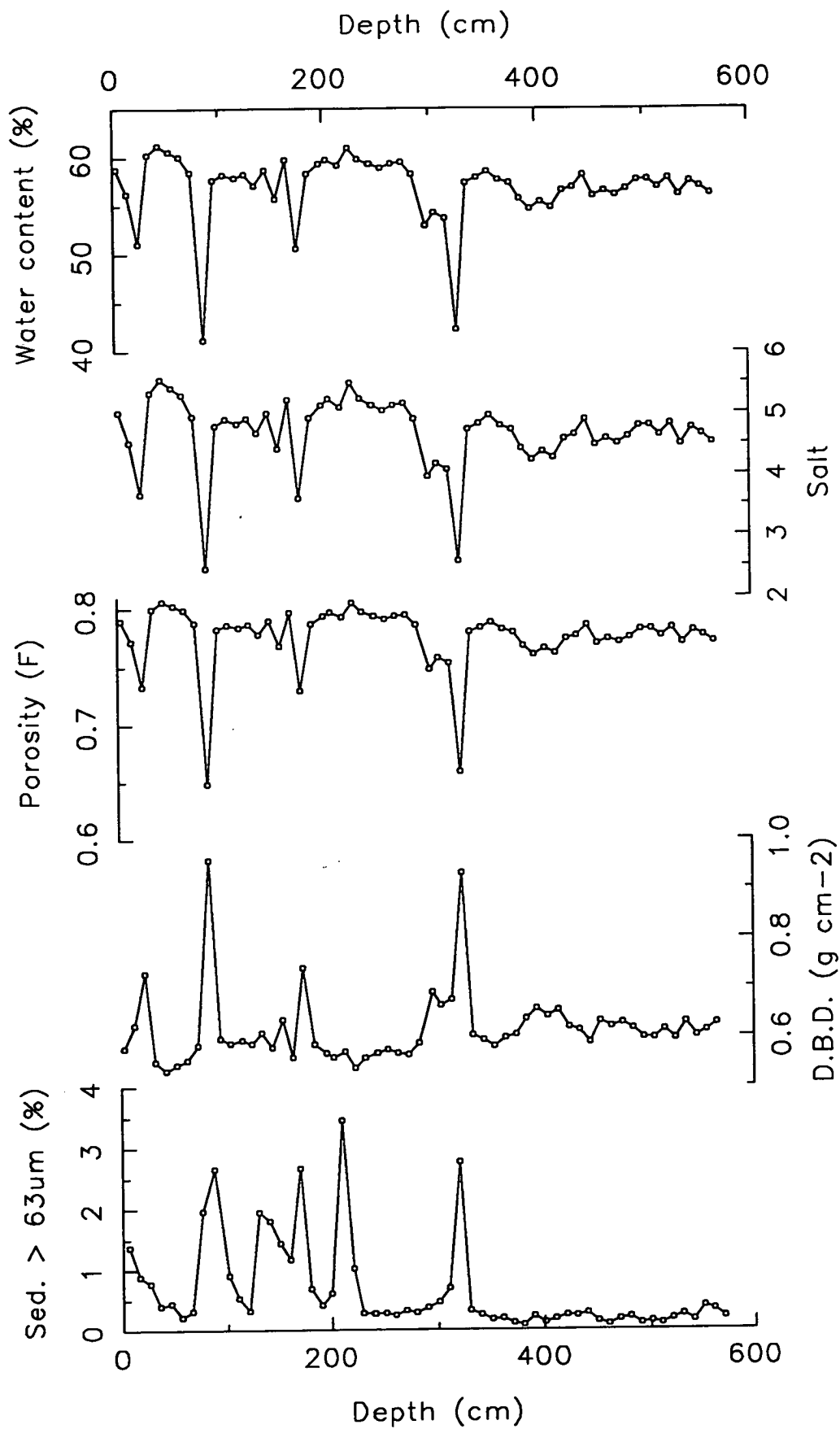


Figure 2.5. Down-core profiles of water content (%), salt content, porosity (F), dry bulk density (g cm⁻²) and sediment > 63μm (%) against depth (cm) for core CD38-11 (3835m).

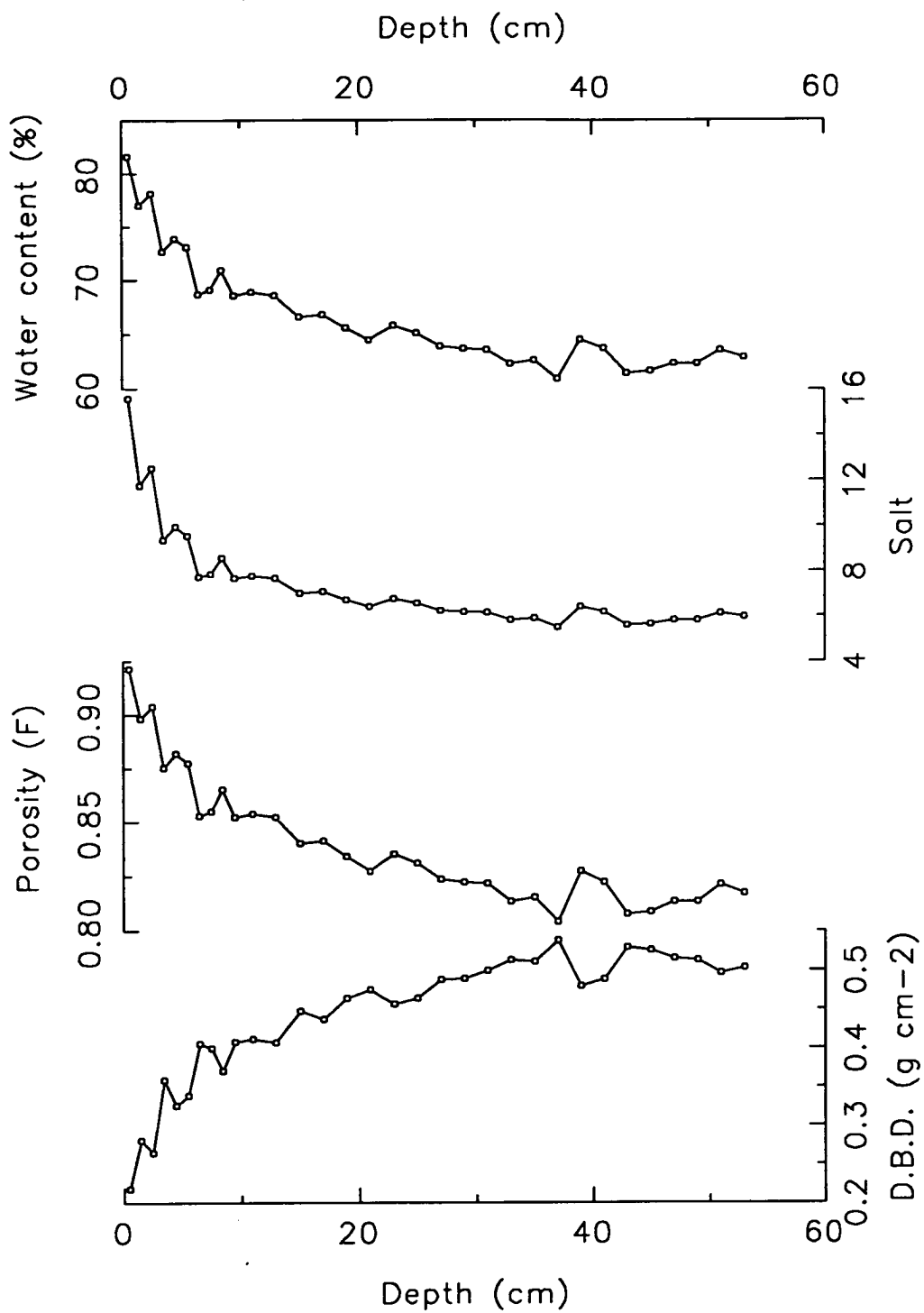


Figure 2.6. Down-core profiles of water content (%), salt content, porosity (F) and dry bulk density (g cm⁻²) against depth (cm) for box core CD38-03 (4289m).

very fine-grained sediments with high organic carbon contents. The profiles of CD38-09 and CD38-10 both show a few anomalous zones of low (< 40%) water content which can be interpreted as horizons, either where the sediment has been compacted more than usual, or where the sediment is coarser-grained and therefore contains less pore space. It will be seen later (Chapter 4) that these zones are of great interest in terms of authigenic mineral growth.

Cores CD38-02 and CD38-11 (Figs 2.4 and 2.5) which are from greater water depths, have water contents which are less than 60%. This possibly indicates that these cores have a lower organic carbon content and/or have a slower sediment accumulation rate compared with cores CD38-09 and CD38-10. The profile of core CD38-02 does, in fact, display a pattern of decreasing water content with depth but it is distorted by regions of steady-state decrease (e.g. 200-240cm and 340-380cm) followed by regions of fairly stable water content (e.g. 240-340cm and 380-510cm). There is also an anomalous increase then sharp decrease of water content in the 540-580cm region. Such a profile may be the result of either variation in concentration of a particular sediment component (e.g. carbonate or clays) which controls the porosity of the sediment, or variation in the sediment accumulation rate. Core CD38-11 has a relatively flat and stable water content profile but, like CD38-09 and CD38-10, it has a number of anomalously low water content regions.

From a geochemical and analytical point of view, the importance of water content measurements is that, by assuming a constant salinity of the pore-waters and using Eqn 2.2, the salt content of each dried bulk-sediment sample can be calculated. The salt content is required for the correction of all geochemical data to allow the true "salt-corrected" concentrations to be calculated (Appendix A.6).

Equation 2.2. Salt content calculation

$$\text{Salt} = (3.513 \times W) / (100 - W)$$

where, W = water content (% Wet wt.).

Figures 2.1 through to 2.6 display the salt content for each core but since this is, in effect, just a recalculation of the water content data, the salt down-core profiles have exactly the same trend as the water content profiles and therefore are not discussed in detail.

Another physical property which can be calculated (Eqn 2.3) directly from the wet and dry weight data is the porosity of the sediment. This is a measure of the total sediment volume that is pore space and its pattern of down-core variation on the Peru margin is again very similar to the water content depth profiles (Figs. 2.1 to 2.6). The values of porosity given in this study are expressed as a fraction of the total sediment volume and the average porosity calculated (0.8-0.9) corresponds well to the % porosity (79-86%) measured by Busch and Keller (1981) for marine sediments from the upper slope mud lens and Peru slope.

Equation 2.3. Calculation of porosity

$$\text{Porosity (F)} = (\text{Water wt.} / 1.025) / [(\text{Dry wt.} / 2.7) + (\text{Water wt.} / 1.025)]$$

where, 2.7 = mean solid-phase sediment density,
 1.025 = mean sea-water density.

In order to express the down-core variation of any particular geochemical component as a flux to the sediment ($\text{g cm}^{-2} \text{ kyr}^{-1}$) instead of a simple concentration in the sediment (wt.%) it is necessary to know the dry bulk density (D.B.D.) of each sample. This can be calculated from knowledge of the wet and dry weights of each sample using Eqn 2.4.

Equation 2.4. Dry bulk density calculation

$$\text{D.B.D. (g cm}^{-2}\text{)} = \text{Dry wt.} / [(\text{Dry wt.} / 2.7) + (\text{Water wt.} / 1.025)]$$

where, 2.7 = mean solid-phase sediment density,
 1.025 = mean sea-water density.

Figures 2.1 through to 2.6 illustrate the fact that the dry bulk density and the water content of each core are inversely related. The zones in cores CD38-09, CD38-10 and CD38-11 (Figs. 2.1, 2.2 and 2.5) where the water contents dropped below 40% have dry bulk densities greater than 1.0 g cm^{-2} which implies that these are regions where the fine-grained, organic-rich sediment ($\text{D.B.D.} = 0.5\text{-}0.6 \text{ g cm}^{-2}$) has been replaced by coarser-grained sediment of a denser nature. The box cores CD38-02 and CD38-03 (Figs. 2.3 and 2.6) show steady-state exponential increases in D.B.D. with depth, as the buried sediment becomes compacted.

2.2.2. Grain-size measurement

The final physical property, whose profiles for the four piston cores are displayed in Figs 2.1, 2.2, 2.4 and 2.5, is a grain-size measurement of the percentage of sediment $> 63\mu\text{m}$. This was measured by sieving during the preparation of the sieved-sediment samples which were used for foraminifera picking (Appendix A.2). The sample depths for the $> 63\mu\text{m}$ fraction measurement are slightly different from the other physical measurements in section 2.2.1, but it is immediately apparent from the down-core profiles that the % sediment $> 63\mu\text{m}$ and the D.B.D. are correlated.* The zones of anomalously high D.B.D. correspond to the peaks ($> 3\%$) in the amount of sediment $> 63\mu\text{m}$, especially in cores CD38-09 and CD38-10. This confirms the hypothesis that these are coarse-grained horizons within the cores (and not errors in the measurement of the water content).

Apart from these anomalous zones, the average amount of sediment $> 63\mu\text{m}$ is only about 1% of the total (wet) weight and this indicates that the sediment accumulating on the Peruvian continental margin is very fine-grained and probably consists mainly of terrigenous, detrital clay particles (Busch and Keller, 1981; Reimers and Suess, 1983).

Core CD38-02 does not contain any large peaks in grain-size (Fig. 2.4) but has a down-core profile which is consistently below 2% sediment $> 63\mu\text{m}$. This core displays a pattern of regions where the amount of sediment $> 63\mu\text{m}$ is either above 1% (e.g. 30-150cm and 350-540cm) or below 1% (e.g. 180-330cm and 550-680cm). This pattern illustrates that the Nazca ridge site has been affected by variation of a particular sediment component which, when present in higher than normal concentrations, can increase the grain-size of the overall sediment above that of fine-grained clays. It will be shown in Chapter 7 that the component whose concentration varies significantly with time, and thereby controls the grain-size pattern of core CD38-02, is the calcium carbonate shell-remains of marine zooplankton (7.3.3).

*It is important to note that in Figs. 2.1 and 2.2 the % sediment $> 63\mu\text{m}$ is displayed as a log scale compared with a normal scale in Figs. 2.4 and 2.5.

2.3. AGE MODELS USING OXYGEN ISOTOPE STRATIGRAPHY

2.3.1. Introduction

Defining an age model for the sediments contained within the four piston cores in this study is of utmost importance, so that the historical record of various geochemical signals can be interpreted. One commonly used method of stratigraphy in the field of marine palæo-studies is foraminifera oxygen isotope stratigraphy. The following is a short explanation of the theory behind its use as a dating tool and more thorough evaluations of its accuracy and reliability can be found in the references cited below, particularly in Patience and Kroon (1991).

The fundamental processes involved in oxygen isotopic fractionation in the oceans are the evaporation and precipitation of water in the natural hydrological cycle. Of the two oxygen isotopes that are of interest, the lighter one, ^{16}O , is preferentially evaporated at low latitudes compared with the heavier one, ^{18}O . During precipitation and atmospheric movement of water towards the high latitudes, ^{18}O is preferentially precipitated first leaving behind a concentration of ^{16}O . This ^{16}O -enriched water is then precipitated at high latitudes and incorporated into ice-sheets. This means that during the glacial periods of the Quaternary, when ice-sheets were much larger than at present, the oceans became enriched in ^{18}O compared with the present ocean $^{18}\text{O}/^{16}\text{O}$ ratio.

The CaCO_3 which is precipitated from sea-water to form the calcareous shells of marine organisms, especially the zooplankton group of foraminifera, records these changes in the oxygen isotope ratio of the oceans during glacial/interglacial periodicity, because it is in approximate isotopic equilibrium with the surrounding sea-water at the time of formation. Other factors, such as water temperature and species vital effects, can distort the oxygen isotopic signal and these are summarised in Patience and Kroon (1991).

Upon death of the living organism, the carbonate shell of a foraminifera will fall to the sea-floor and, if it survives dissolution (7.3.3), will be buried in the accumulating sediment to provide an historical record of the ocean isotope signal, giving an indication of the global glacial/interglacial conditions at the time of its precipitation. It is because of the global synchronicity of the oxygen isotopic changes in foraminifera shells that this method of stratigraphy allows for a high resolution, correlative chronology in marine sediment cores from throughout the world's oceans (Imbrie *et al.*, 1984).

Using the above rationale, a stratigraphy of the Pleistocene was developed by Emiliani (1955), who subdivided the foraminifera oxygen isotope record into "stages" to establish a standard nomenclature. The $^{18}\text{O}/^{16}\text{O}$ ratio of a sample was expressed relative to the $^{18}\text{O}/^{16}\text{O}$ of a fixed standard ($\delta^{18}\text{O}$, Eqn A.2.2) and the negative isotopic excursions (i.e. lighter - less ^{18}O compared with ^{16}O) of the interglacial stages were designated odd numbers (starting with 1 to represent the present interglacial stage) and the positive isotopic excursions (i.e. heavier - more ^{18}O compared with ^{16}O) of the glacial stages were given even numbers (Emiliani, 1955). More recently, a direct link between the climatic effects on isotopic variations and the Earth's orbital changes, explained by the Milankovitch theory, has been suggested (Emiliani and Shackleton, 1974).

Measurement of the foraminifera oxygen isotope record in cores from many sites in the world's oceans has resulted in the correlation and stacking of such records and the construction of the SPECMAP age model (Imbrie *et al.*, 1984). By comparison of the $\delta^{18}\text{O}$ curve for the piston cores in this study with the SPECMAP reference $\delta^{18}\text{O}$ curve and using the stage boundary ages of Martinson *et al.* (1987), it may be possible to create age models for cores CD38-09, CD38-10, CD38-02 and CD38-11 which designate particular sediment depth horizons in each core to particular glacial or interglacial periods.

2.3.2. Methods and results of foraminifera stable isotope analysis

Foraminifera samples were picked from sieved-sediment samples ($> 63\mu\text{m}$) for cores CD38-09, CD38-10, CD38-02 and CD38-11. The oxygen ($\delta^{18}\text{O}$) and carbon ($\delta^{13}\text{C}$) isotopic composition of the carbonate shells was then analysed using mass spectrometry at the Scottish Universities Research and Reactor Centre (Appendix A.2). Benthic foraminifera were used because these were found to be consistently more abundant than the planktonic foraminifera, especially in the two shallow-water cores.

For cores CD38-09 and CD38-10 the species *Bolivina seminuda* was analysed but because of the low carbonate content of these cores, it was impossible in some regions of the core to pick enough of these very light (approx. $3\mu\text{g}$, Heinze and Wefer, 1992) foraminifera and so there are gaps in the oxygen and carbon isotope records. For cores CD38-02 and CD38-11 specimens of the genus *Uvigerina* were picked and analysed. The results of all the isotopic determinations can be found in Appendix C.2.

Figures 2.7 and 2.8 display the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotopic records respectively for the four piston cores. These profiles highlight the isotopic differences between the two infaunal groups of foraminifera, *Uvigerina* and *B. seminuda*, which are the result of species-vital effects (Corliss and Chen, 1988; McCorkle *et al.*, 1990). The down-core profiles show that for core CD38-09 the isotope record is incomplete and the signal is very erratic. This is due to the fact that large areas of the core contained very low concentrations of foraminifera shells and even in the samples from which *B. seminuda* were picked and analysed there were not enough specimens to run duplicate samples where necessary. It is therefore impossible to make any sensible interpretations of the oxygen isotope stratigraphy of core CD38-09.

Although the oxygen isotope record of core CD38-10 (Fig. 2.7) looks fairly continuous, there is a problem in interpreting the $\delta^{18}\text{O}$ signal in terms of designating specific glacial or interglacial periods. As will be discussed in full in Chapter 4, there is a large zone between 80 and 110cm which represents a period of sediment erosion (and possibly another zone lies at about 500cm). This means that the sedimentation history at this shallow-water site has been non-continuous and it is impossible to accurately state how much of the sediment column has been lost by erosion. It may be interpreted, for example, that the region in core CD38-10 from 500 to 550cm represents an interglacial period (more negative $\delta^{18}\text{O}$) and that below 600cm to the base of the core represents a glacial stage (more positive $\delta^{18}\text{O}$). However, because it is unknown how much sediment has been lost in the upper metres of the core, it is impossible to decide whether the above regions represent stages 5 and 6 respectively or stages 7 and 8 or are perhaps even older in age. For this reason core CD38-10 cannot be used for oxygen isotope age modelling.

Throughout the rest of this thesis, cores CD38-09 and CD38-10 will always have their down-core profiles plotted against depth (cm) instead of age (ka). It should be mentioned at this point that the ODP hole 680B, which is situated very close to core CD38-10 (Chapter 1), has been dated by Heinze and Wefer (1992) using only the oxygen isotope stratigraphy of the *B. seminuda* record by comparison with the SPECMAP $\delta^{18}\text{O}$ curve of Imbrie *et al.* (1984). However, Heinze and Wefer (1992) failed to take into account the many erosion horizons (shown as phosphate zones in their Fig. 6b) which are bound to distort their simple age model. It is for this reason that the $\delta^{18}\text{O}$ curve of core CD38-10 (Fig. 2.7) has not been compared with that of ODP hole 680B.

The down-core profiles of the oxygen isotope ratio ($\delta^{18}\text{O}$) shown in Fig. 2.7 for cores CD38-02 and CD38-11 do show a continuous and varying pattern associated with the Late Quaternary glacial/interglacial changes of the $\delta^{18}\text{O}$ ratio in sea-water

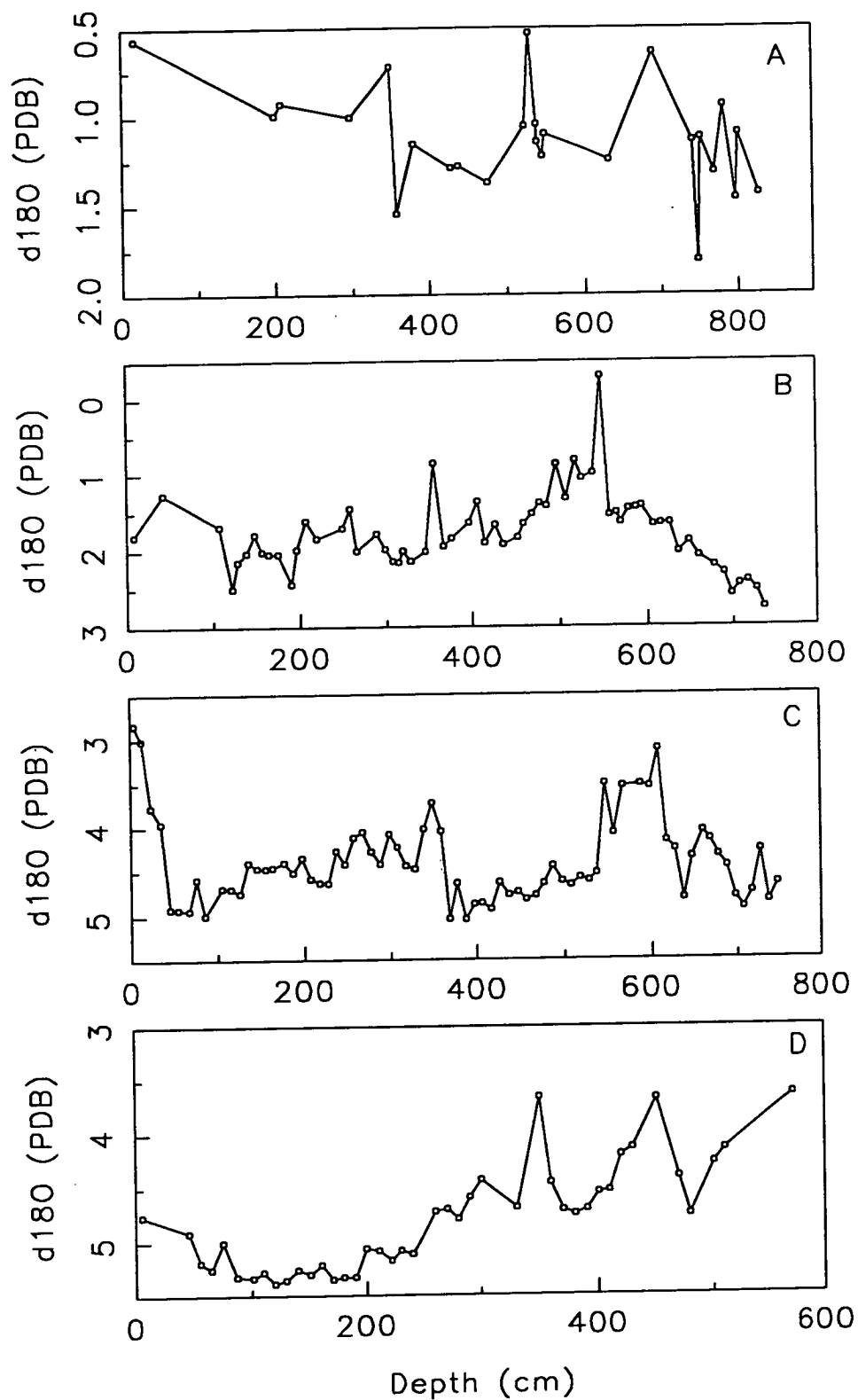


Figure 2.7. Oxygen isotopic composition of foraminifera (expressed as $\delta^{18}\text{O}$ ‰ relative to PDB standard) against depth (cm); A) CD38-09 and B) CD38-10 using *Bolivina seminuda*, C) CD38-02 and D) CD38-11 using *Uvigerina*.

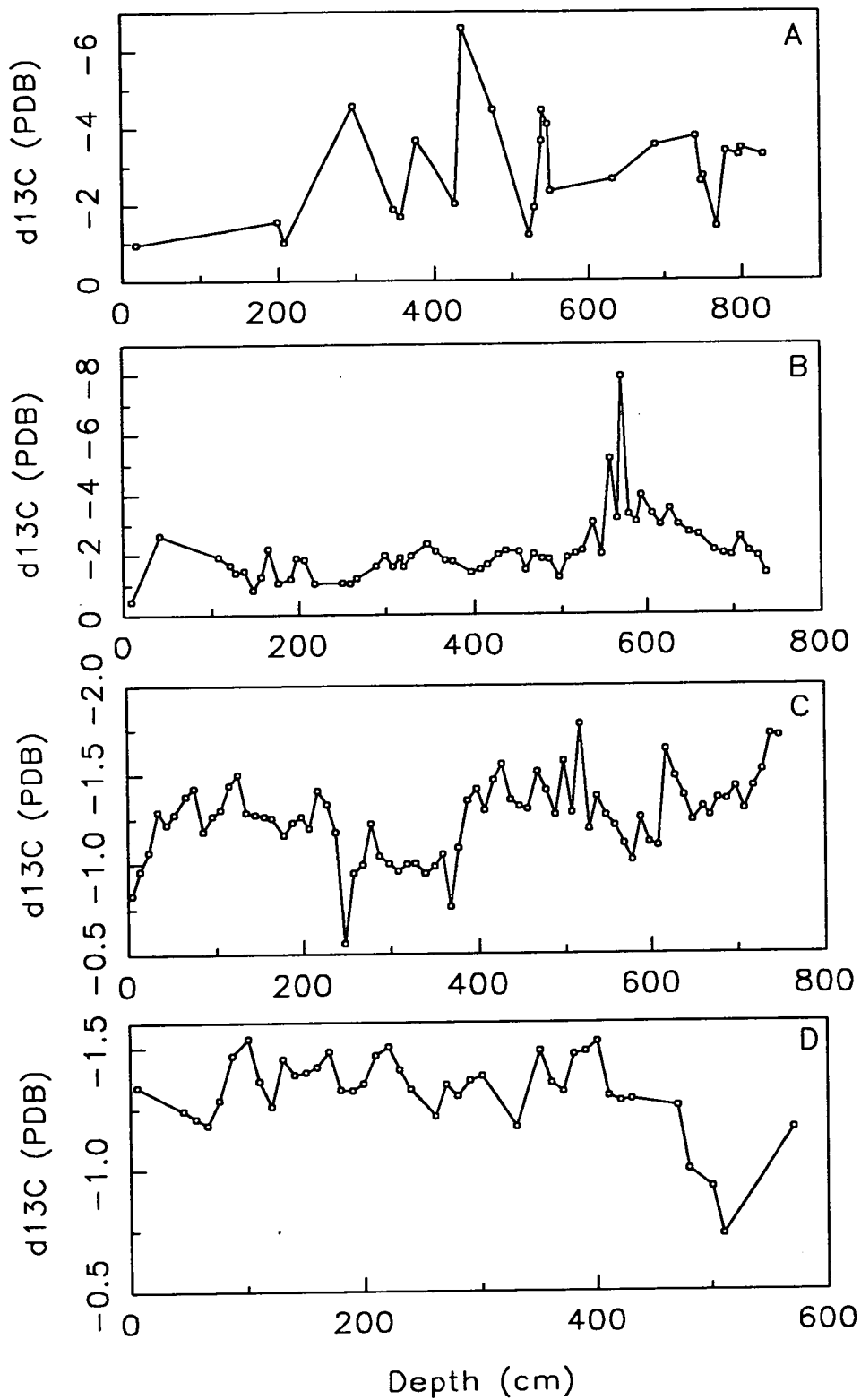


Figure 2.8. Carbon isotopic composition of foraminifera (expressed as $\delta^{13}\text{C}$ ‰ relative to PDB standard) against depth (cm); A) CD38-09 and B) CD38-10 using *Bolivina seminuda*, C) CD38-02 and D) CD38-11 using *Uvigerina*.

(Imbrie *et al.*, 1984). The only region where there is a significant gap is in core CD38-11 between 4 and 24cm, which is thought to be a turbidite deposit (6.2.2) and contains few foraminifera shells.

It is important to note that the profiles in Fig. 2.7 are plotted with the $\delta^{18}\text{O}$ axis reading from isotopically heavier $\delta^{18}\text{O}$ values at the bottom up to isotopically lighter $\delta^{18}\text{O}$ values at the top. This is to allow for easy comparison with the stacked SPECMAP $\delta^{18}\text{O}$ curve as shown in Fig. 8 of Imbrie *et al.* (1984) and with the plots of Ba/Al for the Peruvian piston cores (6.3.2, Fig. 6.8).

Along with the oxygen isotopic measurements made by mass spectrometry of foraminifera, the two isotopes of carbon, ^{12}C and ^{13}C , are also measured (Appendix A.2) and from these results a carbon isotopic signal, $\delta^{13}\text{C}$, can be plotted for each core (Fig. 2.8). As with oxygen isotopes, foraminifera microfossils can record the $\delta^{13}\text{C}$ ratio of the surrounding water (bottom-water, in the case of benthic foraminifera) in their carbonate shells. According to Berger and Vincent (1986), long-period signals reflect global fractionation of carbon isotopes (which changes with respect to the changes in the carbon reservoir in the oceans) whereas short-term variations are due to regional and internal factors (water-mass circulation, organism-specific vital effects and/or ocean temperature gradients). Carbon isotopes are difficult to use for stratigraphic interpretations and will not be discussed in detail in this thesis. More detailed work on foraminifera carbon isotopes in these cores is being carried out by S. King at the University of Southampton (1.5). The only interesting feature of the $\delta^{13}\text{C}$ profiles (Fig. 2.8) is that in cores CD38-02 and CD38-11 variation tends to mirror the $\delta^{18}\text{O}$ signal (Fig. 2.7). However, this inverse relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, as was seen by Dunbar and Wefer (1984) in Peru margin core tops, is not apparent in core CD38-10 where the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ curves seem to run parallel.

The contrast in the dynamic range of down-core $\delta^{13}\text{C}$ values between cores CD38-09 and CD38-10 (about 8 ‰) and cores CD38-02 and CD38-11 (only 1.5 ‰) can be explained either by species vital-effect differences between *B. seminuda* and *Uvigerina* respectively (McCorkle *et al.*, 1990) or by the fact that the down-core variation in the former cores is a result of diagenetic overprinting. Whereas in the latter cores it is a result of fluctuations in the chemical composition of the bottom-water masses which varies due to changes in the pattern of water mass circulation during glacial/interglacial periodicity.

2.3.3. Comparison of the $\delta^{18}\text{O}$ curves for cores CD38-02 and CD38-11 with the SPECMAP record

The method employed for generating an age model for cores CD38-02 and CD38-11 simply involves direct comparison of the peaks and troughs in the $\delta^{18}\text{O}$ curve (Fig. 2.7) with those of the SPECMAP record (Imbrie *et al.*, 1984). There is a noticeable scale difference in the $\delta^{18}\text{O}$ signal between the two Peruvian cores and the SPECMAP record which is caused by the compositional differences between benthic foraminifera in the former cores and planktonic foraminifera in the latter. Control points were designated in both cores which corresponded to the calculated ages of the SPECMAP $\delta^{18}\text{O}$ curve and these are summarised in Table 2.1.

SPECMAP age (ka)	Stage	CD38-02 (cm)	CD38-11 (cm)	SPECMAP age (ka)	Stage	CD38-02 (cm)
12.0	1	35	66	152.0	6	388
18.0	2	67	88	170.0	6	488
24.5	3	86	121	195.0	7a	547
54.0	3	198	261	216.0	7c	608
64.0	4	228	331	238.0	7e	660
80.0	5a	268	351	250.0	8	708
86.0	5b	288	381	258.0	8	728
100.0	5c	299	451	266.0	8	748*
110.0	5d	329	481			
122.0	5e	349	571*			

Table 2.1. SPECMAP control ages (Imbrie *et al.*, 1984) and corresponding depths in core CD38-02 and CD38-11. The base of each core is indicated by *.

Between each control point, it is assumed that the sediment has accumulated at a constant sediment accumulation rate (SAR) and therefore each of the sieved-sediment subsamples can be assigned an age. Figure 2.9 displays the $\delta^{18}\text{O}$ record for cores CD38-02 and CD38-11 plotted against age (ka) along with the SPECMAP profile for comparison.

Finally, the stage boundary ages of Martinson *et al.* (1987) were used to define the depths in both cores at which the sediment changes from accumulation during a glacial period to accumulation during an interglacial period, or vice versa (Table 2.1).

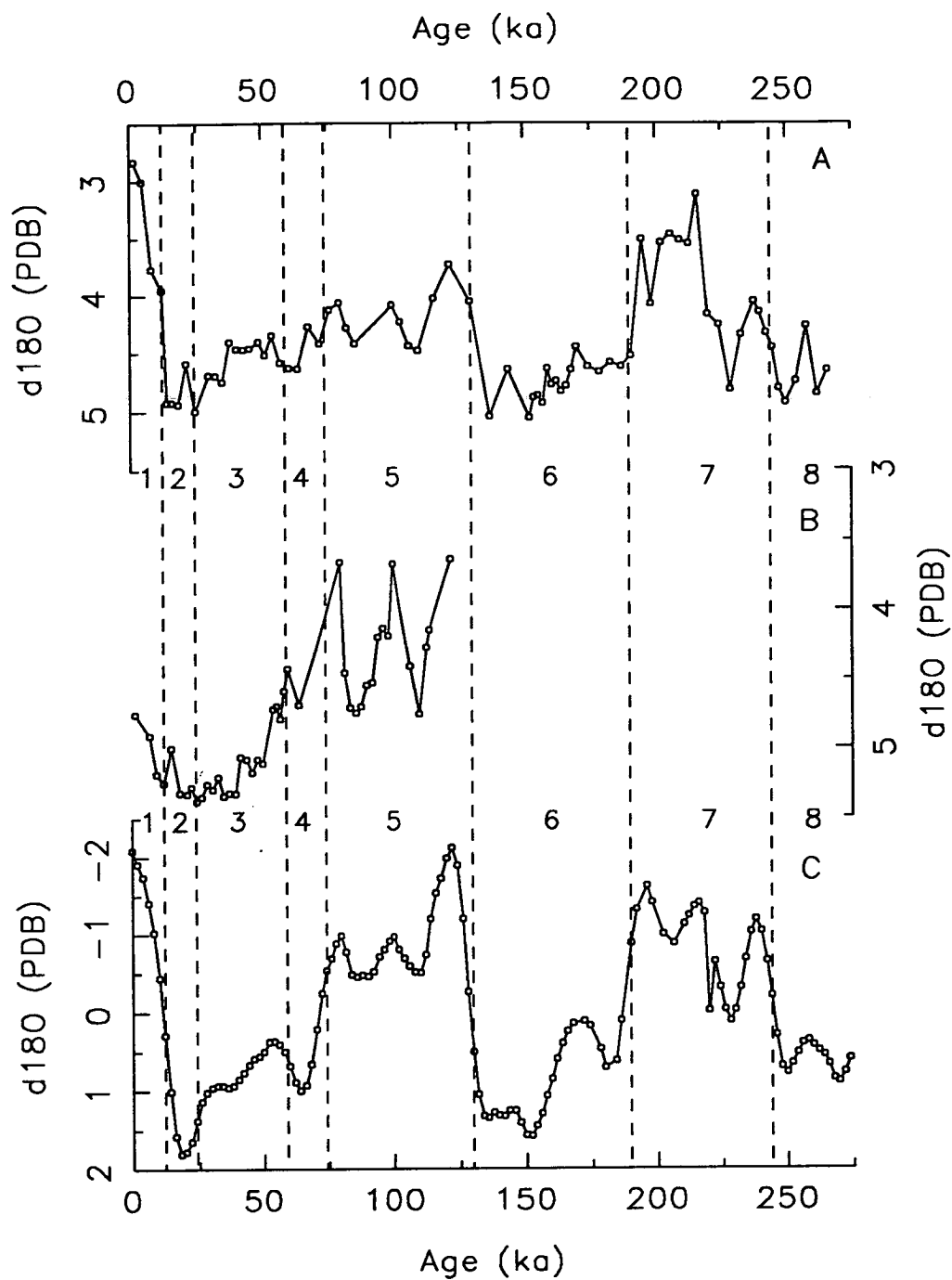


Figure 2.9. Oxygen isotopic composition of foraminifera (expressed as $\delta^{18}\text{O}$ ‰ relative to PDB standard) against age (ka); A) CD38-02 and B) CD38-11 using *Uvigerina* and C) SPECMAP planktonic reference curve (Imbrie *et al.*, 1984). Stage boundary ages from Martinson *et al.* (1987).

From this the age models, shown in Table 2.2, were constructed for cores CD38-02 and CD38-11.

Stage	Boundary Age (ka)	CD38-02 (2525m)		CD38-11 (3835m)	
		Depth (cm)	SAR (cm kyr ⁻¹)	Depth (cm)	SAR (cm kyr ⁻¹)
1			2.90		3.73
	12.05	35		65	
2			4.15		4.56
	24.11	85		120	
3			3.59		5.02
	58.96	210		295	
4			3.01		3.01
	73.91	255		340	
5			1.88		4.80
	129.8	360			
6			2.93		
	189.6	535			
7			2.66		
	244.1	680			
8			3.12		

Table 2.2. Age models for cores CD38-02 and CD38-11. Stage boundary ages are from Martinson *et al.* (1987). Core CD38-11 contains a 20cm turbidite zone within stage 1 and therefore the SAR = 45cm/12.05 kyr.

2.4. SEDIMENT ACCUMULATION RATES AND MASS ACCUMULATION RATES

2.4.1. Introduction

One problem that arises from carrying out a geochemical, marine sediment study using bulk-sediment samples is that the sieved-sediment samples (from which the $\delta^{18}\text{O}$ foraminifera record was obtained) and the bulk-sediment samples (from which all geochemical data are obtained) are taken from different depths down each core. The age models for cores CD38-02 and CD38-11 (Table 2.2) therefore need to be used to calculate the age of each bulk-sediment sample before the mass accumulation rate can be calculated. Sediment accumulation rate (SAR) and mass

accumulation rate (MAR) are used throughout this thesis and can be defined as follows. SAR is the depth rate at which the total sediment is accumulating (measured in cm kyr^{-1}) and MAR is the weight of sediment accumulating in a specific area over time (measured in $\text{g cm}^{-2} \text{kyr}^{-1}$).

2.4.2. Description and use of age model for core CD38-02

The proposed age model for core CD38-02, which is located at a water depth of 2525m on the Nazca ridge, is summarised in Table 2.2. The core is 750cm long and corresponds to continuous sedimentation (but not at a constant SAR) from the present Holocene (stage 1) at the top of the core, back down to glacial stage 8 at the base (270ka).

The sediment accumulation rates for each stage were calculated by simply taking the depth (cm) for a particular stage (e.g. stage 5 = 360cm to 255cm = 105cm depth) and dividing by the corresponding time interval (e.g. stage 5 = 129.8ka to 73.9ka = 55.9kyr); this assumes a constant rate of sediment accumulation for each individual stage. The SARs for core CD38-02 (Table 2.2) display a pattern whereby the glacial stage (even number) SAR is greater than the interglacial stage (odd number) SAR on either side of it. The only exception to this is that stage 3 has a greater SAR than stage 4. The above SAR pattern is to be expected in a core situated on or near a continental margin because the glacial stages are periods when more arid climatic conditions affected the continent, allowing for greater weathering and erosion of the land and, in turn, increasing the terrigenous input to marine sediments (Boyle, 1983; Sarnthein *et al.*, 1988; Patience, 1992). The highest SAR in core CD38-02 is seen during stage 2 (4.15 cm kyr^{-1}) during which time the Last Glacial Maximum occurred. The lowest SAR occurs in stage 5 (1.88 cm kyr^{-1}) which is the interglacial stage when climate conditions were most similar to the present day.

Using the proposed age model for core CD38-02 the age of each bulk-sediment sample was calculated (Appendix C.3) and it is these ages that the geochemical data presented for CD38-02 are plotted against throughout the rest of this thesis (e.g. Fig. 6.4).

There is one final physical property for core CD38-02 that can be calculated and that is the mass accumulation rate (MAR). This requires knowledge of the SARs, from the proposed age model (Table 2.2), and the dry bulk density, from the measured water content (Eqn 2.4), and uses the relationship shown in Eqn 2.5.

Equation 2.5. Calculation of mass accumulation rate (MAR)

$$\text{MAR (g cm}^{-2} \text{ kyr}^{-1}) = \text{SAR (cm kyr}^{-1}) \times \text{D.B.D. (g cm}^{-2})$$

Figure 2.10 displays both the SAR and MAR for core CD38-02 plotted against age and from the down-core profiles, the glacial/interglacial cyclicity pattern of sedimentation can be easily seen. The MAR will be used later in this thesis to examine terrigenous and biogenic fluxes to the sediment (Chapter 7).

2.4.3. Description and use of age model for core CD38-11

The proposed age model for core CD38-11, located at a water depth of 3835m on the lower slope of the Peruvian continental margin (Table 2.2) corresponds to continuous sedimentation (including the 20cm turbidite zone contained within stage 1) from the present Holocene back to interglacial stage 5 at the base of the core (575cm). It should be noted that the amplitude of the isotopically-light, surficial sample (i.e. most recent in age) does not match that of the samples in stage 5 (as seen in core CD38-02, Fig. 2.9) which may imply that some of the true surface sediment of core CD38-11 has been lost during the coring process (Imbrie *et al.*, 1984).

The sediment accumulation rates for each stage in this core were calculated in exactly the same manner as for core CD38-02 in the above subsection and are listed within Table 2.2. The SAR pattern for CD38-11 (Fig. 2.10) contrasts to that of CD38-02 in that the highest SAR is seen in interglacial stage 3 (5.02 cm kyr⁻¹) and stage 5 has a much higher SAR than stage 4 (4.80 cm kyr⁻¹ compared with 3.01 cm kyr⁻¹). The differences between the SARs of cores CD38-02 and CD38-11 are represented graphically in Fig. 2.11. From this simple plot of depth (cm) against age (ka) for both cores it can be seen that within the last few glacial/interglacial periods of the Late Quaternary, CD38-11 has continuously been a site of faster rates of sediment accumulation than the site of core CD38-02. This is due to the fact that the continental slope at site CD38-11 receives a higher input of both terrigenous material from the nearby South American landmass (7.2.3) and biogenic material from the coastal upwelling zone (7.3.3) compared with the Nazca ridge at site CD38-02.

The SAR pattern of core CD38-11 does not conform to the hypothesis (used for CD38-02) that more arid continental conditions during glacial periods will increase the terrigenous input to continental margin marine sediments. This suggests that for core CD38-11 either the stage boundary depths have been incorrectly

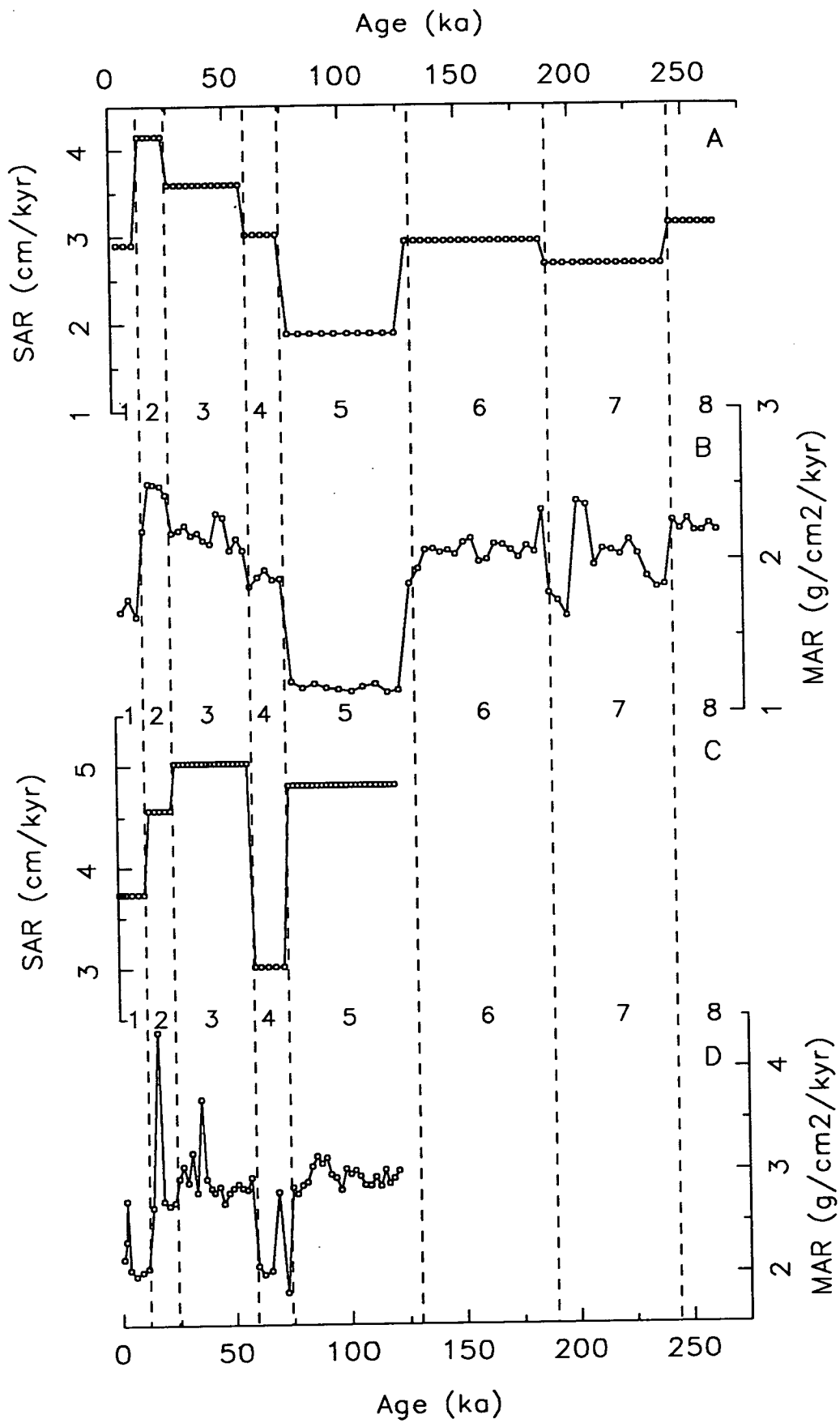


Figure 2.10. Sediment accumulation rate (cm kyr^{-1}) and mass accumulation rate ($\text{g cm}^{-2} \text{ kyr}^{-1}$) profiles against age (ka) for cores CD38-02 (A and B) and CD38-11 (C and D).

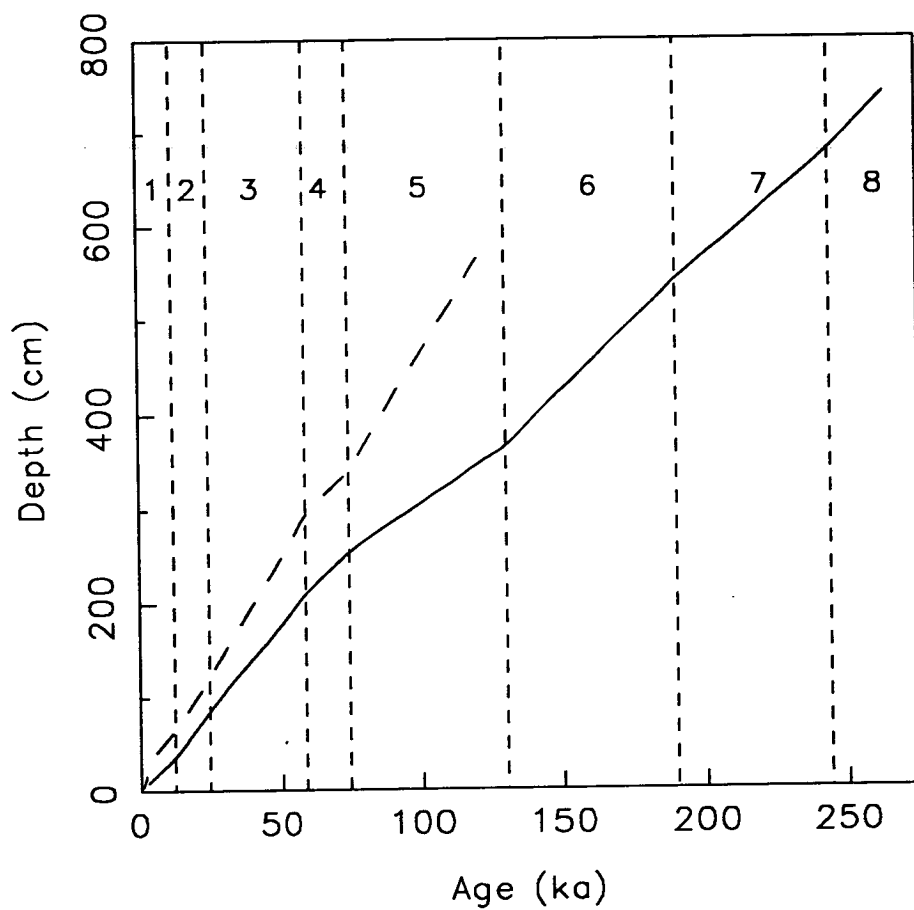


Figure 2.11. Depth (cm) against age (ka) graphic representation of the contrasting sediment accumulation rates for cores CD38-02 (full line) and CD38-11 (dotted line).

designated or, more likely, that higher interglacial biogenic input at this site (6.3.3 and 6.3.4) is controlling the SAR pattern.

The proposed age model for core CD38-11 was then used to convert the depths of each geochemical, bulk-sediment sample from depth (cm) to age (ka) and it is these ages (Appendix C.3) that the geochemical data for this core are plotted against throughout the rest of this thesis.

Finally, as for core CD38-02 above (2.4.2) the mass accumulation rate of each bulk-sediment sample in core CD38-11 was calculated using Eqn 2.5. The down-core profile of MAR for CD38-11 is displayed in Fig. 2.10 and ranges from 2 to 4.5 g cm⁻² kyr⁻¹. These values can then be used in the calculation of fluxes of various geochemical components.

2.5. CONCLUSIONS

This chapter has involved a brief study of some of the physical and geochronological properties of the marine sediments from the Peruvian continental margin. It has yielded vital information contained within the box and piston cores under study; which is needed to allow for the correct and full interpretation of the geochemical data presented in the chapters which follow.

Of most importance has been the calculation of the salt content of each sample, which is used to correct the raw geochemical data*, and the age modelling from the oxygen isotopic composition of foraminifera microfossils. It is unfortunate that the shallow water cores, CD38-09 and CD38-10, were not suitable for precise age modelling because geochemical data plotted on a time scale rather than a depth scale are generally much more meaningful in terms of the interpretation of glacial/interglacial climatic and environmental changes. However, it must be stressed again that throughout this thesis the graphic representations of all geochemical data will be plotted against age (ka) for piston cores CD38-02 and CD38-11 only, and that the other piston cores, CD38-09 and CD38-10, and the two box cores, CD38-02 and CD38-03, will be plotted against depth (cm).

*All geochemical data presented in the following chapters have been corrected to salt-free concentrations (Appendix A.6).

CHAPTER 3

THE SEDIMENT RECORD OF COASTAL UPWELLING

3.1. INTRODUCTION

"No waters in the ocean so teem with life as those
on the west coast of South America."

Buchanan (1886)

3.1.1. Physical oceanography

The physical hydrography of the Pacific Ocean off the coast of Peru is the dominant influence in determining the chemistry and biology of the near-shore waters and hence the geochemistry of the sediments accumulating below.

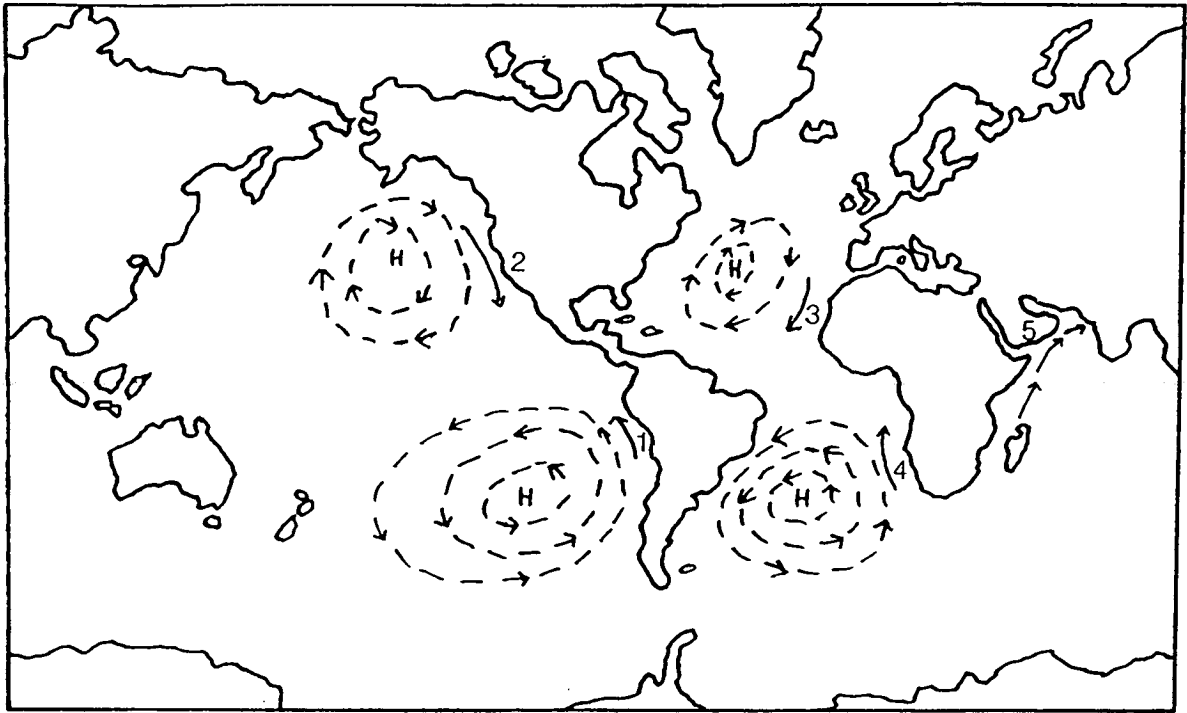
Surface winds controlled by the Earth's weather system, move around high pressure cells over the oceans (clockwise in the northern hemisphere and anti-clockwise in the southern) and therefore the western coastlines of the continental land masses experience prevailing winds which sweep along-shore and toward the equator (Fig. 3.1).

The Coriolis force of these winds deflects the oceanic surface waters (upper 20-30m, Brink *et al.*, 1983; Smith, 1983) off-shore, in a direction determined by the Earth's rotation and the forces of internal fluid friction; a physical process named after the Swedish oceanographer, Vagn Ekman. The angle of deflection, which is about 45° at the surface, increases with depth but the force of the current decreases (Ekman, 1905). This Ekman transport forces colder water from depth (between 70 and 133m, Gunther, 1936; Zuta *et al.*, 1978) to move upward and replace the warmer surface waters (Fig. 3.2). It is this process which is known as **coastal upwelling**.

There are five important oceanic sites where coastal upwelling has been reported to be occurring at present (Diester-Haass, 1978; Hartline, 1980; Thiede and Suess, 1983). These are off Peru-Chile and Oregon-California in the Pacific, off north-west Africa and south-west Africa (Namibia) in the Atlantic and off Somalia-Oman in the Indian Ocean (Fig. 3.1). The latter is at an eastern continental margin rather than the more usual western margin, where upwelling is induced by the southwest monsoon.

Upwelling also occurs along the equatorial and southern divergence zones and, although these too are important areas in the world's oceans, they will not be discussed further in this thesis.

The simple two dimensional model described above is useful to explain the basic concept of coastal upwelling but the actual process is vastly complicated by



1: Peru-Chile 2: Oregon-California 3: NW Africa

4: SW Africa 5: Somalia-Oman

H: High pressure cells

Figure 3.1. World map showing the major zones of coastal upwelling and the wind systems which drive them (adapted from Hartline, 1980).

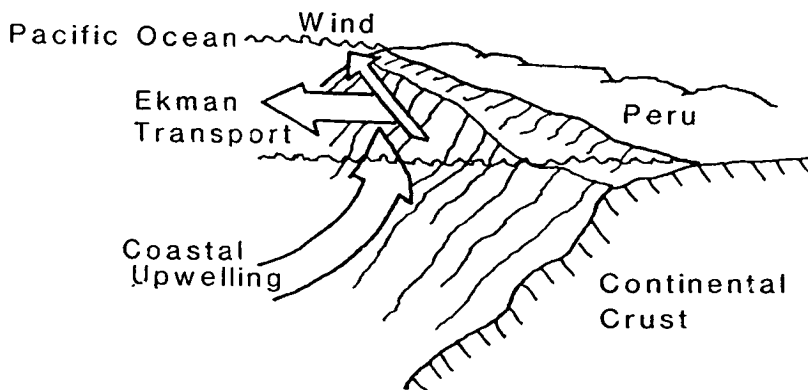


Figure 3.2. Diagram of the processes involved in coastal upwelling .

Along-shore wind stress forces off-shore Ekman transport of the surface water, which is replaced by upwelling of deeper water.

three dimensional sea-floor topography and coastal geometry (Hurlburt, 1974) and by ocean currents and wind fields which can vary both temporally and spatially.

Coastal upwelling off the Peru-Chile continental margin is intense and persistent, and has operated since at least the late Miocene (Schrader, 1992). However, large seasonal and latitudinal variations in the strength of modern-day upwelling have been measured (Zuta *et al.*, 1978). The prevailing wind is the southeasterly trade wind which was measured at 15°S as having a mean direction of $163 \pm 16^\circ$ and speed of 4.6ms^{-1} (Burt *et al.*, 1973). Sea surface temperature mapping in the area highlights the upwelling of colder water near-shore (approx. 17°C compared with $20\text{-}23^\circ\text{C}$ off-shore) and cold patches indicate zones of intense upwelling within the large-scale area of coastal upwelling (between 5 and 20°S). Measurement of seasonal variation shows that these temperatures reduce to a minimum from June to October (the southern hemisphere's winter and spring) which coincides with the strongest winds and most intense upwelling period (Zuta *et al.*, 1978).

The actual size of the coastal upwelling zone at the Peru-Chile margin and the volume of upwelled water can vary depending on the parameters used to measure these quantities. Busch and Keller (1983) quote a distance of 50km off-shore within which coastal upwelling occurs off Peru north of 20°S. Barber and Smith (1981) limited the off-shore dimension of upwelling to the Rossby radius of deformation, a function of the Coriolis force, which varies latitudinally from 270km at 4°S down to 60km at 18°S. This distance can then be used to calculate an upwelling area of $1.82 \times 10^{11} \text{m}^2$ (Chavez and Barber, 1987). However, Smith (1983) gives a Rossby radius of only 20km which would substantially reduce the calculated area of the Peruvian upwelling zone. Estimations of the upward flow of water across the 100m water depth level are about $10^4 \text{m}^3 \text{year}^{-1}$ (Wyrki, 1963) for any point along the coastal region from 6 to 24°S.

Coastal upwelling is not the only water movement that occurs in this area of the Pacific Ocean. The main current on the continental margin, which flows opposite in direction to the surface waters, is the Peru poleward undercurrent (Smith, 1983; Huyer *et al.*, 1991). Brockmann *et al.* (1980) measured this current along the Peru coast from 5 to 15°S at various water depths and concluded that the maximum poleward flow was at about 100m and that it was stronger and more persistent to the north. A study of undercurrent variability by Huyer *et al.* (1991) at 10°S found a well-defined core at 150m, where the (100 day) mean speed was 0.1ms^{-1} with a maximum of 0.25ms^{-1} . It is this undercurrent which supplies the water for upwelling along the

continental margin (Fig. 3.3.).

3.1.2. Nutrients, biomass and organic matter flux

Sea-water contains many dissolved chemical components, some of which are required by marine phytoplankton (microscopic plants) for their growth within the euphotic zone (the surface waters which receive enough sunlight for photosynthesis to occur). These nutrients, principally the silicate, nitrate and phosphate anions, soon get depleted and unless the supplies are replenished, the phytoplankton community will die off. It is because the cold, upwelled water brings with it a fresh supply of nutrients, to replace the nutrient-depleted water pushed off-shore, that coastal upwelling zones are important sites for high and sustainable levels of primary productivity. It should be noted that the relationships between upwelling intensity, euphotic zone nutrient concentrations and biological primary productivity are non-linear (Codispoti, 1983).

Measurements of primary productivity have been published from many studies off Peru and the range of $1.24\text{-}6.26 \text{ g C m}^{-2} \text{ day}^{-1}$ (Ryther, 1969; Chavez and Barber, 1987) is over an order of magnitude greater than normal ocean surface waters ($0.1\text{-}0.2 \text{ g C m}^{-2} \text{ day}^{-1}$; Henrichs and Farrington, 1984). Figure 3.4 illustrates this feature as a high productivity belt along the Peru margin. Conversion of mean primary productivity estimations to a total carbon weight utilised in photosynthesis over the entire coastal zone, gives a value of $1.52 \times 10^{14} \text{ g C year}^{-1}$ (Chavez and Barber, 1987). Brink *et al.* (1983) measured the mixed layer depth off Peru as less than 20m, shallower than the photic zone, and concluded that productivity was not light-limited; this implies nutrient-limitation.

Diatoms are dominant in the phytoplankton community off Peru (De Mendiola, 1981) with a maximum number measured in shallow water stations at 9°S of 195 million cells m^{-3} (Semina, 1971). This is at least 10,000 times greater than the average for ocean surface waters.

The marine phytoplankton are eaten by zooplankton, which in turn are eaten by fish and other marine animals. This results in a greatly enhanced food chain and the coastal waters therefore "teem with life". In fact, the fish stock of the southern anchovy (*Engraulis ringens*) along the Peruvian coast is so high that the anchovy fishery is one of the world's largest (Ryther, 1969; Walsh, 1975 and 1981; Hartline, 1980). The proportion of fish that are not caught and consumed by humans, die along with the rest of the marine biomass, and sink through the water column. Most of this

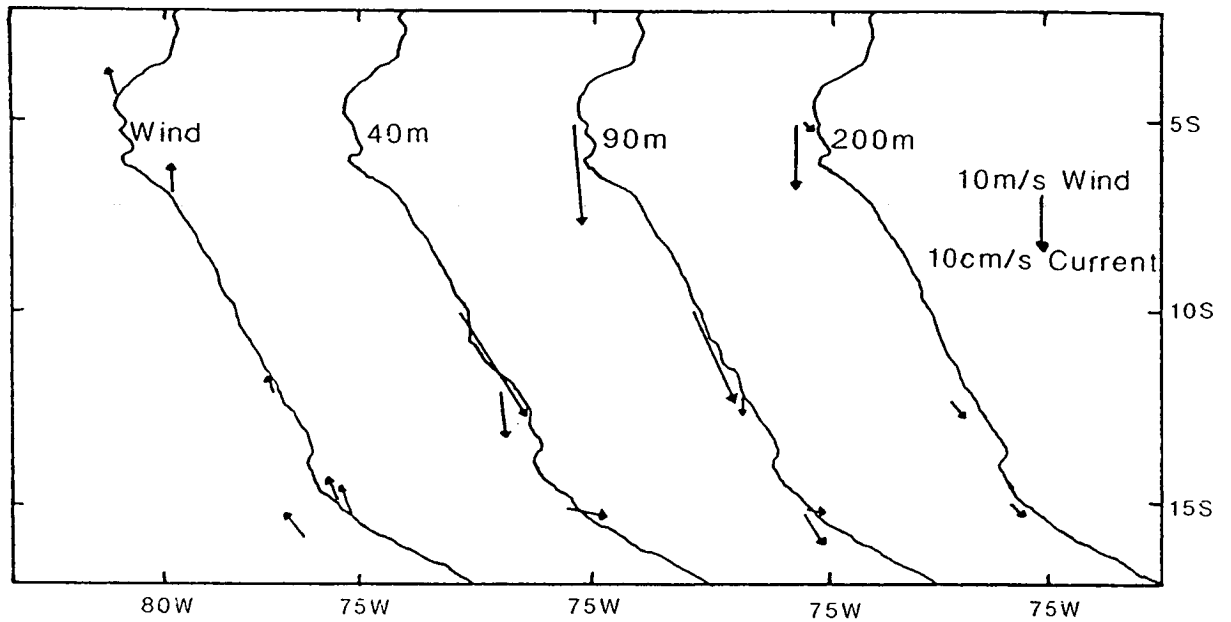


Figure 3.3. Wind and current vectors, at 40, 90 and 200m, along the Peru coast (adapted from Brockmann *et al.*, 1980) illustrating the equatorward wind direction and the poleward undercurrent.

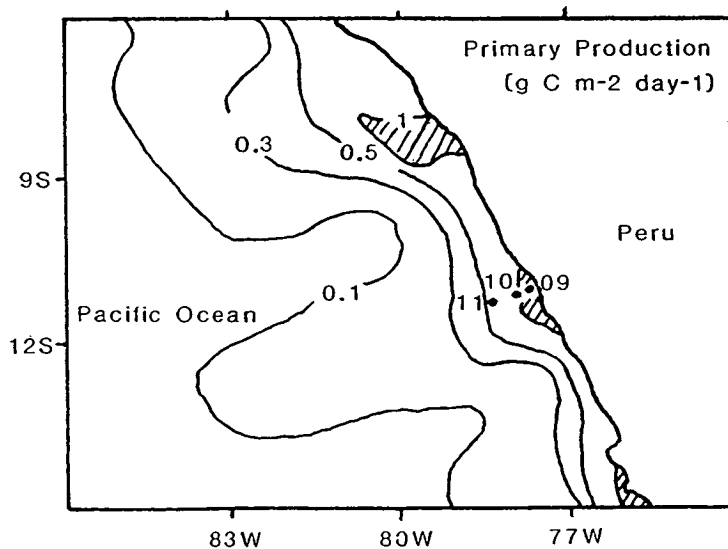


Figure 3.4. Primary productivity ($\text{g C m}^{-2} \text{ day}^{-1}$) map of the Peru coastal upwelling zone. Note the position of core sites CD38-09, CD38-10 and CD38-11 (adapted from Suess *et al.*, 1988).

organic matter is either eaten by other marine organisms or undergoes bacterial decomposition (Baturin, 1982; Henrichs and Farrington, 1984) and there is therefore a recycling of the important nutrients, which are released and dissolved back into the water.

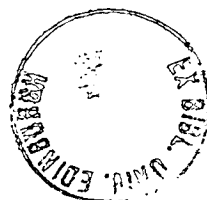
The overall coastal water circulation pattern actually helps to recycle both the nutrients and any phytoplankton communities in a conveyor-belt-like system. Movement off-shore and equatorward by Ekman transport is followed by sinking out of the surface layer. Then the poleward undercurrent acts as the lower part of the conveyor-belt and moves the water back to the zone where upwelling occurs (Brink *et al.*, 1983). This recycling is important in maintaining intense biological productivity in certain centres throughout the Peruvian upwelling margin.

Baturin (1982) stated that only about 0.5% of organic matter does not decompose before deposition in the accumulating sediment but more recent work using sediment traps by Martin *et al.* (1987) as part of the VERTEX experiment, measured the organic carbon flux as it decreases with depth and calculated the increasing percentage regeneration of organic matter down the water column. More than 50% of the original organic matter will still be present at water depths < 300m but by the time the organic matter has sunk to the deep ocean (3000-5000m) less than 5% will remain (Martin *et al.*, 1987). Therefore, the flux of organic matter to the sediment under a zone of coastal upwelling will be much greater than in the open ocean because (a) the surface productivity is greatly enhanced and (b) the water depth to the continental shelf and slope is comparatively shallow.

The data set used by Martin *et al.* (1987) uses the 100m sediment trap as the starting flux, indicative of "new production" sinking down below the euphotic zone. Henrichs and Farrington (1984) however, used sediment traps off Peru at 50m water depth and measured the average downward particulate organic carbon flux as 250mg C m⁻² day⁻¹, which was only 6% of the surface primary productivity. The enhanced marine biomass in coastal upwelling areas is, as expected, utilising most of the organic matter whilst it is still in the euphotic zone. Therefore, the new production of organic carbon [which Martin *et al.* (1987) based their cumulative regeneration calculations on] is at least 1/20th of the total primary productivity in an upwelling zone such as off Peru.

3.1.3. Sediment characteristics

The proportion of organic matter which escapes decomposition and recycling



within the water column, will reach the sea-floor and be incorporated in the accumulating sediments (Baturin, 1982). Organic carbon (C_{org}) rich sediments found on a continental shelf or slope are, therefore, a good indication of accumulation under an upwelling zone (Diester-Haass, 1978; Calvert, 1987). Calvert and Price (1970) measured concentrations up to 26 wt.% C_{org} in muddy sediments off Walvis Bay, S.W.Africa, and a study of the spatial patterns of accumulation of organic matter on the Peru margin (Reimers and Suess, 1983A) showed two maxima areas with levels >10 wt.% C_{org} located within the upper slope muds between 11 and 14°S. Busch and Keller (1981) concluded that it was the high organic matter content on the Peru slope that strongly affected the physical properties of the sediment. The mud lens sediments, with up to 20 wt.% C_{org} , were anomalously fine-grained with high water content and plasticity and low grain specific gravity.

An oxygen-minimum zone (OMZ) is an area within the water column where the dissolved oxygen levels are reduced below 0.2 ml l⁻¹ by the respiration of bottom water zooplankton and bacteria as they decompose the rain of organic matter falling through the water column. Under the Peruvian upwelling system, an OMZ lies between 100 and 500m and where this meets the continental slope the sediments accumulate under suboxic to anoxic conditions (Veeh et al., 1973; Burnett *et al.*, 1980). This impingement of the OMZ was originally thought to enhance the preservation of organic matter within the sediments (Müller and Suess, 1979; Demaison et al., 1984). However, this view is not taken by Calvert (1987) and Pedersen et al. (1992) who saw no relationship between the strong OMZ off Oman and well-preserved organic matter in the sediments below. Calvert and Pedersen (1992) have suggested that it is the settling flux of organic matter, dependant on the surface productivity, that controls the accumulation of organic-rich marine sediments. The preservation versus productivity question will be dealt with in more detail in Chapter 7.

Organic matter is not the only biological product of coastal upwelling which can be incorporated into the sediment record. There are the hard skeletons and shells of marine dwellers and also their waste products.

The frustules of diatoms and radiolarians (marine plankton) are composed of silica (biogenic SiO_2), and their burial in the sediment removes the important silicate nutrient from ocean waters. DeMaster (1981) reports that the highest biogenic silica accumulation rates in the marine environment are under coastal upwelling zones (69 g SiO_2 cm⁻² ky⁻¹). Calvert and Price (1970) measured up to 85 wt.% biogenic silica in

S.W.African sediments and diatom assemblages have been used as coastal upwelling indicators off Portugal (Abrantes, 1988) and Peru (Schrader and Sorknes, 1991).

The calcium carbonate shells of foraminifera and coccoliths are another main biological component of marine sediments. The foraminifera tests have been used in a great number of studies (e.g. Thiede, 1975; Ganssen and Sarnthein, 1983; Wefer *et al.*, 1983; Dunbar and Wefer, 1984; Hermelin and Shimmield, 1990; McCorkle *et al.*, 1990) using both planktonic/benthic species variations and stable isotope chemistry to understand the coastal upwelling environment, both spatially and temporally.*

Fish debris and faecal pellets are also commonly found in continental margin sediments (Busch and Keller, 1981). Fish bones and scales have been observed in shallow-water sediments from the Peru upwelling region (Frankenberg and Menzies, 1968; Ssaidova, 1971; DeVries and Percy, 1982). Faecal pellets are important for the rapid transport of fine-grained clay particles (Scheidegger and Krissek, 1982), diatoms (Schrader, 1971) and trace metals and radionuclides (Osterberg *et al.*, 1963) onto the continental slope.

Geochemical study of the sediments accumulating on the continental margin off Peru should indicate the presence of the above biological components and illustrate any variations in the strength of coastal upwelling in the area through time.

3.2 ANALYSES AND RESULTS

3.2.1. Analytical procedures

The analytical methods used in determining the geochemical parameters described below are detailed in Appendix A. Organic carbon (C_{org}) was measured by combustion after acid digestion of carbonate carbon (Appendix A.3), biogenic silica analysis used colorimetric spectrophotometry of silica and alumina in solution after sodium carbonate leaching (Appendix A.4) and the trace elements were measured by X-ray fluorescence of pressed pellets (Appendix A.5). All analyses were carried out on the dried bulk sediment samples (Appendix A.1). The method of calculation of calcium carbonate ($CaCO_3$) levels is detailed in Appendix B.1.

*The influence of dissolution within the water column for both diatoms and forams is discussed in 7.3.3.

3.2.2. Results

The complete salt-corrected data sets for C_{org} , biogenic silica, $CaCO_3$ and the metals Mo, U, Ni, Cr, V and Cu are listed in Appendices C.10 and C.12. Table 3.1 summarises the data set, giving the range, mean and standard deviation of values for the two shallow water cores, CD38-09 and CD38-10, and gives deep-sea clay values (representative of more normal marine sediments; Turekian and Wedepohl, 1961) for comparison. There is a marked enrichment of the above biogenic indicators for both the near-shore core stations from those found in normal marine sediments, caused by the influence of coastal upwelling and increased biological productivity. The C_{org} mean concentration of 4-5 wt.% for the two near-shore cores is an order of magnitude higher than normal ocean sediments. It should be noted that large, dynamic ranges in metal concentrations are possible under these natural, non-anthropogenic conditions.

	CD38-09				CD38-10				Clay
	Min.	Max.	Mean	S.D.	Min.	Max	Mean	S.D.	Mean
C _{org}	1.6	8.3	4.4	1.45	0.8	11.9	5.4	2.02	
Bio.Sil	3.1	25.8	15.4	4.58	0.5	28.6	13.4	6.11	
CaCO ₃	0	6.6	3.4	1.71	0	26.4	8.9	6.03	
Mo	13	99	52	18.4	11	129	57	25.6	27
U	4	148	9	16.3	206	27	13	4.0	1.3
Ni	28	85	51	15.1	20	165	69	22.4	225
Cr	57	150	111	19.3	46	182	105	22.4	90
V	63	156	119	15.5	46	363	147	60.2	120
Cu	9	51	27	6.6	7	49	28	7.8	250

Table 3.1. Biogenic component and organo-metallic element concentrations. Values for C_{org} , Bio.Sil and $CaCO_3$ are in wt.%, all others are in ppm. Deep-sea clay values from Turekian and Wedepohl (1961).

Depth profiles of the three biogenic components are shown in Figs 3.5 and 3.6 and illustrate the time-varying input to the sediment possibly associated with natural fluctuations in the biological system in the water column above.

In core CD38-09, the C_{org} concentration between 300 and 500cm averages about 6 wt.%, but drops to about 3wt.% below 550cm (Fig. 3.5). The three biogenic components in core CD38-10 seem to increase from a minimum at the base of the core up to about 550cm, before dropping to another minimum at 510cm (Fig. 3.6).

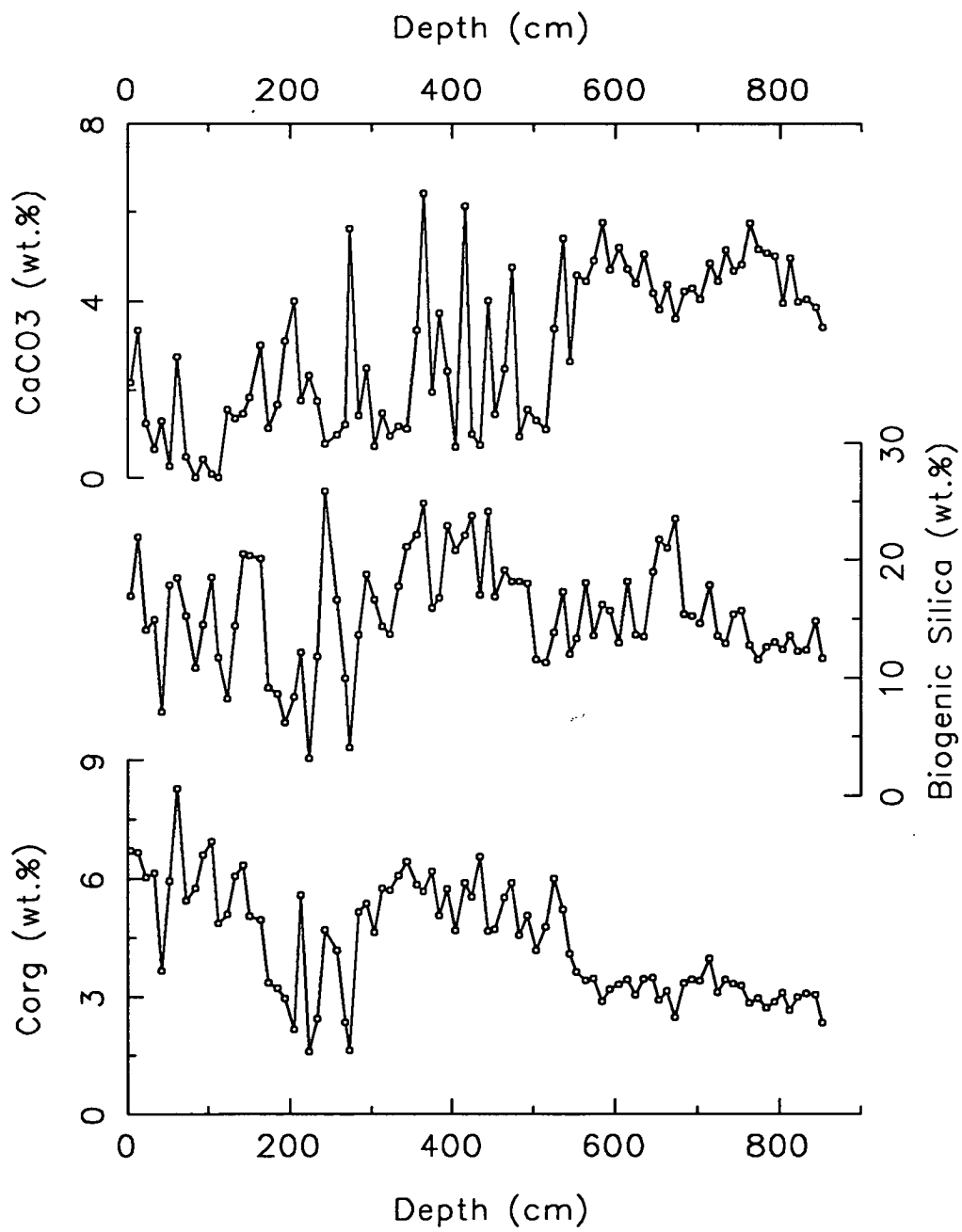


Figure 3.5. Biogenic components (C_{org} , biogenic silica and $CaCO_3$) against depth for core CD38-09 (148m).

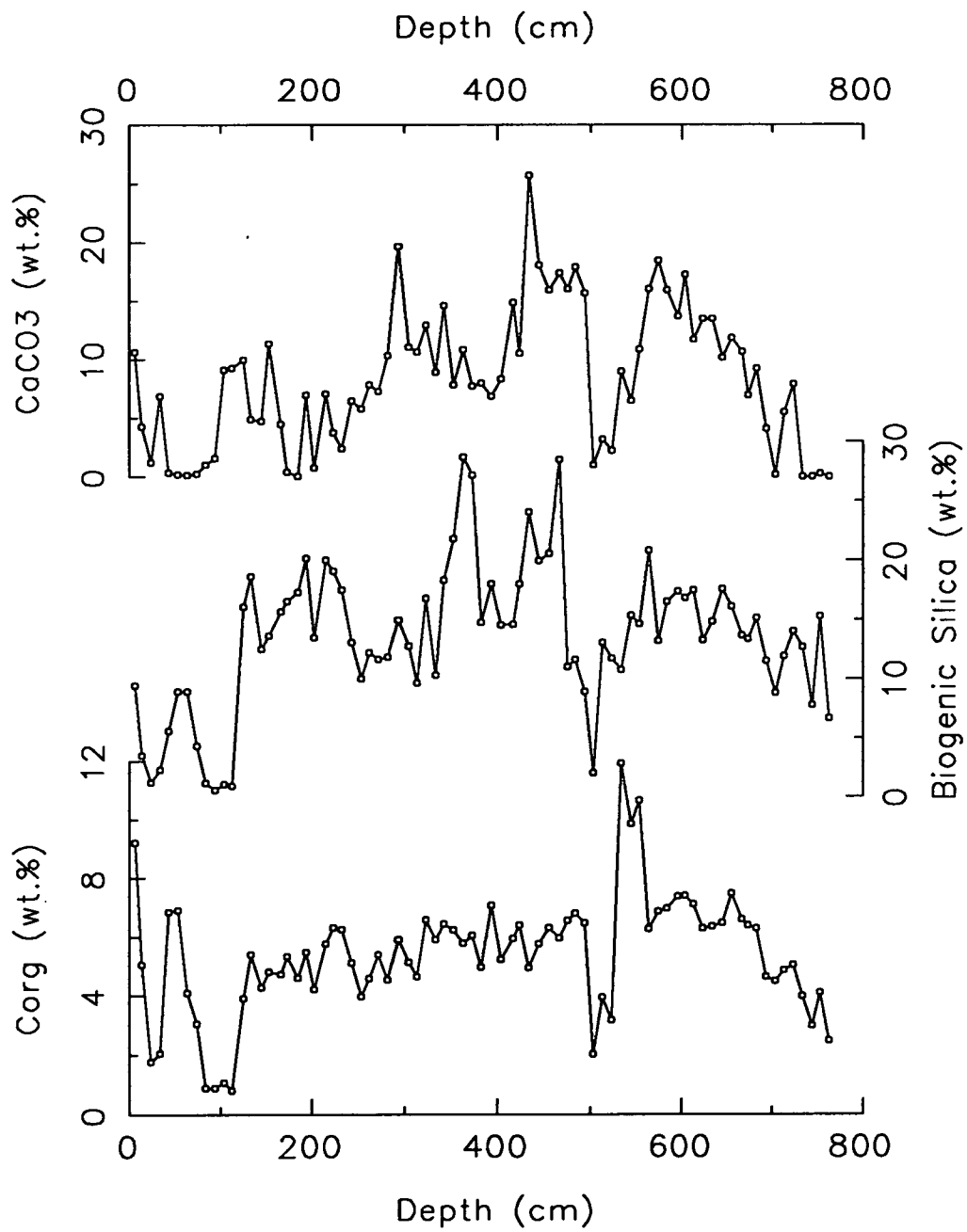


Figure 3.6. Biogenic components (C_{org}, biogenic silica and CaCO₃) against depth for core CD38-10 (257m).

The C_{org} profile is fairly stable between 125 and 490cm in CD38-10 with an average of about 5wt.%.

Table 3.2 lists the statistical information of the above trace metals expressed as enrichment factors ($E.F._{metal}$ - Equation 3.1 and Appendix B.2). Enrichment factors are calculated in order to highlight any proportion of each metal which is not associated with the fraction of the sediment whose input has been from a terrigenous source. They express the enrichment (or depletion) of a metal as a number in order to allow for inter-comparison between each metal and also with other published metal data sets (Balistreiri and Murray, 1986; Shimmield and Pedersen, 1990). An $E.F._{metal}$ above 1.0 implies an extra, non-terrigenous source for the metal.

Equation 3.1. Metal enrichment factors

$$E.F._{metal} = [Metal_{sample}/Al_{sample}] / [Metal_{clay}/Al_{clay}]$$

where, clay values are for deep-sea clay (Turekian and Wedepohl, 1961).

	CD38-09				CD38-10			
	Min.	Max.	Mean	S.D.	Min.	Max.	Mean	S.D.
E.F. _{Mo}	0.70	6.87	2.92	1.27	0.62	9.46	3.82	2.25
E.F. _U	4.21	369.4	12.6	42.1	6.83	37.5	17.4	6.23
E.F. _{Ni}	0.17	0.64	0.34	0.12	0.14	1.37	0.54	0.24
E.F. _{Cr}	0.86	4.42	1.83	0.44	0.76	3.79	2.01	0.57
E.F. _V	0.74	2.34	1.47	0.27	0.57	5.67	2.17	1.12
E.F. _{Cu}	0.05	0.21	0.15	0.03	0.04	0.37	0.19	0.06

Table 3.2. $E.F._{metal}$: for method of calculation see Eqn 3.1 and Appendix B.2.

Figures 3.7 and 3.8 are depth profiles of these enrichment factors for cores CD38-09 and CD38-10, with the C_{org} profiles also displayed for comparison. In core CD38-09, the drop in C_{org} concentration between 500 and 550cm is seen also in the Ni, Cr, Mo and U enrichment factors (Fig. 3.7). In core CD38-10, the profiles look very similar (Fig. 3.8) especially at the zones with low C_{org} at 25-35cm, 80-115cm and 500-525cm which correspond to low enrichment factors for all the metals except uranium, and all the E.F. depth profiles peak at 534cm where the highest concentration of C_{org} is found.

The similarities between the C_{org} and $E.F._{metal}$ depth profiles indicate the possibility of strong organo-metallic relationships within the sediment. These are

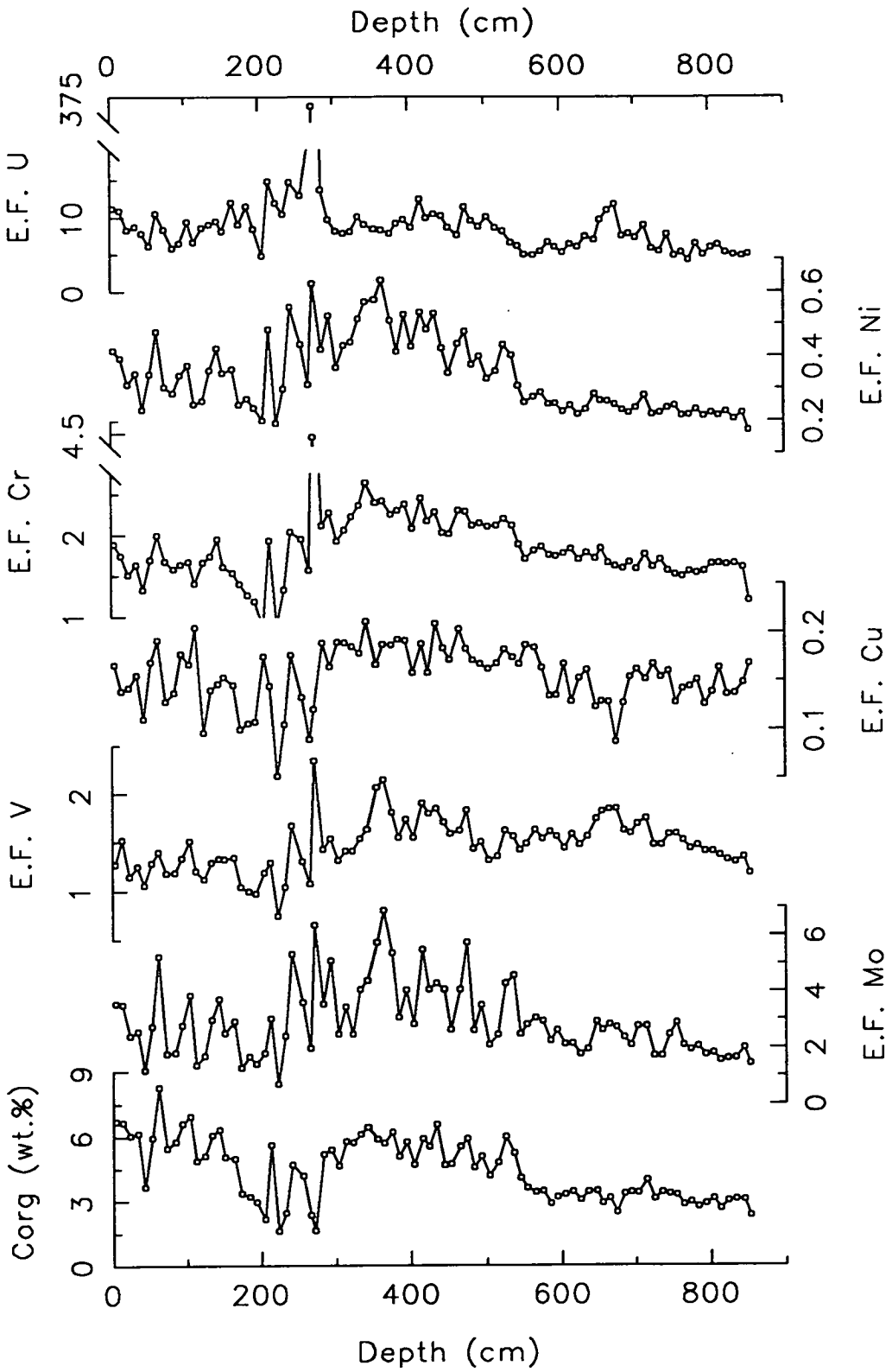


Figure 3.7. Trace metal enrichment factors (E.F._{metal}: Mo, V, Cu, Cr, Ni and U) and C_{org} against depth for core CD38-09 (148m).

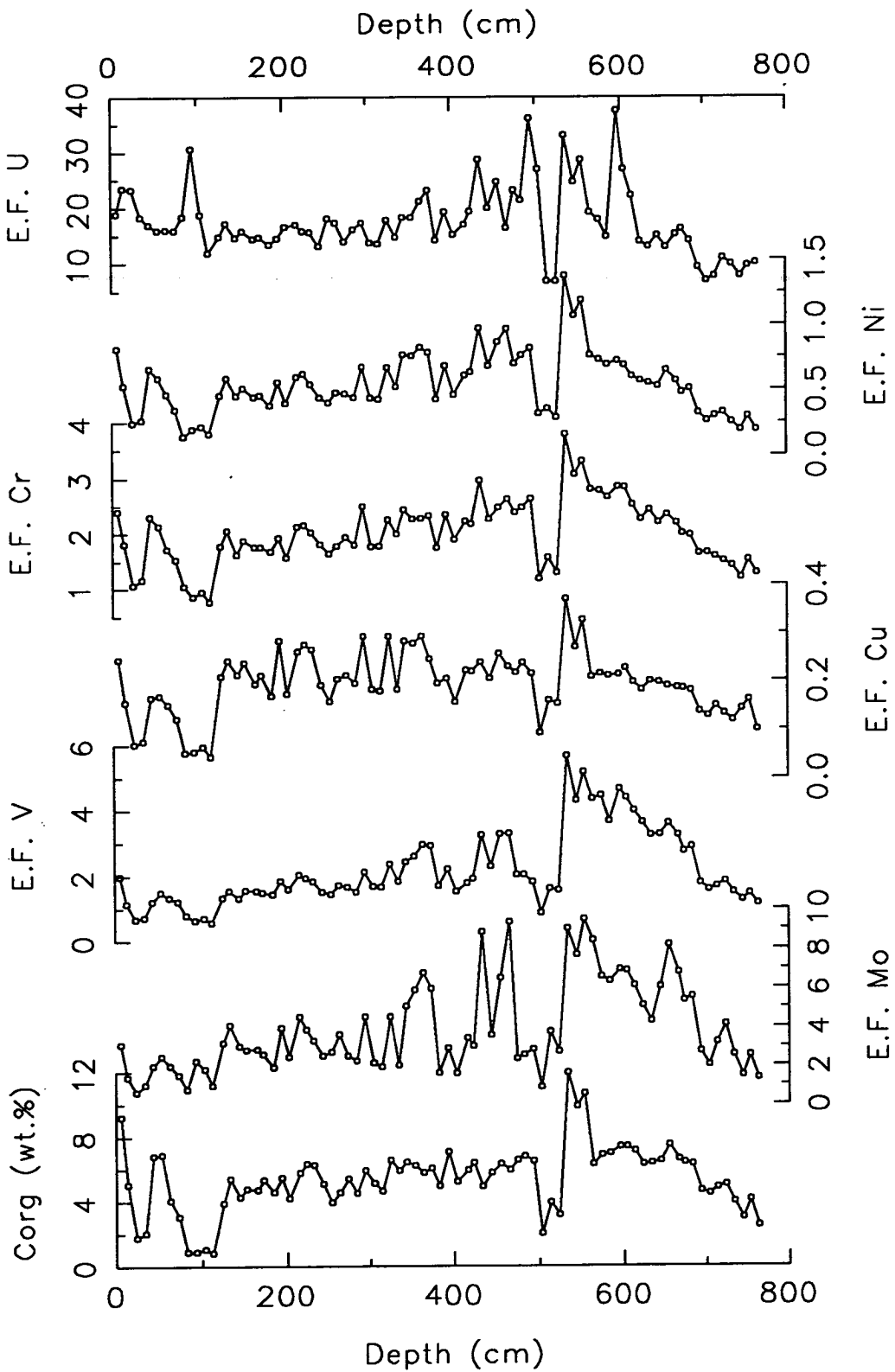


Figure 3.8. Trace metal enrichment factors (E.F._{metal}: Mo, V, Cu, Cr, Ni and U) and C_{org} against depth for core CD38-10 (257m).

highlighted by the correlation plots in Figs 3.9 and 3.10 and in the correlation coefficient matrices in Table 3.3.

CD38-09 (148m)						
E.F.Mo	0.561					
E.F.U	-0.188	0.317				
E.F.Ni	0.681	0.893	0.300			
E.F.Cr	0.346	0.758	0.647	0.789		
E.F.V	0.123	0.709	0.355	0.504	0.694	
E.F.Cu	0.565	0.488	-0.132	0.494	0.418	0.382
	C _{org}	E.F.Mo	E.F.U	E.F.Ni	E.F.Cr	E.F.V

CD38-10 (257m)						
E.F.Mo	0.685					
E.F.U	0.338	0.363				
E.F.Ni	0.864	0.777	0.585			
E.F.Cr	0.916	0.798	0.503	0.944		
E.F.V	0.791	0.910	0.412	0.778	0.868	
E.F.Cu	0.808	0.642	0.303	0.838	0.817	0.624
	C _{org}	E.F.Mo	E.F.U	E.F.Ni	E.F.Cr	E.F.V

Table 3.3. E.F._{metal} and C_{org} correlation coefficients

Strong C_{org} correlations are present in core CD38-09 for Mo, Ni and Cu, and in core CD38-10, Cr shows a very strong correlation, with Mo, Ni, V and Cu having strong correlations*. Although the V concentration in core CD38-09 has a poor correlation with C_{org}, it does correlate strongly with Mo, Cr and Ni. All these correlations are positive which suggests the presence of organo-metallic associations. The possibility that strong correlations are caused by dilution from another component is not suspected because variation in the main dilutant in these continental margin sediments, i.e. terrigenous debris, has already been accounted for by the calculation of enrichment factors for the metals. The poor uranium-C_{org} relationship is interpreted further in 4.3.4.

*Correlation coefficients above 0.9 (or below -0.9) are statistically regarded as being very strongly significant and between 0.5 and 0.9 (or -0.5 and -0.9) as being strongly significant (5.2.1).

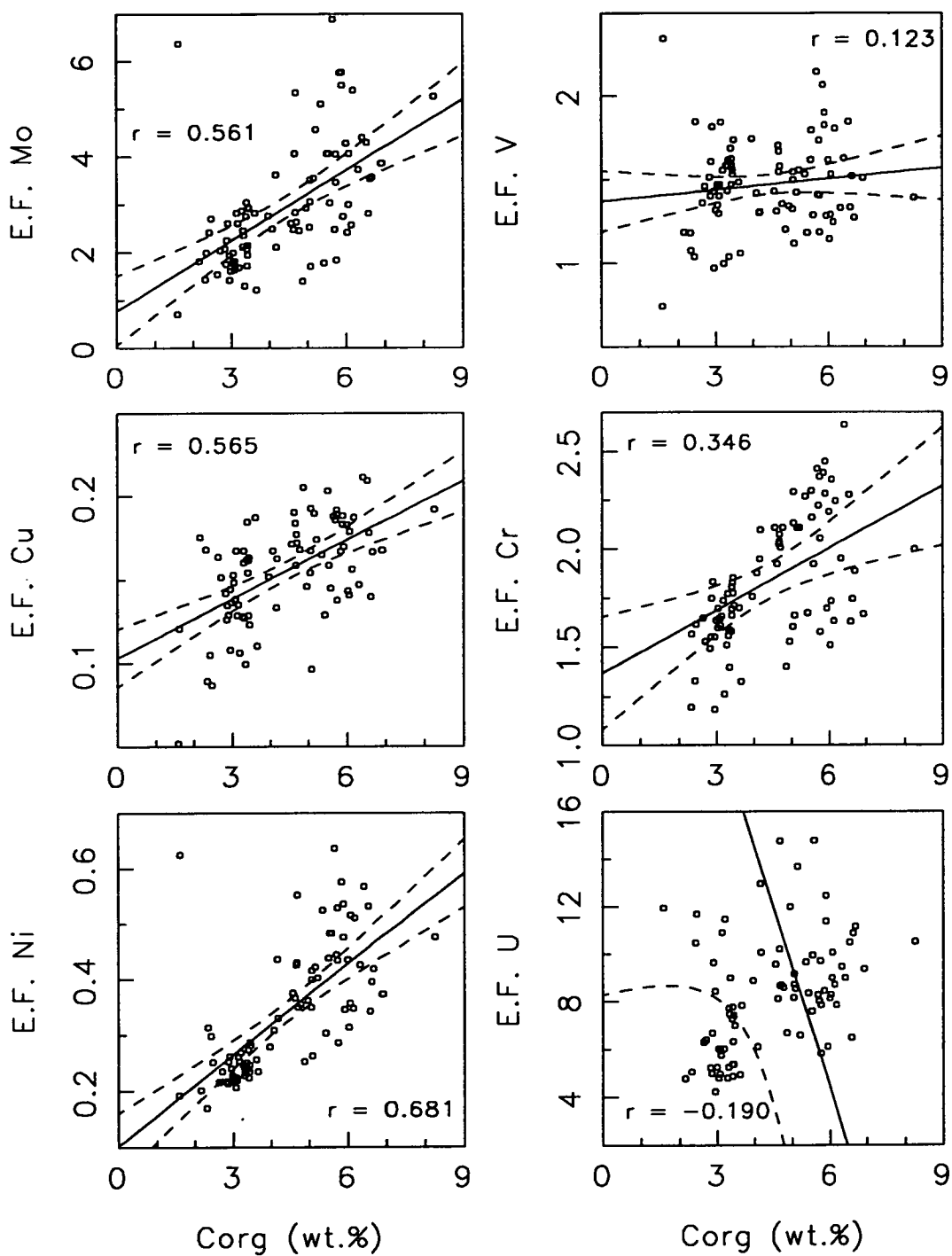


Figure 3.9. Correlation plots of trace metal enrichment factors (E.F._{metal}: Mo, V, Cu, Cr, Ni and U) against C_{org} for core CD38-09 (148m). All with a best fit line, showing 95% confidence limits, and correlation coefficient (r).

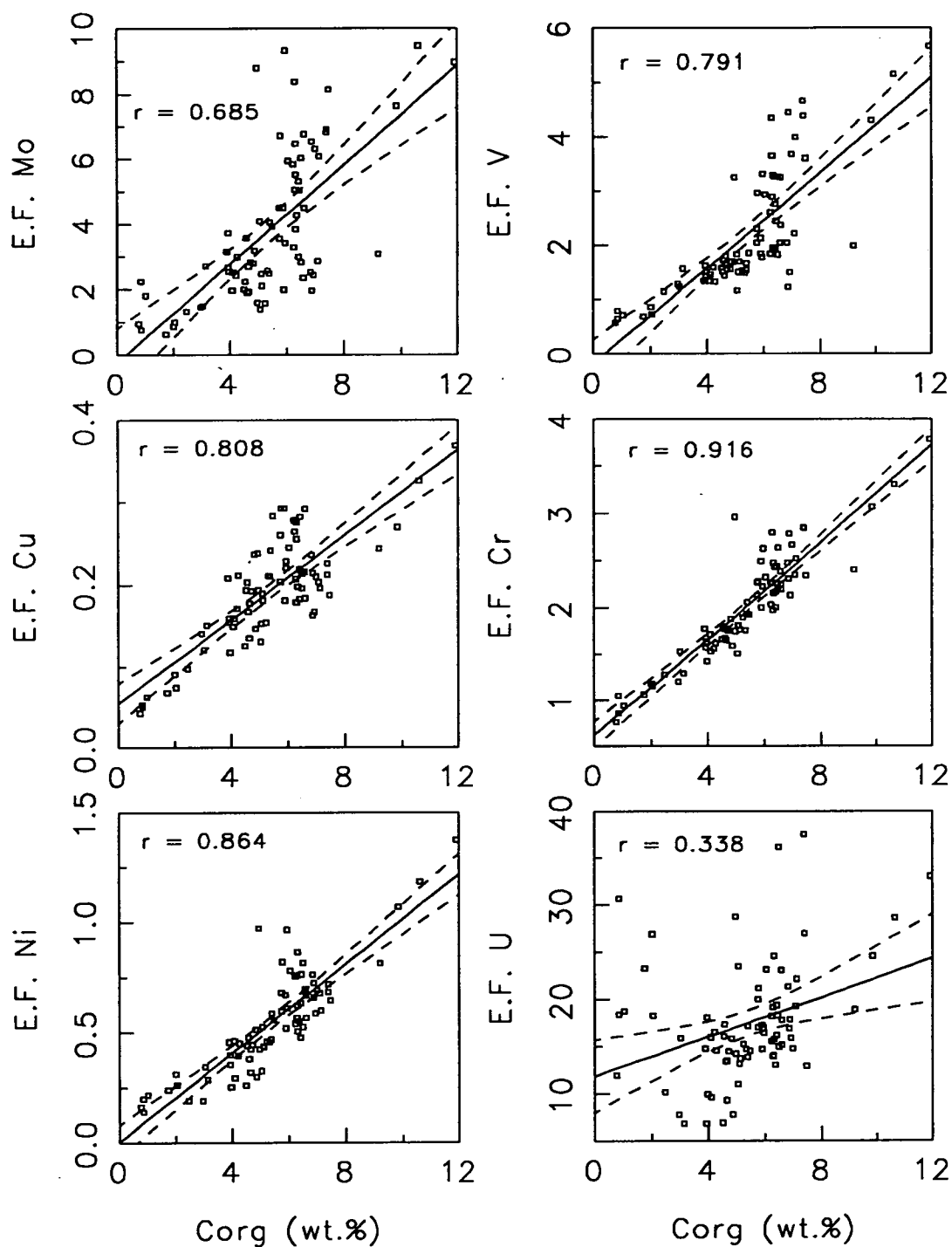


Figure 3.10. Correlation plots of trace metal enrichment factors (E.F._{metal}: Mo, V, Cu, Cr, Ni and U) against C_{org} for core CD38-10 (257m). All with a best fit line, showing 95% confidence limits, and correlation coefficient (r).

3.3. DISCUSSION

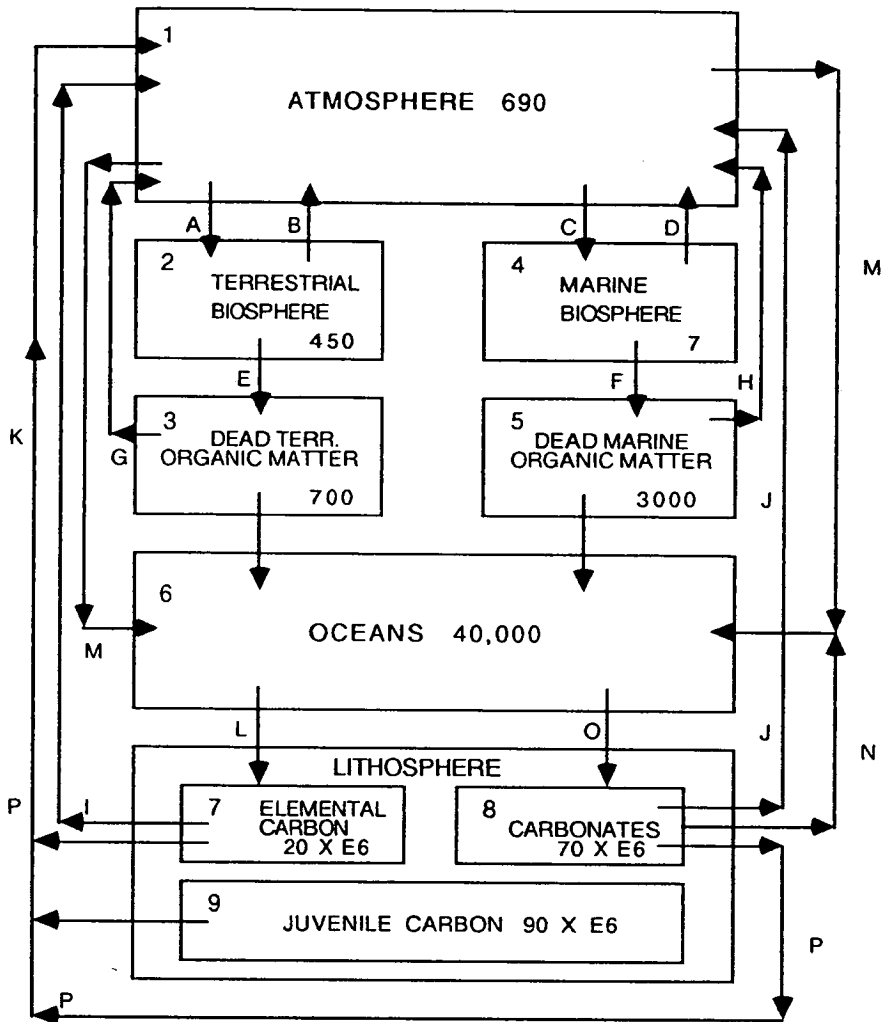
3.3.1. Ocean carbon sink

The global carbon cycle contains the two most important processes necessary to sustain life. It is the fine equilibrium between plant photosynthesis (CO_2 consuming) and animal respiration (CO_2 producing) which keeps the carbon dioxide concentration of the atmosphere at a relatively stable level. As can be seen from Fig. 3.11, the carbon cycle is a very complex series of interactions and one of the major ones is the diffusion of CO_2 from the atmosphere to the hydrosphere and the utilisation of that CO_2 in the photic zone by marine phytoplankton (process C in Fig. 3.11, Holland, 1978).

The carbon remains in the marine biosphere food chain until it is mostly recycled back as dissolved CO_2 in the ocean upon decomposition of the organisms (>99%, Baturin, 1982; up to 96% regeneration in the deep-sea, Martin *et al.*, 1987) or it is buried as organic matter in marine sediments; the latter taking it out of the cycle. Although this carbon sink accounts for only a very small fraction of the carbon moving around the global cycle (process L accounts for only 0.4% of process F, Fig. 3.11), variations in the levels of C_{org} found in marine sediments may be linked to natural fluctuations (or present day anthropogenic increases) in the concentration of atmospheric CO_2 . This assumes that the level of C_{org} accumulation in the sediment column reflects the magnitude of organic matter flux from the euphotic zone to the sea-floor (Müller and Suess, 1979; Müller *et al.*, 1983; Sarnthein *et al.*, 1988).

The vastly increased level of productivity in the surface waters along the Peru continental margin, and other coastal upwelling zones, means that although these areas only cover 0.1% of the ocean surface, they account for about 0.5% of the total ocean productivity (Ryther, 1969). This 5-fold enrichment compared with normal ocean waters is reflected in the elevated concentrations of C_{org} found in sediments accumulating under upwelling areas. This is illustrated by the high mean C_{org} (wt.%) of cores CD38-09 and CD38-10 in this study.

The C_{org} flux data of Martin *et al.* (1987) suggest that site CD38-09 at 147m water depth will receive 70% of the new production sinking out of the euphotic zone, whereas site CD38-10 at 250m will receive only about 50%. The higher mean C_{org} content measured in CD38-10 (5.4 wt.%) compared with core CD38-09 (4.4 wt.%) seems to be a contradiction of the above statement. The reason for this is that the organic matter signal in core CD38-09 is being diluted by more terrigenous clays than



Process	From	To	Description	Rate
A	1	2	Photosynthesis on land	48
B	2	1	Decay of terrestrial organic matter	23
C	1	4	Photosynthesis at sea	35
D	4	1	Decay of marine organic matter	5
E	2	3	Accumulation of dead terr. org. matter	25
F	4	5	Accumulation of dead marine org. matter	30
G	3	1	Decay of dead terr. org. matter	25
H	5	1	Decay of dead marine organic matter	30
I	7	1	Fossil fuel burning	4.2
J	8	1	Cement manufacture	0.7
K	7	1	Oxidation of elemental carbon	0.09
L	6	7	Deposition of elemental carbon	0.12
M	1	6	Flux to carbonates	0.06
N	8	6	Weathering of carbonates	0.16
O	6	8	Deposition of carbonates	0.22
P	7,8,9	1	Degassing (metamorphic and igneous)	0.09

Figure 3.11. The global carbon cycle (adapted from Holland, 1978).

All rates are $\times 10^{15} \text{ g yr}^{-1}$ and amounts of carbon in reservoirs are $\times 10^{15} \text{ g}$.

in core CD38-10 because CD38-09 is situated closer to the source of the terrigenous input, i.e. the continental land mass. Once sedimentation rates are taken into account, organic matter fluxes should be higher at CD38-09.

A similar difference in mean C_{org} is seen in the ODP sites 680B (6 wt.%) and 686 (2 wt.%), the latter of which is situated 200m deeper and 2° further south on the continental margin of Peru (Suess *et al.*, 1988). Schrader (1992) attributes the difference to a combination of (a) a reduced C_{org} flux from the euphotic zone, (b) a weaker OMZ allowing for more organic matter oxidation and/or (c) more recycling of organic carbon because of longer sinking times for organic matter, at site 686.

3.3.2. Glacial/interglacial climate changes

Variations in the concentrations of C_{org} and the other two biogenic components (biogenic silica and calcium carbonate) should reflect changes in the ocean surface productivity, which in turn is controlled by the climatic environment of the area. Under a zone of coastal upwelling, if climatic change alters the strength and persistency of the physical upwelling of water through time (Suess and Thiede, 1983; Bakun, 1990) then the contents of these three biogenic indicators should vary sympathetically (assuming an equal dilution-effect from the terrigenous component input).

In the Late Quaternary, global phases of glacial and interglacial periods have had a great influence on both physical (sea-level and circulation patterns) and biological oceanography (Lyle, 1988; Pedersen, 1983). The extent to which these extreme climatic variations have affected the strength of coastal upwelling has been widely studied (Labracherie *et al.*, 1983; Müller *et al.*, 1983; Reimers and Suess, 1983; Wefer *et al.*, 1983; Schrader and Sorkness, 1991; Schrader, 1992).

Any down-core fluctuations in C_{org} , biogenic silica and $CaCO_3$ concentrations, such as seen in cores CD38-09 and CD38-10 in Figs 2.5 and 2.6, may be attributed to glacial/interglacial cycles by the simple theory that stronger winds during a glacial period produce more upwelling and hence ocean productivity increases (Sarnthein *et al.*, 1988) which is recorded in the sediment column. However, the picture is complicated by other highly variable factors. Dilution from terrigenous debris from the continental land mass (Andean erosion, 7.2.3), preservation of the original biomass (7.3.3) and erosion of the sediment column by stronger bottom water currents during low sea-level stands (4.3.6) are just three of the many influences which affect the accumulation of biogenic components in the continental margin sediments off Peru.

Before an accurate interpretation of the biogenic component concentrations in cores CD38-09 and CD38-10 can be made, sections of the sediment have to be allotted to either a glacial or an interglacial period and this can only be done after accurate age models of the cores have been determined. As described in Chapter 2, age modelling for cores CD38-09 and CD38-10 was not possible due to the unknown amount of erosion of the sediment column that these cores have suffered.

3.3.3. Organo-metallics

As organic matter falls out of the surface waters upon death of the marine organism, it scavenges many redox-sensitive metals (e.g. Mo, U, Ni, Cr, V and Cu) out of their dissolved phase and concentrates them in the solid phase (Goldberg, 1954; Bruland *et al.*, 1974; Craig, 1974; Francois, 1988; Shimmield and Pedersen, 1990). Balistieri *et al.* (1981) concluded that the surface metal chemistry of sinking particles was mainly controlled by the organic matter phase.

Organic matter which reaches the sea-floor before decomposition therefore has a high level of these metals incorporated within it and so the concentrations measured in the sediment should reflect the amount of organic matter in the water column (Shaw *et al.*, 1990).

Under a coastal upwelling zone, such as off Peru, the high organic matter flux produces an anomalous enrichment of the metals in the sediment (Calvert and Price, 1970; Bertine and Turekian, 1973; Calvert *et al.*, 1985; Shimmield and Pedersen, 1990). This enrichment can be calculated as an E.F._{metal} value and this is a measure of the concentration above (or below) that expected if no organic matter was present in the sediment and the only metal source was from a terrigenous association.

The order of organo-metallic enrichment, taken from the mean E.F._{metal} values (Table 3.3), for the two near-shore cores is as follows:

CD38-09	U > Mo > Cr > V > Ni > Cu
CD38-10	U > Mo > V > Cr > Ni > Cu.

It should be noted that Cu and Ni have mean enrichment factors less than one (i.e. depleted). However, the enrichment factors and hence their order is very dependant on the Turekian and Wedepohl (1963) deep-sea clay values being accurate for every metal and so it may not accurately quantify the organic-associated enrichments.

The following is an order of the correlation coefficients of the metal enrichment factors with organic carbon (r from Table 3.2, Figs 3.9 and 3.10) for the two cores:

CD38-09 : Ni > Cu > Mo > Cr > V > U

CD38-10 : Cr > Ni > Cu > Mo > V > U.

This latter order is an indication of the relative strength of any organo-metallic association. However, it is strongly affected by any post-depositional processes operating during the decomposition of organic matter (especially for uranium - 4.3.4).

Differences in the two orders illustrate, for instance, that although the enrichment factors of Cu and Ni are generally less than one, which implies that their concentration can wholly be accounted for by a terrigenous source, the strong C_{org} -Ni and C_{org} -Cu correlations imply that these metals are associated with organic matter as it is buried within the sediment. Ni and Cu maintain strong associations with the C_{org} indicating incorporation into the more refractory fractions of the organic matter. Sclater *et al.* (1976) saw no evidence for direct scavenging of Ni from the water column, but concluded that Ni was involved in the biogeochemical cycle by incorporation into both the hard and soft parts of marine organisms.

Mo and V, on the other hand, are highly enriched within the continental margin sediments off Peru indicating that organic debris can easily scavenge these metals from the water column. However, Mo (in CD38-10) and V (in CD38-09) are low down the order of C_{org} -correlation and this implies that these two metals may be connected to the more labile organic phase and thus are more affected by post-depositional remobilisation. Brumack and Gieskes (1983) observed movement of Mo and V in reducing sediments from the Gulf of California and attributed this to the complexation of these metals with soluble organic material. Mo has been found to be removed from solution by absorption by humic substances and is therefore enriched within the humic fractions of organic matter (Bertine, 1972; Nissenbaum and Swaine, 1976; Calvert *et al.*, 1985).

The relatively large enrichment of Mo, Cr and V relative to the other organo-metallic elements in the two near-shore cores is evidence of accumulation under reducing conditions within the sediment. Shaw *et al.* (1990) reported that near-anoxic conditions produce increased accumulation of the above three metals and low accumulation of Co and Ni.

In a study of sediments in the anoxic environment of the Saanich Inlet, British Columbia by Francois (1988), Mo showed the largest enrichment of all the metals studied. This was due to additional enrichment by sulphide co-precipitation reactions occurring at the sediment/water interface (Bertine, 1972; Shaw *et al.*, 1990).

The presence of naturally metal-stained organic matter in reducing sediments, as investigated by Ittenkkot and Degens (1983) using electron microscope techniques, can help in the preservation of distinct organic matter structures upon burial. If certain organic structures, such as filamentous bacterial mats (Reimers and Suess, 1983A), are characteristic of coastal upwelling sediments, then metal staining could allow them to survive burial and become diagnostic features.

3.3.4. Non-anthropogenic conditions

Marine sediments in the coastal environment are susceptible to pollution from mankind's present day activities. Industrial and sewage waste outflow, land fertiliser run-off and oil tanker spillages are some of the ways in which metals can be mobilised into the marine environment in amounts equivalent to those introduced by natural weathering processes (Bruland *et al.*, 1974).

However, before the effects of anthropogenic pollution on the coastal marine environment can be examined, the complex pathways in which the metals are incorporated from the sea-water to the sediments must be fully understood and the natural, steady-state baseline for metal enrichment associated with organic matter and/or diagenetic processes needs to be quantified.

The sediments off Peru, sampled in cores CD38-09 and CD38-10, have been accumulating under natural, non-anthropogenic conditions throughout the Late Quaternary. The elevated concentrations of C_{org} and its associated redox-sensitive metals found in these sediments allow for accurate quantification of the metal/ C_{org} ratios.

Table 3.4 lists the range, mean and standard deviation of metal/ C_{org} and $E.F._{metal}/C_{org}$ ratios for Mo, U, Ni, Cr, V and Cu for both CD38-09 and CD38-10, and these values could be used in any future studies in a polluted coastal environment as the natural baseline flux for comparison with any additional, anthropogenic input (Bruland *et al.*, 1974). There is generally a very good agreement between the two cores for the mean values of the ratios, implying that the values could be used for sediment sites over a range of water depths on a continental shelf. It would have to be

remembered that these sediments are from a reducing environment (6.2.3). However, according to Bertine and Goldberg (1977) coastal marine pollution records can most easily be found in undisturbed, non-bioturbated, anoxic sediments.

	CD38-09				CD38-10			
	Min.	Max.	Mean	S.D.	Min.	Max.	Mean	S.D.
Mo/C _{org}	7.4	32.6	12.2	3.2	4.9	47.6	11.4	5.8
U/C _{org}	0.9	91.05			1.0	31.3	3.5	4.4
Ni/C _{org}	9.1	26.6	12.0	2.4	9.9	34.9	14.0	4.4
Cr/C _{org}	15.3	75.5	27.2	7.6	11.5	69.0	22.6	10.3
V/C _{org}	14.2	53.3	29.8	9.2	15.0	69.0	29.4	9.9
Cu/C _{org}	3.6	16.4	6.5	2.1	2.8	11.2	5.7	1.8
E.F.Mo/C _{org}	0.29	3.93	0.70	0.40	0.28	2.58	0.73	0.38
E.F.U/C _{org}	0.98	228.0	4.70	27.0	1.55	35.2	4.35	4.96
E.F.Ni/C _{org}	0.05	0.38	0.081	0.04	0.06	0.23	0.106	0.03
E.F.Cr/C _{org}	0.24	2.73	0.46	0.27	0.26	1.19	0.41	0.16
E.F.V/C _{org}	0.17	1.45	0.38	0.17	0.18	0.89	0.41	0.13
E.F.Cu/C _{org}	0.02	0.08	0.038	0.01	0.02	0.06	0.038	0.01

Table 3.4. Metal/C_{org} and E.F._{metal}/C_{org} ratios :all values are x 10⁻⁴.

3.3.5. Fish bones and faecal pellets

High fish production in the plankton-rich waters of a coastal upwelling zone, results in hard-part fish-remains, i.e. bones and scales, being found in the sediments accumulating below in much higher concentrations than in non-upwelling regions (Frankenberg and Menzies, 1968; Diester-Haass, 1979). DeVries and Percy (1982) found that anchovy scales and vertebrae (*E. ringens*) were the most abundant constituent of fish debris (79.4%) in Peruvian continental slope sediments.

A semi-quantitative analysis of fish debris content in cores CD38-09 and CD38-10 was carried out on the sieved (> 63µm) samples used for foraminifera picking (Appendix A.2). The quantity of fish-remains seen in the samples were termed absent (0), rare (1), common (2) or abundant (3), and Fig. 3.12 displays this information plotted against depth for both cores. The fish-remains are well-preserved and easily identified as dark brown, thin scales and small vertebrae.

Figure 3.12A displays some similarity to the C_{org} profile for core CD38-09 (Fig. 3.5) with fish bones consistently in the sediment above 530cm but rare or absent

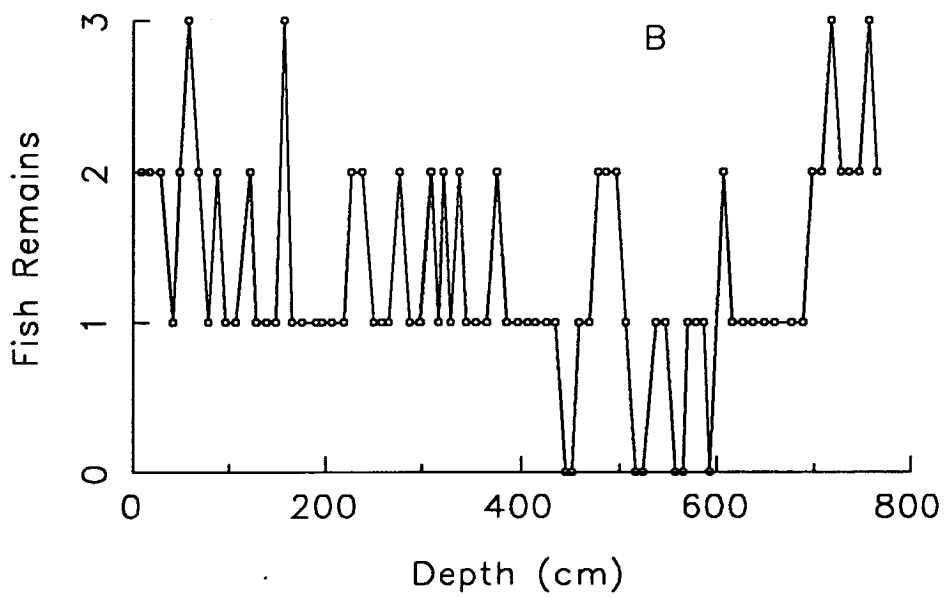
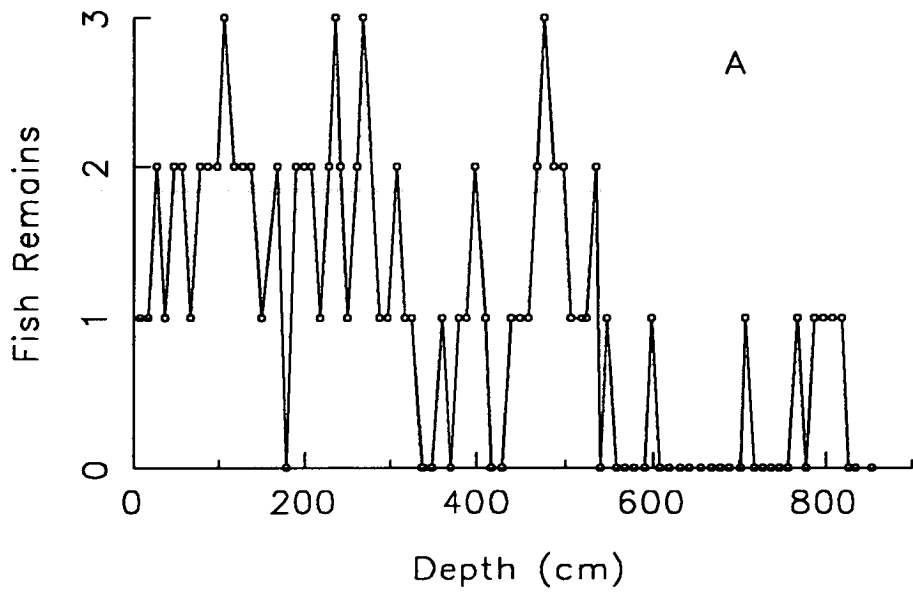


Figure 3.12. Semi-quantitative analysis of fish-remains, A) CD38-09 (148m) and B) CD38-10 (257m). Scale equivalent to: 0 = Absent, 1 = Rare, 2 = Common, 3= Abundant.

below this depth, corresponding to the drop in C_{org} from about 6 to only 3 wt.%. This fish debris- C_{org} relationship is to be expected for a continental margin area such as off Peru because more organic matter falling into the sediment may be the result of higher biological productivity in the surface waters and therefore, more fish should produce more fish-remains which will sink rapidly into the sediment.

The plot for core CD38-10 (Fig. 3.12.B) however illustrates a slightly different story because it does not seem to correlate with the C_{org} content of the core so well (Fig. 3.6). At depths where the C_{org} concentration is very low (e.g. at 30, 80-110, 500 and 735-770cm) the fish-remains are still common or abundant. This is probably due to the fact that fish bones are relatively dense and large in size and therefore, if the sediment is reworked by bottom-water currents, the less-dense, soft organic matter will be resuspended along with fine-grained clays and moved further down the continental slope. This will leave behind a concentration of fish debris (DeVries and Percy, 1982) and other heavy minerals.

A high flux of fish debris in continental margin areas can supply a high concentration of phosphorus (P) and uranium to the sediment. Baturin (1982) states that the P content of fish bones and scales can be up to 16 wt.% and dissolution of these fish-remains off Peru can regenerate dissolved phosphate within pore waters in quantities comparable with those regenerated from decomposition of organic matter (Suess, 1981). The utilisation of this phosphate, and the associated uranium, in phosphorite diagenesis is discussed in Chapter 4.

Faecal pellets were seen at various depths down core CD38-09 (during foraminifera picking). These pellets are covered by a protective, surface membrane (Honjo and Roman, 1978) which makes them resistant to decomposition within the water column. They are most commonly the waste products of herbivorous zooplanktonic copepods and are known to contain about 20-30% of the organic carbon from ingested phytoplankton (Eppley and Peterson, 1979) as well as the actual shells of diatoms and silicoflagellates (Schrader, 1971). Many studies have measured the very fast sinking rates of faecal pellets (up to 400m day⁻¹, Smayda, 1969; 126-862m day⁻¹, Fowler and Small, 1972) which are responsible for the rapid transport of organic matter, trace metals and fine-grained clays (Scheidegger and Krissek, 1982) to the sea-floor.

3.4. CONCLUSIONS

The following conclusions can be made with regards to the geochemical record of coastal upwelling contained within cores CD38-09 and CD38-10.

(1) High concentrations of C_{org} , averaging over a magnitude of order greater than those found in deep-sea sediments, can be found in Peruvian continental margin sediments. This is a reflection of the consistently high biological productivity in the oceanic, surface waters as a result of the physical upwelling of nutrient-rich water into the euphotic zone.

(2) Variations in the strength of coastal upwelling, which has fluctuated as the along-shore and equator-ward trade winds responded to global climate changes during the Late Quaternary, will alter the fluxes of organic matter, silicate- and carbonate- planktonic shell-remains down through the water column and into the sediment.

The concentrations of C_{org} , biogenic silica and $CaCO_3$ in the two shallow-water cores do vary considerably with depth (Figs 3.5 and 3.6) but the interpretation of such changes requires accurate age modelling and the effects of preservation and dilution to the productivity signal have to be taken into account.

(3) Redox-sensitive metals are scavenged from sea-water by organic matter as particles and faecal pellets sink through the water column and hence their concentrations within the sediments of off-shore Peruvian basins are elevated above that expected from a solely terrigenous-association input.

Strong organo-metallic associations are suggested by the high and positive correlation coefficients of the metal enrichment factors with C_{org} . The post-depositional decomposition of organic matter results in the preferential release of U, Mo and V compared with Ni and Cu (taken from the order of correlation coefficients) which implies that the former metals are incorporated into labile organic compounds whereas the latter are associated with more refractory organic fractions.

- (4) Anthropogenic pollution in the marine, coastal environment may result in heavy metal contamination of continental margin sediments. The $\text{metal}/C_{\text{org}}$ or $\text{E.F.}_{\text{metal}}/C_{\text{org}}$ ratios presented for cores CD38-09 and CD38-10 (Table 3.4) could be used as the natural, baseline flux in any future geochemical analysis of polluted, coastal sediments.

An oxygen-minimum zone impinges onto the Peruvian continental margin and the sediments have been accumulating under reducing conditions. Therefore, in any comparative study, the record of marine pollution would have to be taken from similar non-bioturbated, anoxic sediments.

CHAPTER 4

PHOSPHORITES AND EUSTACY

4.1. INTRODUCTION

"Phosphatic nodules are apparently more abundant in the deposits along coasts where there are great and rapid changes of temperature, arising from the meeting of cold and warm waters."

Murray and Renard (1881)

4.1.1. Why study phosphorites?

The first systematic study of marine sediments, during the *Challenger* Expedition of 1872-1876, included the collection and scientific observation of phosphorites. It is from the *Challenger* cruise report that the above quote was taken.

Due to its underwater location, marine phosphorite was discovered nearly a century after the first land deposits were described (Boules, 1782; cited by Daubeny and Widdrington, 1845). During the nineteenth century, phosphorite land deposits were used as agricultural fertilisers and when Lawes dissolved phosphate rock in sulphuric acid, to produce a more soluble phosphatic fertiliser (Buckland, 1843) the phosphate industry began. In order to supply this growing industry, exploration for, and investigation of, phosphorites has continued ever since (Cook *et al.*, 1990).

Today, phosphate is still a principal component in the manufacture of fertilisers and due to intensive farming techniques in the developed world, phosphorite ore deposits are of great economic importance. It is therefore vital to study the chemical and environmental processes which are involved during phosphorite diagenesis, in order to gain more understanding of the mineral's formation and perhaps aid in future exploration of further ore deposits.

Although phosphorites have been found in sediments throughout the world, spanning all geological ages from the Precambrian to the Holocene (Cook *et al.*, 1990), it is only along the narrow zones off the south west coasts of Africa, California and South America that Recent phosphorite formation is known to occur (Manheim *et al.*, 1975; Price and Calvert, 1978; Burnett *et al.*, 1980; Baturin, 1982; Jahnke *et al.*, 1983).

Therefore, examination of the core material from the *R.R.S. Charles Darwin* Leg 38 cruise may reveal the presence of phosphorites and, if so, this mineralogical, geochemical and palaeoceanographical study will attempt to interpret some of the complex processes involved in phosphorite formation.

4.1.2. Phosphorite mineralogy

Though the name phosphorite suggests that the principal element in this mineral is phosphorus, this is not always true because in some cases there is more calcium present (on a weight percent basis) compared with phosphorus. It is probably only because of the economic value of phosphorus in fertilising farmland, that the mineral is so named.

Sedimentary phosphorite is composed principally of the mineral **carbonate fluorapatite** (CFA) (McClellan and Van Kauwenbergh, 1990) and due to its complex mineral structure and an unusually large proportion of ionic substitution, the main elemental components can vary widely between and within phosphorite samples. The composition of phosphorites measured by Baturin and Bezrukov (1979) varied as follows: P_2O_5 from several to 33 wt.%, CaO from 7 to 52 wt.% and fluorine from <1 to 3 wt.%.

Fluorapatite has a hexagonal structure with a unit cell of $Ca_{10}(PO_4)_6F_2$ (Manheim and Gulbrandsen, 1979). CFA is formed by the substitution of CO_3^{2-} for PO_4^{3-} . Ionic substitution is the rule rather than the exception in CFA (McClellan, 1980) and the two factors that influence the stability of an ion in a structure are its ionic radius and its electron charge. The process of carbonate substitution also requires substitution of cations in order to maintain electron-neutrality within the mineral. There is also the effect of lattice deformation to consider, as the planar CO_3^{2-} group substitutes for the tetrahedral PO_4^{3-} group on a 1:1 basis (McClellan and Van Kauwenbergh, 1990).

The most common substitutions which help to accommodate the carbonate ion in the mineral lattice are Na^+ and Mg^{2+} replacement of Ca^{2+} . Presence of a sodium ion reduces the total cationic charge by one electron and although magnesium has the same ionic charge as the calcium that it replaces, it allows for the CFA structure to physically compensate for the carbonate substitution. This is because Mg^{2+} has a much smaller ionic radius than Ca^{2+} ($Mg^{2+} = 0.66\text{\AA}$, $Ca^{2+} = 0.99\text{\AA}$; Ahrens, 1952).

Many other trace element substitutions occur within the lattice framework of the CFA mineral and these can include the incorporation of Ba, Sr, U, S, Y and some rare earth elements (REE) into the mineral structure (Price and Calvert, 1978; Baturin, 1982; Manheim and Gulbrandsen, 1979; Lucas *et al.*, 1990). This variability in the chemical composition of the CFA mineral allows for an enrichment in the concentration of these trace elements to be found in phosphorites, above that of normal marine sediments.

4.1.3. Phosphorite research in the marine environment

The bulk of the world's resources of phosphorus on land, estimated at 67×10^9 tonnes (Stowasser, 1979), occurs in the form of bedded sedimentary phosphorites of marine origin. Therefore, the study of phosphorite formation must be carried out on modern samples from the marine environment.

After the discovery of marine phosphorites during the *Challenger* Expedition and during the early 20th Century, many theories on the origin of phosphorites were proposed. It was accepted that there was some relationship between the biomass and phosphorites and that the mineral diagenesis occurred within the sediments and not in the water column (Murray and Renard, 1891; Blackwelder, 1916; Mansfield, 1918).

Kazakov (1937) proposed that the formation of phosphorites resulted from "direct inorganic precipitation of apatite, from ascending, phosphorus-rich, deep ocean waters and took place in the upper and middle portions of the continental shelf" (approximately 50 to 200m water depth). Kazakov's "Upwelling Hypothesis" received the backing of McKelvey *et al.* (1953) who worked on the US Western Phosphate Field (as a result of the increased interest in uranium-bearing sediments). The facies and chemical composition of this ore deposit reflected "marine deposition of phosphorites controlled primarily by depth, temperature, pH and CO₂ content of the water".

Some recent studies have used experimental and theoretical approaches and concluded that the solubility behaviour of apatite in sea-water can only be described by a complex reaction on the mineral surface (Atlas and Pytkowicz, 1977), that initial apatite precipitation from sea-water is strongly inhibited by magnesium ions (Martens and Harris, 1970) and most importantly, that abundant organic matter must be present (Nathan and Lucas, 1976) to supply high levels of phosphorus to the sediment.

4.1.4. Phosphorus and marine organisms

The phosphate ion is one of the most important nutrients present in the ocean (3.1.2). Phosphorus is vital to both the genetic and metabolic aspects of living organisms because it is a structural element in enzymes, adenosine triphosphate (ATP), ribonucleic acid (RNA), deoxyribonucleic acid (DNA) and phospholipids (Baturin, 1982). The dry weight phosphorus content of terrestrial organisms ranges from 0.1 to 1% but in marine phytoplankton, particularly diatomaceous algae, this can be as high as 3%. Sverdrup *et al.* (1946) give an average C:P weight ratio of 42:1 for

phytoplankton and 40:1 for zooplankton, and this can be recalculated to a C:P molar ratio in marine plankton of 106:1 (Redfield *et al.*, 1963).

The highest concentration of P (up to 16 wt.%) in marine animals is to be found in chitin, scales and fish bones (Baturin, 1982), and it occurs mainly as inorganic phosphorus.

As with all biogenic elements in the ocean, P takes part in an intensive biological cycle and nearly all of the organic-associated P in marine organisms is recycled back into the water column by bacterial decomposition of the organic matter (Baturin, 1982). If sufficient P is to accumulate in marine sediments in order to achieve substantial phosphorite diagenesis, then there must be a high flux of organic matter to the sediment. This situation is known to occur under zones of coastal upwelling (Chapter 3).

Not only is primary productivity vastly increased in these areas and hence organic matter flux, but there is also a high fish bone (DeVries and Pearcy, 1982) and faecal pellet input, both of which supply a certain amount of P to the sediment. Taking the average P content of raw fish as 1wt.% and an area of 200,000 square miles for both the south-west African and Peruvian coastal upwelling zones, Baturin (1982) calculated that up to 50,000 tonnes of P per year is supplied to the sediments as bone detritus.

4.1.5. CFA diagenesis

The supply of high levels of organic-P to a marine sediment is only the precursor to CFA formation. There are many other processes, both chemical and physical, that are needed to bring about phosphorite diagenesis.

Upon bacterial degradation of organic matter within the accumulating sediment, the labile organo-phosphorus compounds, e.g. phospholipids, will release P into the surrounding pore-waters, thus converting particulate P to dissolved P (Froelich *et al.*, 1988). The dissolution of fish debris has been suggested to be the dominant source of pore-water phosphate in Peru margin sediments (Suess, 1981). A third possible source of P is from phosphate released during reduction of iron oxyhydroxide complexes contained within detrital clay particles (Froelich *et al.*, 1988).

Kazakov (1937) originally proposed that apatite precipitated directly from the oceanic bottom waters under an upwelling zone. However, this is unlikely since the

reaction would be in competition with calcium carbonate precipitation and therefore would not occur to any significant degree (Gulbrandsen, 1969; Froelich *et al.*, 1982). A far more likely model is that of CFA precipitating out of the interstitial pore-waters of anoxic sediments which contain elevated concentrations of dissolved phosphate (Baturin and Shishinka, 1973; Manheim *et al.*, 1975; Burnett, 1977; Bremner, 1980; Froelich *et al.*, 1988). Low oxygen levels are required because if the sediments were accumulating under oxic conditions, the dissolved phosphate released from organic matter would form complexes with Fe and Mn ions to become insoluble (Berner, 1973).

Baturin and Bezrukov (1979) quote values of 5-9 mg l⁻¹ phosphorus in pore-waters from both the Peru-Chile and south west African margins, and at such high concentrations supersaturation with respect to CFA is induced and precipitation occurs on the surfaces of mineral grains, diatom frustules, organic detritus etc.

As CFA diagenesis continues, the euhedral apatite crystals can surround the matrix upon which they grow (Burnett, 1977) or even replace the carbonate foraminifera or silica diatoms by slow phosphatisation (Manheim *et al.*, 1975). Phosphatic gels form into small pellets which are usually round or ovule-shaped grains about 125-500µm in diameter (Baker and Burnett, 1988) and include the various sedimentary components upon which diagenesis occurred (Baturin and Bezrukov, 1979). Variation in the chemical composition of phosphorite deposits occur because of large variability not only in the composition of the CFA mineral itself, but also in the composition of the enclosed, non-phosphatic material.

Pellet formation occurs at, or just below, the sediment-water interface (Baker and Burnett, 1988) and, based on fluoride and phosphate uptake rates, Froelich *et al.* (1988) concluded that diagenesis of CFA pellets on the Peru margin takes between 3 and 12 years.

4.1.6. Sea-level change and phosphorite lithification

Authigenic formation of phosphatic material in marine sediments occurs initially as small, disseminated pellets throughout a soft diatom ooze or clay matrix (Baker and Burnett, 1988). The phosphorite minerals are denser than the fine-grained diatoms and clays, and so they can be physically concentrated within the sediment column by any simple sorting process. Reworking of the sediment by bottom-water currents can easily winnow away the less dense, non-phosphatic grains leaving behind a concentrated deposit of heavy minerals (Burnett, 1977; Baturin and Bezrukov, 1979;

Jahnke *et al.*, 1983). Other heavy minerals which can be associated with phosphorites are zircon, rutile and illmenite.

Reworking of a sediment can be caused by a change in the speed or direction of the bottom-water current, which will be most likely to occur because of fluctuations of sea-level (Veeh *et al.*, 1974; Baturin and Bezrukov, 1979). These eustatic variations have the greatest influence on the continental shelf and slope, where a drop in sea-level of between 50 and 100m can dramatically alter the along-shore current systems affecting a particular area. This range in eustacy is known to have occurred throughout the Quaternary (Fairbanks, 1989) associated with glacial/interglacial periodicity.

Baturin (1982) suggests a model of formation for phosphatic muds found off Namibia, which involves precipitation of CFA within organic-rich muds during periods of high sea-level, then winnowing occurring during a regressive period which concentrates the phosphatic pellets.

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- A) Physical upwelling brings nutrient-rich waters to surface-productivity, coastal zone. Phosphate taken up by marine biomass. High flux of organic-P to the sea-floor upon death of marine organisms.
 - B) Organic matter decomposition, fish debris dissolution and/or Fe oxyhydroxide reduction in surface sediment. Release of P into interstitial pore-waters.
 - C) High concentration of pore-water phosphate induces precipitation of CFA. Authigenic mineral growth on surfaces of diatoms, foraminifera and other mineral grains. Uptake of U, Ba, Sr, Y and REE into mineral lattice.
 - D) Phosphorite initially forms as soft nodules and small pellets which need concentration to form deposit. Onset of glacial period in Late Quaternary, brings a lowering of sea-level and stronger bottom-water currents on continental shelf. This winnows away fine grained clays and leaves behind denser phosphatic grains and other heavy minerals.

Figure 4.1. Four stages of phosphorite formation (after Baturin, 1982)

Figure 4.1 summarises the four basic stages of biogenic, chemical and physical processes necessary, under the right oceanographic conditions, for phosphorite

formation (Baturin, 1982). These conditions are to be found at the present day in the waters and sediments on the continental shelf and slope off Peru.

4.1.7. Phosphorites off Peru

A number of previous studies have been carried out on the presence and formation of phosphorites under the coastal upwelling zone off Peru (Veeh *et al.*, 1973; Manheim *et al.*, 1975; Burnett, 1977, 1980; Baturin, 1982; Burnett and Froelich, 1988; Lamboy, 1990) from geochemical, mineralogical and radiometric points of view. Manheim *et al.* (1975) concluded that the four simultaneous requirements for phosphorite diagenesis were found in this off-shore area, i.e. (1) sediments which are rich in organic matter and, (2) covered by bottom water with a low concentration of dissolved oxygen, in an area of, (3) low rates of inorganic (terrigenous) sedimentation and (4) low, but not zero, concentrations of CaCO₃ in the sediment.

U/Th radiometric age determinations of Recent Peru-Chile phosphorite nodules by Burnett (1974, 1980) and Burnett *et al.* (1980) suggest that formation was during high stands of sea-level, i.e. during interglacial, warm periods there is a higher organic-P flux to the sediment and so more phosphorite diagenesis is possible. It may, however, be due to less terrigenous input and lower sedimentation rates. It is only during glacial periods, when a drop in sea-level caused by ice-sheet formation occurs, that reworking of the sediment column concentrates the phosphatic minerals into a phosphorite deposit or hardground (Baturin and Bezrukov, 1979).

The term "hardground" generally refers to an interbedded phosphorite unit which shows signs of burrowing, abrasion and polishing and can be from only a few millimetres up to 1m thick (Cook *et al.*, 1990). Phosphatic hardgrounds are often subsequently broken up by biological or storm activity into shallow-water intraclastic gravel which can be seen on land as "pebble phosphates" (Kennedy and Garrison, 1975; Southgate, 1986).

Phosphatic hardgrounds found off Peru are often irregularly shaped, burrowed and show little internal zonation. They are usually flattened in one dimension with colour variation from pale green to dark grey (Burnett, 1977; Baturin, 1982) and occur in the 120-385m water depth range (Burnett, 1980) which is roughly equivalent to the OMZ depth in this area (Veeh *et al.*, 1973).

A large proportion of such a phosphatic concretion is made up of non-phosphate components such as quartz and feldspar clastic grains and biogenic remains

(Baturin, 1982). Microscopic examination reveals CFA forming a homogeneous cement between the clastic minerals and filling diatom valves. The carbonate tests of foraminifera found, within Peruvian nodules, are sometimes completely replaced by phosphatisation (Manheim *et al.*, 1975).

In 1982, the *R.V. Robert D. Conrad* cruise 23-06 collected many cores from the Peruvian continental margin and results from many studies of both the sediments and pore waters were published in Burnett and Froelich (1988).

One of the most important findings of the cruise was the discovery of small, spherical phosphate pellets, whose distribution and concentration in the surface sediments had not been the result of sediment reworking (Baker and Burnett, 1988). Extensive grain-size analyses by Baker and Burnett (1988) showed that these pellets resided in a poor to very poorly-sorted matrix, which suggested *in situ* production under steady-state conditions, with significant differences in pellet concentration occurring as a result of varying influx rates of detrital sediment. Radiometric age dating by Burnett *et al.* (1988) suggested that some pellets are modern (3 ka) and some were previously formed (250 ka). These pellets from a modern, marine environment are of great interest because most ancient, land phosphate deposits are formed from similar pelletal material.

Factor analysis of the chemical composition of phosphatic pellets and ooids indicated some mineralogical differences (Glenn and Arthur, 1988) and petrographic observations, by these authors, allowed for interpretation of the sequence of authigenic mineral diagenesis, involving glauconite, carbonate fluorapatite and pyrite growth in the suboxic/anoxic environment of Peruvian margin sediments.

Froelich *et al.* (1988) measured pore-water and solid-phase chemical concentrations and found pore-water phosphate levels close to the sediment/water interface which were much higher than that expected if organic matter regeneration was the only source. Other potential sources for the interfacial phosphate release into pore waters are from (1) dissolution of fish debris (Suess, 1981), (2) degradation of microbial mats (*Thiopolca sp.*, Henrichs and Farrington, 1984) and (3) reduction of iron oxyhydroxides (Froelich *et al.*, 1988). Downward-decreasing pore water profiles of fluoride imply diffusion from overlying sea-water into the interstitial pores followed by removal into the sediment column by incorporation into CFA (Froelich *et al.*, 1983; Jahnke *et al.*, 1983).

4.2. ANALYTICAL METHODS AND ELEMENT PARTITIONING

Concentrations of the major and trace elements involved in this geochemical study of phosphorites from off-shore Peru basins, were determined by X-ray fluorescence techniques (Appendix A.5). An actual phosphorite hardground nodule from core CD38-09, found at a depth of 273cm, was sampled and its composition analysed by both X-ray fluorescence and X-ray diffraction. The age of this nodule was determined using U/Th alpha-spectrometry as outlined in Appendix A.8.

To examine the possibility of the presence of phosphorite within each core, particular elemental concentrations in the bulk sediment samples had to be partitioned into various end-member sources. To allow for calculation of the extent of fractionation into terrigenous, organic or phosphorite phases, aluminium (Al) was assumed to be solely present in terrigenous material and organic carbon (C_{org}) levels were assumed to be representative of the amount of organic matter present. Fractionation equations for phosphorus, uranium, yttrium and strontium can be found in Appendix B.4.

4.3. RESULTS AND DISCUSSIONS

4.3.1. Phosphorite hardgrounds

Two zones of coarse-grained pebbles and nodules were seen when the two shallow-water Peruvian continental shelf cores were split open for subsampling. These "hardgrounds" occur at 270-277cm depth in core CD38-09 and at 87-91cm in core CD38-10.

The largest nodule was found at 273cm in core CD38-09; it measured 6x4x1cm and sat horizontally within the core like a 2-dimensional slab. Its outer coating is very dark, olive green in colour with a flat, polished top and base, and small burrows on the top side. One edge is a paler olive green colour with a rough texture indicating that the nodule may have been part of a larger hardground slab.

Due to the similarity with previous phosphorite nodules from the Peru margin (Baturin, 1982; Glenn and Arthur, 1988) the nodule, and others found in cores CD38-09 and CD38-10, were assumed to be phosphorites. The following mineralogical and geochemical analyses were used to test this assumption.

X-ray diffraction

Four samples were obtained by filing away a small amount of material from two nodules and thin smear slides were prepared for X-ray diffraction analysis (Appendix A.9). One sample (GM/HG3) was taken from a small nodule in core CD38-10 (87cm) and three from the large nodule in CD38-09 (273cm) at the top (GM/HG1A), middle (GM/HG1B) and base (GM/HG1C).

X-ray diffraction provided a qualitative identification of the minerals present in the nodules and the spectral patterns shown in Fig. 4.2 illustrate the similarity in mineralogical composition between all four samples. The main minerals that account for the peaks in the diffraction pattern are carbonate fluorapatite (CFA), quartz and calcite (there may also be a small amount of pyrite present). There also seems to be no major mineralogical differences between the dark, outer surfaces and paler centre of the large nodule.

X-ray fluorescence

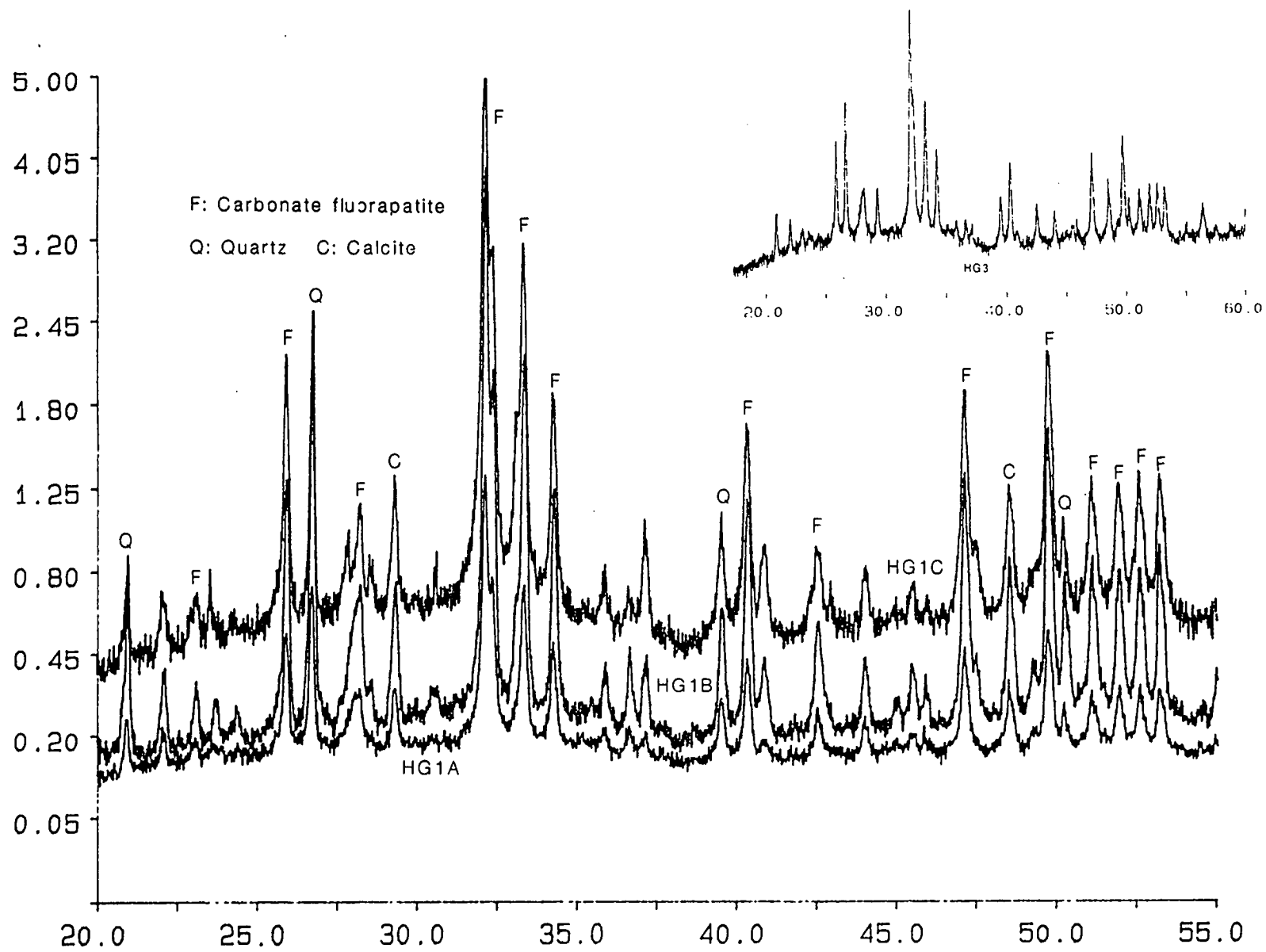
A slice of the large nodule (CD38-09, 273cm) was cut into two samples (09HG/Top and 09HG/Base), which were finely ground and made into pressed pellets for X-ray fluorescence analysis (Appendix A.5). The major and trace element concentrations for both samples are presented in Table 4.1 and from this it can be seen that the bulk chemical compositions of the top and lower halves of the nodule are very similar.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total		
09HG/Top	12.7	2.49	2.30	1.03	32.3	1.39	0.35	19.3	71.85		
09HG/Base	16.6	3.31	2.06	1.03	31.6	1.49	0.47	18.7	75.23		
	Nb	Zr	Y	Ba	U	Rb	Th	Pb	Zr	Cu	Ni
09HG/Top	0	67	7	58	112	20	0	2	36	12	15
09HG/Base	0	81	9	110	153	24	2	3	37	12	14
	Cr	Ce	Nd	La	V	Sc	I	Br	Mo	Sr	
09HG/Top	41	25	3	7	48	5	0	40	68	1692	
09HG/Base	44	19	7	24	56	7	0	35	64	1556	

Table 4.1. X-ray fluorescence analysis of phosphorite nodule.
(Major element oxides in wt.% and trace elements in ppm.)

The two most abundant chemical elements (apart from oxygen) found in the nodule are phosphorus and calcium, which supports the theory that the nodule is

Figure 4.2. X-ray diffraction spectra of phosphorite samples.



dominantly composed of carbonate fluorapatite (CFA). The totals for the major element oxides only add up to 70-75 wt.% because both carbonate and fluorine are not analysed by XRF and they will make up most of the remaining 25-30 wt.%.

Glenn and Arthur (1988) used linear programming to estimate the concentrations of various minerals in a Peru margin nodule using electron microprobe data. Using the end-member mineral compositions from Glenn and Arthur (1988) and following the partitioning steps detailed in Appendix B.3, the above major element oxide concentrations were recalculated into mineral phases (Table 4.2) so that their relative abundances in the nodule from CD38-09 could be studied.

From the mineral data in Table 4.2. it can be seen that CFA is the dominant mineral in the large nodule by a factor of 5-6, over minerals such as feldspars, quartz and opal. The latter minerals form the terrigenous clay and sand particles and diatom frustules around which the CFA originally formed. Pyrite and dolomite are authigenic minerals which are also incorporated into phosphorite nodules (Baturin, 1982). Glenn and Arthur (1988) noted in their study of mineral paragenesis in Peru margin sediments that precipitation of CFA and pyrite appeared to be coincident and often replaced glauconite grains during sediment burial into more strongly reducing conditions.

	CFA	Dolomite	Calcite	Pyrite	Plag.	Orthoc.	Opal/Qtz.
09HG/Top	67.35	3.41	3.43	3.20	9.93	3.21	9.54
09HG/Base	62.35	3.26	3.49	2.74	12.56	4.12	11.72

Table 4.2. Mineral percentage composition of phosphorite nodule
(Plag. = Plagioclase, Orth. = Orthoclase and Qtz. = Quartz.)

The trace element concentrations of the large nodule (Table 4.1.) are anomalously high in uranium, strontium, molybdenum, barium and cerium because it is these elements which are most easily incorporated into the CFA mineral lattice as substitutes for calcium (Price and Calvert, 1978; Manheim and Gulbrandsen, 1979; Lucas *et al.*, 1990). The trace element enrichments (and depletions) in this hardground nodule will be interpreted, along with those for the bulk sediment samples, in 4.3.4.

4.3.2. Pore-water phosphate

The presence of phosphatic, hardground nodules in cores CD38-09 and CD38-10 indicates that on the continental shelf and upper slope at 11°S off Peru, the

biogeochemical and environmental conditions are suitable for phosphorite diagenesis. A second line of evidence to support the mineralogical work in 4.3.1 comes from study of the levels of dissolved phosphate (PO_4^{2-}) anions present in the pore-waters near the sediment/water interface (Baturin and Bezrukov, 1979; Baturin, 1982; Jahnke *et al.*, 1983; Froelich *et al.*, 1988).

Phosphate concentrations in pore-waters from box core material were measured onboard the *R.R.S. Charles Darwin* by G.B. Shimmield, T. Shimmield and A.J. Patience (following the methods described in Appendix A.7). The results for box cores CD38-09, CD38-10 and CD38-11 are tabulated in Appendix C.4. Box cores are used for pore-water analysis because the sediment/water interface can be preserved and sampled, and this is vital for the study of diagenetic processes, such as phosphorite formation, which operate in this zone.

Pore-water PO_4 concentrations from core CD38-11 (3835m) fall in the range 3.9-5.7 μM , which are normal for sediments from the deep-sea. In comparison, the two shallow-water sites are highly enriched in their level of pore-water PO_4 : CD38-09 (148m) = 66-134 μM and CD38-10 (257m) = 38-86 μM . Figure 4.3 illustrates the pore-water PO_4 concentrations for these three cores plotted against depth, along with two profiles from the *R.V. Robert D. Conrad* cruise 23-06 (Froelich *et al.*, 1988) for comparison.

Core CD38-09 has a depth profile which is greatly enriched from bottom-water PO_4 (2.5 μM , Froelich *et al.*, 1988) with levels about 75 μM over the first two centimetres, then displaying a maximum of 134 μM at 4.5cm before slowly decreasing with increasing depth. The profile from CD38-09 is very similar to RC23-06 BX2 (Fig. 4.3) which is from a water depth of 216m and was interpreted by Froelich *et al.* (1988) as resulting from regeneration of organic matter in the upper 5cm and precipitation of phosphate into a solid phase, presumably CFA, below 5cm. It is therefore likely that the same pore-water/solid-phase interactions are occurring at present in the near-surface sediments at site CD38-09 on the Peru margin.

Core CD38-10 also has pore-water PO_4 levels which are greatly enriched from the bottom-water concentration, with a depth profile which peaks directly below the sediment/water interface (86 μM) before sharply dropping to a minimum at 1-1.5cm of 38 μM then levelling out below 5cm at around 50 μM . This unusual profile is virtually identical to that of RC23-06 BX4 (Fig. 4.3) which is from a more southerly site (15°S) on the Peru margin at a water depth of 133m (Burnett and Froelich, 1988). The presence of a phosphate maximum at the sediment/water interface and a minimum just

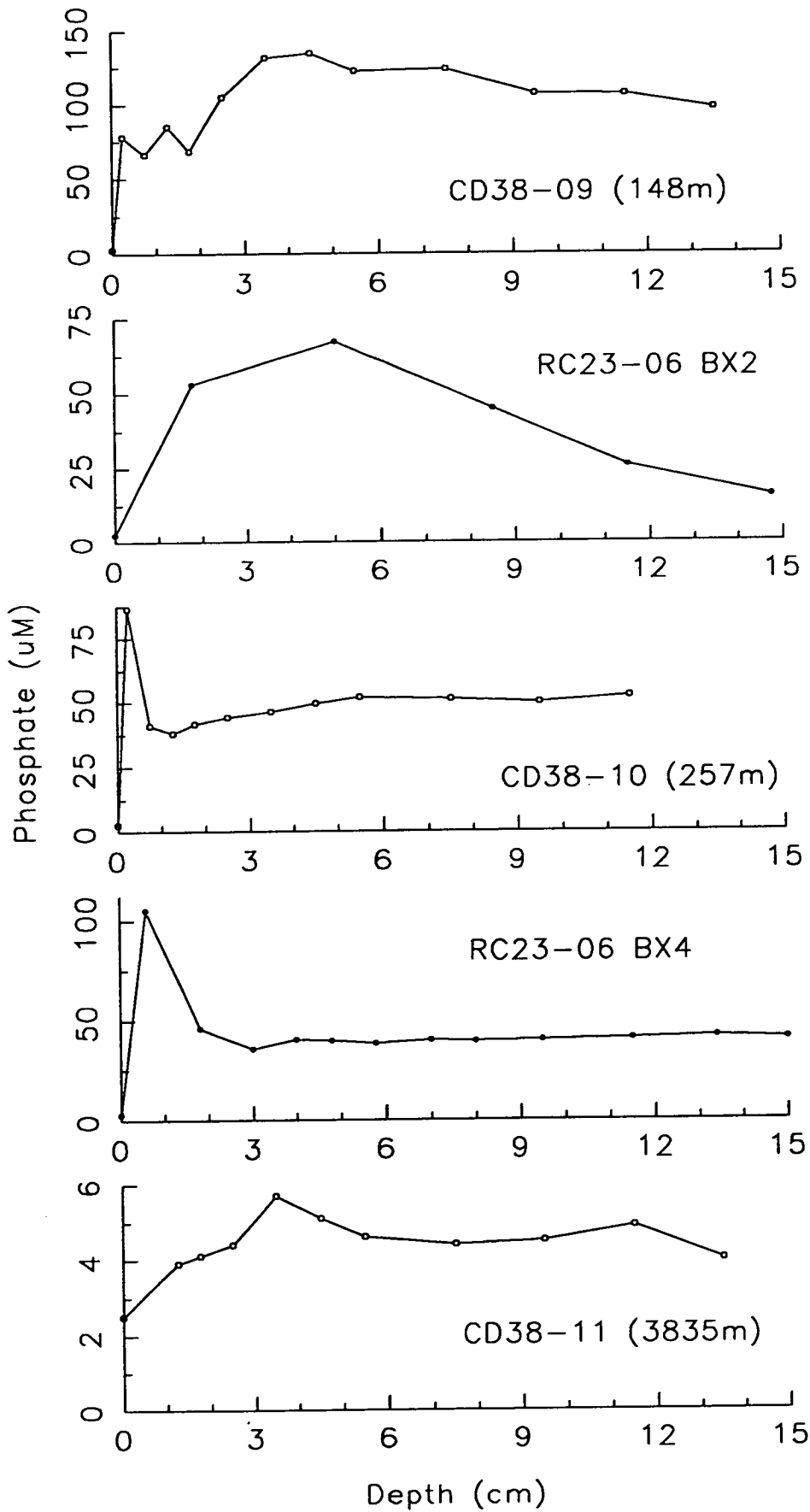
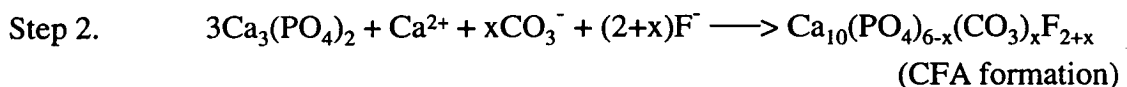
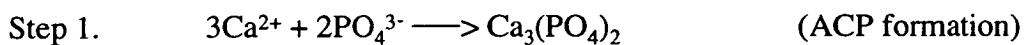


Figure 4.3. Pore-water phosphate (PO_4) concentrations against depth. RC23 cores and bottom-water concentration of $2.7 \mu\text{mol l}^{-1}$ from Froelich *et al.*(1988).

below, requires the precipitation of an inorganic phosphate phase within the upper 5cm of the sediment column and also prevents the diffusion of PO_4 back into the bottom-water, when it is released from organic matter and/or fish debris at depth in the sediment (Froelich *et al.*, 1988).

Froelich *et al.* (1988) also studied other pore-water signals (e.g. silicate, sulphate and nitrate) from core RC23-06 BX4 which displayed suboxic to anoxic diagenetic trends with depth. However, the pore-water fluoride profile did not decrease with depth, as expected if CFA formation is occurring (Froelich *et al.*, 1983). The results of Froelich *et al.* (1988) suggested a two-step process of CFA precipitation, of which only the first step was occurring at site RC23-06 BX4. The two-stage diagenetic sequence involves the formation of amorphous calcium phosphate (ACP) by precipitation of pore-water Ca^{2+} and PO_4^{2-} ions near the sediment/water interface, as the first step, followed by uptake of fluoride and carbonate ions to convert ACP to the more stable mineral, carbonate fluorapatite (CFA).



If the similarity between the phosphate depth profiles of CD38-10 and RC23-06 BX4 is indicative of a similar diagenetic and redox environment at both sites, then at the present day it is possible that CFA is not forming at site CD38-10 due to insufficient ACP-precursor formation (Froelich *et al.*, 1988). This interpretation, however, does not rule out formation of CFA in the recent past, when levels of PO_4 released into the pore-waters, by organic matter decomposition or fish debris dissolution (Suess, 1981), may have been slightly more enhanced.

The model of phosphorite pellet formation proposed by Froelich *et al.* (1988) invokes a steady-state diagenesis, where CFA precipitation is a sediment/water interface-linked process, which occurs in the upper centimetres of the sediment column and continuously moves upwards as more sediment accumulates in order to maintain its near-surface position. This is in contrast to the non-steady-state model proposed by Jahnke *et al.* (1983) for station 145-17 on the Mexican continental margin (off Baja California) which involves the precipitation of apatite only beginning when oxic respiration in the sediments becomes important. However,

Shimmield (1985) related the lower surface levels of organic carbon at this site to grain-size changes and concluded that the lithology change from mud to silt provided a more open-sediment matrix for diagenetic phosphorite precipitation.

The pore-water phosphate profiles of box cores CD38-09 and CD38-10 (Fig. 4.3) support the steady-state model (Froelich *et al.*, 1988) of CFA precipitation, which represents continuous phosphorite formation just below the sediment/water interface and allows for pelletal phosphorite concentrations of up to 5wt.% throughout the sediment column (Baker and Burnett, 1988). This will be shown to be the case for the phosphorite (wt.%) in the piston cores CD38-09 and CD38-10 (4.3.3).

The pore-water PO₄ profile from CD38-11 (Fig. 4.3) is relatively flat and not elevated very much above bottom-water concentrations. It is therefore unlikely that phosphorite formation is occurring at this site to any significant degree at the present day.

4.3.3. Phosphorite zones

Now that the possibility of modern phosphorite diagenesis on the Peruvian continental margin has been examined, it is of great interest in this geochemical study to investigate any variation in phosphorite concentration with depth (i.e. qualitative time-series analysis) occurring in the cores collected on the *R.R.S. Charles Darwin* cruise 38 from off Peru. Using the phosphorus fractionation equation (Eqn 4.1 and Appendix B.4) the distribution and extent of phosphorite diagenesis was examined in the bulk sediment samples for all the cores by calculating P_{phos} (wt.%).

Equation 4.1. Phosphorus fractionation

$$P_{\text{phos}} = P_{\text{total}} - (P_{\text{terr}} + P_{\text{org}})$$

where,

P_{phos} = excess phosphorus incorporated into phosphorite,

P_{total} = concentration from XRF,

P_{terr} = terrigenous phosphorus = Al (wt.%) x 0.0875

(average shale, Turekian and Wedepohl, 1961),

P_{org} = organic phosphorus = C_{org} x 0.0053 (Mach *et al.*, 1987).

A C:P weight ratio of 41:1 in organic matter (Sverdrup *et al.*, 1946; Redfield *et al.*, 1963) is the average value for modern marine plankton and will increase upon

bacterial decomposition of the organic matter due to preferential release of organic phosphorus as dead marine organisms sink down through the water column (Bishop *et al.*, 1980). Therefore, the C_{org}/P_{org} ratio in organic-rich marine sediments is much greater than the Redfield ratio (Froelich *et al.*, 1982). If the organic matter is, however, incorporated in faecal pellets or large aggregates then it will sink rapidly to the sediment surface and phosphorus-deficiency may not occur (Knauer *et al.*, 1979).

Froelich *et al.* (1982) proposed that the P_{org} content of marine sediments is independent of the C_{org} concentration. However, the data set of Froelich *et al.* (1982) was reviewed and updated by Mach *et al.* (1987) who fitted a best-fit straight line with the following relationship: $P_{org} = C_{org} \times 0.0053$. This C:P ratio for organic matter in marine sediments of 190 ± 20 is supported by the results of Ramirez and Rose (1992) who reviewed the analytical procedures used in determining P_{org} in soils and marine and fluvial sediments. The C:P ratio of Mach *et al.* (1987) has therefore been used in calculations of P_{org} from the measured concentrations of C_{org} in Equation 4.1.

The work of Mach *et al.* (1987) indicated no preferential loss of P_{org} or C_{org} associated with organic matter regeneration upon burial in the sediment column. However, Froelich *et al.* (1988) suggest that phospholipids and other labile organo-phosphorus compounds will preferentially decompose in marine sediments and therefore, the calculated P_{org} concentrations may be slightly less accurate towards the base of each core.

The concentrations of the phosphorus fractions for cores CD38-09, CD38-10 and CD38-11 plotted against depth are displayed in Fig. 4.4 (the data is listed in Appendix C.13). For the box and piston cores of CD38-02 and CD38-03, all the P_{total} concentration can be accounted for by the P_{terr} and P_{org} fractions, implying that no phosphorite is present in these cores. Core CD38-09 displays a P_{phos} peak of about 6 wt.% and CD38-10 has three peaks between 2 and 3 wt.% (and 2 other possible peaks at 0.6-0.7 wt.%). However, in core CD38-11 the P_{phos} peaks are no more than 0.5 wt.% which implies that phosphorite formation is only present to any significant degree in the shallow-water shelf environment.

It should be noted that fish bones and scales are enriched in P (Suess, 1981) and therefore, some of the P_{phos} calculated for cores CD38-09 and CD38-10 may in fact, only be concentrations of fish debris and not P in phosphorite minerals. Study of trace metal enrichments will help to solve this problem.

Using the average concentration of P measured in the phosphorite hardground from CD38-09 (8.29 wt.%, Table 4.1) as the end-member concentration for all

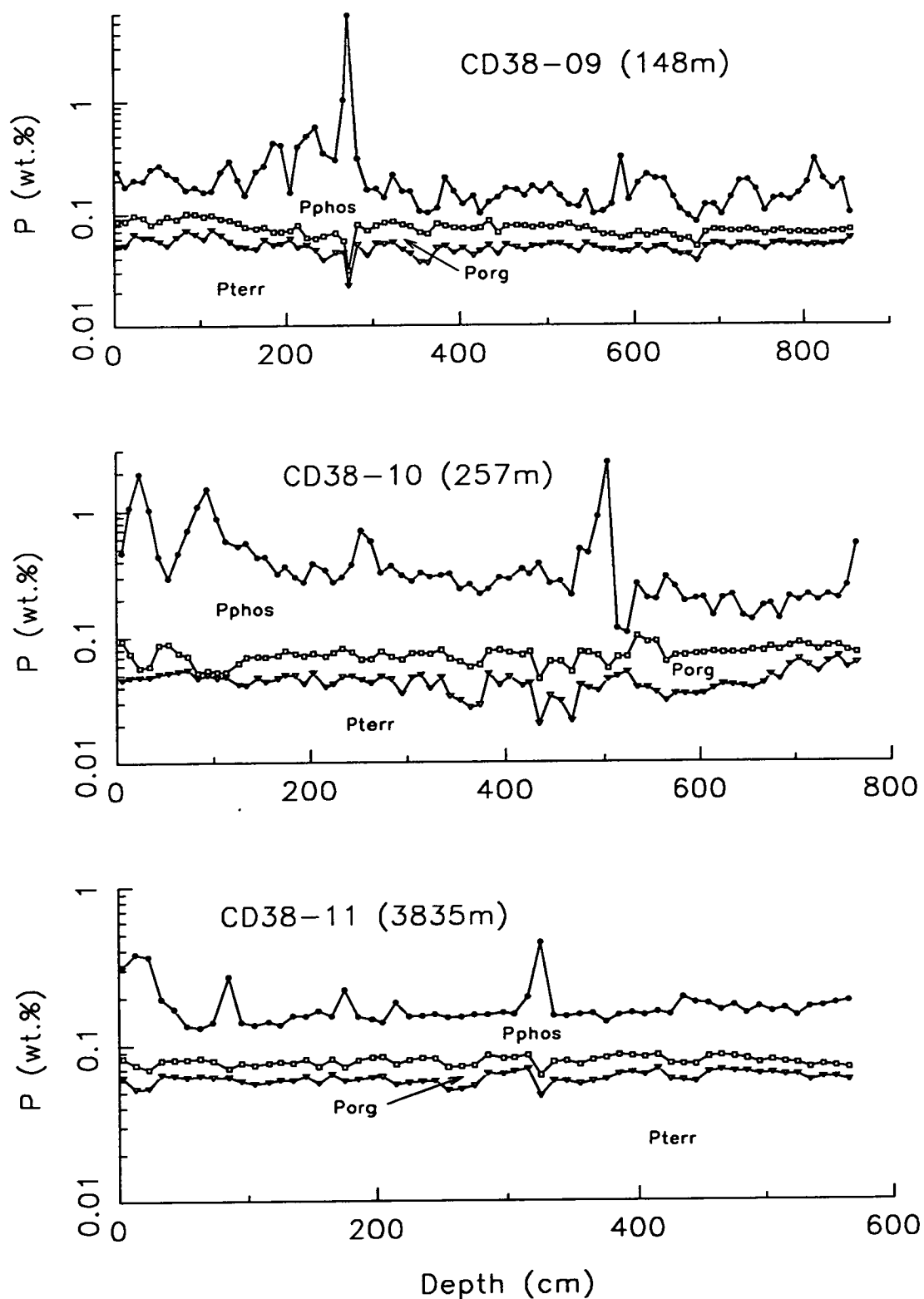


Figure 4.4. Partitioned phosphorus concentration against depth (note the log scale on the P (wt.%) axis). The area under each line represents the fraction of P where,

$$P_{terr} = A_1 \times 0.00875 \quad (\text{Turekian and Wedepohl, 1961})$$

$$P_{org} = C_{org} \times 0.0053 \quad (\text{Mach et al., 1987})$$

$$P_{phos} = P_{total} - (P_{terr} + P_{org}).$$

phosphorites formed in this area off Peru, the percentage amount of phosphorite (CFA and its associated non-phosphatic phases) present in each bulk sediment sample was calculated using Eqn 4.2.

Equation 4.2.

$$\text{Phosphorite (wt.\%)} = P_{\text{phos}} \times (100 / 8.29)$$

It can be seen from Fig. 4.5, which plots the calculated phosphorite percentage against depth for CD38-09, CD38-10 and CD38-11, that in core CD38-09 the background concentration is about 1wt.% but from 170 to 280cm depth there is some phosphorite enrichment. This peaks sharply at 273cm with just under 70 wt.% phosphorite in the sediment sampled and corresponds to the depth at which the hardground nodule was found.

In core CD38-10, the background phosphorite concentration is between 1 and 3wt.%, except in the region between 520 and 680cm where it falls below 1wt.% (this may be due to variability of the $C_{\text{org}}/P_{\text{org}}$ ratio with depth). The background level possibly indicates the presence of disseminated phosphorite gels and small pellets throughout the core. There are five zones in core CD38-10 where there has been enrichment of the phosphatic pellets by some sorting process (Fig. 4.5). These are at 30cm, 80-110cm, 250cm, 480-505cm and 770cm but it was only at the second of these depths that actual hardground nodules were observed during the logging of the core.

In core CD38-11 the phosphorite peaks are much smaller than in the two shallow-water cores, with more than 3 wt.% phosphorite occurring only at 10-30cm (a turbidite zone) and 330cm.

If zones in the sediment column where the phosphorite is greater than 10 wt.% are interpreted as being significant concentration events associated with periods of sediment reworking caused by stronger bottom-water currents during times of low sea-level, then core CD38-09 contains one such event and CD38-10 three events.

However, it must be emphasised that the calculated phosphorite (wt.%) depends greatly on the subsampling procedure: for instance, in core CD38-10 the phosphorite peak at 30cm is about 5% greater than the one at 90cm but it was only at 90cm that any phosphorite nodules were seen. It must also be remembered that if there is a large concentration of undissolved fish debris within the core, then it will be seen as a phosphorite-enriched horizon (Fig. 4.5).

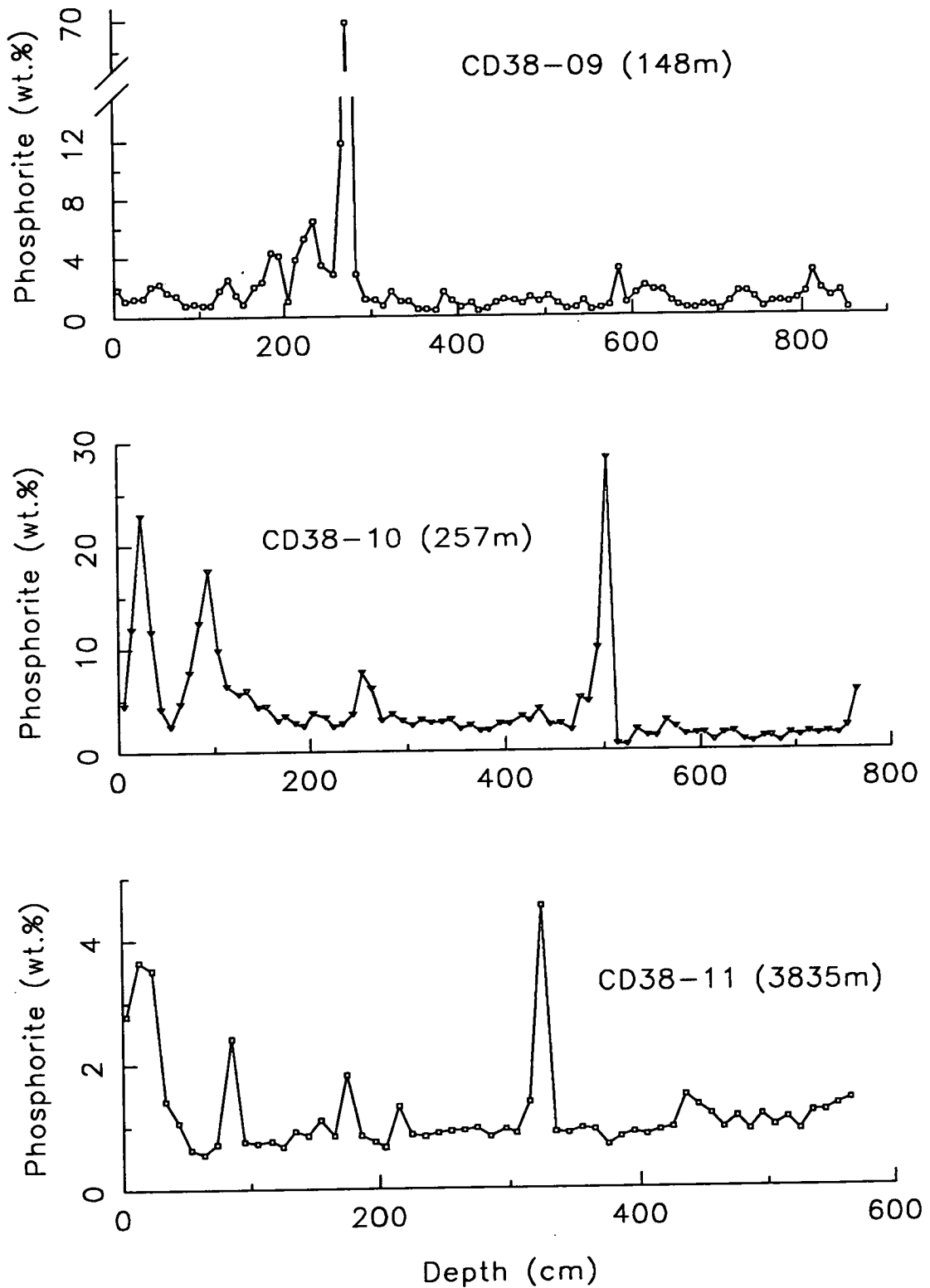


Figure 4.5. Phosphorite concentration against depth, where,

$$\text{Phosphorite} = P_{\text{phos}} \times (100 / 8.29) \quad (\text{Eqn. 3.2})$$

4.3.4. Trace element and phosphorite associations

The trace elements which have high concentrations in the X-ray fluorescence analysis of the large, hardground nodule (Table 4.1) should also be enriched, relative to the normal marine sediment concentrations, in the phosphorite-rich zones found in cores CD38-09 and CD38-10. Many previous studies have focused on the trace element composition of land phosphorites (Altschuler, 1980), marine phosphorites (Price and Calvert, 1978; Baturin, 1982; Piper *et al.*, 1988) and synthetically-grown apatite (Lucas *et al.*, 1990) in which enrichments of uranium (U), molybdenum (Mo), strontium (Sr), barium (Ba), cadmium (Cd), yttrium (Y) and the rare earth elements are common.

The following section will look at a selection of the above trace elements with respect to their concentrations in the sediment column of cores CD38-09 and CD38-10, and interpretations of their distribution, source and association with CFA will be made. Figures 4.6 and 4.7 illustrate the concentrations of U, Sr, Ba and Y, all expressed as element/Al ratios in order to eliminate any variation in concentration resulting from terrigenous input dilution, for both the shallow-water cores. The phosphorite depth profiles are plotted below each set of trace element profiles to allow for easy comparison. Table 4.3 lists the concentrations of trace elements measured in phosphorites from a wide variety of locations and includes the large nodule found in core CD38-09 and the bulk sediment from 273cm.

Uranium

In addition to the small amount incorporated in terrigenous clay particles, organic matter is known to scavenge uranium (as U^{VI}) from sea-water and then transport it to the accumulating sediments (Baturin *et al.*, 1971; Bertine and Turekian, 1973; Baturin, 1982; Shimmiel and Pedersen, 1990). It was seen in Chapter 3 that U is anomalously enriched in the suboxic/anoxic marine shelf sediments off Peru due to its association with the high flux of organic matter down the water column. However, within the sediments of cores CD38-09 and CD38-10, the U concentration displayed poor correlation with C_{org} levels (Table 3.3) as a result of post-depositional decomposition of organic matter and release of U into the surrounding pore-waters.

The U ions dissolved in the near-surface pore-waters (as U^{IV}) are therefore readily available to be incorporated in the authigenic diagenesis of CFA by substitution of calcium in the mineral lattice (Veeh *et al.*, 1974; Price and Calvert, 1978; Manheim and Gulbrandsen, 1979).

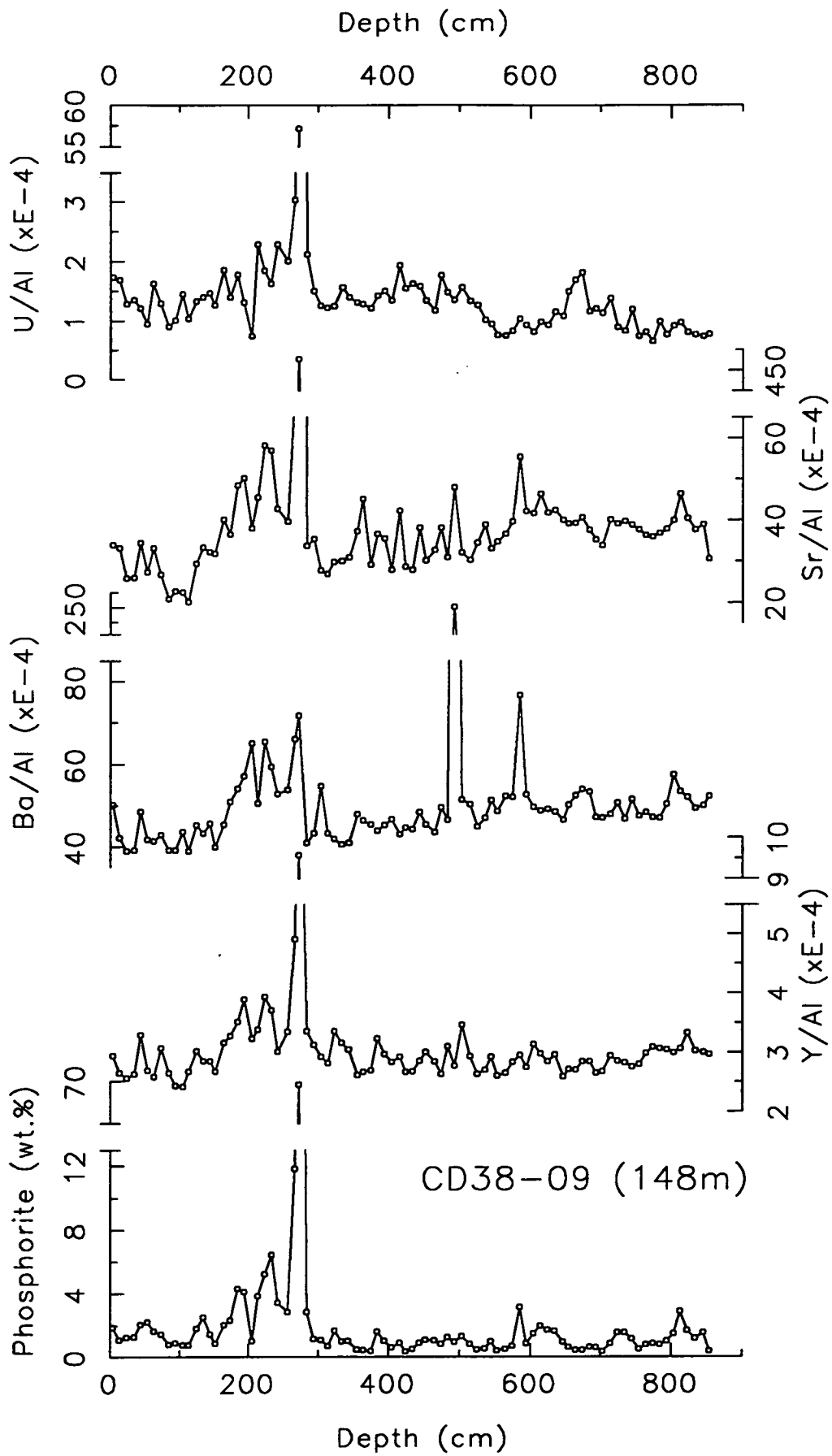


Figure 4.6. Trace element/Al ratios (U/Al, Sr/Al, Ba/Al and Y/Al) and phosphorite concentration against depth for core CD38-09 (148m).

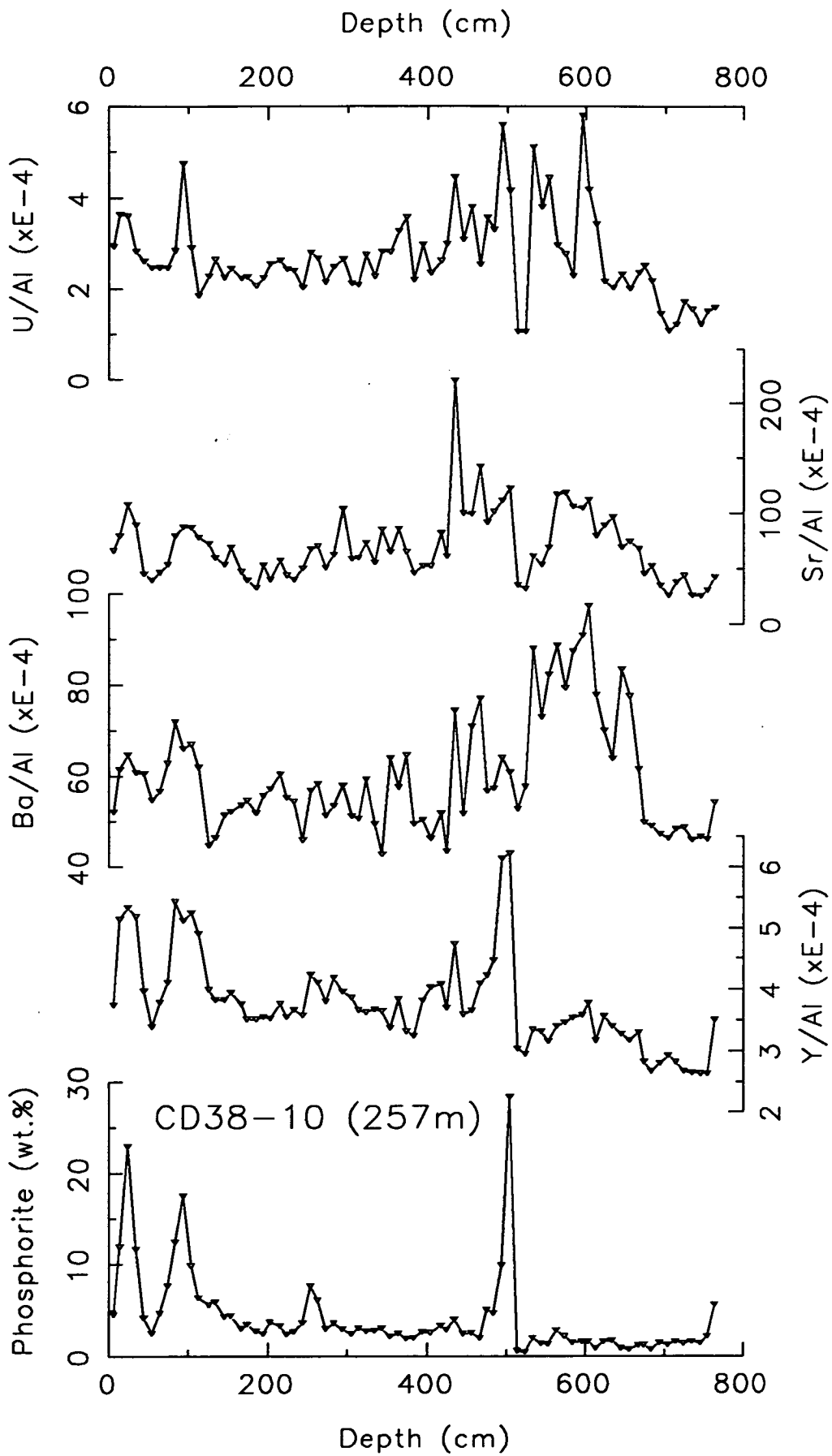


Figure 4.7. Trace element/Al ratios (U/Al, Sr/Al, Ba/Al and Y/Al) and phosphorite concentration vs. depth for core CD38-10 (257m).

Author	Year	Location	U (ppm)	Sr (ppm)	Ba (ppm)	Mo (ppm)	Y (ppm)
Kolodny & Kaplan	1970	Marine environment California Borderland	6-254 36-149				
Veeh <i>et al.</i>	1974	SW African margin	79-158				
Price & Calvert	1978	Namibian shelf (Fish-bones)	40-130 (140)	470-2080 (1640)	200-1100	15-45 (65)	5-302 (128)
McArthur	1978	Morocco sea-floor		53-2130			
Manheim & Gulbrandsen	1979	Marine environment	5-600	800-5000	10-900	2-30	
Altschuler	1980	Average land deposits	120	750	350	9	260
Baturin	1982	Peru/Chile margin	26-219				
Piper <i>et al.</i>	1988	Peru shelf (Fish remains)	51-459				120-150 (16)
This study		CD38-09 hardground Sediment (273cm)	112-153 148	1556-1692 1195	58-110 185	64-68 53	7-9 25
Turekian & Wedepohl	1961	(Deep-sea clay)	1.3	180	2300	27	90

Table 4.3. Trace element concentrations of phosphorites (and fish remains)

The bulk sediment sample at the location of the large hardground nodule in CD38-09, i.e. a phosphorite-rich zone, has a U-enriched concentration of 148ppm (Table 4.3). This U-phosphorite association is illustrated in Figs 4.6 and 4.7 by the similarity between the U/Al and phosphorite depth profiles. The normal, background U/Al level (1.55×10^{-5} , deep-sea clay, Turekian and Wedepohl, 1961) is elevated to about $1-4 \times 10^{-4}$ down both cores by the continuous presence of high organic matter concentrations. However, the phosphorite-rich zones at 270-280cm in CD38-09 and 30, 80-110 and 490-500cm in CD38-10, all correspond to peaks in U/Al (with a maximum of 57.5×10^{-4} at 273cm in core CD38-09) which is due to the incorporation of U into phosphatic pellets and nodules (Price and Calvert, 1978).

One possible problem in this interpretation of the U-phosphorite correlation is brought about by the presence of fish remains. Fish bones and scales are also enriched in uranium (700ppm, Baturin *et al.*, 1971; 140ppm, Price and Calvert, 1978) and, although they can act as an extra source of U by dissolution in marine sediments, if a large concentration of fish debris is buried within the sediment column then its geochemical signal will be an anomalous U (and P) peak.

A correlation plot of the total U content against the calculated P_{phos} content of bulk sediment samples in the phosphorite-rich zones of both CD38-09 and CD38-10, as shown in Figure 4.8, gives a regression line of:

$$U \text{ (ppm)} = [P_{\text{phos}} \text{ (wt.\%)} \times 14.1] + 4.3 \quad (r = 0.905).$$

This relationship is supported by the XRF data of the large, phosphorite nodule which has an average U/P ratio of 16.0 (Table 4.1). The above regression equation accounts for the U enrichment in phosphorite zones and allows for the quantitative partitioning of U into its terrigenous, phosphatic and organic phases for all the sediments from the Peruvian margin cores (Eqn 4.3 and Appendices B.4 and C.13).

Equation 4.3. Uranium partitioning (all in ppm)

$$U_{\text{org}} = U_{\text{total}} - [U_{\text{terr}} + U_{\text{phos}}]$$

where,

U_{org} = excess U associated with organic matter

U_{total} = salt-corrected XRF data

$U_{\text{terr}} = [\text{Al (wt.\%)} \times 0.4625]$

(average shale, Turekian and Wedepohl, 1961)

$U_{\text{phos}} = [P_{\text{phos}} \times 14.1].$

The down-core variations of the three U-phases are displayed in Fig. 4.9 and from this it can be seen that for core CD38-09 the U_{phos} -phase is dominant over the 160-300cm depth range but that U_{org} is significant elsewhere. In core CD38-10, the U_{org} concentrations are high throughout the core reflecting the high organic matter content, but very low (or zero) in the three phosphorite-rich zones. It should be noted that at 30 and 500cm the calculated U_{phos} concentration is greater than the U_{total} as measured by XRF, and this may be an indication that these zones are not composed entirely of phosphorite but that there is a significant concentration of fish debris present, which will have a lower U/P ratio (Price and Calvert, 1978).

In the semi-quantitative analysis of fish-remains in sieved samples from core CD38-10, fish bones and scales were seen to be common in these two zones (3.3.5, Fig. 3.12.B).

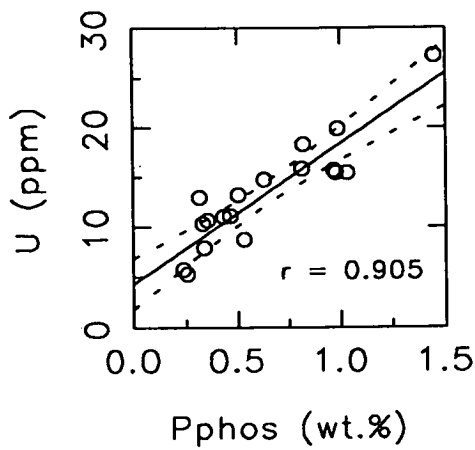


Figure 4.8. Correlation plot of U against P_{phos} for the phosphatic-rich zones in CD38-09 and CD38-10. With a best-fit straight line (showing 95% confidence limits) of:
 $U \text{ (ppm)} = (P_{\text{phos}} \times 14.1) + 4.3 \quad (r = 0.905)$

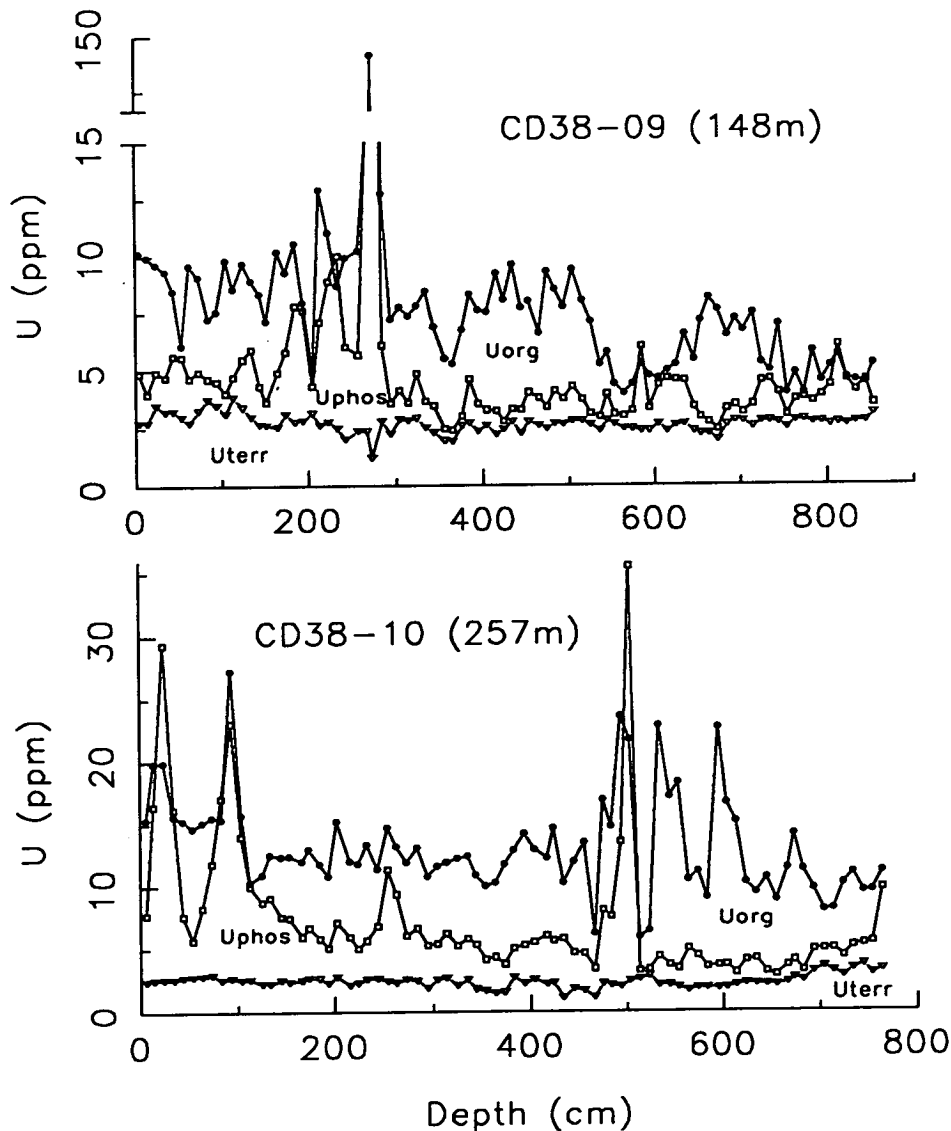


Figure 4.9. Partitioned uranium concentration against depth for CD38-09 and CD38-10 (note the break in scale on the U (ppm) axis for CD38-09). The area under each line represents the fraction of U where,

$$\begin{aligned}
 U_{\text{terr}} &= \text{Al} \times 0.4625 \quad (\text{Turekian and Wedepohl, 1961}), \\
 U_{\text{phos}} &= P_{\text{phos}} \times 14.1 \quad (\text{Fig. 3.8}), \\
 U_{\text{org}} &= U_{\text{total}} - (U_{\text{terr}} + U_{\text{phos}}).
 \end{aligned}$$

The organo-metallic relationship for C_{org} and calculated U_{org} has correlation coefficients of 0.655 for CD38-09 (after eliminating the sample at 273cm) and 0.813 for CD38-10, which are much higher than the original U_{total} - C_{org} coefficients (see Table 3.3).

Strontium

Sr is a group II element which occurs in the same column of the periodic table as calcium. It is most stable as the Sr^{2+} cation and has a very similar ionic radius compared with Ca^{2+} ($Sr^{2+} = 1.12\text{\AA}$, $Ca^{2+} = 0.99\text{\AA}$, Ahrens, 1952) and therefore Sr easily substitutes for Ca in mineral structures. This is true not only for the $CaCO_3$ shells of foraminifera and coccoliths (Emiliani, 1955; Krinsley, 1960) but also for carbonate fluorapatite (McArthur, 1978; Price and Calvert, 1978; Lucas *et al.*, 1990).

Price and Calvert (1978) quote a ratio of $CaO/Sr = 266$ in phosphorites on the Namibian shelf and interpret the consistency of the relationship as caused by Sr incorporation into the CFA structure at the time of formation. McArthur (1978) studied the Sr content of both land and marine phosphorite deposits and concluded that because Sr substitution requires no balancing-anion replacement, it is relatively easy for Sr to be incorporated into CFA and also for it to leave the mineral upon weathering. The concentrations of Sr in phosphorites are tabulated in Table 4.3. and from this it can be seen that the large nodule in CD38-09 has an average Sr content for phosphorites but that it is greatly enriched over normal, deep-sea clay values (Turekian and Wedepohl, 1961).

Figures 4.6 and 4.7 display the Sr/Al depth profiles for cores CD38-09 and CD38-10 which are fairly similar in appearance to the phosphorite profiles. In core CD38-09, the correlation is very good over the 160-300cm depth range but elsewhere the variation in Sr/Al is controlled by changes in $CaCO_3$ concentrations (compare with Fig. 3.5). This carbonate control is also evident in core CD38-10 (compare Figs 4.7 and 3.6) especially at depths below 400cm. The two phosphorite peaks in the top metre of CD38-10 are reflected by elevations in the Sr/Al but there is not such a distinct peak at 500cm. This latter zone may be mainly an enrichment of fish debris, which is characterised by a different Sr/Al ratio.

By selecting the same bulk sediment samples as used for the $U:P_{phos}$ regression analysis, a $Sr:P_{phos}$ relationship in the phosphorite zones can be quantified (Fig. 4.10):

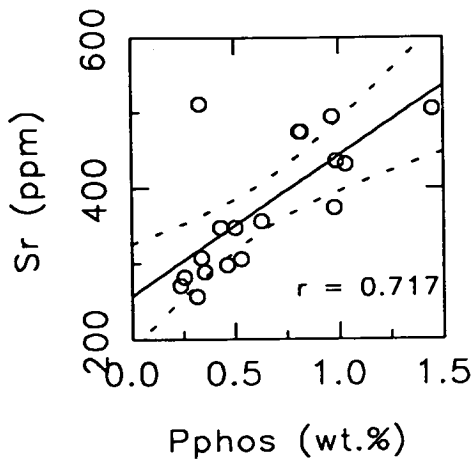


Figure 4.10. Correlation plot of Sr against P_{phos} for the phosphatic-rich zones in CD38-09 and CD38-10. With a best-fit straight line (showing 95% confidence limits) of:
 $Sr \text{ (ppm)} = (P_{\text{phos}} \times 186) + 257 \quad (r = 0.717)$

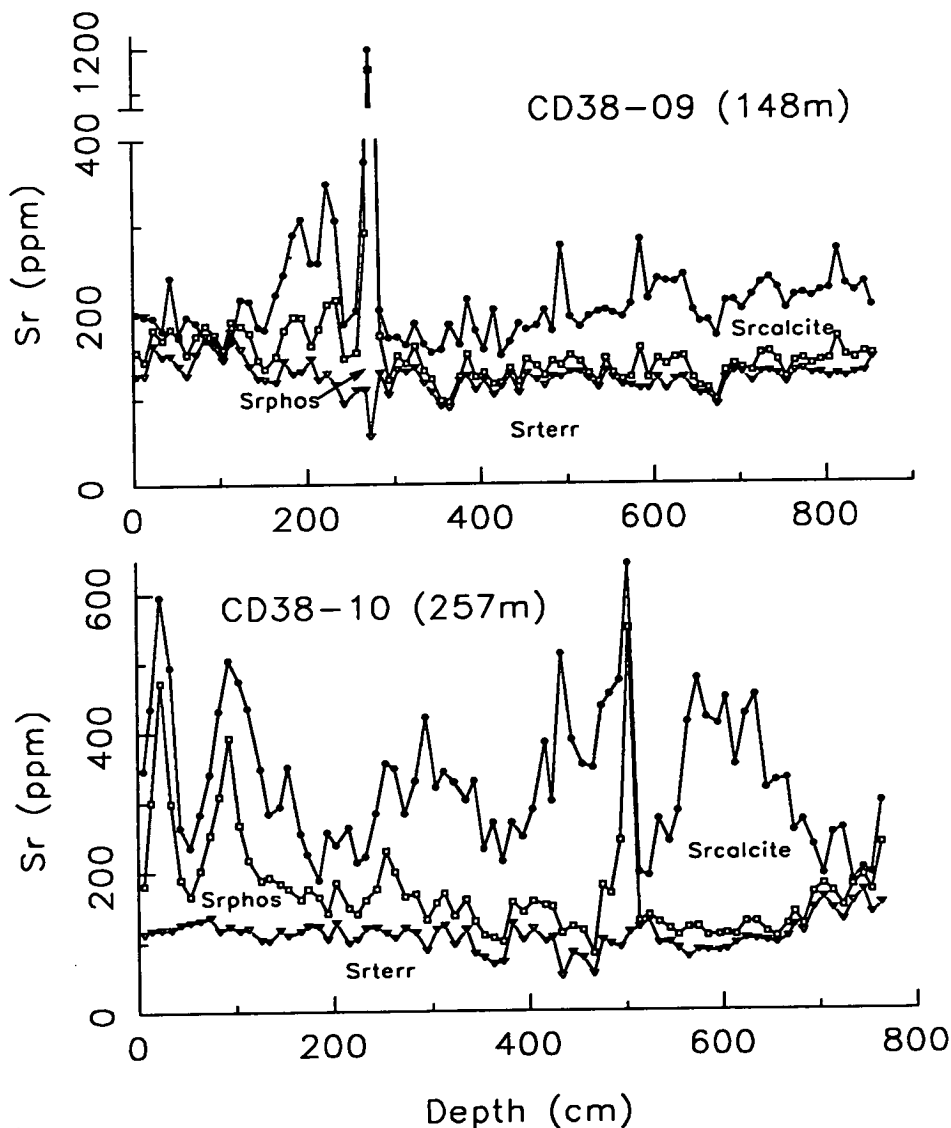


Figure 4.11. Partitioned strontium concentration against depth for CD38-09 and CD38-10 (note the break in scale on the Sr (ppm) axis for CD38-09). The area under each line represents the fraction of Sr where,

$$\begin{aligned}
 Sr_{\text{terr}} &= Al \times 21.43 \quad (\text{Turekian and Wedepohl, 1961}), \\
 Sr_{\text{phos}} &= P_{\text{phos}} \times 186 \quad (\text{Fig. 3.10}), \\
 Sr_{\text{calcite}} &= Sr_{\text{total}} - (Sr_{\text{terr}} + Sr_{\text{phos}}).
 \end{aligned}$$

$$\text{Sr (ppm)} = [\text{P}_{\text{phos}} (\text{wt.}\%) \times 186] + 257 \quad (r = 0.717).$$

The intercept of this regression line is equivalent to the concentration of Sr from terrigenous debris and biogenic CaCO₃ shells found within the phosphorite-rich zones. The Sr/P_{phos} ratio of 186 corresponds well to the measured Sr/P ratio of 190-200 for the hardground nodule in core CD38-09 (Table 4.1). Shimmiel (1985) calculated the quantity of Sr uptake in diagenetic apatite, within sediments from Baja California, as 124ppm Sr per wt.% P.

The above regression equation allows for partitioning of the Sr_{total} concentration into three phases; namely, terrigenous, phosphatic and an excess concentration which is the content associated with biogenic CaCO₃ (Eqn 4.4 and Appendices B.4 and C.13).

Equation 4.4. Strontium partitioning (all in ppm)

$$\text{Sr}_{\text{calcite}} = \text{Sr}_{\text{total}} - [\text{Sr}_{\text{terr}} + \text{Sr}_{\text{phos}}]$$

where, Sr_{calcite} = excess Sr associated with CaCO₃
 Sr_{total} = salt-corrected XRF data
 Sr_{terr} = [Al (wt.%) x 21.43] (Turekian and Wedepohl, 1961)
 Sr_{phos} = [P_{phos} x 186].

The depth profiles of the three Sr-phases (ppm) are plotted in Fig. 4.11 and this illustrates that, for both CD38-09 and CD38-10, Sr_{terr} accounts for about 100ppm of the total Sr content and that there is always a significant amount of Sr_{calcite} present even in the phosphorite-rich zones. This is because of the presence of both biogenic CaCO₃ and secondary-calcite cement within and around phosphorite pellets and nodules (Table 4.2).

The calculated Sr_{calcite} and CaCO₃ concentrations correlate extremely well (in cores CD38-09 and CD38-10, r = 0.723 and 0.924 respectively) and the weight ratio of these two biogeochemical components will be discussed in Chapter 6.

Barium

Lucas *et al.* (1990) studied both Ba and Sr enrichments within synthetic apatites and concluded that Ba²⁺ is a less suitable substituent for Ca²⁺ compared with Sr²⁺ even though the ionic charges are all equal. This is simply because the Ba cation

is much larger (1.34Å, Ahrens, 1952) than the Ca cation. Lucas *et al.* (1990) obtained a continuous solid-solution series for Sr replacement of Ca but could only achieve Ba replacement in apatites at less than 10% by weight.

It is therefore to be expected that in phosphorites from the natural, marine environment, Ba concentrations are significantly lower than the Sr content (Price and Calvert, 1978) and this be seen in the summary table of trace element concentrations in phosphorites (Table 4.3). The hardground nodule from CD38-09 has levels of Ba which are about the average for previously published results of marine phosphorites but much less than the average calculated by Altschuler (1980) for land deposits. This may be an indication that post-depositional weathering can enrich the Ba content of phosphorites.

The Ba ions which are incorporated into CFA minerals (Lucas *et al.*, 1990) must be present in the interstitial pore-waters of surface margin sediments and their flux from sea-water is via a residual solid-phase associated with organic debris and, most commonly, the biogenic silica frustules of diatoms (Dymond *et al.*, 1992 and references therein). In sediments accumulating under oxic conditions the Ba component can be well-preserved, but under reducing conditions, such as found in phosphorite-rich continental margin sediments, low Ba concentrations can occur due to the dissolution of barite and loss of dissolved Ba back into bottom-waters (Dymond *et al.*, 1992).

The Ba/Al depth profiles for the two shallow-water cores (Figs 4.6 and 4.7) display some similarities to the phosphorite profiles but the peaks at 273cm in CD38-09 and at 500cm in CD38-10 are not very pronounced. There are also large peaks in Ba/Al (at 500cm in CD38-09 and 530-650cm in CD38-10) which do not correspond to phosphorite-rich horizons. These may be due to enhanced biogenic flux to the sediment (compare with the biogenic silica profiles in Figs 3.5 and 3.6) and/or enhanced barite preservation (6.3.1).

Molybdenum

Molybdenum is a heavy metal which is known to be associated with organic matter enrichments in suboxic/anoxic sediments accumulating under a zone of coastal upwelling (Chapter 3). Study of the Mo-C_{org} correlation coefficients for the organic-rich sediments of cores CD38-09 and CD38-10 indicated that Mo is released relatively easily upon degradation of organic matter. Therefore, there should be a high concentration of Mo dissolved in pore-waters available for incorporation into any authigenic minerals, such as CFA, or onto the mineral surfaces.

However, possibly because of its high valence state of +6, Mo uptake and enrichment in phosphorites is not common. Although the Mo concentration in the hardground nodule from CD38-09 represents an enrichment of twice the average deep-sea clay (Turekian and Wedepohl, 1961) it only represents a fairly average value for the organic-rich, reducing sediments which surround the phosphorite pellets and nodules (Table 3.1). Therefore, the enrichments seen by Price and Calvert (1978) and Altschuler (1980) are not really due to the authigenic mineral diagenesis of CFA.

Yttrium

One group of elements which can successfully substitute for calcium in the CFA of marine phosphorites are the rare earth elements (REE) (Manheim and Gulbrandsen, 1979; Henderson, 1984) and although Y is not classified as a REE, it does have very similar chemical characteristics to the REE and therefore is found enriched in phosphorites (Price and Calvert, 1978; Piper *et al.*, 1988; Table 4.3).

Y and the REE can be removed from sea-water into marine sediments by association with either terrigenous, hydrogenous or biogenic particles (Henderson, 1984) or, more importantly in the coastal zones such as Peru and south west Africa, incorporated in phosphatic fish-remains (Blokh, 1961; Arrhenius and Bonatti, 1965; Price and Calvert, 1978).

The hardground nodule from CD38-09 does not contain a high concentration of Y (8ppm) and yet the Y/Al depth profiles of the bulk sediment samples show extremely strong similarity to the phosphorite profiles (Figs 4.6 and 4.7). This can be explained either by an inaccurate X-ray fluorescence determination of Y in the hardground (which seems highly unlikely) or by the fact that the Y is still associated with undissolved fish bones and scales which are concentrated in the phosphorite-rich zones, especially at 500cm in core CD38-10.

As for U and Sr, the total Y concentration in these phosphatic horizons can be plotted against P_{phos} (Fig. 4.12) and a regression analysis gives the following relationship:

$$Y \text{ (ppm)} = [P_{\text{phos}} \text{ (wt.\%)} \times 12.1] + 15.2 \quad (r = 0.800).$$

The regression line intercepts the Y-axis at 15ppm which is the average amount of Y associated with terrigenous particles within and around the phosphatic minerals. It is now possible to separate the total Y concentration into two phases; namely the phosphatic and terrigenous associations, using Eqn 4.5 (Appendices B.4 and C.13). It

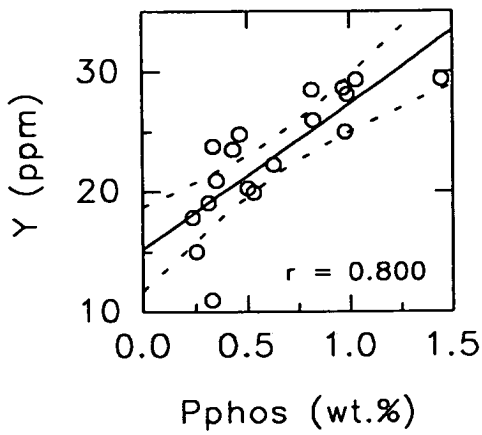


Figure 4.12. Correlation plot of Y against P_{phos} for the phosphatic-rich zones in CD38-09 and CD38-10. With a best-fit straight line (showing 95% confidence limits) of:
 $Y \text{ (ppm)} = (P_{\text{phos}} \times 12.1) + 15.2 \quad (r = 0.800)$

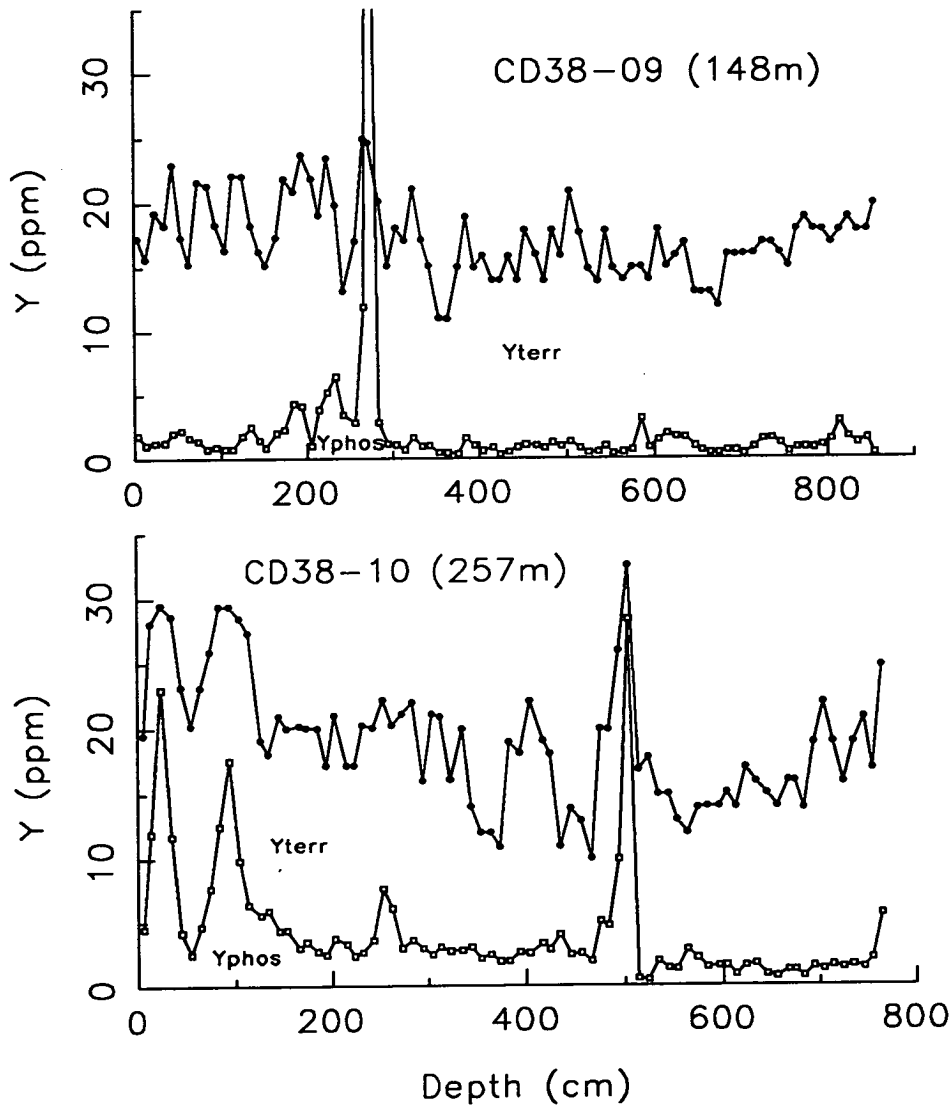


Figure 4.13. Partitioned yttrium concentration against depth for CD38-09 and CD38-10. The area under each line represents the fraction of Y where,

$$Y_{\text{phos}} = P_{\text{phos}} \times 12.1 \quad (\text{Fig. 3.12}),$$

$$Y_{\text{terr}} = Y_{\text{total}} - Y_{\text{phos}}.$$

is not possible, however, to state how much of the Y_{phos} is associated with either CFA and/or fish debris.

Equation 4.5. Yttrium partitioning (all in ppm)

$$Y_{\text{terr}} = Y_{\text{total}} - Y_{\text{phos}}$$

where, Y_{terr} = excess Y associated with terrigenous clay particles
 Y_{total} = salt-corrected XRF data
 Y_{phos} = [$P_{\text{phos}} \times 12.1$].

Figure 4.13 illustrates the concentrations of the two phases of Y down both cores CD38-09 and CD38-10 and it can be seen that Y_{terr} is the most abundant phase. Correlation coefficients of 0.879 for CD38-09 and 0.726 for CD38-10 between Y_{terr} and Al (which is found only in terrigenous clays) gives support to the accuracy of the above partitioning equation.

4.3.5. U/Th age dating of the phosphorite nodule

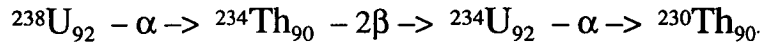
Before the timing of the phosphorite hardground nodules found in the near-shore cores on the Peruvian continental margin can be interpreted with respect to changes in sea-level during the Late Quaternary, the phosphatic material has to be accurately dated.

The analytical technique which is best suited for age determination of phosphorite material is the uranium-series disequilibrium method (Ivanovich and Harmon, 1982; and references therein). This involves measurement of the activity of uranium and thorium radiochemical isotopes and calculation of the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ ratios. A brief outline of the analytical methods involved in U-series disequilibrium determinations by α -spectrometry are given in Appendix A.8 and the equations for calculation of the age of the phosphorite and the initial $^{234}\text{U}/^{238}\text{U}$ ratio are given in Appendix B.5.

The theory behind this method of age determination relies on the natural radiogenic decay of ^{238}U and its daughter isotopes. Following the reaction steps shown in Eqn 4.6, ^{238}U decays by α -particle emission (loss of ^4He) and β -particle emission to ^{234}U and which subsequently loses an alpha-particle to produce ^{230}Th .

Each reaction has a known half-life ($t_{1/2}$) which is the time for one half of the original amount of the parent isotope to decay to its respective daughter isotope.

Equation 4.6. ^{238}U natural radiogenic decay series (Henderson, 1986)



Upon formation of phosphatic material at the sediment/water interface, uranium is incorporated into the CFA mineral lattice (4.3.4) with a $^{234}\text{U}/^{238}\text{U}$ ratio equal to that of sea-water (Veeh, 1967; Veeh *et al.*, 1973; Burnett *et al.*, 1988). It is assumed that the $^{234}\text{U}/^{238}\text{U}$ ratio in sea-water during the last few hundred thousand years has not significantly differed from its present value (1.14 ± 0.014 , Ku *et al.*, 1977) and that the phosphorite has remained a closed system with respect to U and Th since the time of formation (Veeh *et al.*, 1973).

Thus, the ^{238}U in the phosphorite will decay to ^{234}U but at a slower rate (larger $t_{1/2}$) than the rate at which the ^{234}U decays to ^{230}Th , i.e. the $^{234}\text{U}/^{238}\text{U}$ ratio will exponentially decrease (from the initial sea-water value) with increasing age of the phosphatic material and the $^{230}\text{Th}/^{234}\text{U}$ ratio will exponentially increase. If the ^{230}Th content of the phosphatic material at the time of formation is assumed to be zero (i.e. all the ^{230}Th has been formed by U-series decay since formation) then the calculated age, from determination of the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ ratios at present in the phosphorite, can be said to be an absolute age. However, if some ^{230}Th was incorporated into the phosphorite during initial formation then the calculated age can only be said to be a maximum age.

The only phosphorite sample that was measured using the U-series disequilibrium methods was a bulk-sample from the base of the large nodule in core CD38-09 (273cm). From Table 4.1 it can be seen that the Th concentration of this sample is only 2ppm (of which 99.9% is ^{232}Th , G.B. Shimmield, Pers. Comm.). Therefore, although the age calculated below cannot definitely be said to be an absolute age, the low Th content suggests that virtually all the ^{230}Th present in the sample will have been formed by *in situ* radiogenic decay and that the calculated age is probably very close to an absolute age.

The data in Table 4.4 gives the results of the U and Th isotopic determination by α -spectrometry on duplicate samples taken from the base of the large nodule from CD38-09, the calculated age and the original $^{234}\text{U}/^{238}\text{U}$ ratio. The raw data of number

of counts for each isotope and length of counting time are presented in Appendix C.15.

	Sample H	(Error)	Sample I	(Error)
^{238}U (dpm/g)	81.95	± 0.58	82.51	± 0.47
^{234}U (dpm/g)	90.68	± 0.64	92.55	± 0.52
^{230}Th (dpm/g)	58.53	± 0.41	62.53	± 0.76
^{232}Th (dpm/g)	0.61	± 0.03	1.56	± 0.10
$^{234}\text{U}/^{238}\text{U}$	1.1065	± 0.011	1.1216	± 0.009
$^{230}\text{Th}/^{234}\text{U}$	0.6454	± 0.006	0.6756	± 0.009
Age (years)	109895	± 1500	118595	± 2570
Initial $^{234}\text{U}/^{238}\text{U}$	1.145		1.169	

Table 4.4. U/Th isotope results for base of phosphorite nodule found at 273cm depth in CD38-09 (dpm/g = disintegration per minute/gram). Samples H and I are duplicates.

Author	Sample and location	$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{234}\text{U}$	Age (kyr)	Method
Kolodny & Kaplan (1970)	Dredged from sea-floor	< 1.00		> 800	U
Baturin <i>et al.</i> (1972)	S.W. African shelf	1.163		24	U
	Chilean shelf	1.143		55	U
Veeh <i>et al.</i> (1973)	Peru - A183 - surface	1.11	0.61	<100	U/Th
	Peru - A183 - core	1.10	0.70	<125	U/Th
	Peru - KK77161 - surface	1.09	0.46	<66	U/Th
	Peru - KK77161 - core	1.10	0.62	<102	U/Th
	California (15 samples)	0.95-1.02	1.00-1.12	>200	U/Th
Veeh <i>et al.</i> (1974)	S.W. African shelf	0.87-1.02	1.00-1.09		
Jahnke <i>et al.</i> (1983)	Mexican margin apatite			<113	
Kim & Burnett (1985)	Peru shelf nodules			<300	U/Th
Burnett <i>et al.</i> (1988)	Peru shelf pellets	1.05-1.12	0.15-0.73	3-254	U/Th
This study	Peru CD38-09 nodule	1.11-1.12	0.64-0.675	114	U/Th

Table 4.5. U/Th age determinations for phosphorites from Peru, S.W. Africa and Baja California.

The results in Table 4.4 for the large phosphorite nodule can now be compared with the work of previous authors (summarised in Table 4.5) for a range of phosphorite nodules and pellets from the only three sites of modern phosphorite formation; namely, off Peru, S.W. Africa and Baja California. The $^{234}\text{U}/^{238}\text{U}$ and

$^{230}\text{Th}/^{234}\text{U}$ ratios for the CD38-09 nodule seem to have fairly typical values for Recent phosphatic material found in sediments under an upwelling zone. The calculated age, when averaged for the two duplicate samples, of 114.2 ± 6.4 thousand years (kyr) also falls within quite a common age range for phosphorite formation.

Calculation of the original $^{234}\text{U}/^{238}\text{U}$ ratio (using the equation in Appendix B.5) gives an average value of 1.157 which is very close to the present day sea-water $^{234}\text{U}/^{238}\text{U}$ ratio of 1.14 ± 0.014 (Ku *et al.*, 1977). Not only does this give extra confidence to the accuracy of the U-series disequilibrium results but it also supports the theory that formation of the phosphatic material, from which the hardground nodule found at 273cm in core CD38-09 is composed, was initially formed at the sediment/water interface approximately 114 thousand years age (ka).

4.3.6 Phosphorites and eustatic variation off Peru

Given that the large phosphorite nodule in core CD38-09 has a U/Th average age of 114 (± 6) ka and was found at a water depth of 148m and sediment depth of 273cm, what are the possible interpretations for the growth history of this nodule?

The phosphorite nodule is likely to have initially formed as small pellets just below the sediment/water interface (Baker and Burnett, 1988; Burnett *et al.*, 1988). Although each pellet may have only taken between 3 and 12 years to grow (Froelich *et al.*, 1988) from a nucleation point into a grain about 125-500 μm in diameter (Baker and Burnett, 1988), the nodule is likely to consist of thousands of pelletal grains whose ages of diagenetic formation will range over quite a few thousand years. This means that the age of 114kyr is just a mean age for the phosphatic material, some of which may be as old as about 125kyr and some as young as about 100kyr.

One hypothesis may be that this nodule actually consists of pellets (and other non-phosphatic material) which initially formed around 114ka, whereupon it became a closed system with respect to uranium and thorium. In terms of global glacial/interglacial periodicity, 114ka occurs within interglacial stage 5, just after the peak of substage 5e when climatic conditions were very similar to the present day (Imbrie *et al.*, 1984). If the phosphorite nodule formed at this time and has remained *in situ*, slowly being buried under the accumulating sediment since 114ka, then this hypothesis requires an average sediment accumulation rate of only 2.4 cm kyr⁻¹. This rate is exceptionally slow for a shallow-water continental margin site, especially as it lies under a zone of coastal upwelling and the sediment receives a high biogenic flux

(Chapter 3). Also during the period since 114ka, the global climate went through a full glacial cycle which probably means that far more terrigenous material than at present was being weathered off the Andes and being deposited on the Peruvian continental shelf (7.2.3).

It is therefore highly unlikely that sediment at the site of core CD38-09 has been accumulating over the last 114kyr at an average rate of only 2.4 cm kyr⁻¹. Initial formation of the phosphatic material contained in the nodule 114ka may still be possible if, as well as sediment accumulation, the site has also suffered sediment loss. This is very likely due to the shallow water depth of the core and the fact that such fine-grained sediment with high organic matter content will be easily eroded upon a change in direction or strengthening of bottom-water currents. This almost certainly occurred during the last glacial period when the sea-level dropped by up to 120m in response to the global increase in ice-volume (Fairbanks, 1989).

The shape of the nodule (flattened in one dimension) and its horizontal position in the core (4.3.1) point towards a two-phase diagenetic history for this phosphorite hardground deposit, of initial pellet formation followed by a later event of mineral concentration. The radiometric age of the nodule and its depth in core CD38-09, give further proof and support for the established theory of phosphorite hardground formation (Baturin and Bezrukov, 1979; Baturin, 1982; Burnett *et al.*, 1980; Burnett and Froelich, 1988).

The phosphatic material of which the nodule is composed was probably originally introduced to the sediment as organic matter and other biogenic detritus between 125 and 100 ka, during the early stages of interglacial stage 5. At this time, the oceanographic and sedimentological conditions were ideal for diagenetic phosphorite pellet formation, upon bacterial decay of the organic matter (4.1.5), in a reducing pore-water environment (Burnett *et al.*, 1988; Froelich *et al.*, 1988). Thousands of these pellets formed per square metre of ocean floor but it was not until the onset of the next glacial period (stage 4) at about 75ka (Imbrie *et al.*, 1984) when sea-level dropped and bottom-water currents along the Peru shelf became stronger, that the fine-grained clay, diatom and organic matrix (in which the disseminated pellets sat) was winnowed away down the continental slope and the larger-grained, denser pellets were concentrated together (Baturin, 1982).

Although the phosphorite nodule has a U/Th diagenetic age of 114 ±6 ka, it probably only formed after reworking of the sediment column (Baturin and Bezrukov, 1979) sometime during the period from 75 to 19 ka (the latter being the maximum of the last glacial period, stage 2, and lowest sea-level stand; Imbrie *et al.*, 1984). The

nodule was probably part of a larger phosphorite hardground unit, which is suggested by the 2D slab-like appearance, the small burrows seen on its topside and the polished surfaces (Cook *et al.*, 1990). It is quite likely that the hardground unit was subsequently broken up by storm activity when the sea-level was at a minimum (18ka, Fairbanks, 1989) and since that time the nodule has been reburied under 273cm of fresh marine sediment. If this were the correct hypothesis then it would imply a Holocene (stage 1) sediment accumulation rate of about 15 cm kyr⁻¹ which is quite suitable for such a shallow-water site as CD38-09, under a zone of strong coastal upwelling.

4.4 CONCLUSIONS

This geochemical study of phosphorite nodules and pellets which have diagenetically formed in the Peruvian continental margin sediments has led to the following conclusions.

- 1) Hardground nodules found at 273cm in core CD38-09 and at 90cm in core CD38-10 (both cores located in a reducing environment, Chapter 6) have been shown by X-ray diffraction and X-ray fluorescence analyses to be composed of phosphorite. This is a multi-phase mineral deposit which, following the linear programming calculations of Glenn and Arthur (1988), is dominantly (about 65 wt.%) composed of carbonate fluorapatite (CFA).
- 2) Pore-water phosphate profiles from box core material supports the hypothesis of Froelich *et al.* (1988) that phosphorite pellet formation is presently occurring on the Peru shelf and that it is a two-stage process. This involves the initial formation of amorphous calcium phosphate (both at CD38-09 and CD38-10) followed by addition of fluoride and carbonate anions and conversion to CFA (probably presently only at CD38-09).
- 3) Down-core phosphorus partitioning in bulk sediment samples from piston cores allows for calculation of P_{phos} (wt.%) and percentage phosphorite, which indicates the continuous presence of phosphorite pellets and zones of phosphorite concentration. One possible source of error in the phosphorite calculations occurs because fish bone horizons will also give concentrations of excess phosphorus, such as around 500cm in CD38-10.
- 4) The enrichment of certain trace elements (U, Sr, Ba, Mo, Y and REE) in phosphorites due to the necessity of CFA elemental substitution to achieve a stable mineral lattice, allows for the calculation of trace element/P_{phos} ratios in

phosphorite zones. This leads to partitioning equations for the calculation of U_{org} , $Sr_{calcite}$ and Y_{terr} concentrations in all bulk sediment samples, which will be used later in this thesis.

- 5) U-series disequilibrium techniques, used for age calculation of phosphatic material in the large nodule found in core CD38-09, measured U and Th radiogenic isotope activities equivalent to an age of 114 ± 6 ka and with an initial $^{234}U/^{238}U$ ratio of 1.157 ± 0.012 , which is similar to that of present-day sea-water.
- 6) The above radiogenic data and the physical appearance and location of the nodule lead to the following interpretation of the phosphorite's diagenetic history.

Small phosphorite pellets formed from decaying biogenic material at the sediment/water interface in the vicinity of core CD38-09. This occurred over a period of time between 125 and 100 ka, which lies during the early stages of interglacial stage 5. At some time during the next glaciation period, when the sea-level dropped and bottom-water currents strengthened, fine-grained sediment was winnowed away from the site leaving behind a concentration of phosphorite pellets (and other heavy minerals) which slowly lithified into a hardground, bedded unit. This slab-like material was then broken up into flat nodules about 18ka, one of which sat horizontally on the sea-floor at the site of core CD38-09. It was then reburied under accumulating sediment during the Holocene period.

One question that arises from this theory is whether or not the nodule found at 90cm in core CD38-10 has the same diagenetic history as the one found at 273cm in core CD38-09. If it does have a similar history then it implies that, since the last glacial maximum, CD38-09 at 148m water depth has had an average of three times the sediment accumulation rate of CD38-10 at 257m. This may be possible because CD38-09 is situated closer to the source of terrigenous detritus and there may also have been a further period of sediment erosion at CD38-10 (highlighted by the phosphorite peak at 30cm, Fig. 4.5). In order to clarify this hypothesis further U/Th age determinations need to be carried out on the nodules and their surrounding sediments.

CHAPTER 5

STATISTICAL ANALYSIS OF THE DATASET

5.1. INTRODUCTION

"Are you animal, vegetable or mineral?' he said. 'Mineral, I think' replied Alice."

Lewis Carroll

Alice Through the Looking Glass

Just as Alice, in the above quote, had to decide between animal, vegetable or mineral, marine geochemical studies have to interpret the down-core variation in element concentrations, identify element-phase correlations and decide whether or not particular elements are associated with marine animal or plant remains or with diagenetic mineral growth.

This chapter will use statistical analysis and mathematical computational techniques in an attempt to simplify the very large dataset of geochemical parameters (over 25 elements, calculated phases and ratios) measured for all the samples taken from the four piston cores from the Peruvian continental margin (over 250 samples). This is done so that each geochemical variable can be assigned to one or more sediment phases or components, which can be interpreted as the source(s) of that particular element.

The three methods used in this chapter are as follows:

- (a) correlation matrices,
- (b) R-mode factor analysis (principal component analysis - PCA),
- (c) multi-component analysis (MCA).

5.2. CORRELATION MATRICES

5.2.1. Methods

Correlation analysis between each of the 30 geochemical variables was carried out using Minitab statistical programming and involved a least squares correlation of two independent variables. The results, given as r = correlation coefficient of a best-fit straight line in an X-Y plot of the two variables, are tabulated in Appendix C.16 and it is these values that are used throughout this thesis (e.g. Table 6.3).

There are five geochemical variables which are taken to represent five main phases in these marine sediments :

- (1) C_{org} - representative of organic matter phase - as measured (Appendix A.3),
- (2) Biogenic silica - representative of biological silicate-remains phase - as measured (Appendix A.4),
- (3) $CaCO_3$ - representative of biological carbonate-remains phase - as calculated (Appendix B.1),
- (4) Phos. - representative of phosphorite mineral phase - as calculated (Appendix B.4),
- (5) Terr. - representative of terrigenous-input phase = 100 - (sum of above four).

5.2.2. Interpretation of results

Figure 5.1 shows a summary table of the correlation matrix for each of the piston cores, which illustrates the strength of the correlation between the 30 geochemical variables and the five main phases. A strong, positive correlation (++) indicates that there is a probable association between an element and a phase and a positive correlation (+) indicates that an association is possible. Negative correlations (-- and -) occur when the concentration of a particular phase controls the concentration of another due to a strong dilution effect, and therefore an element which is associated with the latter phase will have a concentration which varies antithetically with the former phase.

Using Fig. 5.1 for reference, the following comments can be made about element-phase correlations and associations.

- 1) In all of the cores, the terrigenous phase correlates positively with a large number of elements and strongly with Al, Ti and K in CD38-10, CD38-02 and CD38-11. The association between the terrigenous phase and Al justifies the use of this element in calculations and ratios, used throughout this thesis, which normalise changes in the terrigenous phase and allow study of effects of biogenic dilution.
- 2) In core CD38-09, there are only a few strong correlations, i.e. Ni and Mo with organic matter and U and Sr with phosphorite phases, which may indicate that no one phase dominates the geochemical composition of the sediment in this core.
- 3) The positive correlation in core CD38-09 between the organic matter phase and Zr/Rb (which is a grain-size indicator, 7.2.3) shows that it is possible that the abundance of organic matter arriving at a shallow-water site may have

PC38-02 (2525m)

	Corg	Bio.Sil.	CaCO3	Phos.	Terr.
Corg	1				
Bio.Sil.		1			
CaCO3			1		
Phos.				1	
Terr.					1
Al					++
K					++
Ti					++
I	++				
Br	+				
Mo	+				
U					
Ni	+	+			
Cr		+			+
V					++
Cu					+
Sr			++		-
Ba		+		+	+
Zn		+			++
Rb					++
Zr					++
Zr/Rb					
Nb					+
Pb					+
Th					+
La					+
Ce					+
Nd					+
Y					++
Sc					++

PC38-09 (148m)

	Corg	Bio.Sil.	CaCO3	Phos.	Terr.
Corg	1				
Bio.Sil.		1			
CaCO3			1		
Phos.				1	
Terr.					1
Al					+
K					+
Ti					+
I					
Br	+				
Mo	++	+			
U				++	-
Ni	++				
Cr	+				
V					
Cu	+				
Sr				++	-
Ba					
Zn					
Rb					-
Zr					
Zr/Rb	+				
Nb					
Pb					+
Th					+
La					+
Ce					+
Nd					+
Y					+
Sc					+

PC38-10 (257m)

	Corg	Bio.Sil.	CaCO3	Phos.	Terr.
Corg	1	+			
Bio.Sil.	+	1			
CaCO3			1		
Phos.				1	
Terr.					1
Al					++
K					++
Ti					++
I					
Br	+				
Mo	+	+			
U				+	
Ni	++				
Cr	++				
V	+				
Cu	+				
Sr				+	
Ba					+
Zn					+
Rb					+
Zr				+	+
Zr/Rb				++	
Nb					++
Pb					+
Th					+
La					+
Ce					++
Nd					++
Y				+	+
Sc					+

PC38-11 (3835m)

	Corg	Bio.Sil.	CaCO3	Phos.	Terr.
Corg	1				
Bio.Sil.		1			
CaCO3			1		
Phos.				1	
Terr.					1
Al					++
K					++
Ti					++
I	+				
Br	++				
Mo	+		+		
U					
Ni	++				
Cr					
V					+
Cu		+			
Sr			++		-
Ba		++			
Zn		+			
Rb					+
Zr				+	+
Zr/Rb				++	
Nb					++
Pb					+
Th					+
La					+
Ce					+
Nd					+
Y	+				+
Sc	+				+

Symbol Max. Min.
 ++ +0.999 +0.800
 Symbol Max. Min.
 + +0.799 +0.500

Symbol Max. Min.
 - -0.500 -0.799
 Symbol Max. Min.
 - -0.800 -0.999

Figure 5.1. Summary tables of correlation coefficients for piston cores CD38-09, CD38-10, CD38-02 and CD38-11.

some control over the grain-size of the sediment. However, there may be an external component, such as bottom-water current activity, which controls both variables. In cores CD38-10 and CD38-11, the Zr/Rb ratio correlates strongly with the phosphorite mineral phase and this is indicative of the fact that bottom-water current strength has an influence on both phosphorite nodule growth and sediment grain-size (Chapter 4).

- 4) In cores CD38-02 and CD38-11, strong, positive correlations exist between the carbonate phase and Sr. This association is due to the uptake of Sr^{2+} by substitution of Ca^{2+} in the carbonate shells of zooplankton (6.4). The carbonate phase also displays in core CD38-02 strong, negative correlations between the terrigenous phase and elements such as Al, K, Ti, Zn, Zr and Y. This implies that, in this sediment, dilution by one phase is strongly controlling the other. However, correlation analysis cannot indicate whether it is the carbonate phase or the terrigenous phase which is the dominant, controlling phase in core CD38-02.
- 5) The halogens (I and Br) show some positive correlation to the organic matter phase in all of the cores, except for I in CD38-10. This indicates that a halogen-organic matter association exists in marine sediments but for some reason I has been lost from core CD38-10. The same may be said for a Ba-biogenic silica association, which shows a strong correlation in CD38-11, a positive one in CD38-02 but no correlation and a negative one in CD38-09 and CD38-10 respectively. Chapter 6 studies these associations in more detail.

The main problem with correlation analysis is that if one phase is dominating over all the others and therefore diluting all the elements in the other phases to the same degree, then there may be a strong, positive correlation between two elements which are not related in any true, geochemical association, e.g. Ba and Cr in CD38-02 (Appendix C.16). Also, there may be an element whose phase association changes over time due to loss upon burial and/or diagenetic remineralisation or an element which has more than one phase association. Correlation analysis will not pick up such associations because they have a low correlation coefficient.

Using a dataset-reduction technique which allows for simple, graphic representations of the element-element and element-phase associations may help to solve the above problems. This is possible with principal component analysis.

5.3. PRINCIPAL COMPONENT ANALYSIS

5.3.1. Introduction and methods

Principal component analysis (PCA) is a statistical data reduction technique which identifies a small set of variables ("principal component factors" each having "eigenvalues") which can account for a large proportion of the total variance in the dataset. A number of authors (Li, 1981, 1982; Gardner *et al.*, 1990; Hermelin and Shimmiel, 1990; Shimmiel and Mowbray, 1991; Patience, 1992) have used PCA to simplify large datasets from marine sediment studies in an attempt to identify a few factors or components with which various geochemical elements (variables) are associated.

PCA was carried out on the data from the piston core sediments of the Peruvian continental margin using Minitab R-mode factor analysis. This technique of data reduction has advantages over correlation analysis because of ease of graphic representation of the results and also over Q-mode factor analysis because in PCA the multiple-regression coefficient of variables is normalised to one for a perfect correlation (Li, 1982), which allows for easy inter-core comparison.

The results of PCA include the eigenvalues of the principal component factors (PCFs), their proportion (and the cumulative proportion) of the total variance and the principal component matrix. Appendix C.17 tabulates the results of the first 8 PCFs, using the same dataset used for correlation analysis (5.2) for each of the four piston cores. Any possible association of a group of geochemical elements within the dataset can usually be deduced from the coherence of these elements in the first three PCFs.

Before an interpretation of the PCA results is made, it should be noted that this technique only provides good statistical proof that elements are associated and therefore such associations should always be checked against some form of independent evidence. Errors in interpretation of PCA results can arise if an apparent correlation is caused by a systematic error in the chemical analysis or if it is an indirect one. Also, an apparent lack of correlation may exist if the natural variability is less than the uncertainty in the chemical analysis (Li, 1982). However, it is thought that such errors are likely to be low because of the high precision and accuracy of the X-ray fluorescence technique (Appendix A.5) and wet chemical methods in measuring the composition of sediments in this study and their high, natural variability (as seen in the down-core profiles).

5.3.2. Interpretation of results

The extracted PCFs 2 and 3 are plotted against PCF 1 in Figs 5.2 to 5.5 for cores CD38-09, CD38-10, CD38-02 and CD38-11 respectively. The plots all have the same scales for the axes so that inter-core comparisons are easy to make. Elements which plot close to each other in both the PCF diagrams are highly likely to have an association within the same sediment component phase. The same five end-member phases as used in the correlation analysis (C_{org} , Bio. Silica, $CaCO_3$, Phos. and Terr. - 5.2.1) are also plotted on the diagrams.

Each sediment phase will now be examined with respect to its location on the PCF plots (Figs. 5.2 to 5.5) and the elements which group around it.

Organic matter phase

Under a zone of high biological productivity associated with coastal upwelling (Chapter 3) the organic matter flux can vary considerably over time and therefore it may be expected that the variation in the organic matter phase down each core would play a large part in the total variation of the sediment composition.

This is certainly true for core CD38-10 (Fig 5.3), and to a lesser extent for CD38-11 (Fig. 5.5), in which C_{org} plots strongly positive for both factors 1 and 2. This implies that the organic matter phase variation has a strong influence on the total variation. In core CD38-09, C_{org} is positive for factors 2 and 3 but slightly negative for factor 1 (Fig. 5.2) which indicates that another phase is dominating the total variation in sediment composition of this core. Core CD38-02 has a variation in C_{org} which plots in nearly the same place as core CD38-09 (compare Fig. 5.4 with 5.2) for the PCF 2 vs. 1 diagram. This means that although CD38-02 has a much lower concentration of C_{org} , its variation control on the sediment composition is at a similar level to core CD38-09 (which has a very high C_{org} concentration).

The elements which have an organic matter phase association (i.e. they plot close to C_{org}) are the halogens (I and Br) and the heavy metals (Ni, Cr, V, Mo, Cu and U; 3.3.3).

Of the two halogens, Br always plots closer than I to C_{org} (except for the PCF 3 vs. 1 plot for CD38-02) which implies a stronger organic-matter association for bromine (Chapter 6.2). The two cores which have the highest concentration of C_{org} (CD38-09 and CD38-10) tend to have the organic matter-associated elements plotted much closer to C_{org} than in the other cores. However, in some cases an element does

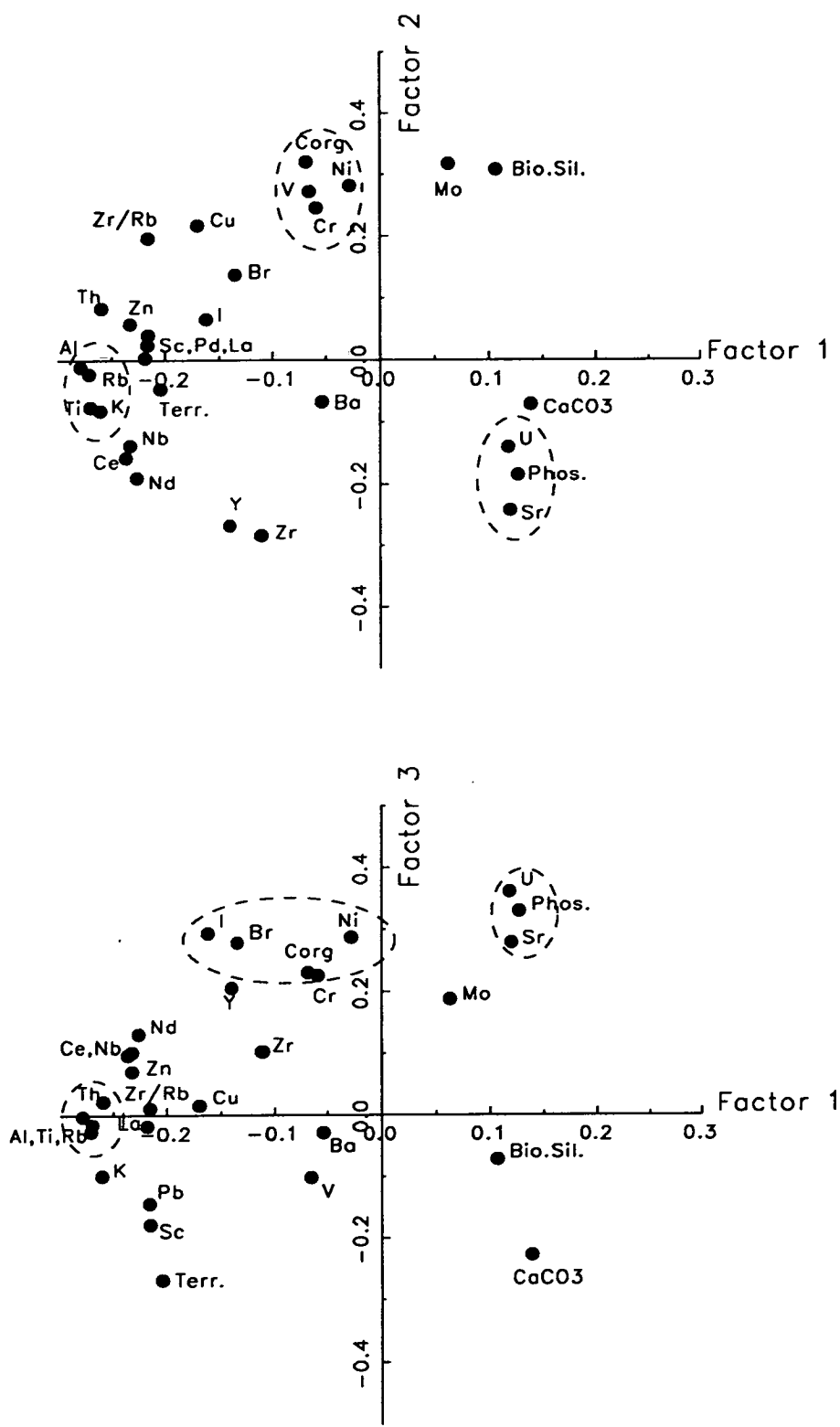


Figure 5.2. Principal component factor diagrams for core CD38-09 (148m).

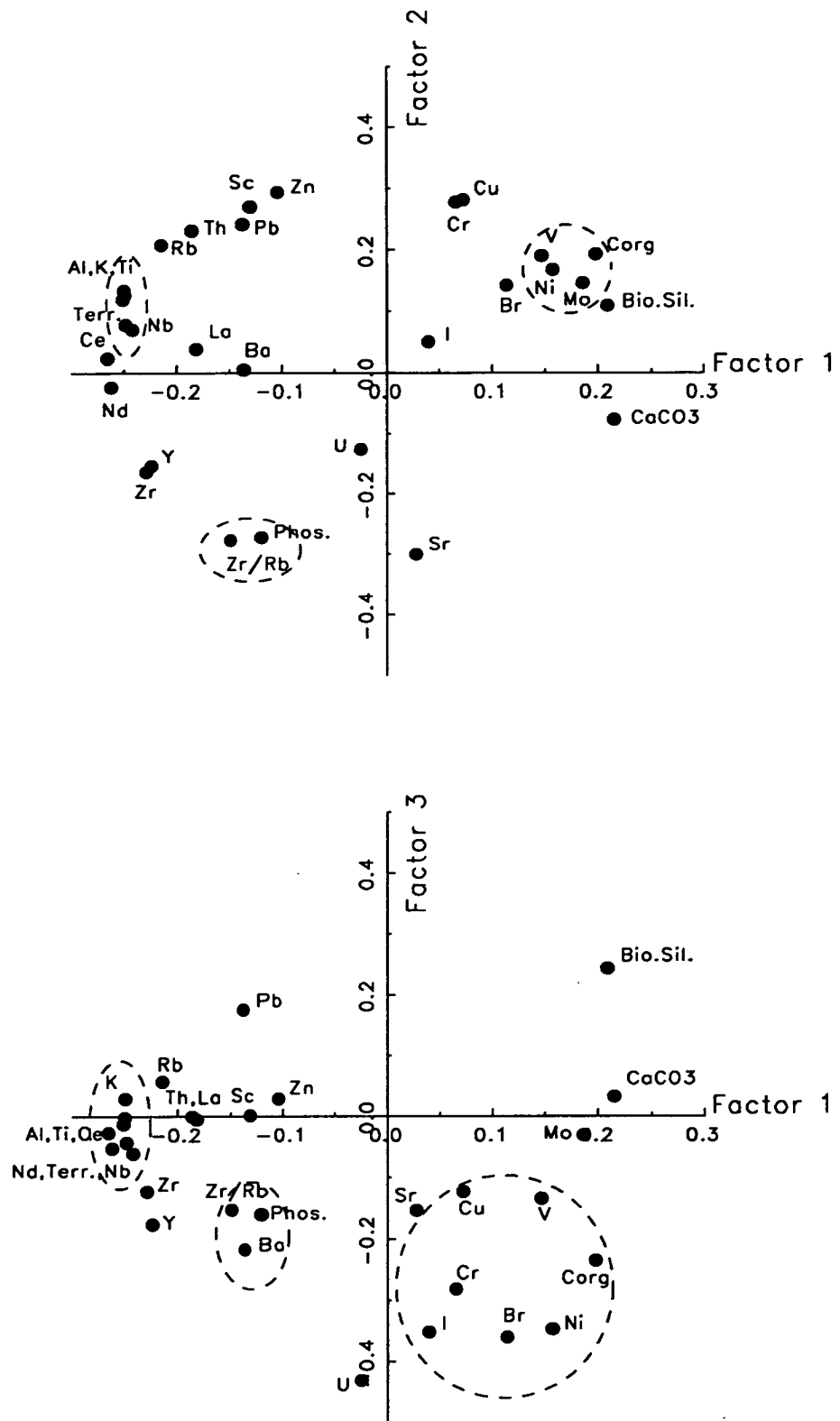


Figure 5.3. Principal component factor diagrams for core CD38-10 (257m).

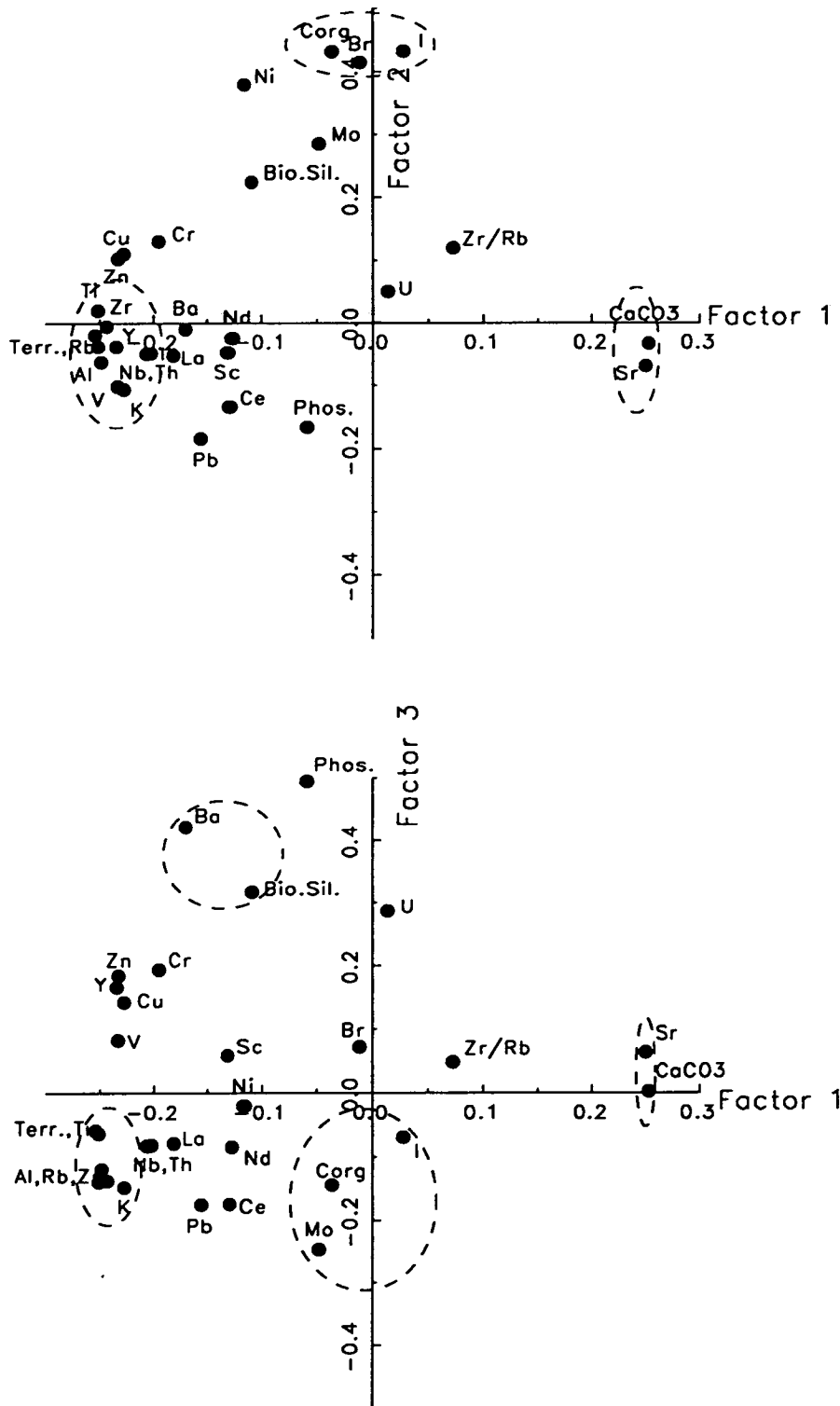


Figure 5.4. Principal component factor diagrams for core CD38-02 (2525m).

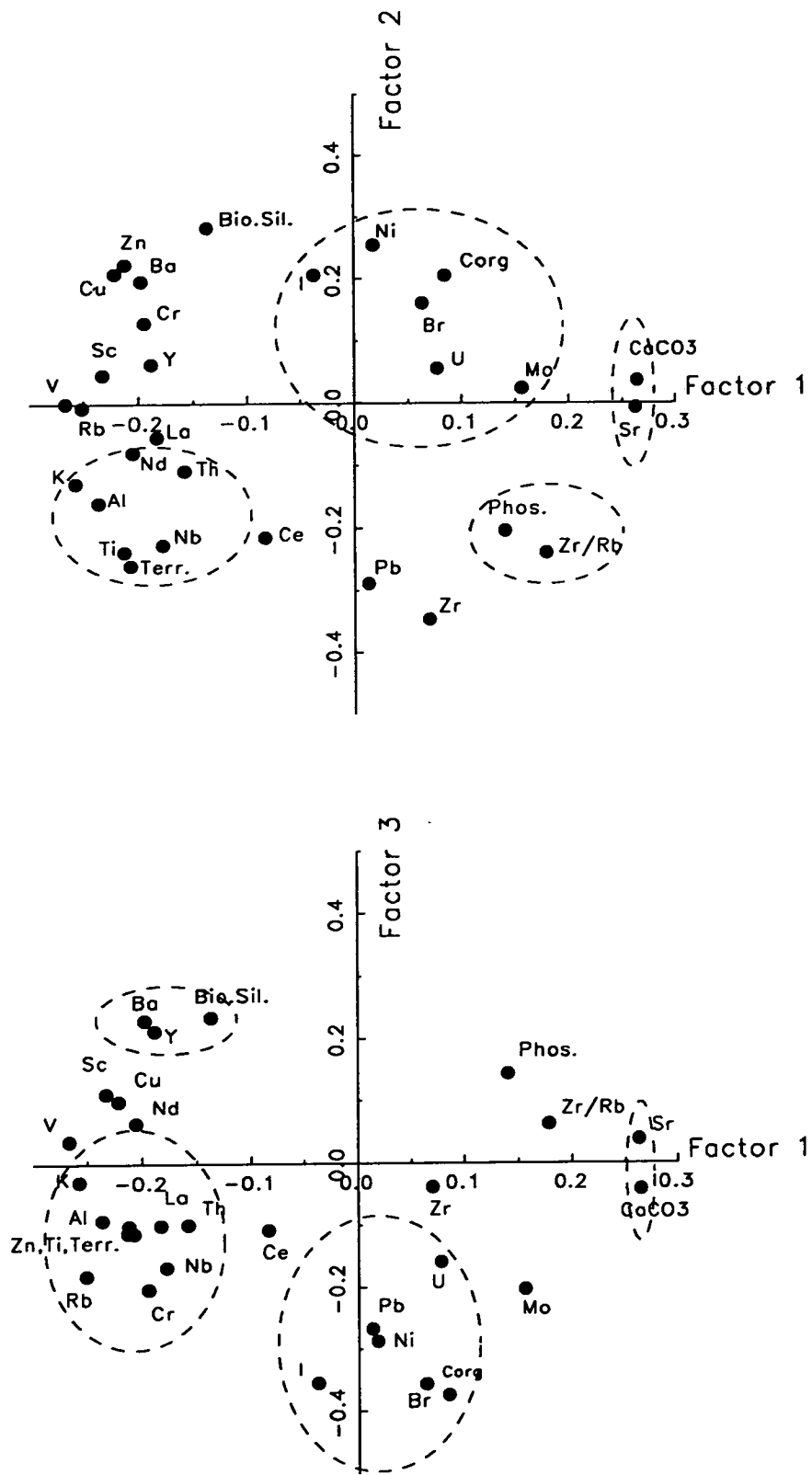


Figure 5.5. Principal component factor diagrams for core CD38-11 (3835m).

not plot close to a particular phase because it is also associated with another phase. These multi-phase elements, e.g. U, Sr, Ba, will be discussed later in this section.

Biogenic silica phase

The sediment phase which consists of the hard, silicate shell-remains of marine plankton is another biogenic component in marine sediments and, as for organic matter, it would be expected to influence the total variation of the sediment composition quite strongly in cores situated under high productivity zones. Cores CD38-09 and CD38-10 have strong, positive PCFs 1 and 2 for biogenic silica and the other two cores have negative values for factor 1 and positive for factors 2 and 3. The latter cores are located slightly further away from the Peruvian coastal upwelling zone and therefore the variation in biogenic silica flux would be expected to have less influence on the total sediment variation than in the two shallow-water cores.

There is little evidence from the PCF plots of any element being strongly associated with the biogenic silica phase in the sediments, except perhaps Ba and Y in CD38-11.

Carbonate phase

This third and final biogenic phase is composed of the hard, carbonate shell-remains of foraminifera and coccoliths, whose variation in concentration can often play a large part in the total sediment variation, especially in sediments away from the strong influence of a terrigenous input near a continental margin (Patience, 1992).

In the four piston cores studied here, the variation in CaCO_3 concentration is always strongly positive along the PCF 1 axis, implying that carbonate dilution is a dominating influence in sediment composition on the Peruvian continental margin. The value of the factor 1 for CaCO_3 and its distance away from any other sediment phases on the PCF diagrams indicates that in core CD38-02 the effects of carbonate dilution are strongest, followed by CD38-11, CD38-10 and CD38-09 in decreasing order of dominance.

In the two deeper-water cores, Sr shows a very strong association with the carbonate phase but this is the only element whose variation in PCA seems to be of a similar value to CaCO_3 .

Phosphorite phase

This is an authigenic mineral phase which does not necessarily appear in all marine sediments but which may have a strong influence on the compositional variation of sediments on the Peru margin (Chapter 4).

From the PCF diagrams, it can be seen that cores CD38-09 and CD38-11 have a phosphorite variation which is positive for both factors 1 and 3 but negative for factor 2. Core CD38-10 which, like the above two cores, has zones of phosphorite pellet formation and concentration (4.3.3) is, however, negative for all three factors in terms of phosphorite variation. Accurate interpretation of the influence of phosphorite formation on total sediment compositional variation is difficult to make because its effects can be strong in some parts of the core but weak in others.

The geochemical elements which were studied in Chapter 4, i.e. U, Sr, Ba and Y, do have PCFs which plot close to, or nearby, Phos. for cores CD38-09 and CD38-10. This supports their use in the interpretation of phosphorite-trace element associations (4.3.4). It should also be noticed that Zr/Rb in cores CD38-10 and CD38-11 plots very close to Phos. which may indicate that the variation in the phosphorite phase and the variation in grain-size of the sediment are controlled by the same external influence.

Elderfield *et al.* (1981) showed that the rare earth elements (Nb, La, Ce, Nd) are mainly associated with phosphate minerals in the Wahine area sediments. However, from the PCF plots for CD38-09 and CD38-10, no such REE-phosphorite association can be seen for the sediments in this study. The REEs show closer association with the terrigenous phase.

Terrigenous phase

Shimmield and Mowbray (1991) used PCA to interpret sediments from ODP core 722B in the north-western Arabian Sea, and found that an "aluminosilicate, detritus factor" plotted with strong, positive values for PCF 1 and therefore its variation dominated the total sediment variation at this site. The opposite situation can be seen in the sediments from the Peruvian continental margin where the terrigenous phase (Terr.) has a strong, negative factor 1 value implying that another sediment phase is more dominant in its variation and is diluting the terrigenous phase.

The elements most closely grouped around Terr. on the PCF plots are Al, Ti, K, Zn, Rb, Zr, Ce, Nd, Th and La which are all associated strongly with aluminosilicate clay minerals. These elements are of terrigenous origin whose input to the ocean, and hence the marine sediments, is either riverine or aeolian (Chapter 7). Each of the four cores has a slightly different grouping pattern to the element-terrigenous phase association (such as an arc around Al, Ti and K in core CD38-09 and a long, thin zone in CD38-10) which may be indicative of slight differences in the mineralogical composition of the terrigenous phase.

Mixed-phase elements

One advantage that PCA has over simple correlation analysis is that the graphic representation of variance within a dataset allows for identification of elements which are associated with more than one end-member phase. If correlation analysis was the only statistical analysis method used on the dataset then such "mixed-phase" elements would probably have a non-significant correlation coefficient with the end-member phases, even though an association was present. Such mixed-phase associations would therefore not be noticed.

In the geochemical datasets from the four piston cores used in this study there are a few mixed-phase elements whose association with two or more end-member phases can be examined using PCA (Figs. 5.2 to 5.5). These are uranium, strontium and barium; as detailed below.

Uranium

In core CD38-09, uranium has a strong association with the phosphorite phase in both the PCF plots but this element is also known to be a heavy metal associated with the organic matter input to the sediment (3.3.3). For the other three piston cores, U can be seen to plot on the PCF diagrams somewhere on an imaginary line between the organic matter phase (C_{org}) and the phosphorite phase (Phos.) end-member components.

This mixed-phase characteristic of U can be interpreted as the variation in supply of the metal to the sediment being primarily associated with the variable organic matter input, but upon increasing organic matter decay during burial and diagenesis of phosphorite minerals (Chapter 4), the uranium becomes associated less with the C_{org} phase and more with the Phos. phase. Therefore, simply from the position of U in the PCF diagrams it is possible to interpret that the uranium in core CD38-09 has undergone an almost complete remobilisation from organic matter to phosphorite minerals, whereas in core CD38-10 the remobilisation has not occurred to such a high degree.

The uranium in core CD38-11 plots closest to C_{org} , implying that it is still mainly associated with the organic matter which was responsible for introducing the metal into the sediment, and that very little phosphorite formation has occurred.

Strontium

In core CD38-10, strontium can be seen to be a mixed-phase element which, on the PCF 2 vs. 1 diagram, lies between the carbonate and phosphorite end-member phases. Cores CD38-02 and CD38-11 both show close correlation in the variance of

Sr and CaCO_3 (see above) which indicates a strong association between the two geochemical parameters, but in core CD38-09 the Sr is associated with the phosphorite phase only.

It is known that both carbonate and phosphorite minerals can easily incorporate Sr into their crystal lattices due to the similarity in ionic size and charge of Ca^{2+} and Sr^{2+} (4.3.4). Therefore, the mixed-phase characteristic of Sr in core CD38-10 indicates that both the carbonate and phosphorite phase variance are controlling the Sr concentration variance to roughly the same extent. In core CD38-09 it is the phosphorite phase which dominates the Sr variance and in CD38-02 and CD38-11 it is the carbonate phase.

The position of Sr on the PCF diagrams reflects the nature of the relative abundances, and therefore the dominance in variation control, of the carbonate and phosphorite end-member phases.

Barium

This mixed-phase element can be seen to plot in a variety of locations on the PCF diagrams of the four piston cores. Barium plots somewhere between the terrigenous, biogenic silica and phosphorite end-member phases which reflects its association with three possible sources, i.e. with detrital clays, diatom frustules (6.3.1) and diagenetic phosphorite mineral growth (4.3.4).

5.3.3. PCA Conclusion

Principal component analysis has helped to assign various elements to one (or more than one) particular end-member phase and also to indicate which phase is the most dominant in controlling the total variation in the geochemical composition of the piston cores from the Peruvian continental margin.

In cores CD38-02 and CD38-11, it is the CaCO_3 content of the sediment which dominates the dataset variation and, therefore, carbonate-dilution controls the down-core variation of the other four phases. This interpretation comes from the fact that for PCF 1 in CD38-02 and CD38-11, CaCO_3 has a high, positive value (0.253 and 0.265 respectively, C.17). Cores CD38-09 and CD38-10 do not, however, have one dominant end-member phase but seem to have three phases each whose relative abundances control the variation in the dataset. Biogenic silica, CaCO_3 and Phos. in core CD38-09 all have positive and roughly equal values for PCF 1 (0.107, 0.139 and 0.127 respectively, C.17) and in core CD38-10 it is the three biogenic phase

components which have high, positive values for PCF 1 ($C_{\text{org}} = 0.198$, Bio. Sil. = 0.209 and $\text{CaCO}_3 = 0.215$, C.17).

PCA is therefore very useful in the interpretation of complex datasets such as used by marine geochemists. From examination of the proportion and cumulative percentages of the eigenvalues of each PCF (Appendix C.17) it can be seen that the highly variable chemical composition of marine sediments results in a high degree of complexity in the total variance of the dataset. It requires more than six PCFs to account for over 90% of the total variance in each of the four piston core datasets.

Also, PCA normalises the PCF eigenvalues to one for each dataset which allows for easy inter-core comparison. Of the four piston cores in this study, CD38-02 has the highest PCF 1 eigenvalue at 48.9%, which implies that the variation in carbonate concentration in this core accounts for just under half the total variation (compared with only 40.7% in core CD38-11). The cumulative variance of the first three PCF eigenvalues, which were the three used in the PCF diagrams (Figs. 5.2 to 5.5) statistically illustrates that only in core CD38-10 can over 80% of the total variance be accounted for by PCFs 1, 2 and 3. This indicates that core CD38-10 is, statistically, the least complex in its total geochemical variation of the four piston cores studied.

5.4. MULTI-COMPONENT ANALYSIS (MCA)

5.4.1. Introduction

Marine sediments are composed of a complex mixture of many chemical elements and these can be grouped into various components depending on their origin. The purpose of this section is to use multi-component analysis (MCA) in order to calculate, for each piston core sample, the relative proportions of the main components which can combine to form marine sediments. The concentration of each component and its down-core variation will then be interpreted for each piston core in this study to identify the main sources of input to the continental margin sedimentary environment.

The principles behind MCA as a computational technique used to simplify a set of geochemical data into a meaningful component composition, were set out by Heath and Dymond (1977, 1981) and Dymond (1981). These authors decided that a five-component system could be used to describe most marine sediments and allow

for estimations of the temporal variability of various depositional processes and for comparison with modern spatial variability (specifically on the Nazca plate of the Pacific Ocean). The five components defined were detritus, biogenic, authigenic, dissolved opal-solution residue and hydrothermal, and their models allowed for the simultaneous partitioning of elements using either algebraic algorithms or linear programming.

The models of Heath and Dymond (1977, 1981) and Dymond (1981) all assumed that each of the five components had a constant, end-member composition that was uniform across the Nazca plate and then converted bulk geochemical data (concentrations of Al, Si, Fe, Ni, Mn, Ba, Zn and Cu) into quantitative estimates of the mixture of components that best accounted for the measured composition of the sample.

It must be noted that the five components used in the MCA are not the same as the five end-member phases used in the regression analysis (5.2) and the principal component analysis (5.3) sections. Instead, the five components of Dymond (1981) are used so that the results of the MCA algorithm using the Peru margin sediment data can be compared to previous and/or future studies of multi-component analysis of marine sediments from other locations.

5.4.2. MCA methods, results and interpretations

It was decided to carry out the MCA of the four piston cores in this study by adapting the algorithms and component end-member compositions of Heath and Dymond (1977, 1981) and Dymond (1981) to create my own MCA algorithm.

The algorithm is listed in full in Appendix B.6 and uses seven geochemical variables (Al, C_{org}, Bio. Silica, CaCO₃, P_{phos}, Ba and Fe) to calculate the relative concentrations of five components; namely the terrigenous (TERR), biogenic (BIOG), authigenic (AUTH), residual (RESID) and hydrothermal (HYDRO) inputs to the sediment. The basic assumption used by the MCA algorithm is that the composition of each of the components is constant (in the above geochemical variables) both spatially along the Peru margin and temporally throughout the depth of each core. Also, it was assumed that each end-member component can be defined by the content of one (or more than one) characteristic geochemical variable.

For example, the algorithm assumes that all the Al present in a sample is present in the terrigenous component (5.2 and 5.3) and that the concentration of Al in a pure, end-member terrigenous sediment would be 8.40 wt.% (equivalent to the Al concentration of average deep-sea clay; Turekian and Wedepohl, 1961). The above

assumptions are, of course, not entirely accurate throughout all the marine sediment samples but in order to simplify the geochemical dataset and interpret the concentration and variation of each component present in the cores, the assumptions are justified.

The final step of the algorithm (Appendix B.6) recalculates all five components to percentages so that comparisons both within and between cores from different marine environments can be made. The results from MCA of the piston cores CD38-09, CD38-10, CD38-02 and CD38-11 are tabulated in Appendix C.18 and summarised in Table 5.1. (the hydrothermal component was absent in the MCA results for all the samples in this study).

Core	TERR (%)		BIOG (%)		AUTH (%)		RESID (%)	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
CD38-09 (148m)	26.9-85.5	73.12	8.4-42.8	24.51	0.3-60.9	2.35		
CD38-10 (257m)	31.9-88.6	65.69	32.-63.4	29.74	0.5-29.6	4.57		
CD38-02 (2525m)	52.5-89.4	69.27	10.1-47.0	30.21	0.2-0.8	0.49	0-0.26	0.04
CD38-11 (3835m)	66.7-88.3	80.07	10.4-30.8	18.75	0.5-4.7	1.16	0-0.22	0.02

Table 5.1. Summary of MCA results for Peru margin piston cores.

The down-core profiles shown in Figs. 5.6 through to 5.9 graphically display the MCA results for cores CD38-09, CD38-10, CD38-02 and CD38-11 respectively. It can be seen from these plots that cores CD38-09 and CD38-10 contain sediments which can be described by a three-component system, and CD38-02 and CD38-11 are four-component systems. In all four cores, it is the terrigenous-source component which is the most common input (highest %) and the biogenic-source component is the second most abundant input to the sediment. This dominance of material from either a terrigenous or a biogenic origin contained within these sediments is to be expected from a marine environment which is close to a continental landmass and which is strongly influenced by high biological productivity as a result of coastal upwelling (Chapter 3). Chapter 7, which studies the environment of deposition of the Peru margin sediments, will focus on these two major components.

CD38-09

The MCA of CD38-09 (Fig 5.6) reveals that this core is located in an environment receiving an input of terrigenous-derived material which consistently makes up greater than 60% of the total input to the sediment, reaching a maximum of 85% (Table 5.1). The biogenic-derived material contained within the core generally

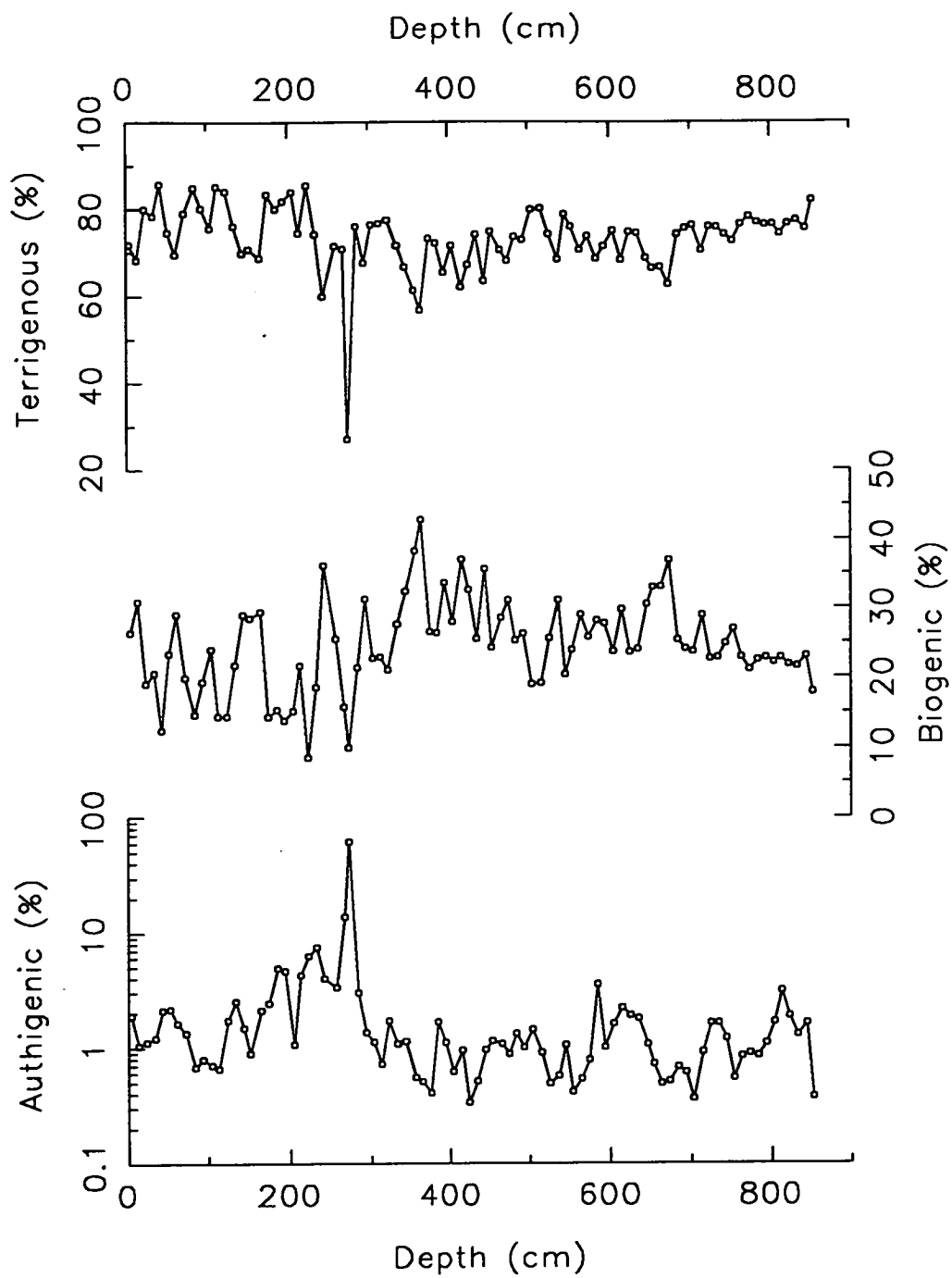


Figure 5.6. Multi-component analysis down-core profiles against depth (cm) for core CD38-09 (148m).

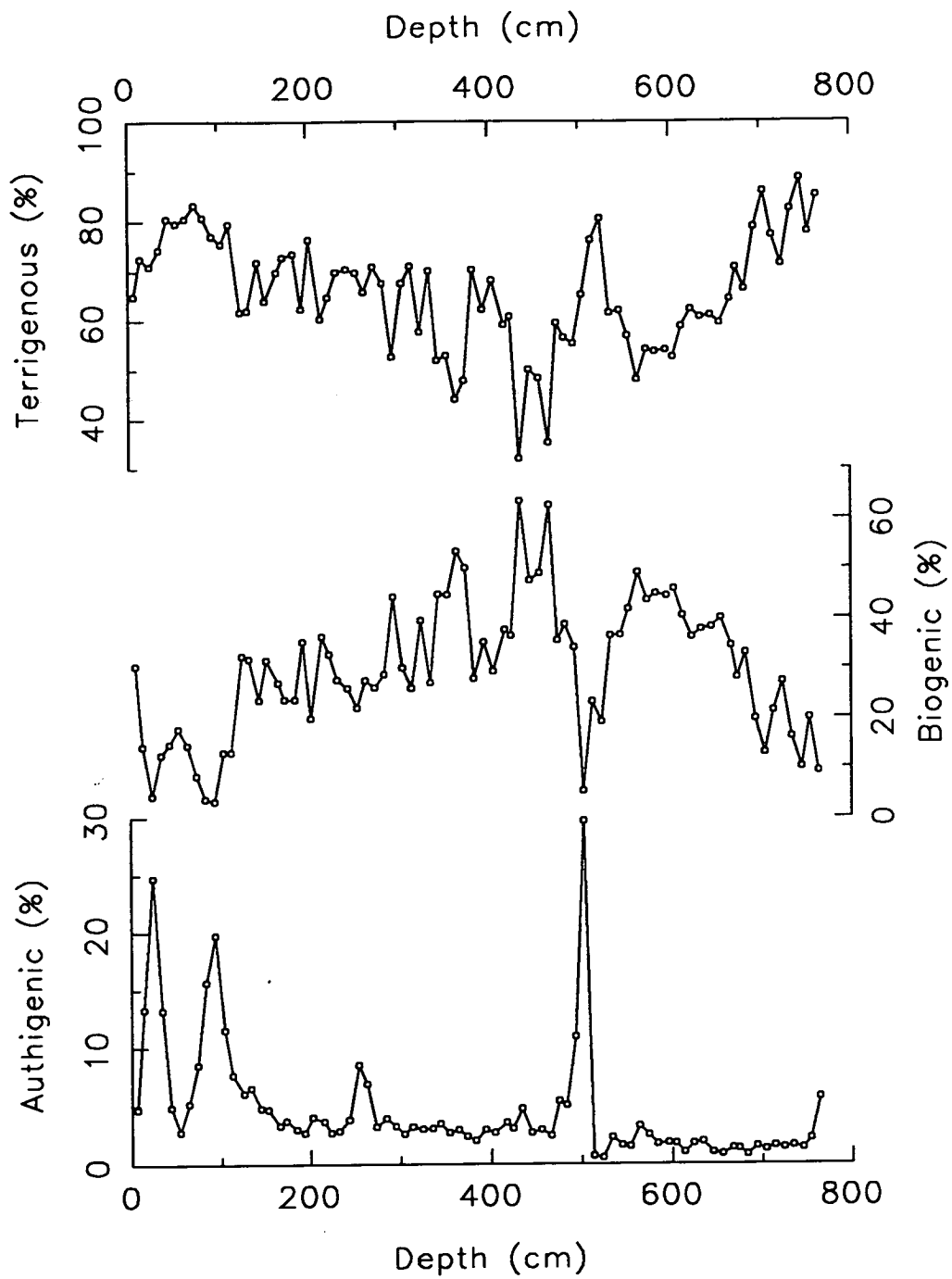


Figure 5.7. Multi-component analysis down-core profiles against depth (cm) for core CD38-10 (257m).

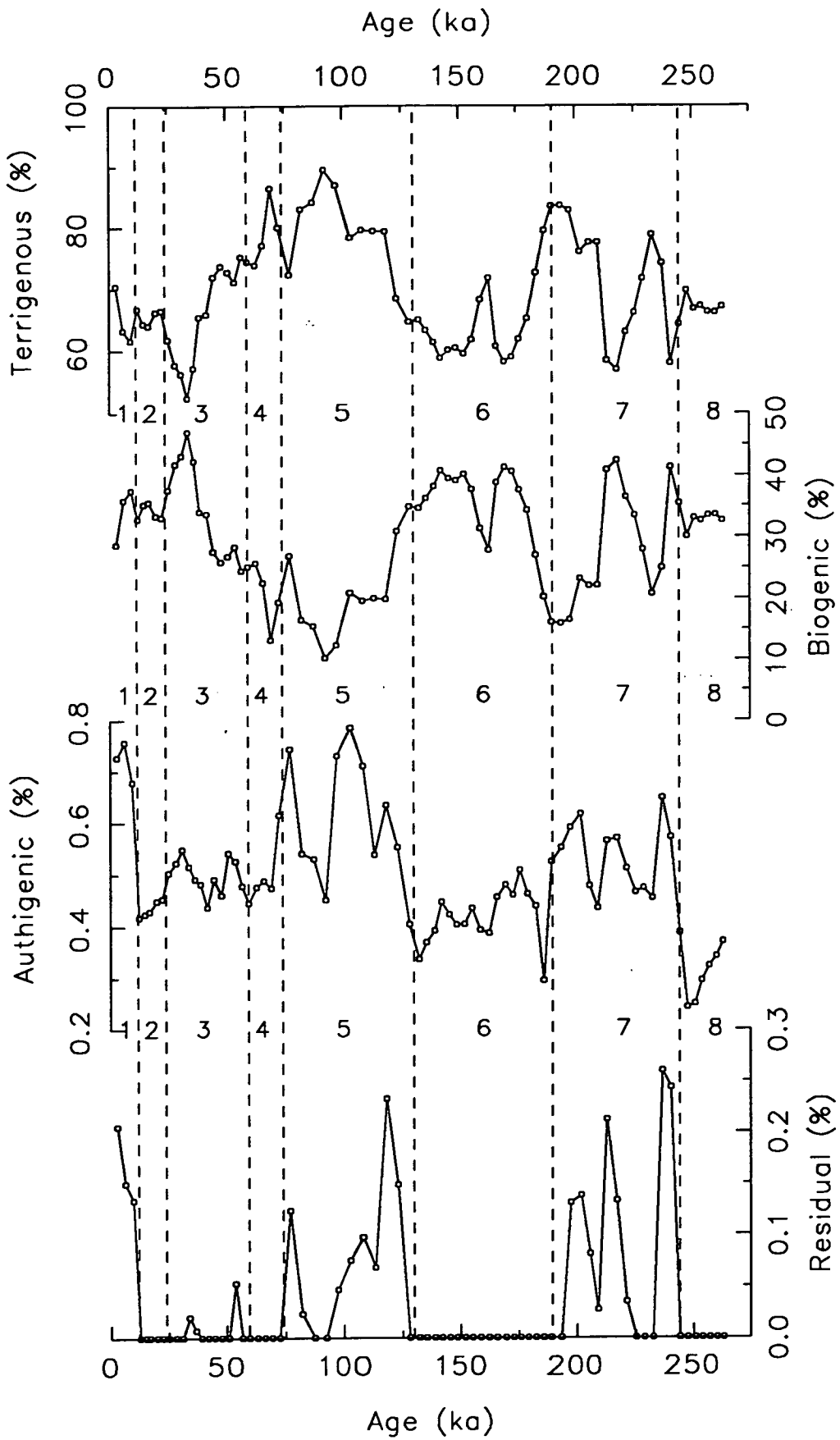


Figure 5.8. Multi-component analysis down-core profiles against age (ka) for core CD38-02 (2525m).

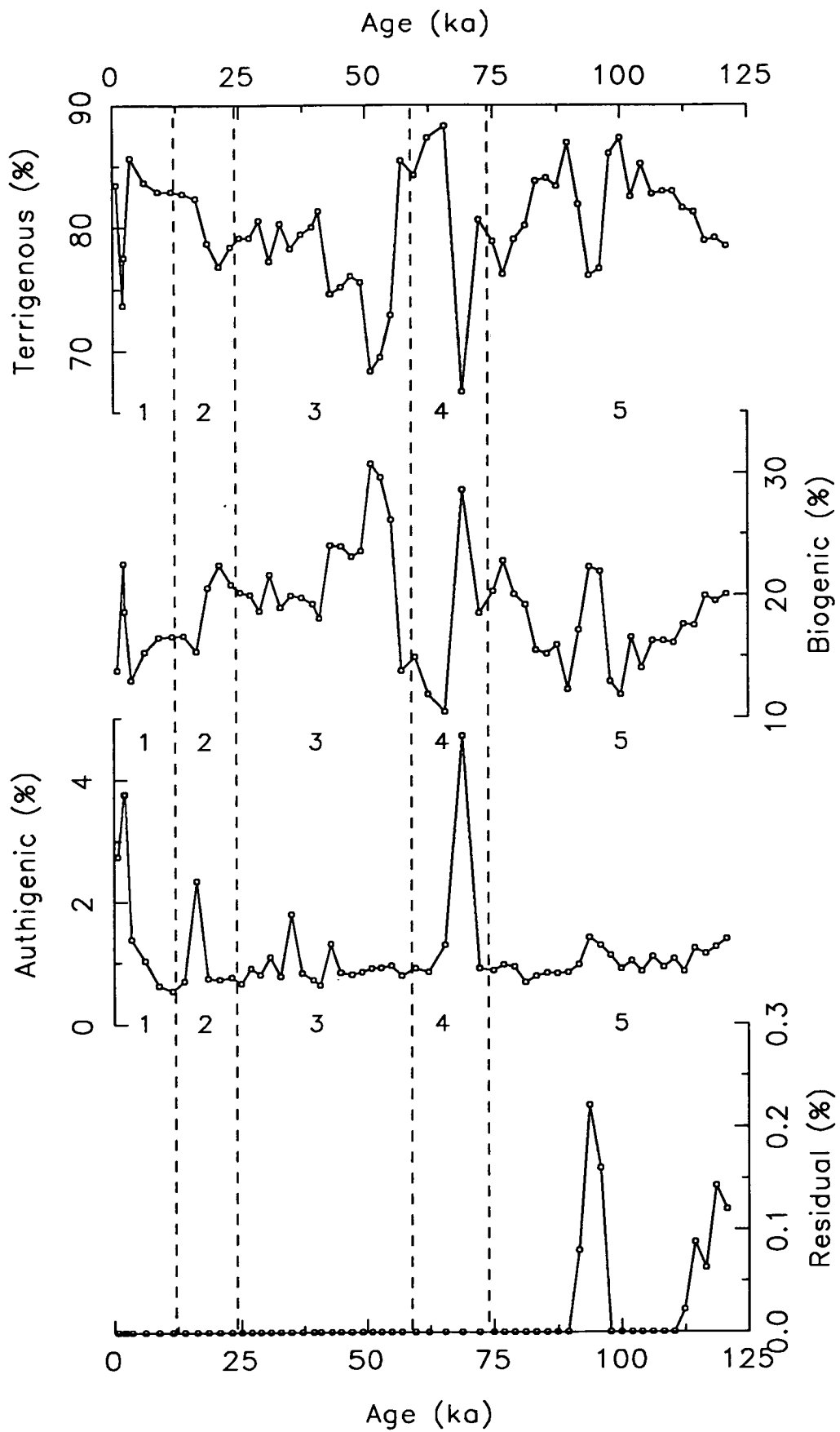


Figure 5.9. Multi-component analysis down-core profiles against age (ka) for core CD38-11 (3835m).

contributes greater than 10% of the sediment and can reach above 40%. The only other source component present in this core is the authigenic phosphorite component which is usually only a background of 1-2% but can be concentrated up to a maximum of 61% in the area around 273cm (4.3.3). It is interesting to note that below this strong authigenic zone, the terrigenous component averages 72.3% and the biogenic component averages 26.5%, but above this zone (i.e. since the last major change in sea-level at the time of phosphorite concentration; 4.3.6) the average terrigenous component has noticeably increased and the biogenic component decreased (to 76.5% and 20.7% respectively). It is, however, impossible to interpret from the MCA results whether this change in the component input to core CD38-09 is due to either increased continental weathering and input of more terrigenous material to the oceans or decreased marine biogenic productivity (and/or preservation) since the phosphorite concentration event.

CD38-10

The three-component system of core CD38-10 (Fig. 5.7) is essentially very similar to that of CD38-09. There is only a 100m water depth difference between the two core sites and it is therefore expected that both sets of sediment would be influenced by the same terrigenous and biogenic inputs and by zones of high authigenic input. The down-core profiles of the three components in core CD38-10 show an interesting pattern, whereby the terrigenous component is most dominant around the zones of authigenic phosphorite concentration (e.g. in the upper 100cm, between 490 to 520cm and at the base of the core) and the biogenic component is at a maximum between these zones. One possible interpretation of this pattern is that higher biogenic productivity occurred during interglacial periods and, relatively, an increased terrigenous input occurred during glacial periods (when sea-level dropped and phosphorite minerals were concentrated, 4.3.6). However, as with core CD38-09, the correct interpretation of core CD38-10 is difficult due to the lack of an accurate age model (2.3.2).

It should be noted that of the four piston cores, CD38-10 has the lowest average terrigenous-component input (Table 5.1) and yet it is situated closer to the continental landmass than both CD38-02 and CD38-11. The reason for this apparent irregularity is that CD38-10 also has high average biogenic and authigenic components (Table 5.1) and therefore the terrigenous component is relatively depleted.

CD38-02

Core CD38-02 is situated on the Nazca ridge and does have an accurate age model and, therefore, it is possible to interpret the four-component system (Fig. 5.8) in terms of Late Quaternary climatic changes. The terrigenous and biogenic inputs dominate the sediment composition and their down-core profiles mirror each other showing an inverse relationship of glacial/interglacial variation. The terrigenous component varies approximately $\pm 15\%$ about an average of 70% (Table 5.1) and is predominantly higher during the interglacial stages 1, 5 and 7 compared with the glacial stages 2, 6 and 8. The biogenic component varies to the same extent around an average of 30% (Table 5.1) and its concentration is relatively lower during the interglacial and higher during the glacial stages.

It was seen in the PCA interpretation (5.3.3) that in core CD38-02 it is the variation of CaCO_3 concentration which dominates the total variation and yet the MCA results show that the biogenic source component (of which CaCO_3 is the major contributor in this core) only makes up about one third of the total input to the sediment and is approximately half of the terrigenous component, in terms of relative concentrations. Therefore, core CD38-02 is an example of a marine sediment system in which the concentration of the major component (terrigenous) is controlled by the variation of input to the sediment of another component (biogenic).

The down-core profiles shown in Fig. 5.8 support this biogenic-dilution interpretation for core CD38-02 because when compared with the profile of the mass accumulation rate (Fig. 2.10) for the same core, it can be seen that the biogenic (and not the terrigenous) component is the most similar to the mass accumulation rate in its glacial/interglacial pattern. This implies that the variation in the biogenic component is controlling the total mass accumulation rate pattern and that the geochemical composition of core CD38-02 is strongly affected by biogenic (carbonate) dilution. A full explanation of the reasons for (i.e. productivity or preservation variation of carbonate microfossils), and the effects of, the biogenic component fluctuations over the past 250,000 years will be given in Chapter 7.

In the study of phosphorite minerals (4.3.3) it was stated that the amount of phosphorus present in core CD38-02 was not sufficient to indicate the presence of any phosphorite material. However, the algorithm used in this multi-component analysis has resulted in a small amount ($<1\%$) of the authigenic component being required to account for the geochemical composition of the sediment. The down-core profile of this third component in core CD38-02 (Fig. 5.8) also suggests an interesting glacial/interglacial variation with slightly higher interglacial production of authigenic material. The most plausible reason for this is that the authigenic component of

CD38-02 is the result of the limitation of the algorithm, in that it assumes constant end-member compositions throughout the core (Appendix B.6). There are errors in calculating the P_{phos} concentration (4.3.3) and the presence of the authigenic component in this core could easily be removed by slight adjustments to the $P_{\text{org}}/C_{\text{org}}$ ratio used in Eqn 4.1.

Core CD38-02 is, therefore, probably only really a three-component system with inputs from terrigenous, biogenic and residual sources. Inaccuracies in the MCA algorithm could also be used to explain the presence of the small percentage of the residual component but it must be stressed that this component is calculated from the barium concentration which is measured in ppm and not a weight % (as for all the other geochemical variables used in MCA). It is because a very high end-member Ba concentration of the residual component is used (equivalent to 270,000ppm; Dymond, 1981) is used, that the MCA results in a very low % residual component compared with the other more dominant components. However, it will be shown later (6.3.4) that the residual component, derived from the excess Ba concentration, is a true component whose down-core signal (Fig. 5.8) demonstrates a pattern of presence only during interglacial periods. Dymond (1981) stated that the "dissolution residual component should be high in areas of high productivity" which implies that in core CD38-02 there was higher surface biological productivity during interglacials compared with glacial stages. The use of barium as a palæo-productivity indicator will be examined later in this thesis (6.3.4)*.

CD38-11

The results of the MCA on core CD38-11 show it to be a true four-component system (Table 5.1 and Fig. 5.9) with high inputs of the terrigenous and biogenic components and significant quantities of the authigenic phosphorite component in a few horizons above a background level of about 1%. The residual component is not present until the lowest (and therefore oldest) region of core CD38-11 and, as in core CD38-02, it is only present during an interglacial stage.

The fact that CD38-11 has the highest average terrigenous component (80%) of the four piston cores in this study, supports the previous work of Dymond (1981) who produced a contour map of surficial sediment component concentrations on the Nazca plate and found that, except for the coastal upwelling region where biogenic

*It may be expected that cores CD38-09 and CD38-10 which are located under a high biological productivity zone, associated with coastal upwelling (Chapter 3), would show a strong residual component signal. However, it will be shown later that these sediments are situated in an environment which is unsuitable for the preservation of a barium-residual component (6.3.2).

dilution occurs, sediments from areas closer than 1000-1500km to the South American continent are composed of >80% terrigenous component.

5.4.3. MCA conclusions

The algorithm used in this multi-component analysis of the geochemical data from the four piston cores on the Peruvian continental margin obviously has its drawbacks and inaccuracies which are due to the basic assumptions made during the mathematical calculations. However, MCA does allow for the complex mixture of various components contained within marine sediments to be separated and their down-core variations and relative abundances to be examined individually.

One example of how the results of MCA can be used to help in the interpretation of geochemical and/or physical measurements is the comparison of the grain-size signals for each core (Figs 2.1, 2.2, 2.4, 2.5 and 7.7) with the respective down-core profiles of the MCA components (Figs 5.6 to 5.9). In both the shallow-water cores, CD38-09 and CD38-10, the authigenic component profile is most similar to the grain-size signal. This may indicate that the formation and concentration of authigenic phosphorites is affecting the overall grain-size of the sediment in these two cores (4.3.6). In core CD38-02, it is the biogenic component which is similar to the grain-size signal (compare Figs 2.4 and 5.8). This is because the variation in the concentration of carbonate microfossils can strongly influence the percentage of sediment which is >63 μm in grain-size. Core CD38-11 does not have any component profile which is similar to the grain-size down-core profile but it is probably the relative proportion of both the authigenic and biogenic components which is influencing the overall grain-size.

CHAPTER 6

GEOCHEMICAL PALÆO- PRODUCTIVITY AND PALÆO-REDOX INDICATORS

6.1. INTRODUCTION

"Biogeography cannot confine itself simply to describing the occurrence of living forms, arranging them regionally, investigating the ecological causes of distribution. It must also proceed historically"

S. Ekman (1953)

One of the main purposes for undertaking geochemical studies of sediment core material from the marine environment, is to measure and interpret variations, cycles and anomalies of a certain element or ratio of elements in a down-core profile. If the concentration of an element in the sediment can be related to the condition of an oceanographic parameter then its profile against depth or, better still, age, can be used for palæo-reconstruction of certain physical, chemical and/or biological ocean conditions in the past.

The level of marine biological productivity in surface-waters and the concentration of dissolved oxygen in bottom- and pore-waters are two oceanographic parameters which are of utmost importance in controlling many processes operating within the water and sediment columns. Therefore, if certain geochemical elements can act as indicators of palæo-productivity and/or palæo-redox conditions, their study in marine sediments will help to broaden our understanding of the physical and biological changes which have occurred in the oceans throughout the Late Quaternary associated with glacial/interglacial periodicity. The above quote from Sven Ekman stresses the importance of using historical records, in this case marine sediment cores to study indicators of ocean productivity.

This chapter will examine four geochemical, environmental records, from the cores used in this study, in an attempt to evaluate their potential as palæo-productivity and palæo-redox indicators in the sediments from the Peruvian continental margin. This area is strongly influenced by coastal upwelling (Chapter 3) and therefore both the level of biological productivity and the strength and location of the oxygen minimum zone have affected the concentration and distribution of important geochemical indicators accumulating in the sediments through time.

The chapter will be divided into the following four sections and then conclude with a summary of the interpreted palæo-oceanographic conditions, allowing for a palæo-climatic reconstruction of Peruvian coastal upwelling.

- 1) Halogens: iodine and bromine and their association with organic matter.

- 2) Barium: Ba/Al record of biogenic silica and/or organic matter flux.
- 3) Strontium: variations in the Sr/Ca ratio within carbonate shell remains.
- 4) Molybdenum and uranium: use of the Mo/U ratio to distinguish between oxic and anoxic sediments.

6.2. THE HALOGEN SIGNAL

6.2.1. Introduction

Before an accurate interpretation of the geochemical signature from the two halogens, iodine (I) and bromine (Br), can be made for the off-shore Peruvian sediments, the basic marine chemistry of the elements and their sea-water/sediment/pore-water interactions need to be understood. This introduction will review some of the large number of marine geochemical studies of I and Br, with specific reference to their association with organic matter (Price and Calvert, 1977; Pedersen and Price, 1980; Shimmiel and Pedersen, 1990) and the redox conditions within the sediment (Price and Calvert, 1973; Wong and Brewer, 1977; Kennedy and Elderfield, 1987).

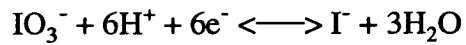
The geographical locations of such studies have included the deep-sea abyssal plains of the Atlantic (Kennedy and Elderfield, 1987), anoxic basins such as the Black Sea (Wong and Brewer, 1977), shallow-water polar regions (Price *et al.*, 1970) and coastal regions such as the Panama basin (Pedersen, 1979; Pedersen and Price, 1980; Patience, 1992), off south-west Africa (Price and Calvert, 1973, 1977) and Baja California (Price and Calvert, 1973, Shimmiel, 1985). However, no high-resolution study of the halogens and their organic matter-association has been published for the marine sediments from off Peru.

Iodine

The concentration of total dissolved I in sea-water is only 0.5 μ M (Wong, 1980) and it displays a nutrient-like behaviour in the oceans, being slightly depleted in surface waters (Wong and Brewer, 1974; Elderfield and Truesdale, 1980). In natural waters, I is known to exist in more than one oxidation state and the relative proportions of iodate (IO₃⁻) and iodide (I⁻) is strongly dependant on the redox environment (Wong, 1980). Iodate is dominant in normal, oxygenated waters (Sillen, 1961) but the opposite situation is found in anoxic basins, where high concentrations of I⁻ and undetectable levels of IO₃⁻ have been measured, e.g. in the Cariaco Trench and the Black Sea (Wong and Brewer, 1977). It is the interconversion between the

two species (Eqn 6.1) occurring at an Eh of +10.5 (at pH = 8.1), which makes iodine a potentially useful indicator of early diagenesis in hemipelagic sediments (Shimmield and Pedersen, 1990).

Equation 6.1. Iodate-iodide interconversion



The processes responsible for the removal of iodine from sea-water into the sediment column have been studied extensively (Wong and Brewer, 1974, 1977; Truesdale, 1975; Harvey, 1980; Francois, 1987) but are still not fully understood.

Author	Location	I (ppm)	I/Corg (x 10 ⁻⁴)	Br (ppm)	Br/Corg (x 10 ⁻⁴)
Price <i>et al.</i> , 1970	South west Barents Sea	60-828	380	12-257	120
Price and Calvert, 1973	South west Africa	96-1990	90		
Price and Calvert, 1977	South west Africa (anoxic)	200-350	20	500-800	60
	South west Africa (oxic)	750-2000	250	250-500	72
Pedersen and Price, 1980	Panama Basin	76-861	395	11-278	146
Shimmield, 1985	Baja, California	116-569	173	71-279	97
Pedersen <i>et al.</i> , 1992	Oman margin	134-870	140		
Patience, 1992	Panama Basin	37-252	104	17-182	49

Table 6.1. Iodine and bromine concentrations and their weight ratios to organic carbon, in surface sediments

As can be seen from Table 6.1, the concentration of I in surface, hemipelagic marine sediments can be greatly enriched (up to 2000 ppm) above the levels found in the open marine environment (Kennedy and Elderfield, 1987). The two most important factors in determining the level of I enrichment are the flux of organic matter to, and the redox-state of, the sediment (Price and Calvert, 1973, 1977; Shimmield and Pedersen, 1990). The association of I with organic matter was initially suggested by Vinogradov (1939) and Price *et al.* (1970) found a strong linear correlation between I and organic carbon (C_{org}) in the surface sediments of the Barents Sea.

Price and Calvert (1973, 1977) measured I/C_{org} weight ratios of surface, oxidised sediments (about 250×10^{-4}) from south west Africa and the Gulf of California which were an order of magnitude higher than in reduced sediments (20×10^{-4}) from the same locations (Table 6.1), and proposed that the enrichment of iodine in an oxic environment occurred at the sediment/water interface. One possible mechanism for such an enrichment involved the sequestration of I by plankton seston using an iodide-oxidase enzyme which requires free-oxygen to perform any reaction (Shaw, 1962).

Harvey (1980) proposed that the association of I with organic matter involves nitrogenous compounds (e.g. polypeptides) which are labile upon decomposition. More recent experimental work by Francois (1987) concluded that the humic fraction of organic matter readily absorbs IO_3^- which is the dominant I species in oxic bottom-waters and therefore I is enriched in oxic environments. In oxygen-deficient conditions, I^- is the dominant species of I and is not adsorbed to the same extent (Pedersen *et al.*, 1992).

Shimmield and Pedersen (1990) reviewed surface I/C_{org} ratios from a wide range of hemipelagic, oxic marine environments and stated that an I/C_{org} molar ratio of $25 (\pm 10) \times 10^{-4}$ (equivalent to $265 \pm 100 \times 10^{-4}$ weight ratio) was a global-average for continental margin sediments. The surface I/C_{org} weight ratio can therefore be used as a redox-indicator, where values of $165\text{-}365 \times 10^{-4}$ imply normal, oxic conditions and much lower values are indicative of anoxic conditions.

If organic matter did not decay upon burial within marine sediments or if I decayed at the same rate as the bulk of organic matter during decomposition, then the down-core I/C_{org} ratio could easily be used as a palæo-redox signal, to indicate whether oxic or anoxic conditions were prevalent at any particular site over time. However, this is not the case, and as has been shown by many authors (Price *et al.*, 1970; Pedersen and Price, 1980; Shimmield, 1985; Kennedy and Elderfield, 1987; Patience, 1992), the I/C_{org} ratio decreases exponentially down the sediment column upon preferential release of I during the post-depositional decomposition of organic matter. The complex interactions and recycling between solid-phase I incorporated with organic matter, and dissolved IO_3^- and I^- in bottom-waters and pore-waters has been studied by Francois (1987) and Kennedy and Elderfield (1987) and this will be looked at in more detail later, with respect to the I concentration profiles of the Peruvian continental margin sediments.

Bromine

This halogen occurs as one of the major anions present in sea-water at a concentration of 0.84mM (at salinity = 35 parts per thousand) and displays conservative properties (Riley and Chester, 1971). Bromine has a much more simple marine geochemical behaviour compared with I because it exists only as the bromide ion (Br^-) in sea-water and therefore does not display any redox-associated properties (Shimmield and Pedersen, 1990). However, as can be seen from Table 6.1, Br is present in marine surface sediments in quite high concentrations (up to 800 ppm) and is found in association with organic matter (Price *et al.*, 1970; Price and Calvert, 1977; Pedersen and Price, 1980).

Price and Calvert (1977) measured relatively low $\text{Br}/\text{C}_{\text{org}}$ ratios compared with $\text{I}/\text{C}_{\text{org}}$ in oxic sediments from the Namibian shelf and concluded that the two halogens must display different forms of association with organic matter. The fact that the I/Br ratio in Panama basin surface sediments was 3500 times greater than in sea-water, implied to Pedersen and Price (1980) that uptake of the halogens was by different organic ligands. Shimmield and Pedersen (1990) quote a $\text{Br}/\text{C}_{\text{org}}$ molar ratio of 19.6×10^{-4} (equivalent to 131×10^{-4} weight ratio) for surface continental margin sediments, regardless of the redox state of the water or sediment column.

Very little study has been carried out on the mechanism for, and the nature of, Br uptake by organic matter but Harvey (1980) concluded that Br exists in a large range of water-soluble and organic-soluble compounds including aliphatic molecules.

Upon burial of organic matter in marine sediments, microbial degradation will occur which should release Br to the interstitial pore-waters. Measurement of the down-core variation in $\text{Br}/\text{C}_{\text{org}}$ suggests that Br is released much slower in relation to I and this implies that Br is bound more strongly to the organic matter (Price and Calvert, 1977; Pedersen and Price, 1980; Shimmield, 1985). In Panama Basin sediments, Pedersen and Price (1980) measured $\text{Br}/\text{C}_{\text{org}}$ ratios down to depths of about 160cm which displayed zones which increased with depth. This is an indication that, in hemipelagic sediments, Br is less labile than the bulk of organic matter during diagenesis (Shimmield and Pedersen, 1990) i.e. that Br is associated with refractory organic compounds.

Of the two halogens, Br is therefore the less useful in terms of both redox and productivity signals in marine sediments. However, it is still important to study the concentrations of both halogens together, as well as their relative associations with organic matter, e.g. correlation coefficients and halogen/ C_{org} ratios, in the sediments on the continental margin of Peru.

6.2.2. Analytical methods and results

Both I and Br concentrations (ppm) were measured in all the sediment samples in this study using X-ray fluorescence techniques on pressed-pellet samples (Appendix A.5). It should be noted that there is a larger degree of error in calculating the salt-corrected concentrations of Br than for I, because there is a significant concentration of Br contained in the salt, which has to be subtracted from the raw data (Appendix A.6). As previously stated, C_{org} levels were determined by combustion techniques after initial acid-removal of carbonate (Appendix A.3).

	I (ppm)	Br (ppm)	I/Br	I/Corg ($\times 10^{-4}$)	Br/Corg ($\times 10^{-4}$)
SURFACE					
CD38-09	93	456	0.21	14.0	68.0
CD38-10	134	461	0.29	14.6	50.0
CD38-02 (Box)	350	103	3.38	343.1	101.4
CD38-02	222	132	1.68	148.7	88.4
CD38-11	469	300	1.56	121.0	77.6
CD38-03 (Box)	540	189	2.87	314.2	109.6
RANGE					
CD38-09	3-93	40-456	0.05-0.4	0.9-14.4	14-68
CD38-10	3-134	22-461	0.05-0.5	1.4-16.8	16-53
CD38-02 (Box)	139-379	47-148	1.8-3.7	128-357	47-131
CD38-02	74-355	47-213	0.8-3.2	67-170	39-101
CD38-11	136-469	86-300	0.7-1.9	43-135	43-78
CD38-03 (Box)	174-624	68-266	1.6-3.0	110-330	46-135
MEAN					
CD38-09	25.0	112.9	0.20	5.4	24.7
CD38-10	24.1	132.0	0.19	4.9	25.0
CD38-02 (Box)	229.2	89.5	2.62	195.8	77.4
CD38-02	161.8	91.9	1.77	107.1	62.0
CD38-11	283.2	190.5	1.51	86.1	57.6
CD38-03 (Box)	291.3	140.4	2.12	162.8	78.0

Table 6.2. Iodine and bromine concentrations and weight ratios (surface, range and mean) for Peruvian margin sediments.

The data in Table 6.2 summarises the halogen concentrations (ppm), the I/Br ratio and their weight ratios to organic carbon (all surface, range and mean) for the two box cores and four piston cores used in this study (the full data set is listed in Appendix C.11). From the surface I/C_{org} ratios an initial interpretation of the redox environment at each core site will be made by comparison with the results of Price and Calvert (1977, Table 6.1).

Care must be taken when interpreting surface data from piston cores because these cores do not contain the sediment/water interface and the first sub-sample was taken up to 10cm down the core. In the study of a geochemical indicator whose concentration varies dramatically over the first few centimetres of the sediment column, such as the halogens, box cores give a much more detailed picture close to, and at, the sediment/water interface.

The profiles in Figs 6.1 through to 6.6 are plots of I, Br, C_{org}, I/C_{org}, Br/C_{org} and I/Br against depth/age for the above cores. It can be seen that all the I and Br profiles display strong similarities to their respective C_{org} profile and the strength of this halogen-C_{org} relationship can be illustrated by the high correlation coefficients shown in Table 6.3, especially for the four piston cores.

			Core position	
Iodine	0.567	0.390	CD38-09	CD38-10
	0.120	0.825	CD38-02 (Box)	CD38-02
	0.673	0.362	CD38-11	CD38-03 (Box)
Bromine	0.702	0.745	0.923	0.732
	0.017	0.766	0.534	0.810
	0.815	0.565	0.724	0.731
	Organic carbon		Iodine	

Table 6.3. Iodine, bromine and organic carbon correlation coefficients.

From the data presented in Figs 6.1 to 6.6 and Table 6.2, the following points should be noted.

- a) The surface I concentrations are lowest in the shallow-water, shelf cores and highest at the deep-water sites, even though cores CD38-09 and CD38-10 have the highest organic matter content. This results in very low surface I/C_{org} ratios for these two cores.
- b) In contrast, the highest surface Br concentrations are found in the two shallow-water cores and the inter-core variation seems to be dependant on the level of

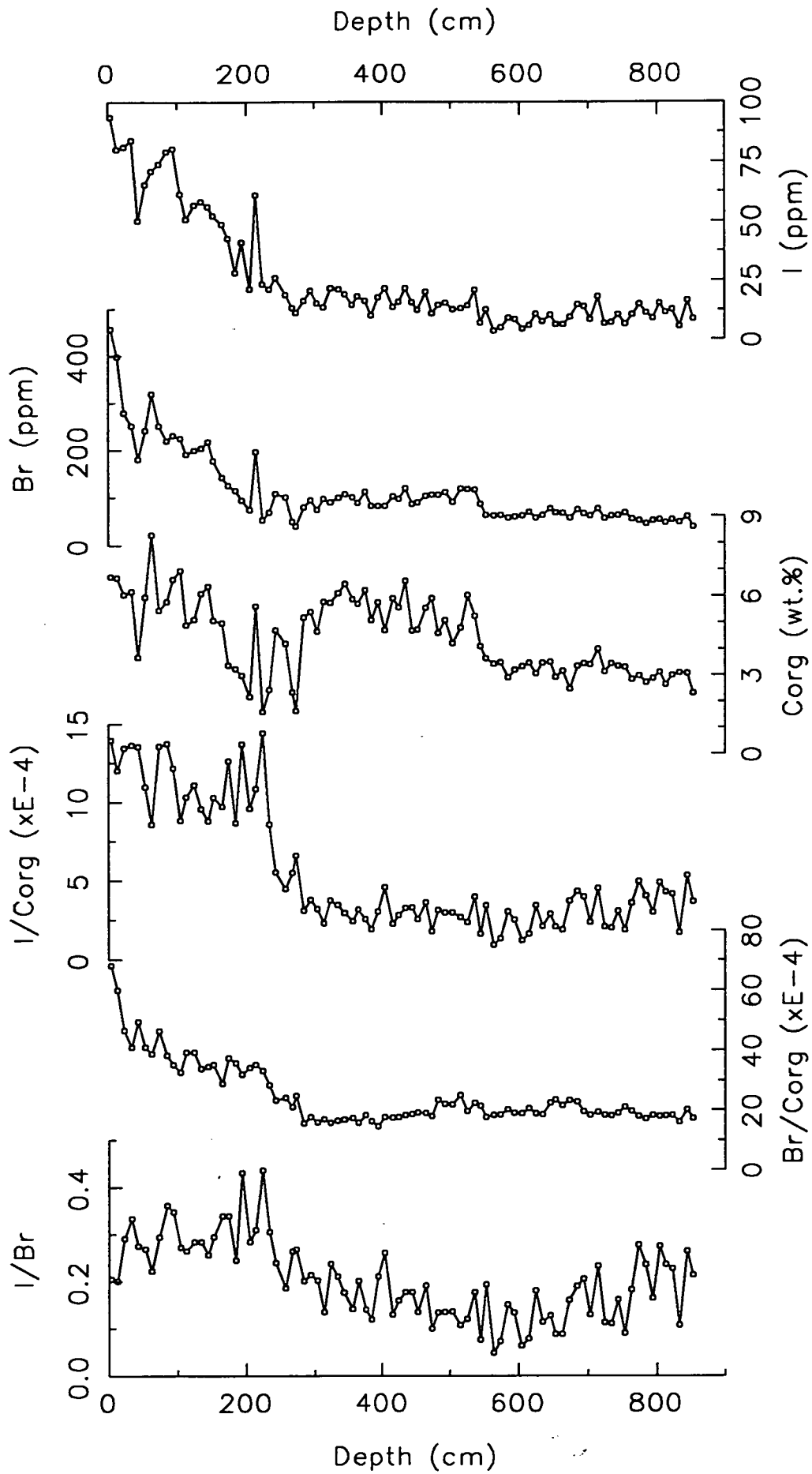


Figure 6.1. Core CD38-09 (148m) halogen depth profiles : iodine, bromine, organic carbon, I/C_{org} , Br/C_{org} and I/Br against depth (cm).

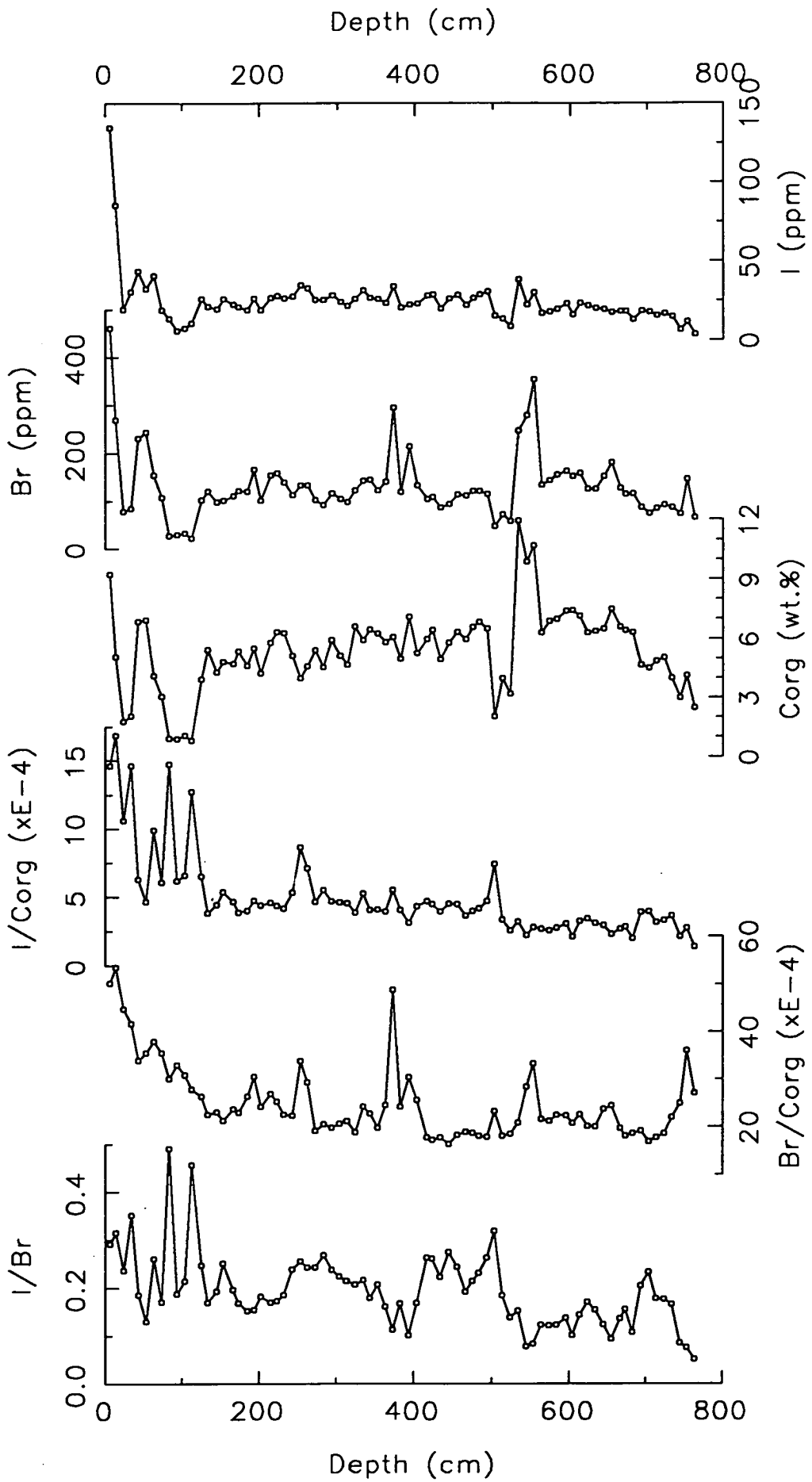


Figure 6.2. Core CD38-10 (257m) halogen depth profiles : iodine, bromine, organic carbon, I/C_{org} , Br/C_{org} and I/Br against depth (cm).

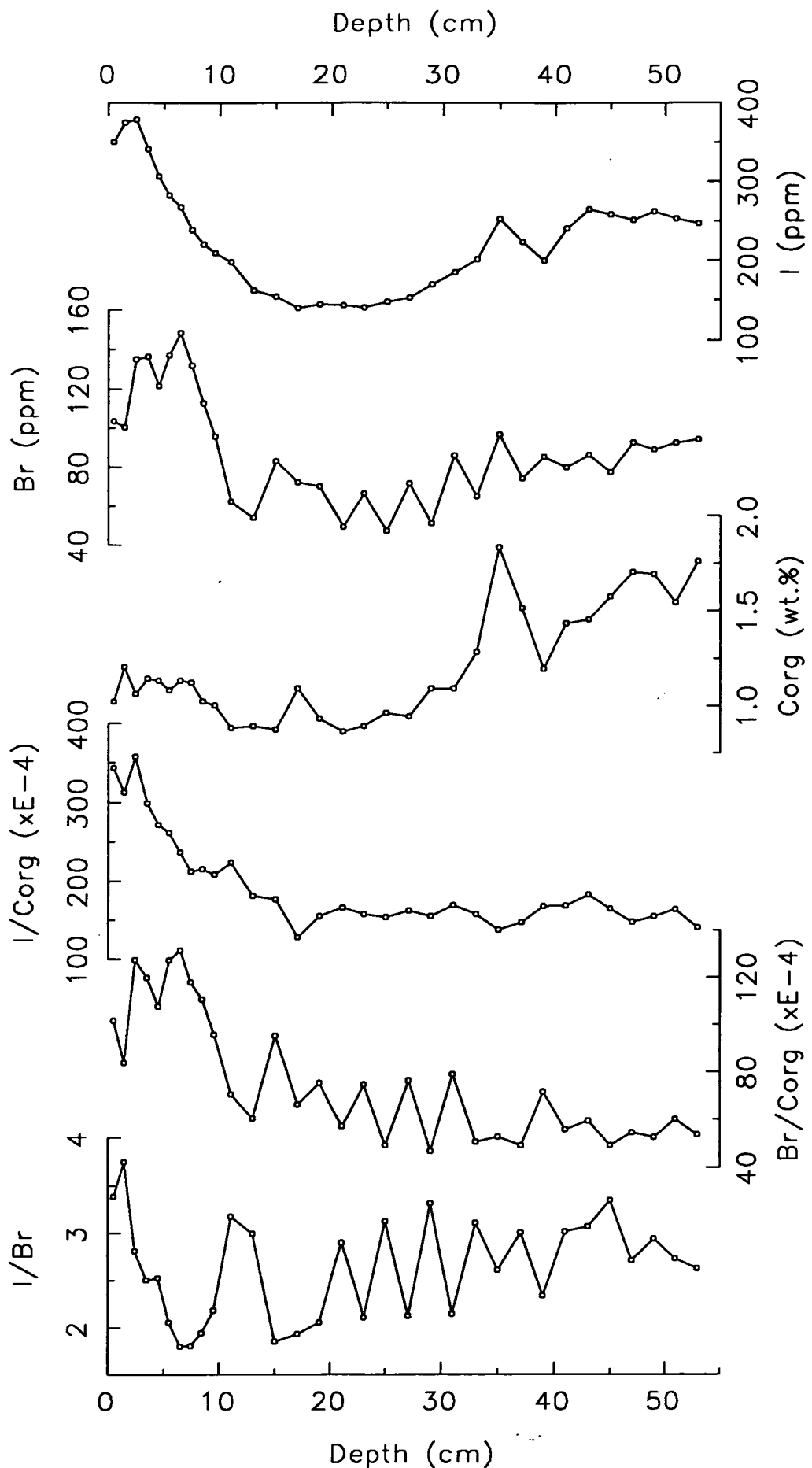


Figure 6.3. Box core CD38-02 (2530m) halogen depth profiles : iodine, bromine, organic carbon, I/C_{org} , Br/C_{org} and I/Br against depth (cm).

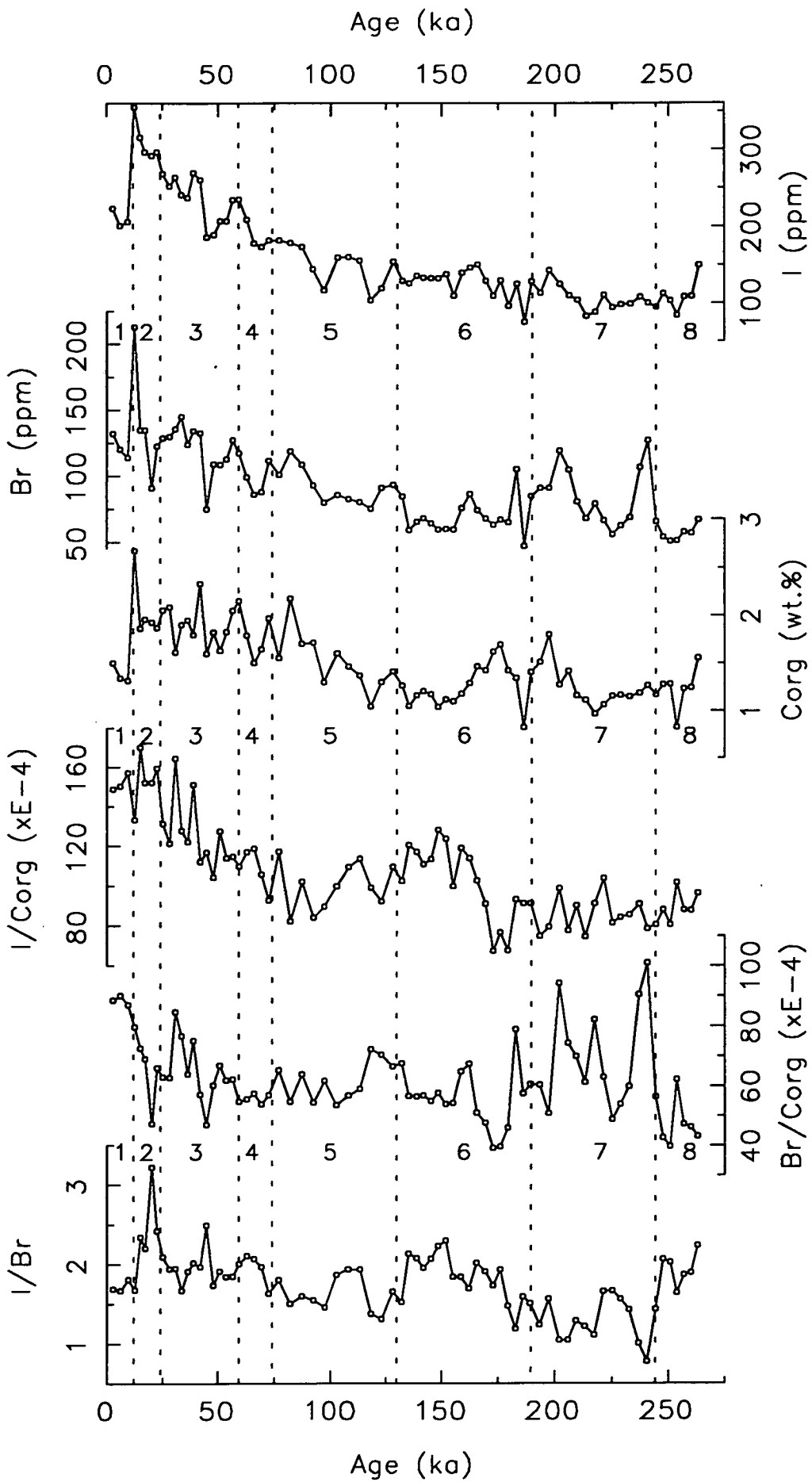


Figure 6.4. Core CD38-02 (2525m) halogen age profiles : iodine, bromine, organic carbon, I/C_{org} , Br/C_{org} and I/Br against age (ka).

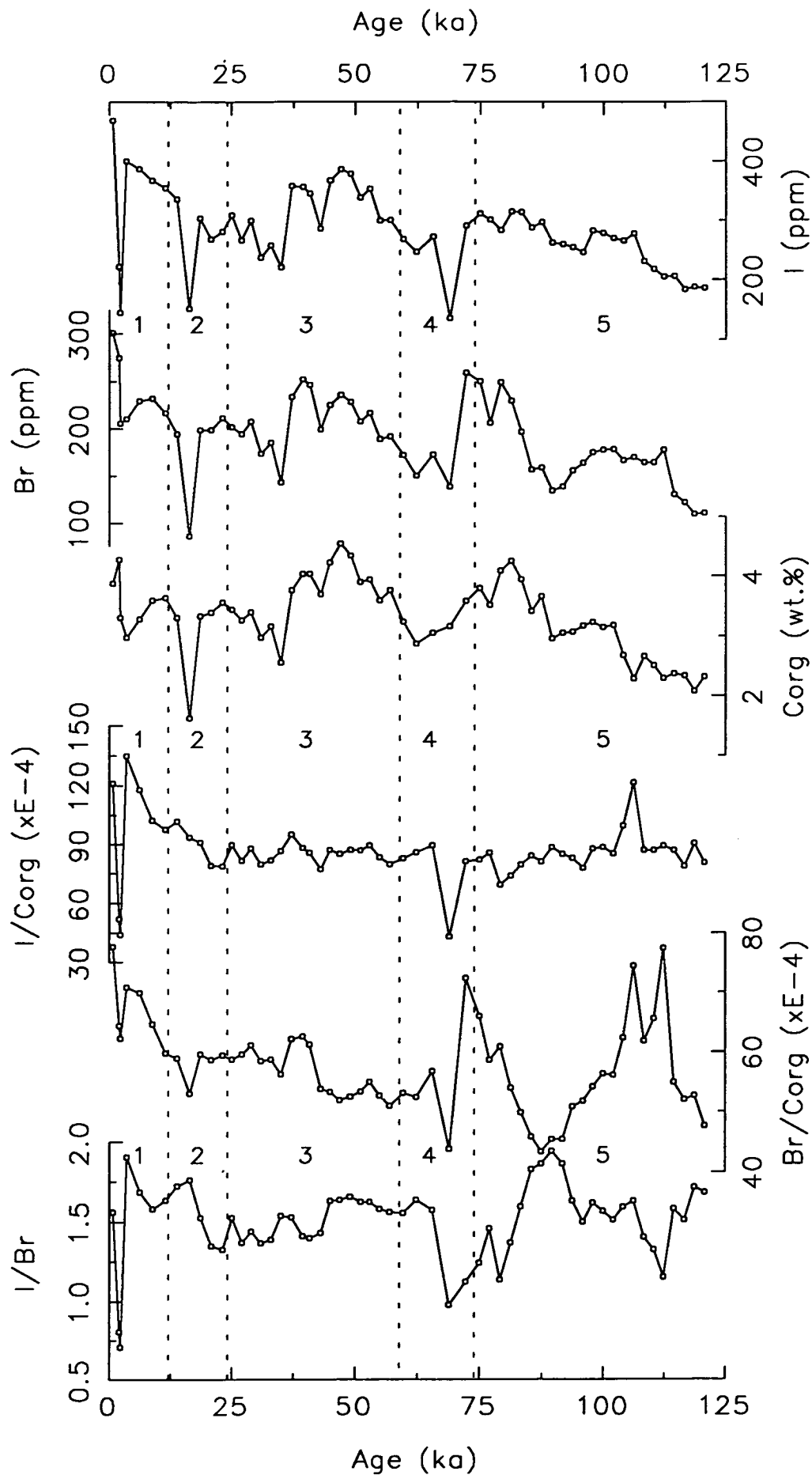


Figure 6.5. Core CD38-11 (3835m) halogen age profiles : iodine, bromine, organic carbon, I/C_{org} , Br/C_{org} and I/Br against age (ka).

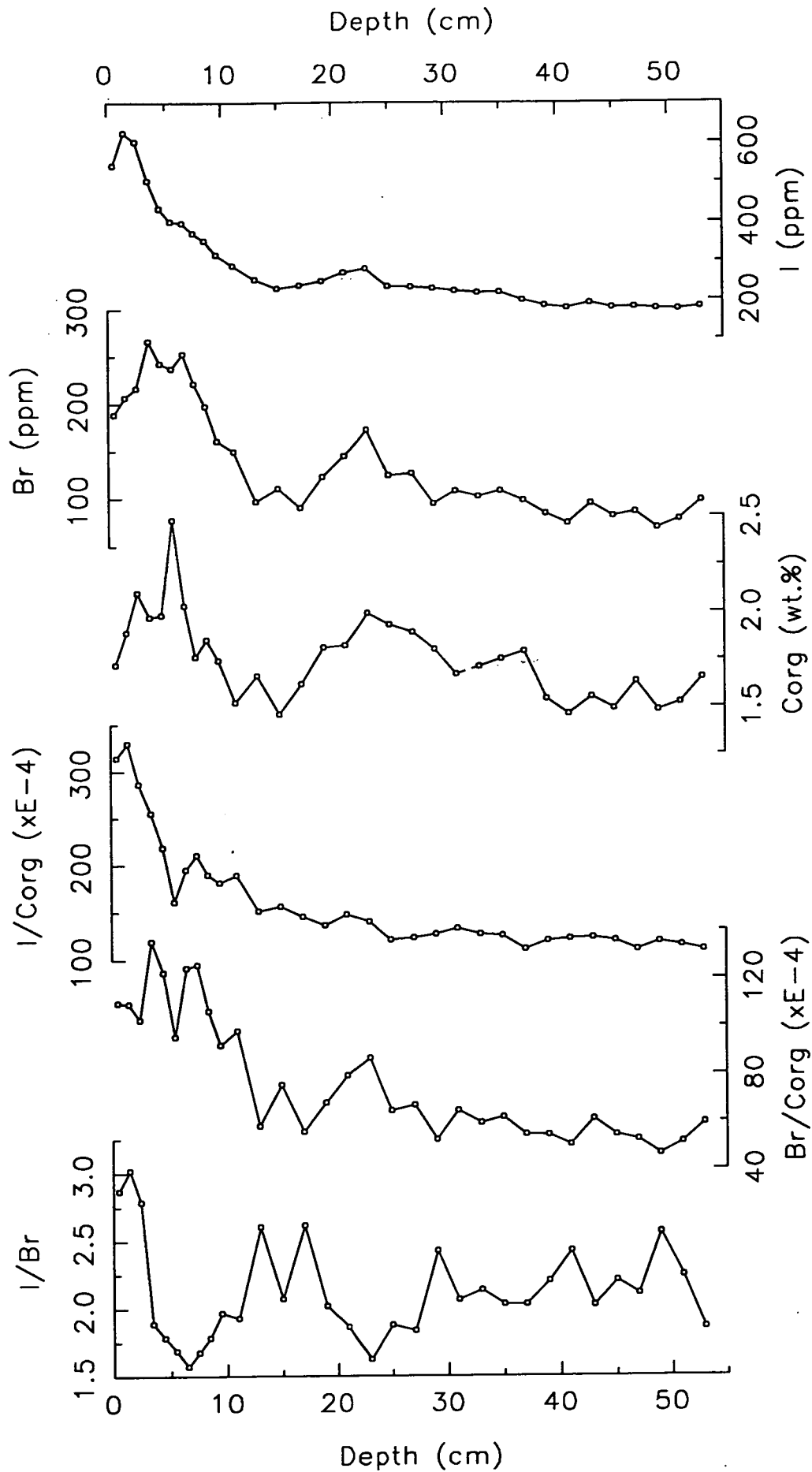


Figure 6.6. Box core CD38-03 (4289m) halogen depth profiles : iodine, bromine, organic carbon, I/C_{org} , Br/C_{org} and I/Br against depth (cm).

C_{org} , resulting in fairly similar surface Br/C_{org} ratios, which are within the range, $50-110 \times 10^{-4}$.

- c) In the two box cores (Figs 6.3 and 6.6), the peak of I (ppm) is not exactly at the sediment/water interface but is just below it, at the 1-2cm range. The pattern is similar for Br (ppm) which peaks at 2-7cm. The surface sample concentrations in the four piston cores are very dependant on the actual depth of the first sub-sample and so the near-surface peaks are not seen.
- d) There is a fairly smooth exponential decrease in the I/C_{org} ratios of the two box cores, which levels out within 20-30cm to an average of 160×10^{-4} for CD38-02 and 120×10^{-4} for CD38-03. The deep-water piston cores display similar profiles with a sub-surface maxima in CD38-11 at 40cm (135×10^{-4}) decreasing smoothly down to a background level of $80-90 \times 10^{-4}$ below 100cm. The decrease in piston core CD38-02 is not as smooth and there is a broad zone (300-500cm) where the I/C_{org} increases again.
- e) The two shallow-water, iodine-depleted cores have I/C_{org} weight ratios which are very variable ($5-15 \times 10^{-4}$) above the zones of major phosphorite formation (4.3.3) but below 280cm in CD38-09 and 120cm in CD38-10 the ratio is less than 5×10^{-4} and much more steady.
- f) There is a steady-state, exponential decrease in the Br/C_{org} weight ratios of cores CD38-09 and CD38-10 which levels out to about 20×10^{-4} . However, in all the piston cores except CD38-09, sub-surface maxima in Br/C_{org} are found and the ratio is highly variable in CD38-02.

The relative enrichments of the two halogens can be expressed as an I/Br weight ratio and the lowest plot in Figs 6.1 to 6.6 displays the depth profile of I/Br for each of the cores. The four piston core I/Br profiles illustrate the difference in halogen enrichment between the shallow-water (surface $I/Br = 0.2-0.3$) and deep-water (surface $I/Br = 1.5-1.7$) environments. In core CD38-11, it is thought that a turbidite-like zone occurs at 4-24cm and the two sub-samples in this horizon (Fig. 6.5) have I/Br ratios < 1.0 (as well as anomalously low I/C_{org} ratios) which may be an indication that the sediment in this zone contains organic matter which was originally deposited further up the continental slope at a much shallower depth.

The very low I/Br weight ratio in sea-water ($8.5 \times E^{-4}$, Pedersen and Price, 1980) is due to the fact that Br is a major sea-salt anion (Riley and Chester, 1971). Therefore, surface sediment I/Br ratios of between 0.2 and 3.4 (Table 6.2) indicate that on the Peruvian continental margin the uptake of I is being favoured over Br by a factor of between 235 and 4000.

6.2.3. The halogens as palæo-indicators

The various factors which control the halogen composition of marine sediments must be examined before any interpretation of their down-core variation can be made. This discussion section will look at the two halogens separately, with respect to the results from this study, in terms of their geochemical controls and then make some interpretations about their use as palæo-indicators. Finally, their relative concentrations will be considered, using the I/Br weight ratios of piston core CD38-02 (for which a glacial/interglacial age model has been assigned; 2.4.2), for their use as indicators of global climate change.

Iodine

The level of organic matter flux to the sediment and its actual concentration within the sediment does not seem to control the level of I enrichment in the Peru margin sediments, even though it is the organic matter which is the vital component in the mechanism of I uptake from sea-water (Harvey, 1980; Francois, 1987). This can be seen by the inverse relationship for surface sediment concentrations of I against C_{org} in Fig. 6.7.A.

If the surface sediments with the highest C_{org} content have the lowest I concentration, and vice versa, and yet there is a fairly strong I- C_{org} correlation in all the sediments (Table 6.3) there must be another, more dominant factor controlling the I concentration. Figure 6.7.B is a plot of the surface I concentration against water depth of the core site, which has a positive straight-line relationship [where, I (ppm) = $0.0996 \times \text{water depth (m)} + 75.8$ ($r = 0.956$)]. This can be interpreted either as uptake of I by organic matter within the water column (where longer sinking times allow for higher I enrichment) or uptake at the sediment/water interface by organic matter before it is buried, in which case more I enrichment would depend on slower sedimentation rates.

Previous work by Price and Calvert (1977) implies that the latter of the two, i.e. bulk sedimentation rate, is the correct interpretation, and this hypothesis is backed up by the I recycling model of Kennedy and Elderfield (1987) which is very dependant on the bulk sedimentation rate. Recycling involves initial release of I from freshly deposited organic matter in the form of the thermodynamically-unstable I^- anion, which can be oxidised to I_2 . This free iodine can then react with organic matter or be hydrolysed to HOI, which is readily sequestered by humic compounds.

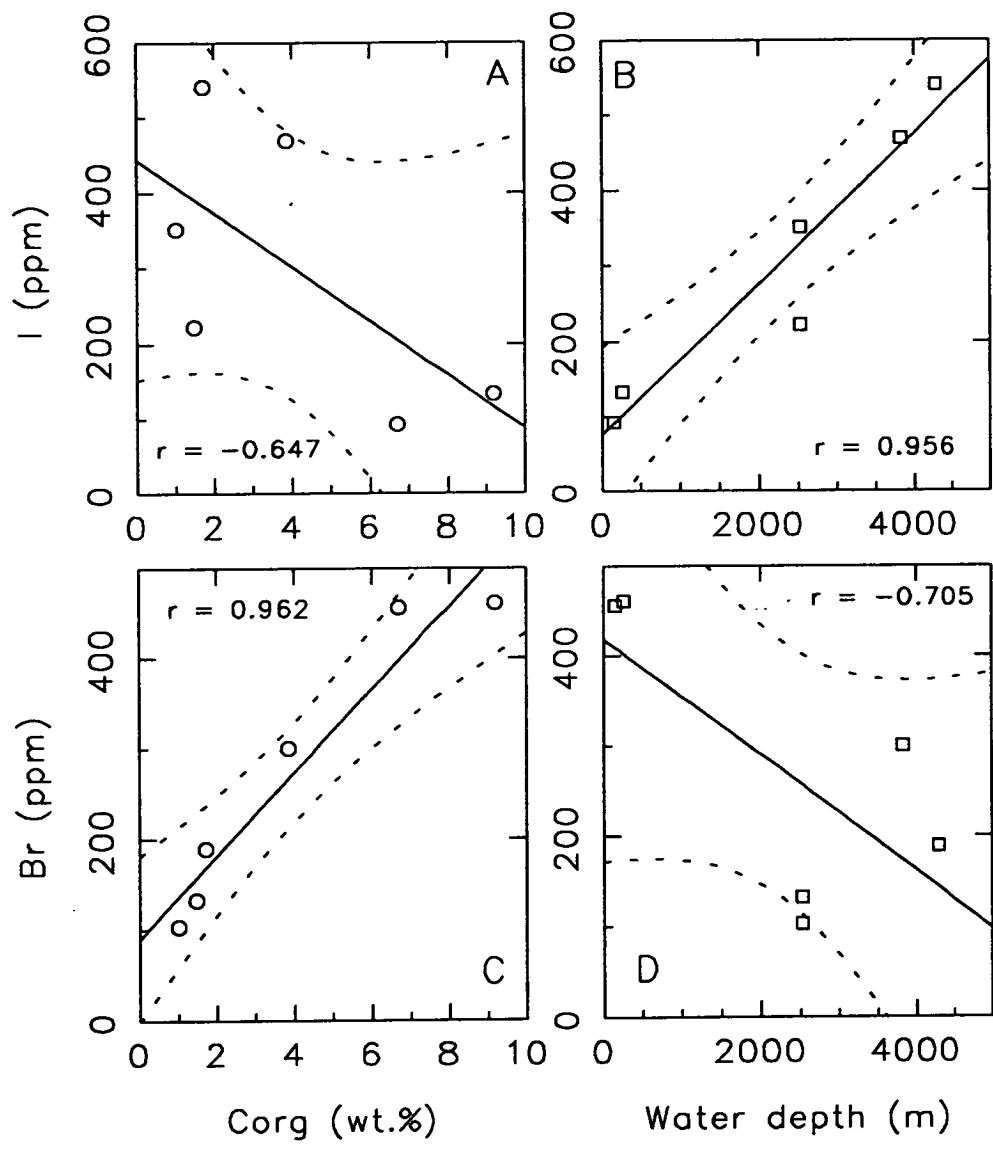


Figure 6.7. Correlation plots for surface samples in this study: A) I against C_{org} , B) I against water depth, C) Br against C_{org} and D) Br against water depth. All show best fit straight line (full line) and 95% confidence limits (dotted lines).

Therefore, slower burial of organic matter allows for a longer residence time near the sediment/water interface and greater I enrichment by organic matter.

However, even if sedimentation rates and organic matter fluxes are similar, there is one physio-chemical property of the sediment/pore-water system which dominates the control of I concentration in marine sediments and that is the redox environment of deposition (Price and Calvert, 1973, 1977; Shimmiel and Pedersen, 1990; Pedersen *et al.*, 1992).

Price and Calvert (1977) state that on the Namibian shelf, under a zone of coastal upwelling similar to that found off Peru, the I/C_{org} weight ratio in surface sediments is about 250×10^{-4} in oxic sediments but only about 20×10^{-4} in reduced sediments. From the surface I/C_{org} data in Table Z.2, it can therefore be interpreted that the sediments in cores CD38-09 and CD38-10 are presently accumulating under reduced, anoxic conditions, in contrast to the deeper-water cores which are situated in an oxic environment. The two shallow-water cores are located within the 100-400m water depth where the oxygen-minimum zone (OMZ) impinges on the Peruvian continental shelf (Veeh *et al.*, 1973) and therefore the bottom-waters and pore-waters at these sites are very deficient in dissolved oxygen (Chapter 1).

As previously mentioned, Price and Calvert (1973, 1977) concluded that I uptake at the sediment/water interface involves an iodide-oxidase enzyme within organic matter which requires the presence of free oxygen to react (Shaw, 1962). This I-organic matter reaction, therefore does not operate in sediments within the OMZ off Peru, resulting in the relatively low I concentrations in CD38-09 and CD38-10. Laboratory experiments by Francois (1987) suggested that humic substances can reduce iodate to electropositive iodine species, which then electrophilically substitute onto organic molecules. This reaction did not occur when humic compounds were exposed to iodide-bearing solutions, such as found in anoxic systems (Francois, 1987). Therefore, sediments accumulating under such conditions are less enriched in I than those exposed to oxic, iodate-bearing waters.

The problem with relating this redox-indicating property of I to sediments which are no longer at the surface, arises from the preferential release of I back into pore-waters upon post-depositional decay of organic matter and recycling of the halogen (Kennedy and Elderfield, 1987; Shimmiel and Pedersen, 1990). The exponential decrease of the I/C_{org} ratio with increasing depth, can result in sediments

which were initially deposited under oxic conditions displaying a very low I/C_{org} ratio.

The iodine concentration is of limited use as a palæo-redox indicator but when applied in conjunction with C_{org} measurements, it can be used to distinguish between past oxic conditions ($I/C_{org} = 250$ down to 80×10^{-4}) and anoxic conditions ($I/C_{org} < 20 \times 10^{-4}$) existing at the sediment/water interface.

From the I/C_{org} profiles in Figs 6.1 to 6.6, it can be seen that the sediments in cores CD38-09 and CD38-10 have been continuously deposited under anoxic conditions and all the other cores within an oxic environment. The shallow-water, anoxic conditions on the Peruvian continental shelf indicate that over the length of time that the sediments in cores CD38-09 and CD38-10 were deposited, the OMZ was always present. This, in turn, probably means that coastal upwelling has existed in this area throughout the Late Quaternary (Schrader, 1992).

One other application of this I/C_{org} palæo-redox indicator is in the determination of possible breaks in the sedimentation pattern of a core, which can be either due to loss (i.e. erosion of the column) or gain (i.e. a turbidite) of sediment. In core CD38-11 (Fig. 6.5), the turbidite zone at 4-24cm is highlighted by anomalously low I/C_{org} weight ratios ($40 \times E^{-4}$) below which an exponential, steady-state decrease occurs. In cores CD38-09 and CD38-10 (Figs 6.1 and 6.2), there is a non-steady-state decrease pattern of I/C_{org} in the upper part of each core, then a sharp break at the zones of phosphorite formation (220-270cm in CD38-09 and 80-110cm in CD38-10) followed by much lower I/C_{org} ratios which show less variation. This unusual I/C_{org} profile implies that the smooth exponential decrease of I/C_{org} has been disturbed by a period of erosion of the sediment column (occurring at the same time as phosphorite concentration, 4.3.6) and that the sediment below the phosphorite horizon is relatively older than its current depth would imply.

Bromine

The ability of an element to act as an indicator of surface ocean productivity or bottom-water oxygen conditions in a marine sediment record depends respectively on the mechanisms of preservation of the element's original surface sediment signal and the number of valence states in which the element exists in sea-water.

As previously mentioned, bromine cannot easily be used as a palæo-indicator because,

- a) the mechanisms of release of Br upon organic matter degradation are not fully understood (Harvey, 1980; Shimmiel and Pedersen, 1990) and therefore a

palæo-measurement of Br concentration cannot be accurately interpolated back to an original surface Br content and thus organic matter/ocean productivity level, and,

- b) bromide is the only form of Br that exists in sea-water and therefore it displays no redox behaviour (Shimmiel and Pedersen, 1990).

There is a linear correlation between Br and organic carbon for the surface sediments from all the cores in this study, regardless of the redox state of the sediments or water column (Fig. 6.7.C). However, this relationship does not hold for sub-surface samples due to inter-core differences in the decay of organic matter and release of Br.

Measurement of Br and its ratio to C_{org} in marine sediment cores can help to indicate possible sediment loss at the top of piston cores and possible inter-core variations in the sedimentation rate and/or the composition of organic matter present.

Shimmiel and Pedersen (1990) produced a correlation plot of Br against C_{org} for surface, hemipelagic sediments with a straight line molar ratio of 19.6×10^{-4} , which is equivalent to a weight ratio of 131×10^{-4} . The two box cores in this study have surface Br/C_{org} weight ratios of 102×10^{-4} for CD38-02 and 110×10^{-4} for CD38-03 (Table 6.2), which agree well with the combined data set used by Shimmiel and Pedersen (1990). In fact, the Br/C_{org} weight ratios measured between 2 and 3cm, where the sub-surface peak of Br (ppm) occurs, are 130×10^{-4} and 135×10^{-4} respectively. It can also be seen from Figs 6.3 and 6.6 that within the upper 30cm in the two box cores, the Br/C_{org} ratio has dropped to $50-60 \times 10^{-4}$.

This information can now be used for all the piston cores to determine whether or not much of the surface sediment has been lost during the coring procedure. A surface value of 130×10^{-4} for Br/C_{org} can be applied to all the Peruvian continental margin sites including the two shallow-water, anoxic cores because the redox state should not affect the surface Br/C_{org} ratio (Pedersen and Price, 1980; Shimmiel and Pedersen, 1990). The top samples in the four piston cores from this study fall within the range $50-90 \times 10^{-4}$ for Br/C_{org} (Table 6.2) which indicates that very little (up to 30cm) of the original surface sediment has been lost during coring.

The depth at which the Br/C_{org} ratio reaches a background, steady level in marine sediments can suggest differences in sedimentation rates between cores. If the sedimentation rate is relatively slow, any Br associated with labile organic matter should have enough time to be released before being buried too deep. The cores CD38-02 and CD38-11 both seem to reach background Br/C_{org} ratios of about $60 \times$

10^{-4} within the upper metre of sediment (Figs 6.4 and 6.5) suggesting a slower sedimentation rate at these sites compared with CD38-09 and CD38-10 which take 3 and 1.5m respectively to reach their background $\text{Br}/\text{C}_{\text{org}}$ level of about 20×10^{-4} (Figs 6.1 and 6.2). This is as expected, since the shallow-water cores are situated on the continental shelf, close to the terrigenous-input source (7.2.3).

This picture may, however, also be influenced by differences in the type of organic matter and/or its flux to the sediment at each site. It is of interest to note that the two cores situated directly under the zone of coastal upwelling display a much lower background level of $\text{Br}/\text{C}_{\text{org}}$ when compared with the cores on the Nazca ridge and deep continental slope (20×10^{-4} compared with 60×10^{-4}). This difference may be due to contrasts in the composition of organic matter at these sites, e.g. if different organic compounds take up variable quantities of Br in labile forms compared with more refractory forms, then more Br will be released upon post-depositional decomposition from the organic matter containing more labile-Br. This will result in a lower background $\text{Br}/\text{C}_{\text{org}}$ ratio.

I/Br

In previously published studies of marine sediments which measured both I and Br (Price *et al.*, 1970; Price and Calvert, 1977; Pedersen and Price, 1980; Patience, 1992) the concentrations of the two halogens have generally been considered separately and then conclusions drawn about their contrasting geochemical behaviours. Pedersen and Price (1980) used the surface sediment I/Br ratio to quantify the degree of enrichment of I in relation to Br in Panama Basin sediments compared with sea-water, but did not study down-core variations in I/Br. Patience (1992) plotted temporal variations in I/Br which showed a general decrease down-core indicative of preferential release of I relative to Br during burial diagenesis. The I/Br weight ratio profiles for the piston cores in this study also show this down-core decreasing trend (Figs 6.1, 6.2, 6.4 and 6.5) but these are complicated by zones of higher I/Br as well.

As described above, the two halogens are taken up at the sediment/water interface by organic matter to different degrees due to the redox state of the pore-waters, the flux of organic matter and/or the sedimentation rate. They are then released upon burial at different rates. This would seem to imply that the I/Br ratio would be of little use as a palæo-indicator of the possible changes in surface biological productivity associated with glacial/interglacial periodicity throughout the Late Quaternary.

The two near-shore cores, CD38-09 and CD38-10, have exceptionally low (<0.5) I/Br ratios due to the lack of I uptake in the anoxic environment. Although the

down-core plots of I/Br for these two cores (Figs 6.1 and 6.2) do show a possible cyclic pattern, interpretation is difficult because of the lack of accurate age models and the breaks in the sediment column caused by erosion. However, for piston core CD38-02 an accurate age model has been determined by foraminifera oxygen isotope profiling (2.4.2) and the lowest plot in Fig. 6.4, which displays the I/Br ratio plotted against calculated age, shows that on the Nazca ridge the I/Br profile does show a possible palæo-environmental record of glacial/interglacial variation. The sediments in core CD38-02 have accumulated under surface oxic, steady-state conditions resulting in I/Br ratios which vary between 0.9 and 3.1, with the interglacial stages displaying relatively lower values. This is the case both in the near-surface sediments, which contain organic matter which is still releasing the halogens during decomposition, and in the deeper sediments, which have reached a stable state with respect to organic matter decay.

Why should hemipelagic sediments from the Peruvian continental margin display I/Br ratios which seem to fluctuate in correspondence to Late Quaternary climate changes? The I/Br against age profile of CD38-02 could be interpreted as a palæo-productivity record because climate change, caused by ice-sheet build-up during glacial periods, is known to affect the strength of coastal upwelling, which in turn can alter the structure and volume of the marine biomass in the surface waters and change the organic matter flux to the sediment (Chapter 3). Variations in the quantity and/or composition of organic matter at the sediment/water interface could affect the relative amounts of uptake of the two halogens into organic compounds thus altering the I/Br ratio measured throughout the sediment column. There seems to be either a relatively greater uptake of I or less uptake of Br during glacial periods, resulting in higher I/Br ratios in core CD38-02. This interpretation is, however, very speculative and no such I/Br-climate change relationship was seen in core CD38-11. Until a more detailed understanding of the complex mechanisms of halogen incorporation in hemipelagic sediments is known, it is difficult to interpret these I/Br variations further.

6.2.4. Conclusions

The following conclusions can be made with regards to the use of I and Br as indicators of palæo-productivity and palæo-redox conditions in the Peru continental margin sediments.

- 1) I and Br are closely associated with organic carbon and with each other (Table 6.3). However, their post-depositional diagenetic mobility means that the halogens are unreliable as indicators of palæo-productivity.
- 2) Surface sediment concentrations of I and the I/C_{org} ratio can be used to distinguish between oxic and anoxic environments of deposition. Piston cores CD38-09 and CD38-10 show very low surface I/C_{org} ratios, and are therefore located in an anoxic environment, where the OMZ impinges on the sea-floor under the Peruvian coastal upwelling zone. All other cores used in this study contain much higher surface I/C_{org} ratios which indicates that they are situated in a more normal, oxic marine environment.
- 3) Interpretation of down-core I/C_{org} ratios is made complicated by the decay of organic matter and recycling of I (Kennedy and Elderfield, 1987) but they seem to imply that palæo-redox conditions at the above sites on the Peru continental margin have not changed throughout the Late Quaternary, i.e. cores CD38-09 and CD38-10 have accumulated under generally anoxic conditions, which implies that coastal upwelling has affected bottom-water oxygen levels throughout the history of sediment deposition.
- 4) Surface Br/C_{org} ratios are independent of redox conditions (Shimmield and Pedersen, 1990) and therefore this halogen cannot be used as a palæo-redox indicator. Stronger statistical correlation in the piston cores between Br and C_{org} compared with I and C_{org} (Table 6.3) suggests that Br is associated with less labile compounds within marine organic matter.
- 5) Down-core variations in halogen content and their ratios to C_{org} can help to identify breaks in the sedimentation pattern (turbidite zone in CD38-11 and erosion in CD38-09 and CD38-10), loss of sediment at the top of piston cores and inter-core variations in sedimentation rate and/or organic matter composition.
- 6) The I/Br ratio in sediments from an undisturbed, oxic core, such as CD38-02, may indicate changes in the composition and/or flux of organic matter associated with glacial/interglacial climate change, where glacial periods display relatively higher I/Br ratios. Until the complex interactions involved in the uptake and release of halogens by organic matter are more fully understood, this I/Br - climate change hypothesis cannot be substantiated.

6.3. THE BARIUM SIGNAL

6.3.1. Introduction

A major aim of palæo-oceanography is to find a geochemical record in marine sediments of past levels of sea-surface biological productivity and because most of the proxy indicators previously used (C_{org} , CaCO_3 , biogenic silica; Chapter 7) are indicators of more than one oceanographic process, the ideal palæo-productivity indicator has still to be found (Rea *et al.*, 1991).

However, since Revelle *et al.* (1955) first noticed a link between barium (Ba), opal (biogenic silica) and biogenic sedimentation, many authors (Chow and Goldberg, 1960; Church, 1970, 1979; Schmitz, 1987; Nair *et al.*, 1989; Dehairs *et al.*, 1991; Shimmield and Mowbray, 1991; Dymond *et al.*, 1992; Patience, 1992; Von Breyman *et al.*, 1992) have studied Ba in terms of its usefulness as a palæo-productivity indicator.

Ba in sediments occurs mainly as barite (BaSO_4), a marine mineral which was first reported by Murray and Renard (1898) and whose production in the water column from dissolved Ba seems to be related to the marine biogeochemical cycle. There are two sets of hypotheses for the production of barite in the ocean:

- 1) formation in microenvironments, such as siliceous plankton tests, marine snow, faecal pellets etc., where decay of organic matter provides an enrichment of dissolved sulphate (Chan *et al.*, 1976; Dehairs *et al.*, 1980; Bishop, 1988); and
- 2) active precipitation by marine organisms, such as benthic foraminifera (Lea and Boyle, 1989), corals (Lea and Boyle, 1990A) and benthic protozoans (Bishop, 1988).

Church (1970, 1979) found a correlation in East Pacific Rise sediments between Ba, CaCO_3 and C_{org} but the relationships and causes of such trends have still not been firmly established (Schmitz, 1987; Shimmield and Mowbray, 1991; Shimmield, 1992; Patience, 1992). Recently, Dymond *et al.* (1992) used sediment traps in the Atlantic and Pacific oceans to measure particulate fluxes of Ba and C_{org} . They found that the C_{org}/Ba ratio decreased with increasing water depth as a result of the simultaneous uptake of Ba in settling particles during organic matter decomposition. The results from Dymond *et al.* (1992) support the first of the above

two hypotheses as a cause of deep-sea barite production, i.e. formation of barite in microenvironments rather than secretion by specific organisms. Their water column observations imply that Ba could be used as a quantitative productivity signal in marine sediments and, because Ba can resist dissolution and/or remineralisation upon burial (Heath and Dymond, 1977, 1981; Dymond, 1981), its "residual" signal has potential for use as a palæo-productivity indicator.

6.3.2. Analytical methods and results

Barium is classified as a trace element and its concentration in the sediments in this study was determined by X-ray fluorescence techniques on pressed-pellet samples (Appendix A.5). As previously stated, Al determination used X-ray fluorescence analysis of fused discs (Appendix A.5) and C_{org} and biogenic silica concentrations were measured using wet chemical techniques (Appendices A.3 and A.4 respectively).

A proportion of the Ba concentration present in marine sediments is associated with the terrigenous, detrital aluminosilicates and, therefore, in order to examine any variation in the "biogenic-source" Ba (Ba_{bio}), the total Ba concentration (ppm) can be expressed as a ratio to Al ($Ba/Al \times E^{-4}$). Table 6.4 shows the range and mean values of total Ba, Ba_{bio} and the Ba/Al ratio for the four piston cores, which is a summary of the Ba data in Appendices C.10, C.11 and C.14.

The Ba/Al depth/age profiles for the above piston cores are illustrated in Fig. 6.8 and this shows that even after normalising for the variation of terrigenous-Ba input, there is still a large dynamic range in the Ba/Al ratio, especially for cores CD38-02 and CD38-11. The reasons for such variation over time will be discussed shortly.

	Ba (ppm)			Ba/Al ($\times E^{-4}$)			Ba_{bio} (ppm)		
	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean
CD38-09 (148m)	185	1438	292	38.8	250.1	51.1	-299	1006	-140
CD38-10 (257m)	164	397	296	42.7	97.2	59.8	-225	89	-84
CD38-02 (2525m)	1098	2424	1600	167.0	425.1	277.8	620	1941	1166
CD38-11 (3835m)	385	2495	1390	63.1	369.2	199.2	-73	1988	868

Table 6.4. Range and mean of Ba, Ba/Al and Ba_{bio} (calculated using Eqn 6.3).

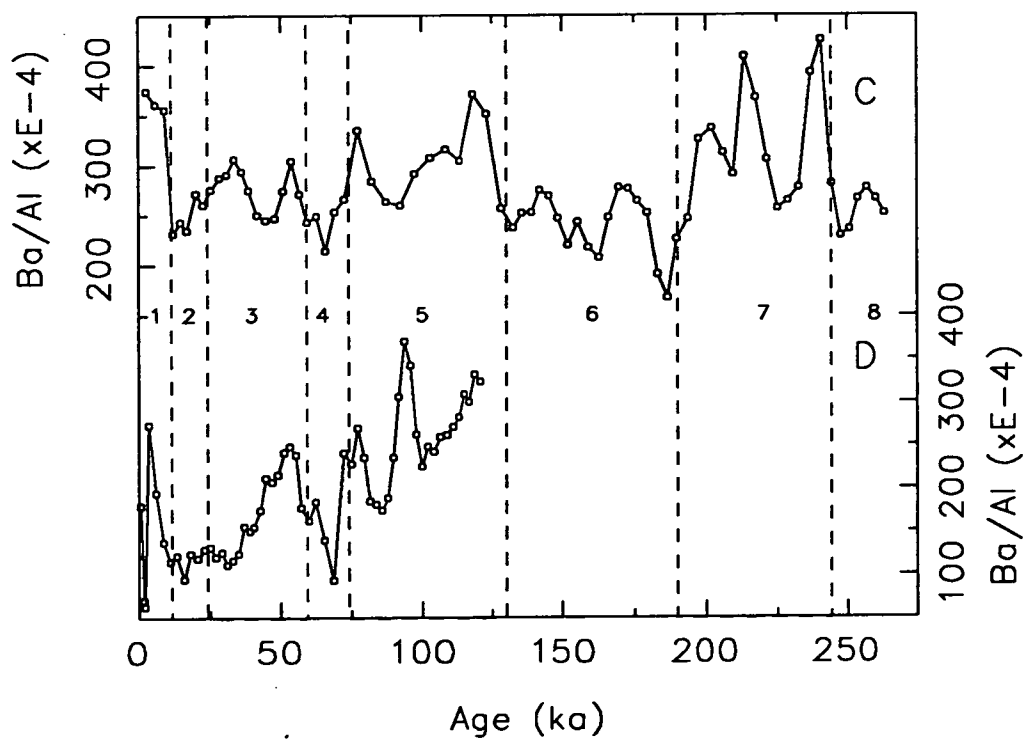
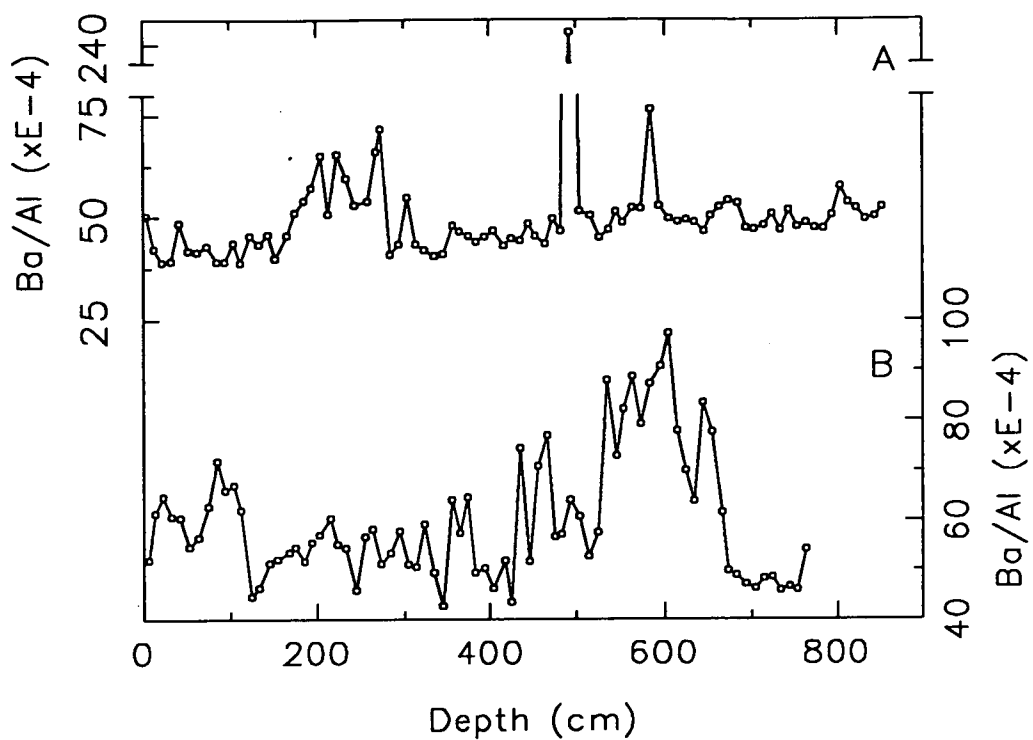


Figure 6.8 Ba/Al weight ratio down-core profiles: A) CD38-09, B) CD38-10, C) CD38-02 and D) CD38-11.

If Ba is to be a useful palæo-productivity tracer then study of the correlation coefficients between Ba and C_{org} and biogenic silica (Table 6.5) may indicate the presence of any biogenic relationships (Dehairs *et al.*, 1980; Von Breymann *et al.*, 1992).

Ba correlation	Corg	Bio. Silica
CD38-09	-0.094	-0.648
CD38-10	-0.191	-0.171
CD38-02	-0.066	0.540
CD38-11	-0.357	0.822

Table 6.5. Correlation coefficients of Ba (ppm) with C_{org} and biogenic silica for piston cores.

The lower concentration of Ba found in the two shallow-water cores (CD38-09 and CD38-10) compared with the deeper-water cores (Table 6.4) supports the work of Von Breymann *et al.* (1992) who found a water depth/sedimentation rate dependence on the biogenic-Ba content of many Peru shelf and slope sites. This theory might initially suggest less biogenic-Ba input at CD38-09 and CD38-10. The shallow-water cores are very near the coast, which is the source of aluminosilicate, terrigenous detritus (aeolian and riverine) and so this source of Ba can dominate over a biogenic source. However, as was seen in Chapter 3, it is these cores which are situated directly under the zone of Peruvian coastal upwelling and therefore there is also a high biogenic flux to the sediment. At these two sites a high total Ba concentration (terrigenous and biogenic) would be expected.

The main reason for the low Ba concentrations and Ba/Al ratios (and negative Ba_{bio}) is that Ba is being lost upon burial in the sediment during diagenetic mobilisation (Von Breymann *et al.*, 1992). This can only occur in sediments within a suboxic/anoxic environment (Dymond, 1981; Dymond *et al.*, 1992) due to pore-water undersaturation with respect to barite at the base of the sulphate reduction zone (Von Breymann *et al.*, 1992). The low Ba concentrations in cores CD38-09 and CD38-10 therefore supports the theory that the sediments at these shallow-water sites are accumulating under reducing conditions (6.2.3) and high sedimentation rates. In terms of using Ba as a palæo-productivity indicator, the cores taken at these two sites are of no use and will not be studied further in this section.

6.3.3. Ba and oxygen isotope profiles

On the Owen Ridge in the north-western Arabian Sea (ODP site 722B), Shimmield and Mowbray (1991) measured a Ba/Al depth profile which had a very large dynamic range and bore an almost perfect correlation with the foraminifera $\delta^{18}\text{O}$ stratigraphy. Elevated Ba contents were seen during interglacial stages in core 722B, even when considered in terms of Ba flux, which according to the authors, reflected periods of enhanced productivity (Fig. 6.9).

This remarkable capacity for Ba concentrations to parallel the SPECMAP oxygen isotope curve (2.3.1; Shimmield, 1992) is also seen in cores CD38-02 and CD38-11 from the Peruvian continental margin (compare Figs 6.8C and D with Fig. 2.9). Figure 6.9. illustrates the similarity between the Ba/Al age profiles of cores CD38-02 from the Peru margin and ODP 722B from the Arabian sea (Shimmield and Mowbray, 1991). There is the possibility that variation in the Ba content of the sediment is caused by changes in the strength of dilution by another component within the sediment, e.g. calcium carbonate. However, any carbonate dilution will affect the Ba and the Al concentrations to the same degree and therefore the variation in the Ba/Al profile is independent of such dilution effects (Figs 6.8.C and D). The Ba/Al profile could be caused simply by fluctuations in the ratio of these two elements in purely terrigenous material but it is thought that the degree of natural variation of Al (7.2.3) is much less significant than the biogenic-associated fluctuations of Ba, displayed by the Ba/Al ratios.

Use of the Ba/Al ratio for age modelling obviously needs further, detailed study and this would be possible by comparing Ba/Al ratios and foraminifera $\delta^{18}\text{O}$ records when both sets of measurements are taken from the same depth samples. Unfortunately, in this study (as in most due to the limitations in volume of sample material from a specific depth) the geochemical bulk-sediment sub-samples were taken up to 5cm away from the sieved-sediment sub-samples used for foraminifera studies. If the same sub-sample were used for both measurements then comparison of exact variations between peaks and troughs in the Ba/Al and *Uvigerina* profiles would be possible and a relationship could be established between the concentration of Ba in a sediment and the oxygen isotope signal recorded by foraminifera living at that time.

All that can be said from comparison of the Ba/Al and $\delta^{18}\text{O}$ records in CD38-02 and CD38-11 (compare Figs. 2.9 and 6.9) is that higher Ba_{bio} contents are found during the interglacial periods and seem to correspond closely to heavier (more negative) values of $\delta^{18}\text{O}$ in *Uvigerina* shells. This in turn implies that during the Late

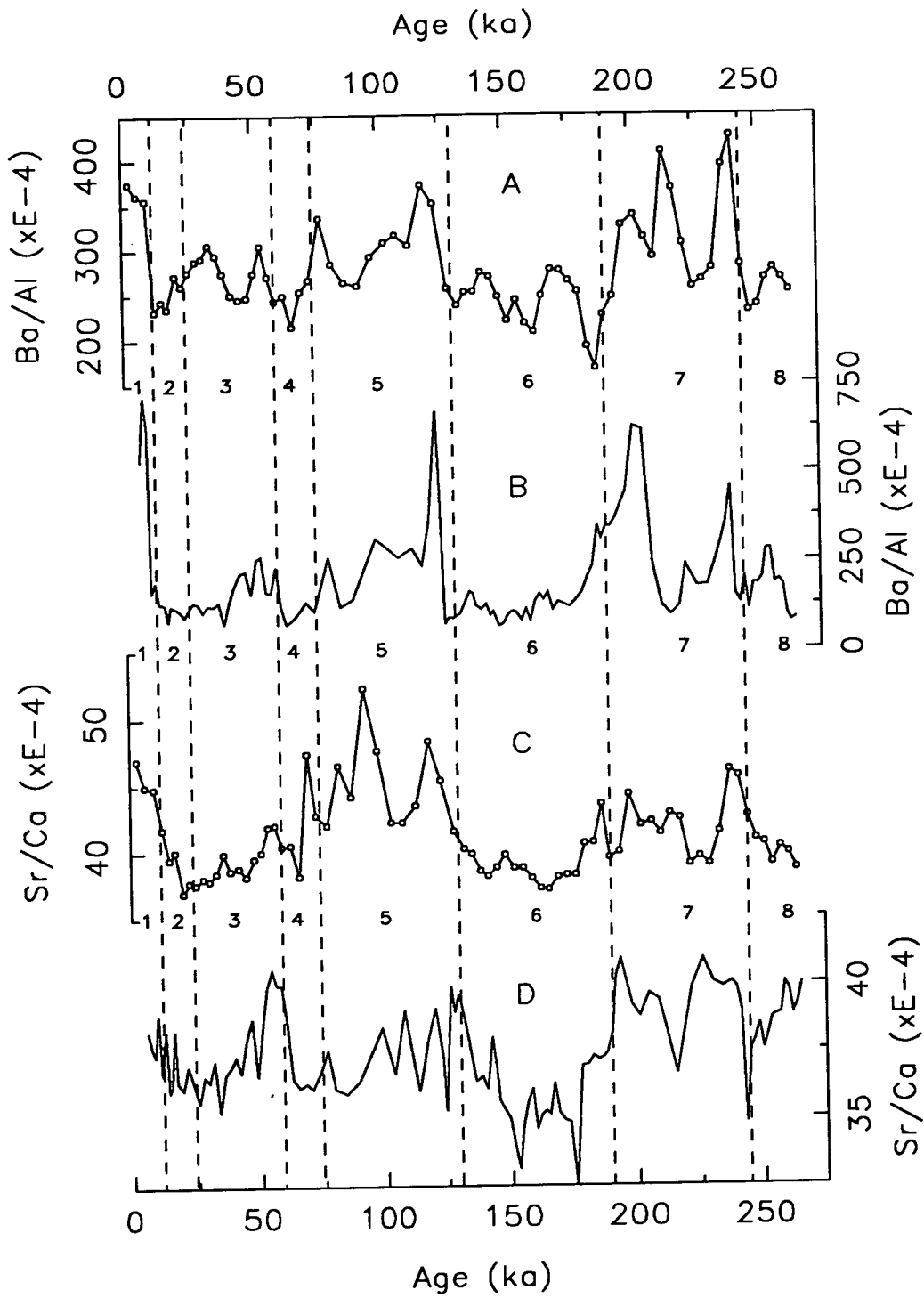


Figure 6.9. Ba/Al weight ratios against age: A) CD38-02 and B) ODP 722B (Shimmield and Mowbray, 1991). Sr/Ca weight ratios against age: C) CD38-02 and D) ODP 722B (Shimmield and Mowbray, 1991).

Quaternary at these two sites, more Ba_{bio} accumulated in the sediments when the global ice-sheet volume was at a minimum. The question that then arises is; are the Ba/Al ratios in the sediment recording changes in sea-surface productivity associated with global climate changes? If so, then barium may be one of the best proxies for palæo-productivity available to marine geochemists.

6.3.4. Palæo-productivity from Ba fluxes

This section will review the recent paper by Dymond *et al.* (1992) which advocates the use of Ba as a palæo-productivity proxy. Once their sediment trap Ba- C_{org} relationship and the Ba_{bio} -new production equation have been explained, the Ba data from core CD38-02 will be used to establish a proxy record of palæo-productivity in the waters off the continental margin of Peru.

Dehairs *et al.* (1980) proposed that the particulate Ba content of the upper 1000m of the water column was positively correlated with diatom productivity and further analyses of water from the Southern Ocean (Dehairs *et al.*, 1990, 1991) provided support for this theory. Dymond *et al.* (1992) takes the work of the above authors one stage further with the basic hypothesis that the flux of particulate Ba to the sea-floor (i.e. input to the sediment record) has a quantifiable relationship to the level of new productivity in the oceans. New production is defined as "the fraction of total primary production supported by the input of nutrients into the euphotic zone rather than by the recycling of nutrients from particulate organic matter within the euphotic zone" (Eppley and Petersen, 1979). Using sediment traps located in the Atlantic, Equatorial Pacific and California Current, the authors measured particulate C_{org} , Ba and Al fluxes and plotted C_{org}/Ba_{bio} ratios against water depth for the three sites. The ratios all decreased sympathetically with increasing water depth, and the best-fit curves predicted a C_{org}/Ba_{bio} ratio of 200 at the 200m base of the euphotic zone.

By converting the carbon flux-new production relationship equation of Sarnthein *et al.* (1988) and incorporating terms which depend on the dissolved Ba content of the water through which the organic debris settles, Dymond *et al.* (1992) produced an equation (Eqn 6.2) from which new production can be calculated.

The authors addressed the problem which affects all geochemical productivity indicators, i.e. the preservation factor - how much, if any, of the original signal reaches the sediment and is then retained upon burial? Marine biological systems use chemical elements and components for essential life processes which are easily

recycled, e.g. carbon, nitrogen, phosphorus. Therefore, the concentration of a productivity indicator in marine sediments is usually only a small fraction of the original signal or it can be lost altogether (completely recycled). Barium, however, has been shown to be an element which is fairly resistant to recycling and post-depositional mobilisation (Dymond, 1981) because in oxic sediments, the pore-waters are saturated with respect to barite (Church and Wolgemuth, 1972).

Equation 6.2. Calculation of new production (Dymond *et al.*, 1992)

$$P_{\text{new}} = \{[(F_{\text{Bbio}}) \times (0.171 \times \text{Ba}^{2.218}) \times z^{(0.476-0.00478\text{Ba})}] / 2056\}^{1.504}$$

where, P_{new} = new production ($\text{g C m}^{-2} \text{ year}^{-1}$),
 F_{Bbio} = flux of biogenic-Ba to the sea-floor ($\mu\text{g m}^{-2} \text{ year}^{-1}$),
 Ba = dissolved Ba concentration at 1700m ($\mu\text{mol kg}^{-1}$),
 z = water depth of core site (m).

Equation 6.3. Calculation of Ba_{bio}

$$\text{Ba}_{\text{bio}} = \text{Ba}_{\text{total}} - (\text{Al} \times \text{Ba}/\text{Al}_{\text{aluminosilicate}})$$

where, Ba_{bio} = biogenic barium,
 Ba_{total} and Al = as measured by X-ray fluorescence,
 $\text{Ba}/\text{Al}_{\text{aluminosilicate}} = 0.0075$ (Dymond *et al.*, 1992).

Dymond *et al.* (1992) carried out a series of selective leaching experiments on sediment trap samples and found that the total Ba content consisted of a small aluminosilicate fraction (1-2%) and a barite fraction, which occurred mainly in two forms; an absorbed, calcite-bound phase (22-43%) which was soluble in acetic acid ($\text{pH} = 5$), and a residual phase (48-70%). The authors partitioned the total Ba concentration into aluminosilicate and biological phases using Eqn 6.3 (used to calculate Ba_{bio} in Table 6.4), and then, by comparing the Ba/Al ratio in sediment traps with the $\text{Ba}_{\text{bio}}/\text{Al}$ ratio in sediments directly below (using Eqn 6.4), they produced a best-fit line of approximately 30% Ba preservation (i.e. 70% Ba_{bio} recycled before reaching the sea-floor) which is the highest preservation factor for any productivity proxy measured so far.

However, preservation of Ba upon burial in the sediment was seen to have a non-linear relationship with the mass accumulation rate (MAR), and Eqn 6.5 predicts the original total Ba_{bio} flux to the sea-floor from the MAR and accumulation rate of Ba_{bio} in the sediment (both in $\mu\text{g cm}^{-2} \text{ year}^{-1}$). This work allowed Dymond *et al.* (1992) to specify a step-by-step scheme for calculating new production in the ocean from knowledge of the Ba concentration and MAR in the sediment at any particular age (Eqn 6.2), assuming that an accurate concentration of dissolved Ba in the water column (1700m) can be measured or calculated (Lea and Boyle, 1990B).

Equation 6.4. Calculation of barium preservation factor

$$\% \text{ Ba preserved} = [(Ba_{bio}/Al)_{\text{sediment}} / (Ba/Al)_{\text{sed. trap}}] \times 100$$

Equation 6.5. Calculation of original Ba_{bio} flux

$$F_{Ba_{bio}} = (Ba_{bio} \text{ accumulation rate}) / [(0.209 \times \log \text{MAR}) - 21.3]$$

Using the step-by-step scheme of Dymond *et al.* (1992) the Ba concentration data from piston core CD38-02 was converted to Ba_{bio} (Eqn 6.3) then to $F_{Ba_{bio}}$ (Eqn 6.5) and finally to the palæo-productivity signal of P_{new} (Eqn 6.2).

The final calculation involved using a value of 145 nmol kg^{-1} for the dissolved Ba concentration at 1700m in the water column, which is actually the level measured at the GEOSECS site in the California Current (Lea and Boyle, 1990B). The value was chosen because it was thought to be a close approximation for the Nazca ridge core since both sites are located on continental margins affected by coastal upwelling (2.1.1). In effect, this means that the values of P_{new} for CD38-02 may not be completely accurate, but the calculation should give a good approximation of the new production levels at this site. The shape of the down-core palæo-productivity signal will not, however, be affected by this estimation of the dissolved Ba because each sample point uses the same value of 145 nmol kg^{-1} in the calculation (Eqn 6.2).

The values of P_{new} for core CD38-02 are tabulated in Appendix C.14 and range from 7 to 30 $\text{gC m}^{-2} \text{ yr}^{-1}$ with a mean value of 14.4 $\text{gC m}^{-2} \text{ yr}^{-1}$. The age profile of this new production record is shown in Fig. 6.10.C and from it can be seen an interesting glacial/interglacial pattern of palæo-productivity.

The most obvious feature of this signal is the two large peaks in interglacial stage 7 which drop sharply on either side into the glacial stages 6 and 8. There are

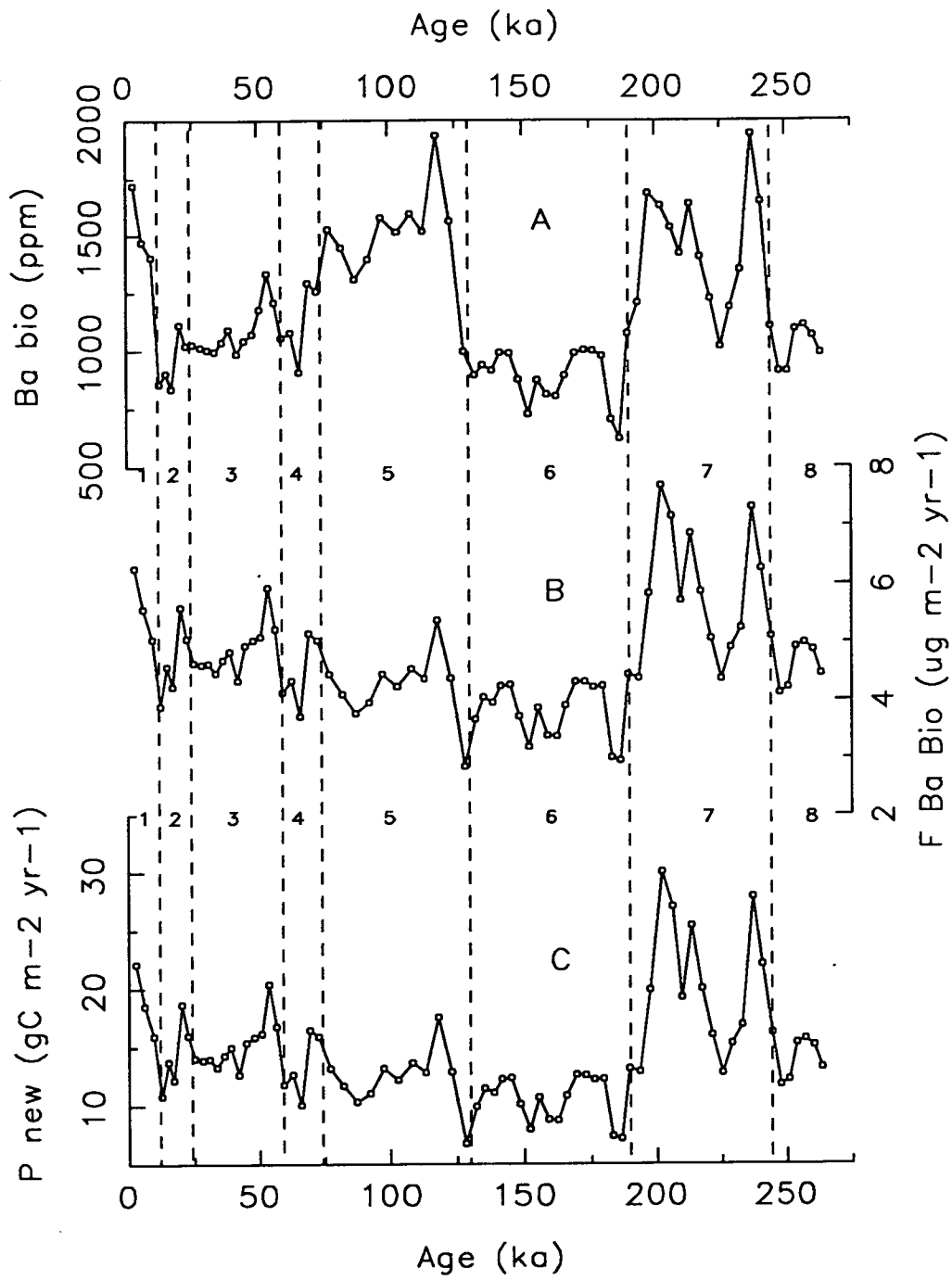


Figure 6.10. The barium palaeo-productivity signal for core CD38-02 (2525m) against age: A) Ba_{bio} (ppm), B) $F_{Ba_{bio}}$ ($\mu\text{g m}^{-2} \text{yr}^{-1}$) and C) P_{new} ($\text{g C m}^{-2} \text{yr}^{-1}$).

other interglacial maxima ($>16 \text{ gC m}^{-2} \text{ yr}^{-1}$) in the P_{new} profile, which lie at the top of stage 1 and the base of stages 3 and 5, and glacial minima ($<12 \text{ gC m}^{-2} \text{ yr}^{-1}$) which occur during stages 2, 4 and 6; all of which indicate that there is a glacial/interglacial periodicity control on the levels of new production in the waters above the Nazca ridge site. This in turn suggests that the coastal upwelling primary productivity along the Peruvian continental margin has been strongly affected by the global climate during the Late Quaternary and has been more intense during the interglacial stages.

However, the P_{new} profile of CD38-02 is much more complex than the simple hypothesis above suggests. Figure 6.10 also shows maxima at the base of glacial stages 2 and 4 and the intensity of the peaks in stage 7 cannot be easily explained. The equation to calculate P_{new} from Dymond *et al.* (1992) depends strongly on the mass accumulation rate. This means that the age model from the foraminifera $\delta^{18}\text{O}$ record needs to be correct. Simply moving some of the stage boundaries in the original age model for CD38-02 (Chapter 2) can significantly change the mass accumulation rates, which alters the concentrations of P_{new} and can give a down-core profile which peaks strongly in glacial stages 2 and 4.

It is also wrong to assume that interglacial peaks on the P_{new} profile are caused by more intense coastal upwelling and higher biological productivity on the Peruvian continental margin. It may be that lateral movement of the main coastal upwelling zone along the coast, caused by changes in the wind patterns during global climate change, brought a higher biogenic flux to the sediments accumulating on the Nazca ridge during interglacial periods. Other factors such as the dissolved Ba concentration may also have varied with time. Lea and Boyle (1989, 1990A and B) have examined the Ba/Ca ratio of benthic foraminifera from many deep-sea cores in the Atlantic and Pacific oceans and concluded that because of water mass circulation variations during the Late Quaternary, the deep-waters of the Pacific during glacial conditions were about 25% lower in their dissolved Ba concentration (at about 3000m water depth) compared with today's interglacial levels.

In conclusion, it is likely that the levels of new production at CD38-02 have altered significantly over the past 250,000 years associated with the variation in global climate. However, until other cores with accurately defined age models in this area are also used for the calculation of P_{new} , the precise reasons for such variation in this palæo-productivity signal cannot be known. The equations of Dymond *et al.* (1992) are the first attempt to use and quantify sediment Ba concentrations as an ocean biological productivity indicator and hopefully this and many future studies (e.g. Shimmiel *et al.*, 1992) will help to clarify both the relationship between Ba and

organic matter in the water column, and the variation of dissolved Ba concentrations in water masses over time.

6.4. THE STRONTIUM SIGNAL

6.4.1. Introduction

The marine biomass is a complex mixture of phytoplankton, zooplankton and many other larger marine organisms, which are all inter-related by the food chain. It has been shown that barium can be used as an indicator of the total palæo-productivity in the oceans but it is possible that other geochemical signals in the sediment record can indicate changes over time in the relative abundance of one type of marine organism compared to another. This section will examine the biological relationship of strontium (Sr) with calcium carbonate shell-remains and interpret temporal variations in the biogenic Sr/Ca ratio with respect to variation in the relative abundances of foraminifera and coccoliths; two important groups of marine plankton.

Strontium in marine sediments occurs mainly in carbonate minerals but can also be found in phosphorite, barite and aluminosilicates (El Wakeel and Riley, 1961; Church, 1970). As previously stated (4.3.4), it is because the Sr^{2+} cation has a similar ionic radius as well as the same ionic charge as Ca^{2+} , that Sr easily substitutes for Ca in most minerals. Sr substitution for Ba in marine barite only occurs to a relatively small degree (0.2-3.4 mol% Sr, Church, 1979) which allows for a potential contribution of 30-150ppm Sr to the total Sr concentration in most marine sediments (Patience, 1992).

Table 6.6 lists the Sr concentration previously found in marine organisms and sediments and from this it can be seen that the Sr content of pelagic foraminifera (1500-1710ppm) is slightly higher than that of coccoliths (1000ppm), with the result that a foraminiferal ooze has a higher Sr/Ca ratio (33×10^{-4} , Thompson and Chow, 1956) compared with a coccolith-rich ooze ($26-26 \times 10^{-4}$, Turekian, 1964).

6.4.2. Analytical methods and results

Strontium and calcium concentrations in the sediments in this study were determined using X-ray fluorescence on pressed pellet samples and fused discs respectively (Appendix A.5). The amount of CaCO_3 present was then calculated by

correcting for the calcium content of aluminosilicates and phosphorite present (Appendix B.1). Using the strong correlation between Sr and P_{phos} in phosphorite zones (4.3.4, Fig. 4.10) the total Sr concentration can be partitioned into terrigenous (Sr_{terr}), phosphatic (Sr_{phos}) and calcium carbonate (Sr_{calcite}) phases using Eqn 4.4 (Appendix B.4). This then allows for the true Sr/Ca ratio in biogenic carbonate shell remains (Sr/Ca_{bio}) to be calculated.

Author	Organism/sediment type	Sr (ppm)	Sr/Ca ($\times 10^{-4}$)
Emiliani (1955)	Foraminifera tests	1200	
Thompson & Chow (1956)	Foraminifera tests	1300	
	Pacific Globigerina ooze		33
Turekian (1957)	Foraminifera tests	1200	
Krinsley (1960)	Foraminifera tests	1150	
Turekian & Wedepohl (1961)	Deep-sea clay	180	
	Deep-sea carbonate	2000	
Turekian (1964)	Pure foraminifera ooze	1600	
	Pure coccolith ooze	1000	25-26
Martin & Knauer (1973)	Mean marine organism	862	
Shimmield and Mowbray (1991)	NW. Arabian Sea sediments	740-1489	33-45
Patience (1992)	E. Equatorial Pacific sediments	330-1207	32-64
Carpenter & Lohmann (1992)	Foraminifera tests	1190-1710	

Table 6.6. Sr concentration and Sr/Ca weight ratio of marine organisms and sediments.

Table 6.7 summarises the strontium data for the four piston cores from the Peruvian continental margin (listed in Appendices C.10 and C.13) and includes the range and mean of total Sr, the mean CaCO_3 concentration, the range and mean of Sr_{calcite} and the Sr/Ca_{bio} ratio and the correlation coefficient of total Sr with CaCO_3 .

The $Sr_{\text{total}}:\text{CaCO}_3$ correlation coefficients are much lower for cores CD38-09 and CD38-10 compared with CD38-02 and CD38-11 (Table 6.7) because in the shallow-water cores there is less calcium carbonate present, more aluminosilicate detrital material and significant zones of phosphorite formation; all of which have different Sr/Ca ratios in the minerals. It is because of the complication of the phosphorite zones, that cores CD38-09 and CD38-10 will not be considered further in this section.

		CD38-09 (148m)	CD38-10 (257m)	CD38-02 (2525m)	CD38-11 (3835m)
Sr (ppm)	range	149-1195	185-642	311-812	222-423
	mean	220	329	567	277
CaCO ₃ (wt.%)	mean	2.9	8.2	26.9	10.7
Sr _{calcite} (ppm)	range	0-138	7-400	143-700	43-238
	mean	61	156	434	110
Sr/C _{abio} (x10 ⁻⁴)	range			36.9-52.2	14.7-33.6
	mean			41.0	25.1
Corr. coeff. of Sr with CaCO ₃		0.235	0.451	0.980	0.948

Table 6.7. Strontium data summary table

A plot of Sr_{total} against CaCO₃ concentration for core CD38-02 is shown in Fig. 6.11 and has the following straight-line relationship:

$$\text{Sr (ppm)} = 13.01 \times \text{CaCO}_3 \text{ (wt.\%)} + 216.$$

The best-fit straight line intercepts the Y-axis of Fig. 6.11 at 216ppm Sr, which is equivalent to the average amount of Sr in each sample which has been introduced to the sediment by a non-carbonate source, i.e. associated with terrigenous, aluminosilicate material. If the sediments in core CD38-02 were to contain purely carbonate shell remains then the total Sr concentration would be $13.01 \times 100 (\%) = 1301\text{ppm}$. This calculation of the Sr content of marine organisms in sediments on the Nazca ridge corresponds well with the Sr analyses of the foraminifera tests shown in Table 6.6. This calculation gives confidence to the use of the equation to calculate CaCO₃ levels from X-ray fluorescence analysis of total Ca concentration (Appendix B.1).

It is therefore of no surprise that the down-core age profiles for both CD38-02 and CD38-11 of Sr_{total} and Sr_{calcite} in Figs 6.12 and 6.13 show remarkable similarity to their respective CaCO₃ profiles.

6.4.3. Sr/Ca temporal variations

In sediments from the Northwest Arabian Sea (ODP core 722B), Shimmield and Mowbray (1991) found ratios of Sr/Ca which were higher than previously reported (up to 45×10^{-4} , Table 6.6) and whose down-core profile showed a close similarity to the $\delta^{18}\text{O}$ foraminifera curve, although the peaks were damped or

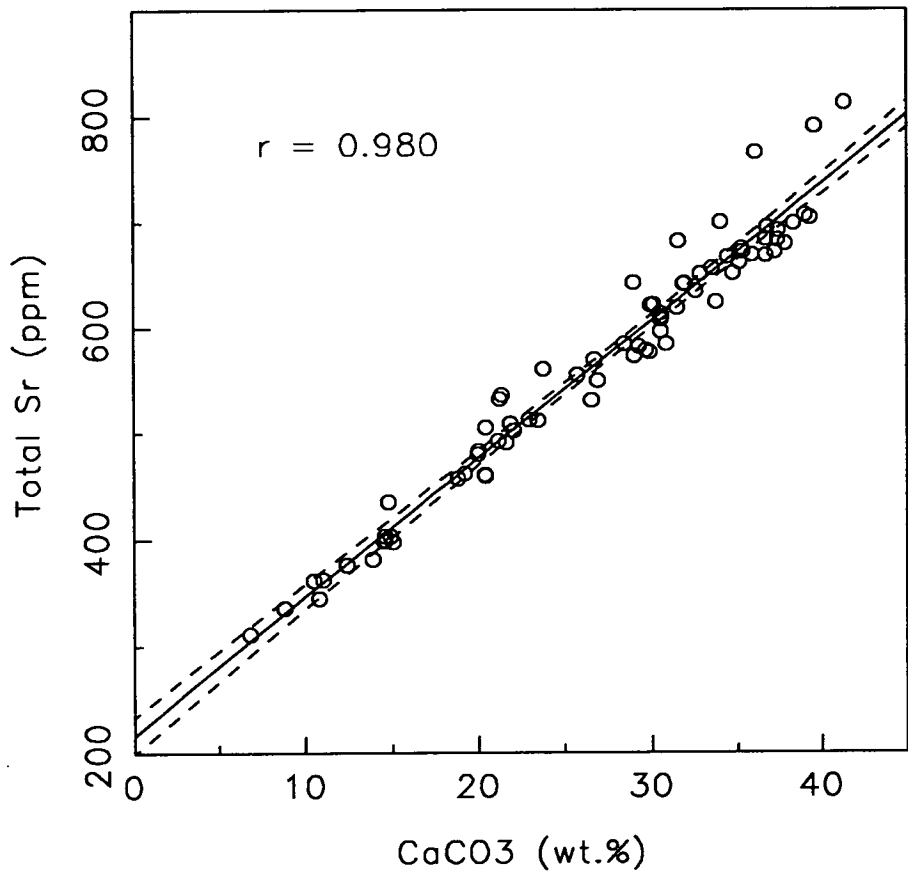


Figure 6.11. Core CD38-02 (2525m): total strontium against calcium carbonate. Shows best fit straight line (full line) and 95% confidence limits (dotted lines) representing,

$$\text{Sr (ppm)} = 13.01 \times \text{CaCO}_3 \text{ (wt.\%)} + 216.2 \quad (r=0.980)$$

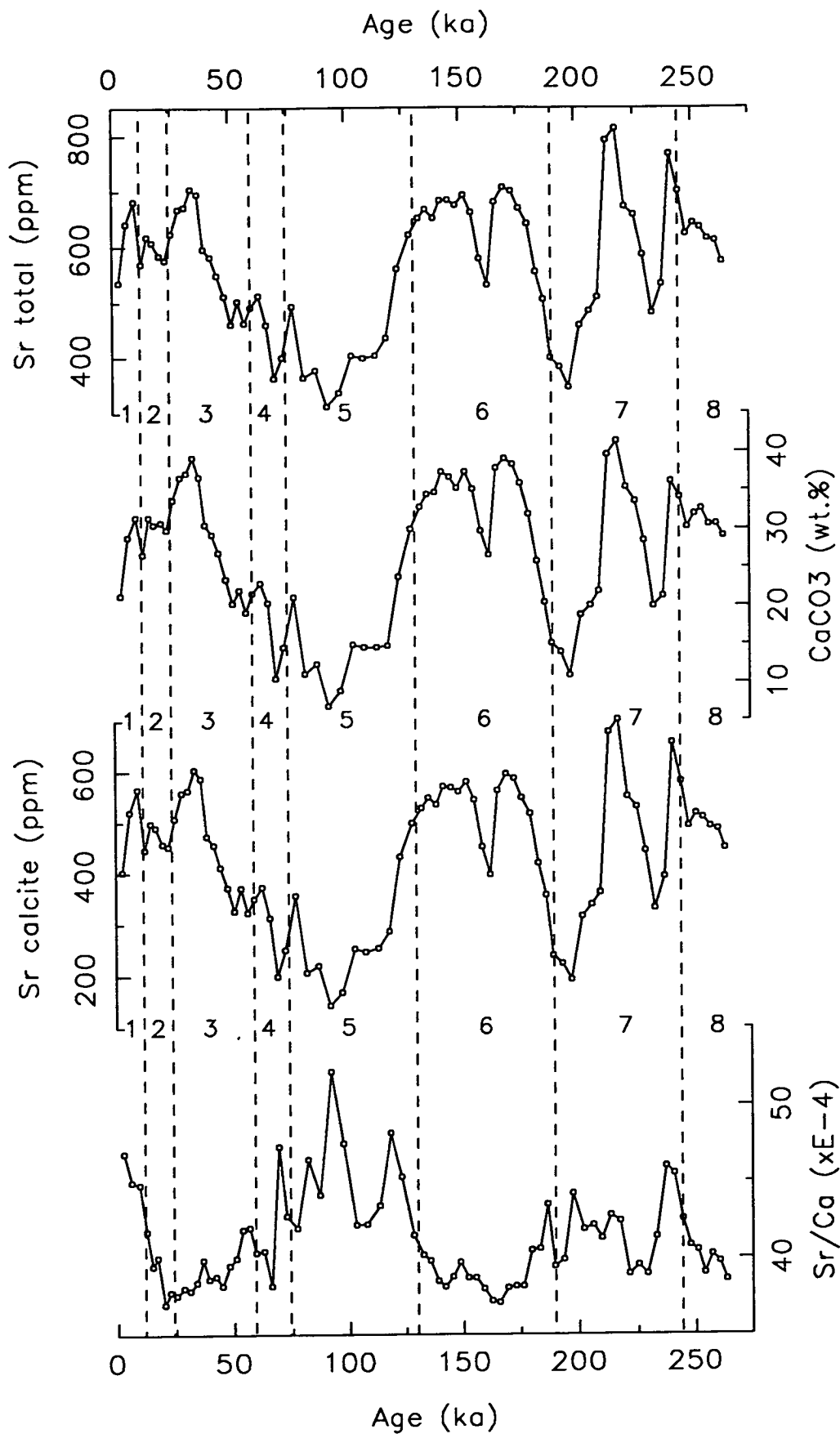


Figure 6.12. Core CD38-02 (2525m): Sr_{total} , $CaCO_3$, $Sr_{calcite}$ and Sr/Ca down-core profiles against age (ka).

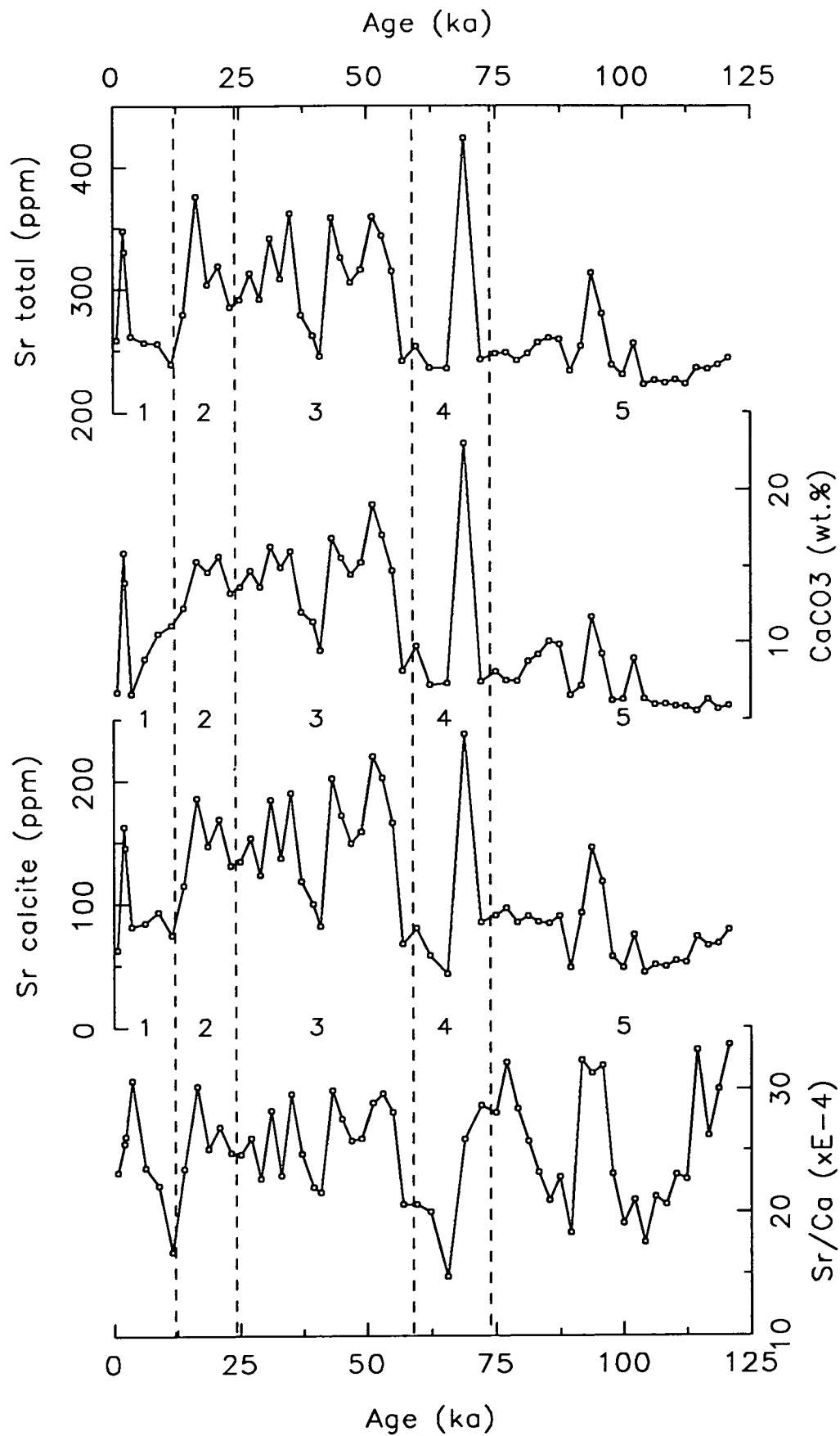


Figure 6.13. Core CD38-11 (3835m): Sr_{total}, CaCO₃, Sr_{calcite} and Sr/Ca down-core profiles against age (ka).

modulated (Fig. 6.9). The authors measured elevated concentrations of Sr with respect to Ca in the interglacial stages and suggested that the Sr content of the biogenic carbonate was indicating a temperature/species/vital effect control, which fluctuated with changes in the global climate. Patience (1992) concluded that variations in the excess Sr/excess Ca ratio (similar to Sr/Ca_{bio}) in Eastern Equatorial Pacific sediments illustrated changes in the relative dominance of coccoliths to foraminifera in the oceanic waters.

The age profiles of biogenic Sr/Ca ratio for cores CD38-02 and CD38-11 are plotted in Figs 6.12 and 6.13, and both illustrate temporal changes which have higher ratios during the interglacial stages (most pronounced in CD38-02, shown in Fig. 6.9 with ODP 722B for comparison). The most obvious interpretation of such a geochemical signal in terms of palæo-productivity is that during interglacial periods, when the overall CaCO_3 concentration is lowest, the production of foraminifera is more dominant over that of coccoliths (the latter having a lower Sr content in their shells). Whereas during glacial periods, when total carbonate production (or preservation?) is much higher, coccolith production is increased at a greater rate relative to the rate of increase in foraminifera production and this results in significantly lower Sr/Ca_{bio} ratios. However, this simple hypothesis may be strongly affected by increased rates of CaCO_3 dissolution in the sediment, increased barite production and/or diagenetic overprinting (Baker *et al.*, 1982).

Shimmiel and Mowbray (1991) discounted diagenetic overprinting as being responsible for the Sr/Ca profile in core 722B due to the "shallow depth of the core". Their core was situated at a water depth (2028m) fairly similar to core CD38-02 (2525m) and therefore the same statement can be made for the Nazca ridge core. However, core CD38-11 is from much deeper water (3835m) and therefore diagenetic overprinting may be responsible for the more noisy Sr/Ca signal.

The question of variable carbonate dissolution affecting the Sr/Ca ratio profiles can be discounted because dissolution is thought to affect foraminifera shell remains more than coccoliths (Broecker, 1971; Honjo, 1977) and its influence to have been greater during the interglacial periods. This would mean that the dominance of foraminifera over coccoliths would be less significant during interglacials and the Sr/Ca_{bio} ratio would be expected to decrease (Patience, 1992). This is clearly the opposite of what is seen for the Sr/Ca_{bio} ratio in cores CD38-02 and CD38-11 (Figs 6.12 and 6.13).

The possibility that increased barite production during interglacial periods due to higher organic matter settling fluxes (6.3.4) may also be bringing more Sr,

incorporated within the mineral (Church, 1979), to the sediment cannot, however, be discounted. This extra source of "biogenic" Sr may be able to account for some of the variation seen in the biogenic Sr/Ca profiles.

It can only, therefore, be concluded that fluctuations in the Sr/Ca ratio of carbonate shell-remains in the sediments from cores CD38-02 and CD38-11 may be a palæo-productivity signal of temporal changes in the relative dominance of foraminifera over coccoliths off the Peruvian continental margin during global climate change. There may, however, be a temperature and/or species related control on the uptake of Sr by marine plankton and the influence of increased barite production (itself a palæo-productivity indicator, which is not accounted for in the calculation of Sr_{calcite}) must also be examined. Before any definite statements about the Sr/Ca palæo-productivity signal can be made more detailed studies of the Sr content of both marine organisms and diagenetic minerals need to be carried out.

6.5. THE MOLYBDENUM-URANIUM SIGNAL

6.5.1. Introduction

The final section in this palæo-indicators chapter will examine the use of the ratio of two heavy metals, molybdenum (Mo) and uranium (U), for identification of the redox environment under which deposition of marine sediments occurs. The Mo and U geochemical data of the four piston cores from the Peruvian continental margin will be used to calculate Mo/U ratios and to critically review the following hypothesis made by Bertine and Turekian (1973).

Their data of Mo and U concentrations from a wide variety of marine sediments indicated that two different chemical associations are responsible for the removal of Mo from sea-water; namely, with ferromanganese minerals under oxidising conditions and with a sulphide or high organic matter phase under reducing conditions. The authors stated that due to the different Mo/U ratios measured in samples from deep-sea, oxic sediments ($Mo/U = 3-4$) and from near-shore anaerobic sediments (Mo/U about unity), the two mechanisms of Mo accumulation in marine sediments could be distinguished. This means that, in terms of using the Mo/U ratio as a palæo-redox indicator, Bertine and Turekian (1973) implied that a ratio of about one is indicative of reducing conditions and a ratio above three is indicative of oxidising conditions at the sediment/water interface at the time of deposition.

6.5.2. Analytical methods and results

Both Mo and U concentrations were analytically determined using X-ray fluorescence techniques on pressed pellet samples and are expressed as parts per million (ppm) (Appendix A.5). In contrast, Bertine and Turekian (1973) measured Mo and U by neutron activation analysis and expressed their results as ppm on a carbonate-free basis. Since this section is examining the Mo/U ratio, it does not matter if the data has not been corrected for the carbonate content of the sample because both the metal concentrations would be affected by the recalculation to the same extent.

		CD38-09	CD38-10	CD38-02	CD38-11	Bertine & Turekian (1973)	
		(148m)	(257m)	(2525m)	(3835m)	Oxic	Anoxic
Mo/U	Min.	0.36	0.56	0.00	0.18	1.24	0.36
	Max.	17.29	13.12	0.62	2.10	4.92	2.19
	Mean	7.37	4.81	0.23	1.07	2.77	1.08
Mo/U _{org}	Min.	0.81	3.76	0.00	0.27		
	Max.	617.7	50.9	1.63	16.9		
	Mean	35.3	11.0	0.39	2.62		

Table 6.8. Summary of Mo/U and Mo/U_{org} data.

The Mo/U ratios of the sediments from the four piston cores are summarised in Table 6.8 (full data listed in Appendix C.11). This table also includes the Mo/U_{org} ratio data, which has been determined after calculation of the U content associated with the organic carbon fraction of the sediment (using the partitioning equation 4.3). The use of the Mo/U_{org} ratio may give a more accurate indication of the true Mo-U relationship in the near-shore cores CD38-09 and CD38-10, where phosphorite mineral diagenesis can preferentially concentrate U (4.3.4) and therefore distort the original Mo/U signal. The results from Bertine and Turekian (1973) for deep-sea sediments (oxic) and near-shore sediments (anoxic) are also given in Table 6.8 for comparison.

6.5.3. Interpretation and discussion of Mo/U ratios

Previously in this chapter, it has been interpreted from the iodine/C_{org} ratio down-core profiles that of the four piston cores, two have been collected from a depositional environment of reducing conditions (CD38-09 and CD38-10) and two from an environment of oxidising conditions (CD38-02 and CD38-11). The

knowledge of the redox state of each core throughout its depositional history can now be used to interpret the Mo/U and Mo/U_{org} ratio profiles for each core (Figs 6.14 and 6.15) and determine the usefulness of these ratios as palæo-redox indicators, following the work of Bertine and Turekian (1973).

From consideration of the mean values of Mo/U and Mo/U_{org} for cores CD38-09 and CD38-10 (Table 6.8) and from the depth profiles (Figs 6.14 and 6.15) it is obvious that the statement of Bertine and Turekian (1973) that near-shore reducing sediments have a Mo/U ratio close to unity (with a maximum of about two) is invalid.

It also seems that the authors were wrong in their hypothesis that oxidising sediments have a Mo/U ratio of between 3 and 4, when considering the Mo/U and Mo/U_{org} mean ratios (Table 6.8) of cores CD38-02 and CD38-11. In fact, if the Mo and U data from the piston cores used in this study had been available to Bertine and Turekian then they may have arrived at a completely opposite hypothesis. They may then have stated that the two mechanisms of the removal of Mo from sea-water could be distinguished by,

- 1) Mo/U ratios of near unity for removal under oxidising conditions associated with ferromanganese minerals and,
- 2) Mo/U ratios of between 5 and 10 (or higher, if considering Mo/U_{org} ratios) for removal under reducing conditions associated with a high organic matter phase.

In conclusion, the Mo and U concentration data from this study of both reduced and oxidised sediments from the Peruvian continental margin imply that the simple hypothesis of Bertine and Turekian (1973) is invalid. In fact, uptake of these two heavy metals and their relationship in marine sediments is highly complex and does not just depend on the redox state of the depositional environment. Therefore, until more detailed work into the relationship of Mo and U with organic matter, ferromanganese and phosphorite minerals and of their post-depositional mobility is carried out, the Mo/U ratio cannot be used as a reliable palæo-redox indicator in marine sediments.

6.6 CONCLUDING INTERPRETATIONS OF PERUVIAN PALÆO-OCEANOGRAPHIC CONDITIONS

Of the three groups of palæo-chemical tracers described by Elderfield (1990), namely tracers of oceanic (1) chemistry, (2) fluxes and (3) processes, this chapter has

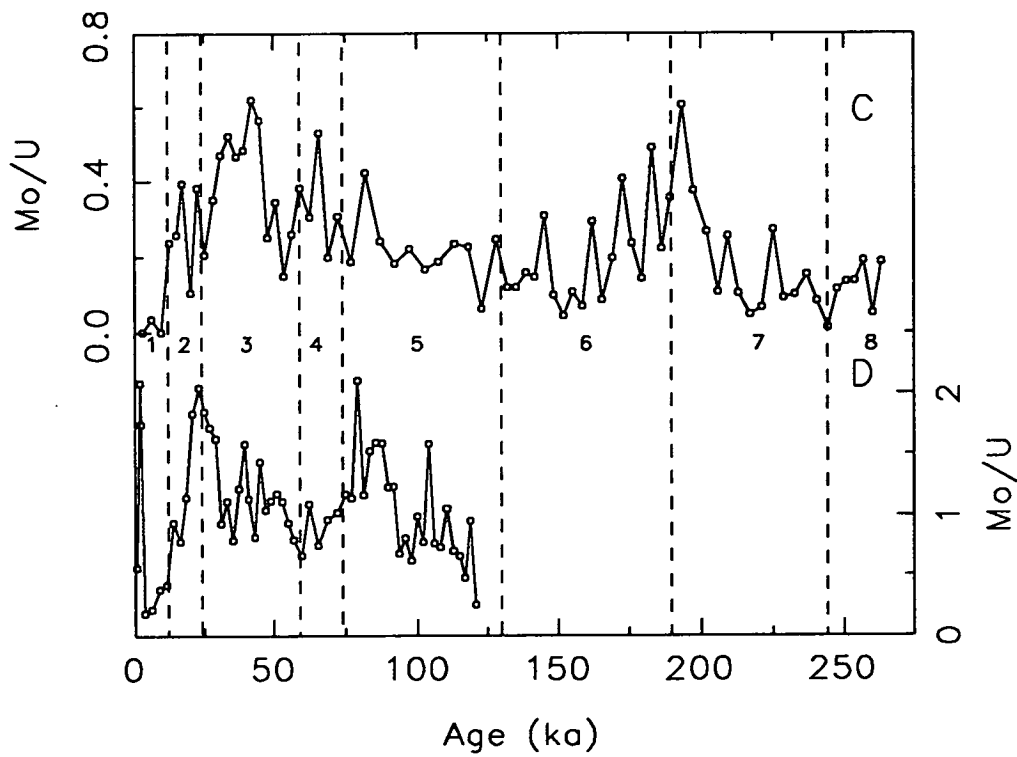
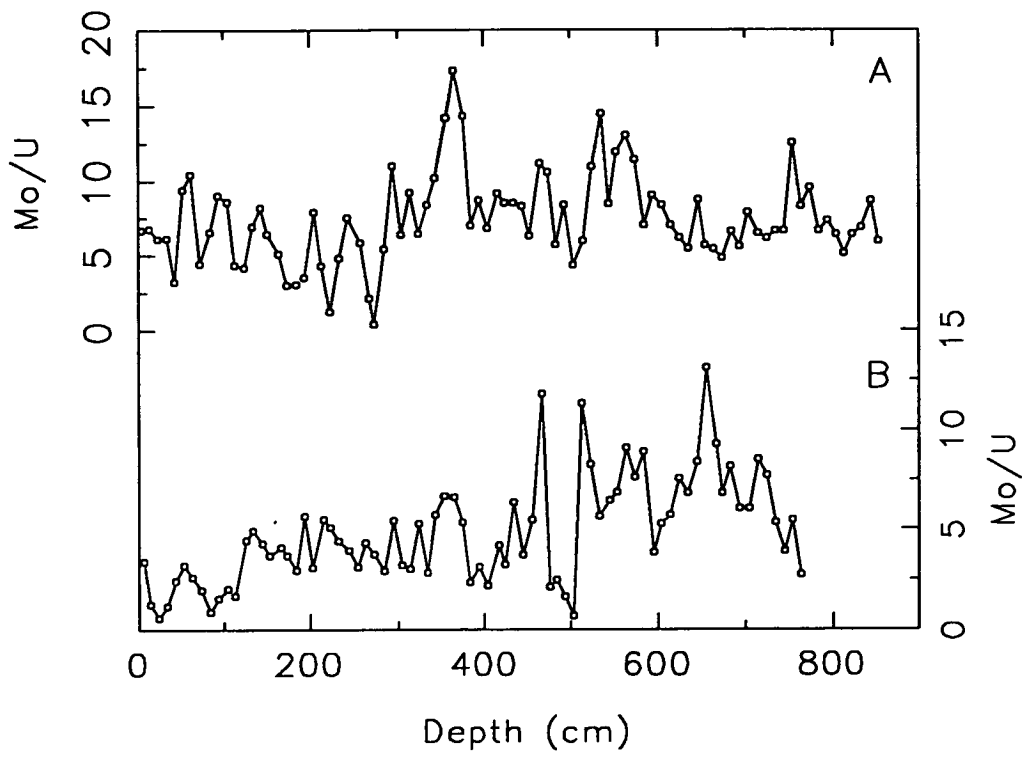


Figure 6.14. Mo/U weight ratio down-core profiles: A) CD38-09, B) CD38-10, C) CD38-02 and D) CD38-11.

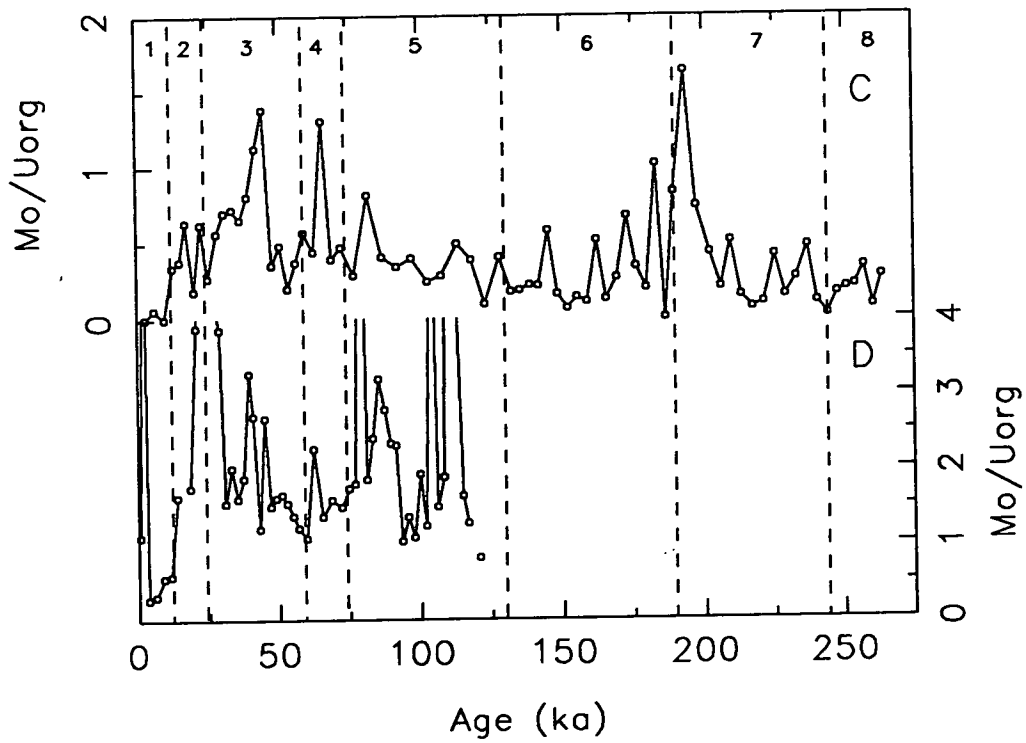
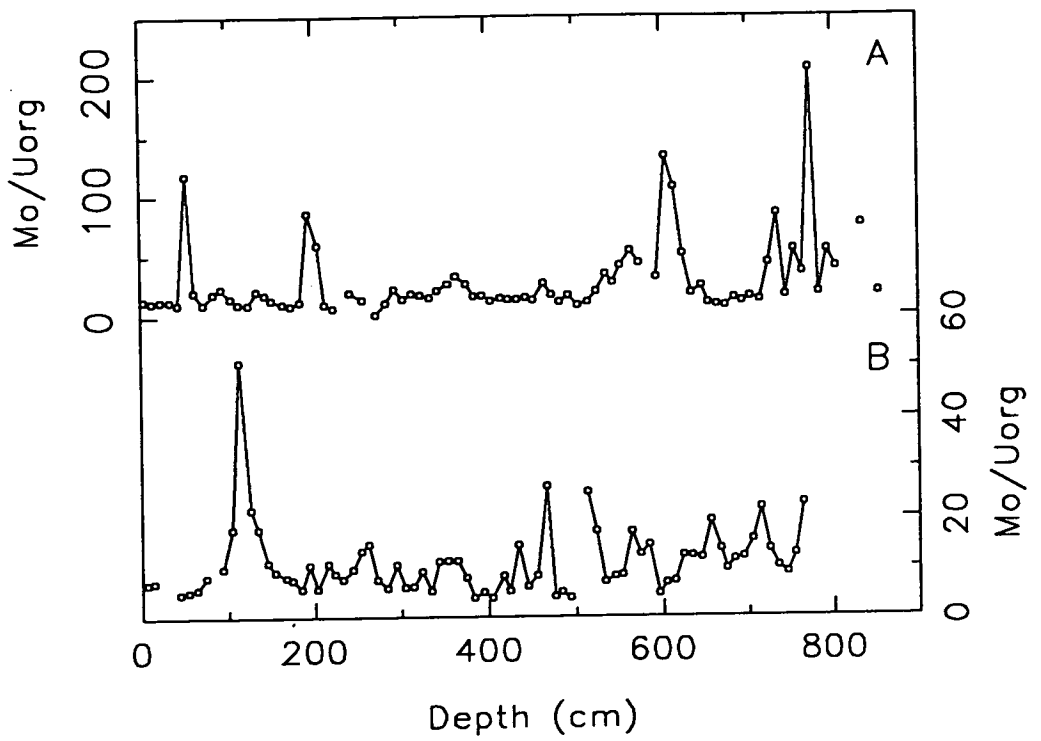


Figure 6.15. $\text{Mo}/\text{U}_{\text{org}}$ weight ratio down-core profiles: A) CD38-09, B) CD38-10, C) CD38-02 and D) CD38-11.

concentrated on the last group by examining the use of trace element geochemistry in the interpretation of two important oceanic processes. These are the level of biological productivity in the surface-waters and the state of the redox environment which exists at the sediment/water interface, each in terms of both the present day condition and the historical record contained in the box and piston cores from the Peruvian continental margin.

Elderfield (1990) stressed the importance of the above two processes by stating that chemical records can lead to "an examination of how climate-related processes such as increased production or lowered bottom-water oxygen concentrations might modify element accumulation rates." Therefore, if trace element signals can be used as palæo-productivity and palæo-redox indicators, it is necessary to study, interpret and fully understand their chemical record before other element accumulation rates can be examined. The following conclusions summarise the information that has been interpreted from the halogen, barium, strontium, molybdenum and uranium signals contained in the CD38 cores.

- 1) The post-depositional diagenetic mobility of the halogens renders them unreliable as palæo-productivity indicators. However, iodine concentrations, used in conjunction with organic carbon measurements, allow for the classification of marine sediments in terms of the redox state (oxic or anoxic) that existed at the sediment/water interface at the time of deposition. The sediment in piston cores CD38-09 and CD38-10 has been deposited within a reduced, anoxic environment, whereas all the other cores in this study have been sites of deposition under oxic conditions.

The halogens may also be used to identify breaks in the sedimentation pattern, inter-core variations in sedimentation rate and/or organic matter composition and the I/Br ratio in CD38-02 (an undisturbed, oxic core site) may indicate organic matter flux changes associated with glacial/interglacial climate change.

- 2) The lack of Ba in cores CD38-09 and CD38-10 supports the theory of reduced conditions during their sediment deposition but this trace element can be used as a palæo-productivity signal as well as a simple palæo-redox indicator. Following the algorithm of Dymond *et al.* (1992) the level of new production above site CD38-02 has been calculated and from the age profile of this productivity signal (Fig. 6.10), it could be interpreted that the interglacial periods of the Late Quaternary were associated with more intense biological production in the surface-waters on the Peru margin.

- 3) Temporal variations in the Sr/Ca ratio of sediments containing a significant quantity of CaCO₃ shell-remains (CD38-02 and CD38-11) are a geochemical record which is more likely to be a productivity signal rather than a preservation effect. It may be interpreted as fluctuations in the degree of the dominance of foraminifera over coccoliths and seems to be related to glacial/interglacial periodicity.
- 4) The use of the Mo/U (and the Mo/U_{org}) ratio as a palæo-redox indicator in the Peruvian margin sediments contradicts the previous work of Bertine and Turekian (1973). The anoxic, shallow-water cores (CD38-09 and CD38-10) display higher Mo/U ratios compared with those in the oxic, deeper-water cores (CD38-02 and CD38-11). This implies that until more detailed work is carried out on the complex processes involved in Mo and U movement into and within marine sediments, the Mo/U ratio is highly unreliable as a palæo-redox indicator.

CHAPTER 7

ENVIRONMENT OF DEPOSITION

7.1. INTRODUCTION

"Factors controlling element distributions in sediments are difficult to induce, because the distributions are frequently the result of non-equilibrium processes."

Spencer *et al.* (1968)

It is because the environment of marine sediment deposition is both complex and highly variable, in terms of geology, chemistry, biology and physics, that the study of such sediments can reveal a great deal of information about the natural processes responsible for its composition. This study has so far attempted to interpret some of the factors controlling the geochemical element distributions in marine sediments from the Peru margin. In this chapter the overall environment of deposition will be considered in order to understand a particular element concentration and/or its down-core variation.

The cores sampled in this study have been taken from a range of depositional environments, widely varying in water depth, proximity to the Peruvian continental margin, redox potential at the sediment/water interface etc. This allows for the element distributions contained within the cores and the processes controlling them to be examined both spatially and temporally.

The marine environment contains such a complex mixture of many "non-equilibrium processes" that this chapter has had to be divided into various sections which, in effect, separate the inter-twined processes. The two main sections which follow correspond to the two most important input components to marine sediments which are accumulating on a continental margin affected by strong coastal upwelling (i.e. terrigenous and biogenic inputs, Chapter 5). The conclusions will, however, attempt to tie the various processes together again.

7.2. THE TERRIGENOUS INPUT

7.2.1. Introduction

Multi-component analysis (MCA) of the geochemical dataset from the Peru margin sediments (5.4) suggested that an average of 72% (on a weight basis) of the material was of a terrigenous origin. In some samples the abundance of the terrigenous component was as high as 90%, and on this fact alone, a detailed

examination of the major component in these marine sediments is merited. The terrigenous material is land-derived (i.e. not oceanic or biogenic) and can originate either from terrestrial (continental landmass) sources or from the alteration of oceanic basalts and/or hydrothermal exhalations (Bonatti *et al.*, 1983; Nath *et al.*, 1989). However, the results of the MCA indicated that hydrothermal deposits were completely absent from the sediments in this study and, therefore, this discussion of the depositional and environmental controls on the terrigenous input can concentrate solely on material whose source is the South American continent, in particular the Andes mountain range and the arid Peruvian coastal plain (Prospero and Bonatti, 1969; Scheidegger and Krissek, 1982; Boyle, 1983).

As well as the natural, continuous erosion and weathering of the continental rocks and soils, a second (but much less significant, in quantitative terms) source in this area, for terrigenous-derived material contained within marine sediments, is from land (and oceanic island) based volcanic activity (Ninkovitch and Shackleton, 1975; Ledbetter, 1982, 1985). Such volcanic ash deposits ("tephra") can form distinct layers which have characteristic geochemical compositions and can aid in the dating and correlation of marine sediment cores. The presence of any such ash layers within the Peru margin cores may be highlighted by the following geochemical interpretation of the terrigenous component.

There are a number of important questions which this section will try to interpret and answer, with respect to the spatial and temporal records of terrigenous material deposition in the marine environment of the Peruvian continental margin.

- 1) Is the composition, abundance and/or variation of terrigenous material strongly controlled by the proximity of each core site to the continental landmass?
- 2) Are there temporal variations which can be explained by climatic changes in sea-level, wind strength, continental aridity etc. during glacial/interglacial periodicity in the Late Quaternary (Boyle, 1983)?
- 3) Can the mechanism of transport of terrigenous material (wind-blown, river or ocean currents) be examined by any geochemical indicators?
- 4) What are the possible source differences that exist between (and within) cores from varying oceanographic locations and environments (Krissek *et al.*, 1980; Scheidegger and Krissek, 1982)?

7.2.2. Analyses and results

The geochemical parameters described below (namely aluminium, silicon, iron, manganese, potassium, rubidium, titanium and zirconium) were all analysed by X-ray fluorescence techniques using fused and pressed discs (Appendix A.5) and all data are presented on a salt-free basis (Appendix A.6). Regression analysis (5.2) and principal component analysis (5.3) both highlight the above elements as having strong correlations with the terrigenous phase and, therefore, they are likely to be most useful in the interpretation of this important sediment phase.

The only correction that has been made to the salt-free XRF data was for silicon (Si). The total Si concentration (Si_{total}) has been recalculated to remove the contribution of biogenic silica (as measured using the techniques described in Appendix A.4) which results in a terrigenous Si value (Si_{terr}) for all samples (using Eqn 7.1 and Appendix B.4).

Equation 7.1. Calculation of terrigenous silicon

$$Si_{terr} = Si_{total} - [Bio. Sil. \times 0.466]$$

where, Si_{terr} = terrigenous silicon (wt.%),
 Si_{total} = XRF Si concentration (wt.%),
 Bio. Sil. = biogenic silica concentration (wt.%),
 0.466 = atomic weight conversion from biogenic silica to
 biogenic silicon.

Terrigenous element ratios

As previously stated (e.g. 5.2.2 and 6.3.2), the element which is known to be exclusively associated with the terrigenous component is aluminium (Al) (Arrhenius, 1952; Bostrom, 1973; Bischoff *et al.*, 1979) and it has often been used in marine sediment studies as an indicator of clay detritus of terrestrial origin (e.g. Shimmield, 1985; Finney *et al.*, 1988; Shimmield and Mowbray, 1991; Patience, 1992; Pedersen *et al.*, 1992). In order to illustrate any variations in the composition of the terrigenous material, it is necessary to convert the simple elemental wt.% (which can be influenced by dilution effects of another component) into an element/Al ratio. The data and down-core profiles in this section are therefore expressed as elemental ratios to Al (or, in some cases, to Rb).

The complete dataset for Si_{terr}/Al , Ti/Al , Fe/Al , Mn/Al , K/Al , K/Rb and Zr/Rb for all the cores in this study can be found in Appendices C.8 and C.11. Table 7.1 summarises this large set of data by displaying the mean and range of values of the above geochemical parameters. The average deep-sea clay composition from Turekian and Wedepohl (1961) is also listed, for comparison with the Peru margin cores.

		Si_{terr}/Al	Ti/Al ($\times 10^{-3}$)	Fe/Al	Mn/Al ($\times 10^{-3}$)	K/Al	K/Rb ($\times 10^{-3}$)	Zr/Rb
CD38-09 (148m)	Range	2.51-5.28	46.3-56.6	0.29-1.14	3.39-7.30	0.20-0.26	18.3-25.3	1.40-5.11
	Mean	3.85	52.29	0.46	5.48	0.226	21.48	1.94
CD38-10 (257m)	Range	2.99-5.79	43.5-55.2	0.26-0.49	1.23-6.29	0.22-0.27	17.5-25.9	1.26-5.17
	Mean	4.02	49.74	0.39	4.24	0.240	20.86	2.125
CD38-02 (Box, 2530m)	Range	2.43-2.82	44.5-48.2	0.49-0.62	3.43-6.63	0.26-0.29	19.5-21.7	1.36-1.52
	Mean	2.65	46.37	0.55	4.70	0.278	20.73	1.43
CD38-02 (2525m)	Range	2.05-3.13	38.5-53.7	0.38-0.62	4.14-5.94	0.19-0.34	12.1-24.6	1.19-1.41
	Mean	2.54	49.46	0.51	4.95	0.266	17.76	1.27
CD38-11 (3835m)	Range	1.67-3.82	44.5-60.4	0.34-0.50	3.11-5.94	0.22-0.28	16.4-21.4	1.20-2.98
	Mean	2.32	49.59	0.41	4.20	0.254	17.84	1.39
CD38-03 (Box, 4289m)	Range	1.89-2.54	45.4-49.1	0.41-0.64	3.24-12.5	0.25-0.28	19.9-22.6	1.24-1.42
	Mean	2.20	47.69	0.47	4.74	0.268	21.43	1.34
T & W (1961)		2.97	54.76	0.77	79.7	0.297	22.72	1.364

Table 7.1. Range and mean of terrigenous ratios for all cores in this study and average deep-sea clay values from Turekian and Wedepohl (1961).

From the information contained within Table 7.1 it can be seen that there is a wide range of variation of each of the terrigenous element ratios both within and between each core in this study. When compared with the average deep-sea clay ratios (Turekian and Wedepohl, 1961) the data displays the following interesting points.

- a) An enrichment (above 3.0) in the mean Si_{terr}/Al ratio is seen only for the two shallow-water cores, CD38-09 and CD38-10. The deeper-water sites all have mean Si_{terr}/Al ratios which are significantly depleted from the average clay value.
- b) The majority of the Ti/Al ratios fall within the range of approximately 45-55 $\times 10^{-3}$, with this upper limit representing the average clay ratio. The only

exceptions to this range are the minimum in core CD38-02 (38.5×10^{-3}) and the maximum in core CD38-11 (60.4×10^{-3}).

- c) The mean Fe/Al and Mn/Al values are all significantly depleted compared to the average deep-sea clay composition. However, Turekian and Wedepohl (1961) do not indicate whether their sediment samples are restricted to purely surface samples or if they are a mixture of surface and core samples. As will be shown later by the down-core profiles of the two box cores, this information is significant because of near-surface migration of both Mn and Fe relating to the redox environment of the sediment (Calvert and Price, 1977; Heath and Lyle, 1981; Graybeal and Heath, 1984).
- d) The K/Al and K/Rb ratios from the Peru margin show only slight inter-core variation and the mean ratios are slightly depleted compared with the world average clay composition.
- e) Cores CD38-09, CD38-10 and CD38-11 show Zr/Rb maxima which are 2-4 times the average deep-sea clay but of these, only the two shallow-water sites have mean Zr/Rb ratios which are enriched in Zr compared with Rb.

It is important in this examination of terrigenous input variation to study the down-core profiles of the above element ratios. Figures 7.1 through to 7.7 illustrate the temporal fluctuations of Si_{terr}/Al , Ti/Al, Fe/Al, Mn/Al, K/Al, K/Rb and Zr/Al (against depth or age) respectively and because each figure shows all six core profiles together, the spatial pattern of terrigenous composition can also be easily studied.

The following section (7.2.3) will give detailed interpretations of Figs 7.1 to 7.7 in terms of environmental and depositional conditions but described below are some of the most interesting features of the profiles.

- a) With the knowledge that core CD38-09 contains a concentrated phosphorite horizon at 273cm and core CD38-10 contains similar zones at approximately 30, 80-110 and 500cm (4.3.3) then the down-core profiles display variations in the terrigenous composition which occur either around these zones (e.g. the Zr/Rb ratio peaks significantly at the above depths, Fig. 7.7) or between these zones. Examples of this latter variation pattern are, 1) in core CD38-10 where the Ti/Al ratio is on average around 45×10^{-3} below 500cm but above the phosphorite zone it shifts to an average of around 52×10^{-3} (Fig. 7.2) and, 2) in core CD38-09 where below the phosphorite zone (273cm) the Fe/Al and the Si_{terr}/Al ratios have significantly higher average ratios compared with those

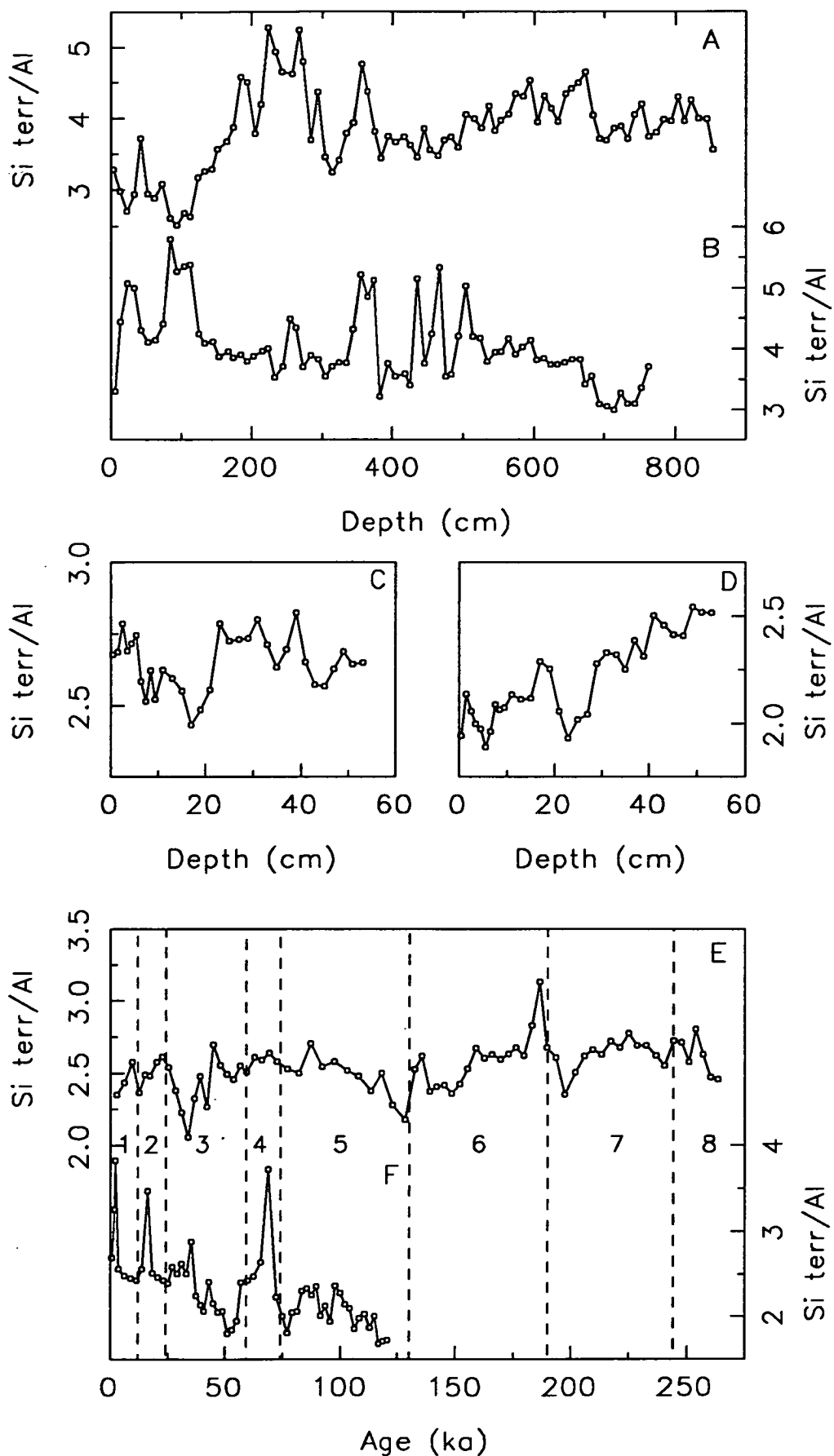


Figure 7.1. Si_{terr}/Al ratio down-core profiles: A) CD38-09, B) CD38-10, C) box core CD38-02, D) box core CD38-03, E) CD38-02 and F) CD38-11.

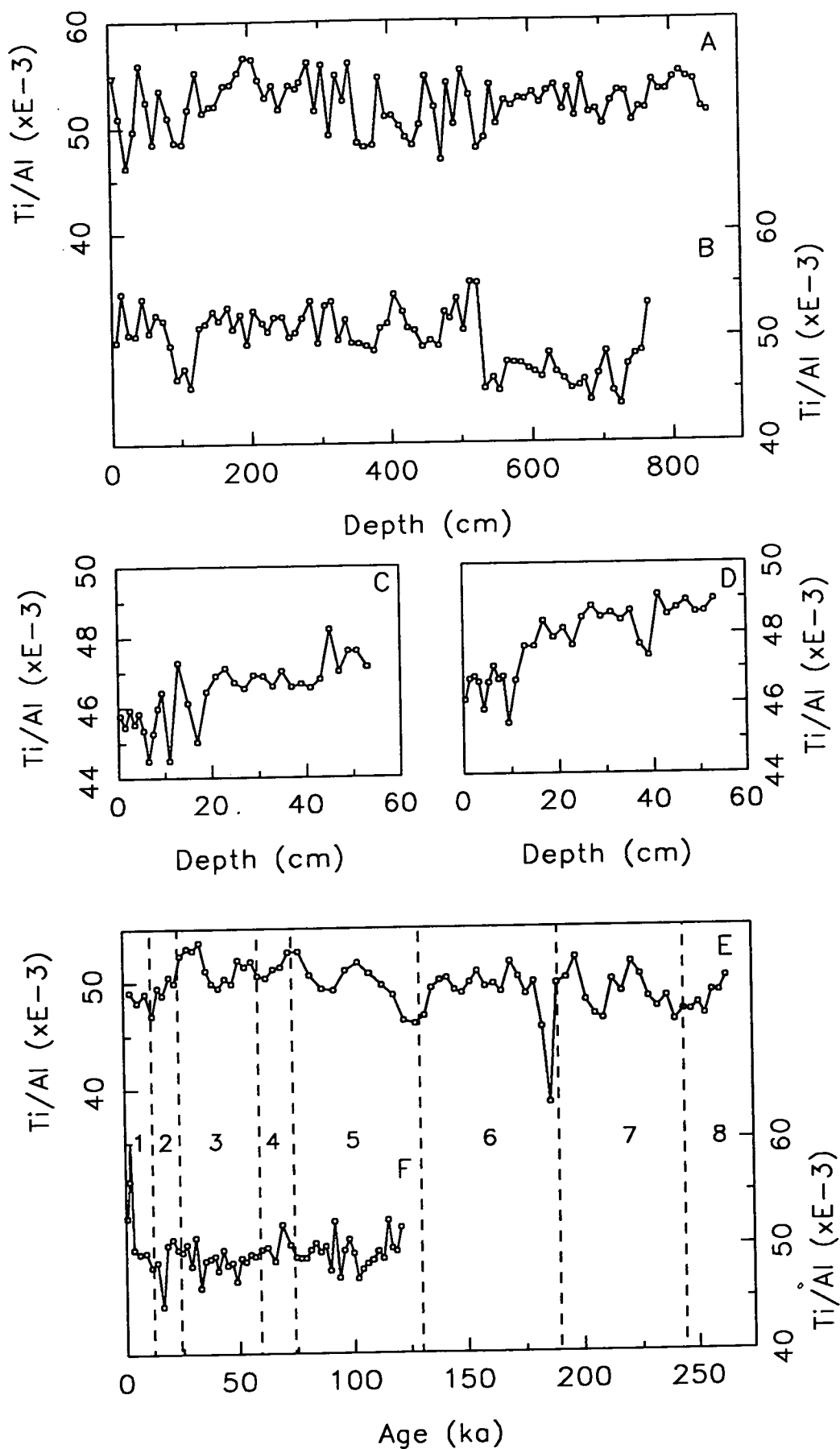


Figure 7.2. Ti/Al ratio down-core profiles: A) CD38-09, B) CD38-10, C) box core CD38-02, D) box core CD38-03, E) CD38-02 and F) CD38-11.

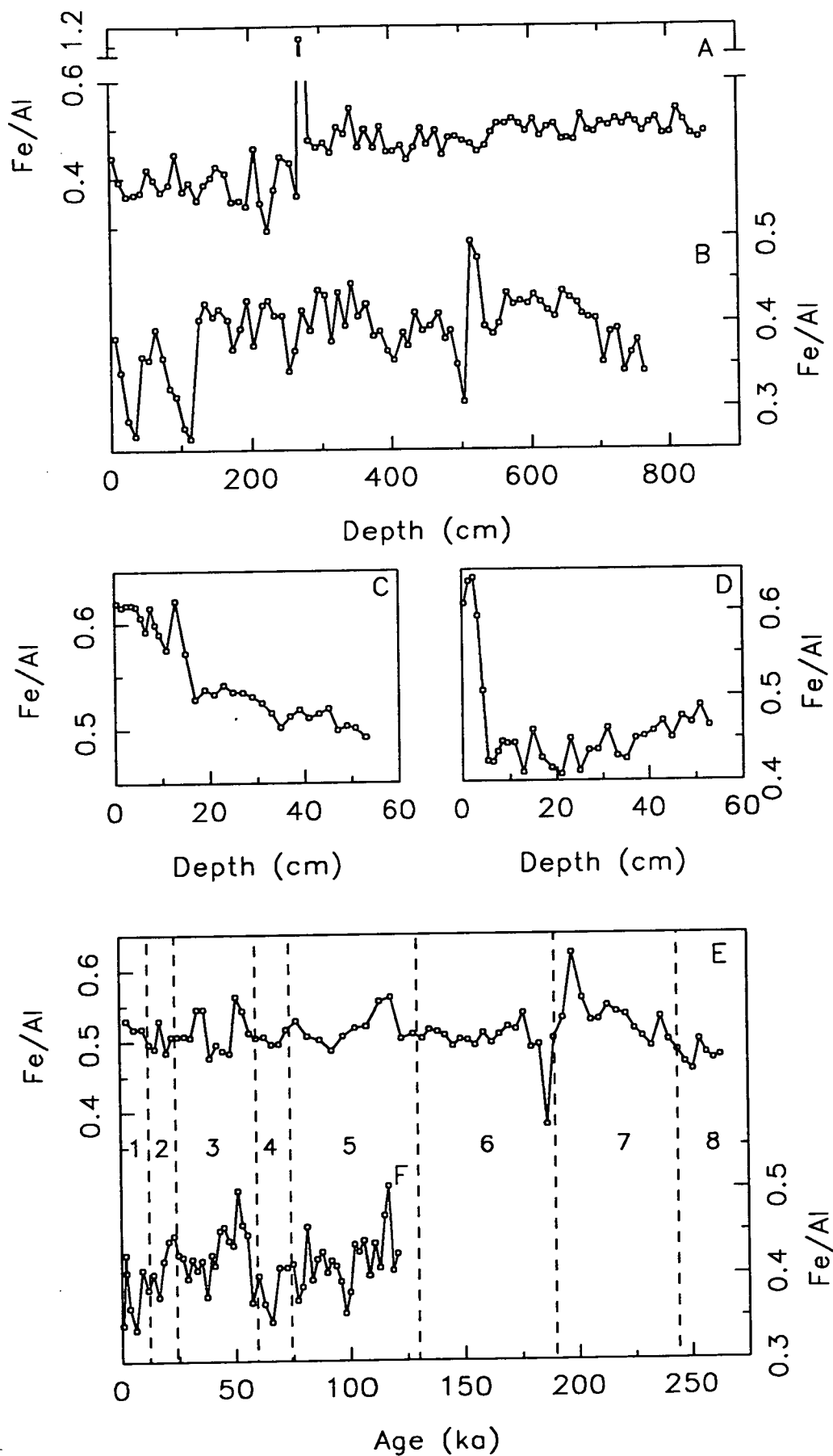


Figure 7.3. Fe/Al ratio down-core profiles: A) CD38-09, B) CD38-10, C) box core CD38-02, D) box core CD38-03, E) CD38-02 and F) CD38-11.

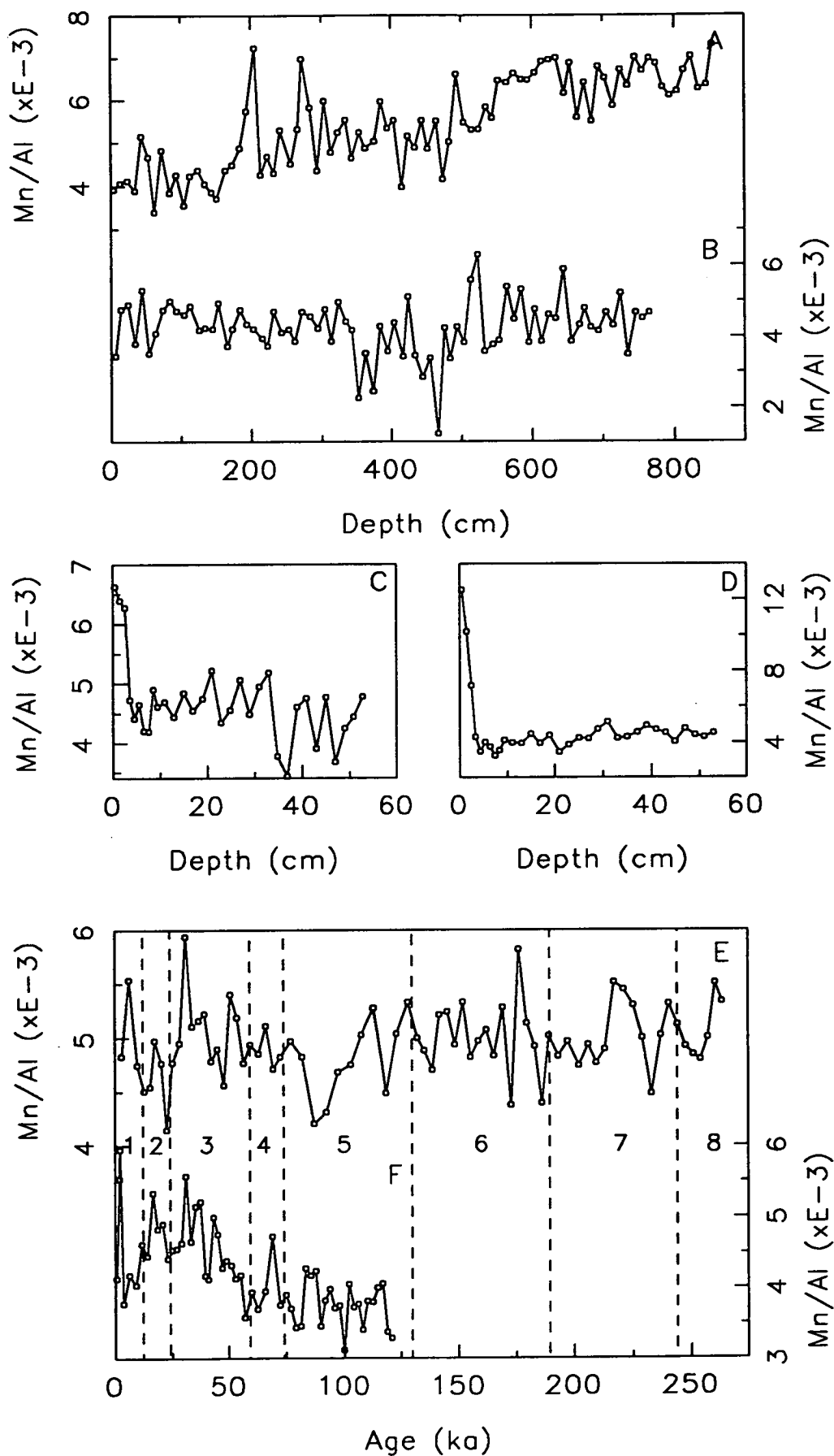


Figure 7.4. Mn/Al ratio down-core profiles: A) CD38-09, B) CD38-10, C) box core CD38-02, D) box core CD38-03, E) CD38-02 and F) CD38-11.

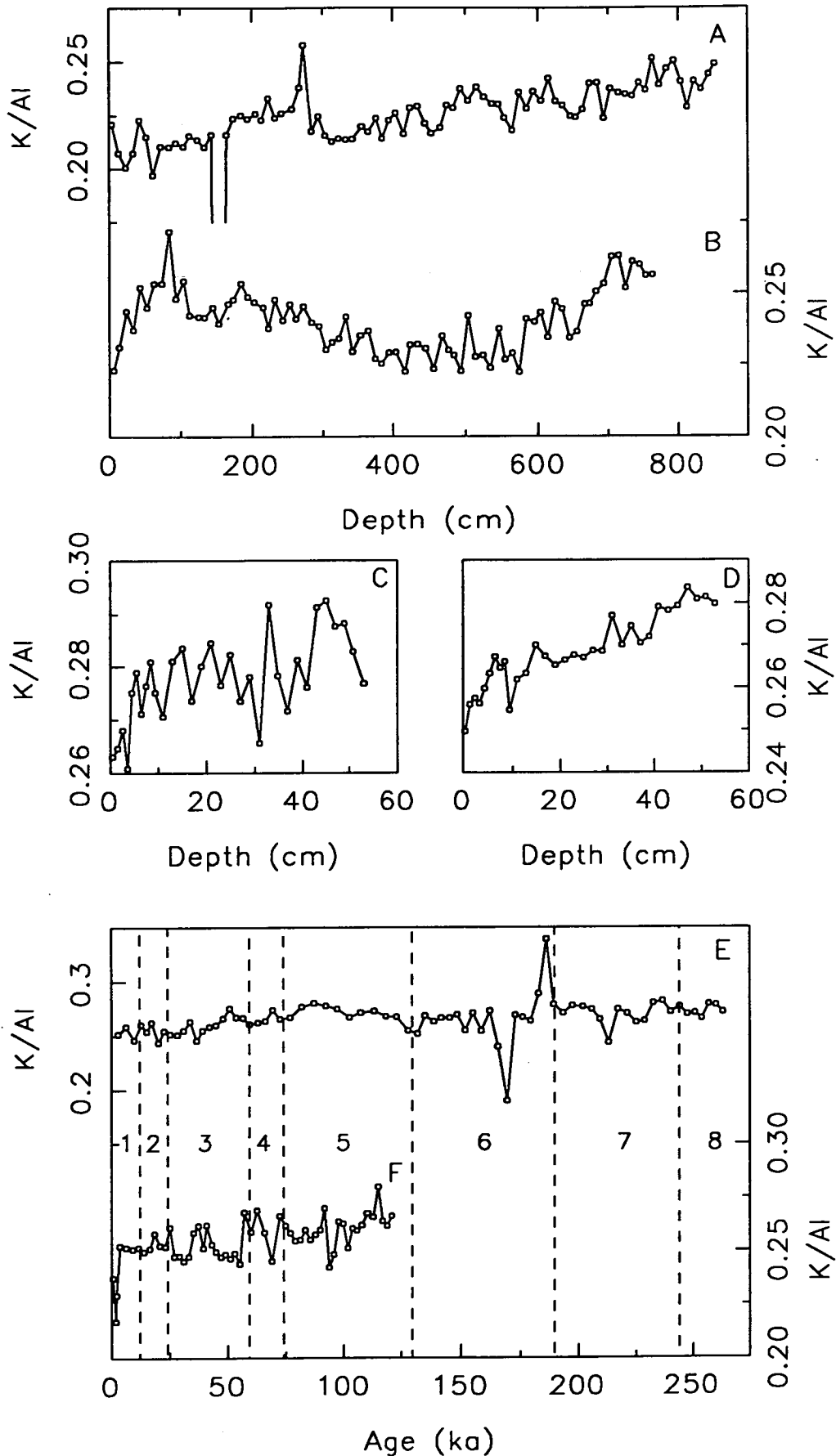


Figure 7.5. K/Al ratio down-core profiles: A) CD38-09, B) CD38-10, C) box core CD38-02, D) box core CD38-03, E) CD38-02 and F) CD38-11.

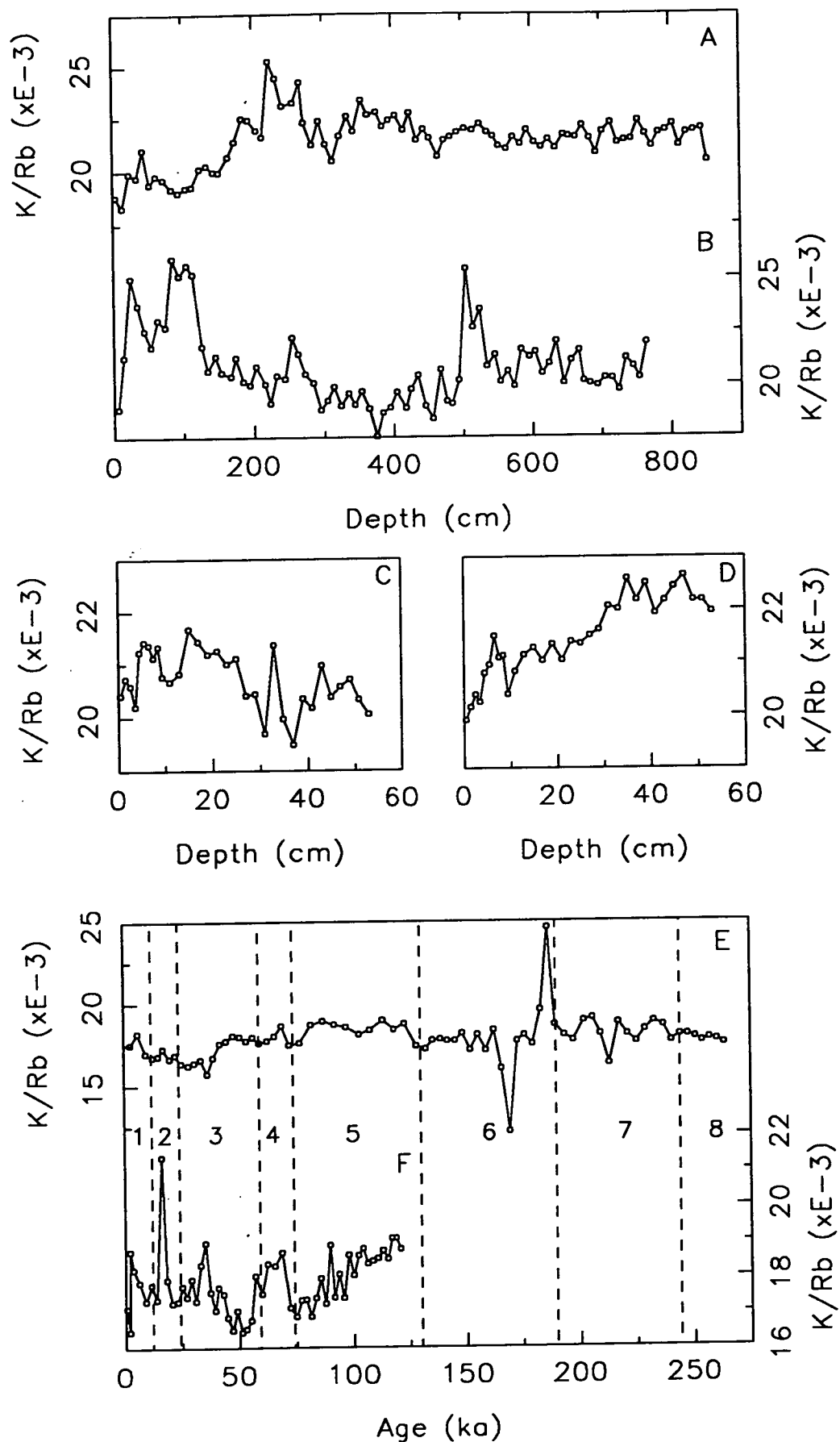


Figure 7.6. K/Rb ratio down-core profiles: A) CD38-09, B) CD38-10, C) box core CD38-02, D) box core CD38-03, E) CD38-02 and F) CD38-11.

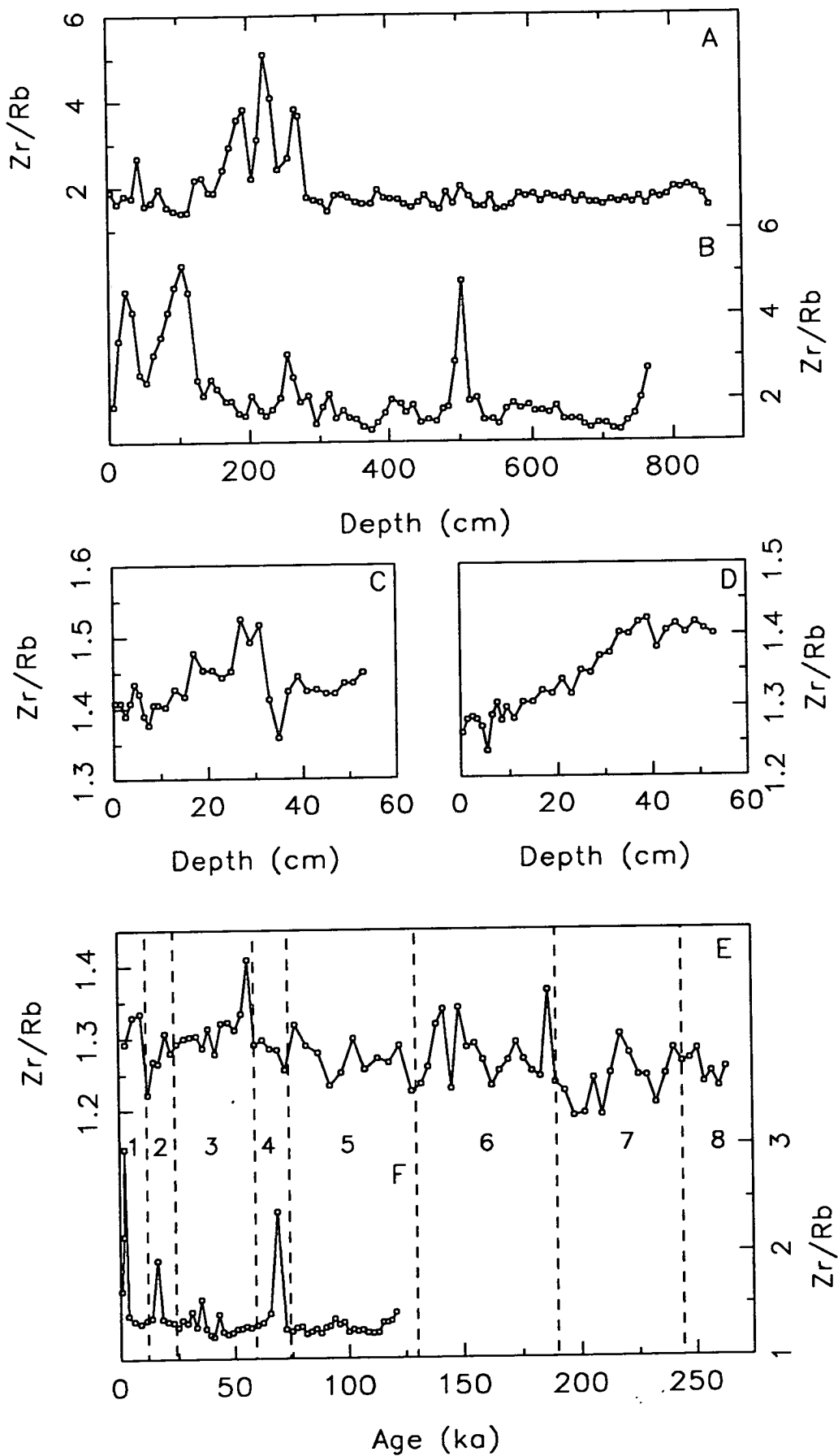


Figure 7.7. Zr/Rb ratio down-core profiles: A) CD38-09, B) CD38-10, C) box core CD38-02, D) box core CD38-03, E) CD38-02 and F) CD38-11.

- above the phosphorite concentration event (from about 0.5 to 0.4 and from 4.0 to 3.0 respectively, Figs 7.3 and 7.1).
- b) The two box cores (CD38-02 and CD38-03) display diagenetic, surface enrichment profiles of Fe/Al and Mn/Al (Figs 7.3 and 7.4) and in both sediment columns, it is the Mn/Al which drops at a shallower depth than the Fe/Al.
 - c) All the profiles for piston core CD38-02 contain anomalous troughs or peaks at about 186ka (lower stage 6); the most significant of which is the drop in Ti/Al (Fig. 7.2) down to $38.5 \times E^{-3}$.
 - d) The turbiditic zone in core CD38-11 (6.2.3) at about 2.5ka shows strong enrichments in Si_{terr}/Al , Ti/Al, Mn/Al and Zr/Rb but a depletion in K/Al compared with the rest of the sediment in this core. The glacial stages 2 and 4 also show peaks in Si_{terr}/Al and Zr/Rb in this core but because of the lack of a Ti/Al enrichment (and from the I/C_{org} data, 6.2.3) these areas are not considered to be turbidite (secondary sedimentation) layers.
 - e) Accurate temporal studies are only possible using the two cores with age models, however, there seems to be very little obvious glacial/interglacial variation contained within the terrigenous composition profiles. The Si_{terr}/Al profile during stage 5 perhaps shows some similarity between CD38-02 and CD38-11 (Fig. 7.1) with the ratio starting low after glacial stage 6, rising steadily during interglacial stage 5 before dropping again just before the stage 4/5 boundary. The Ti/Al record of core CD38-02 displays a trend of decreasing ratios at the end of each glacial stage (2, 4, 6 and 8) followed by a double peak/trough system within the interglacial stages 3, 5 and 7. However, core CD38-11 shows no such pattern in its Ti/Al profile (Fig. 7.2).
 - f) Of the four piston cores, CD38-10 and CD38-02 show no obvious trend in their Mn/Al down-core profiles (Fig. 7.4) whereas core CD38-09 displays a generally increasing trend with depth (up to 7.3×10^{-3}) and core CD38-11 shows a generally decreasing trend (down to 3.3×10^{-3} at the base of the core).
 - g) The K/Al record of core CD38-10 (Fig. 7.5) looks like it contains a smooth and continuous cycle of changing relative concentrations of K and Al in terrigenous material with time. However, it must be remembered that this is a depth profile and not an age profile and, therefore, variations in the sedimentation rate and periods of sediment erosion (2.3.2) must be taken into account. The peak in K/Al at around 80-100cm in core CD38-10 is related to the phosphorite horizon and can also be seen in core CD38-09 at 273cm (where there is a significant break in the trend of increasing K/Al with depth).

Obviously, the mineralogical composition of the terrigenous component is of concern in this study of the Peru margin sediments and Table 7.2 lists the chemical composition of some of the most common minerals (including quartz, heavy minerals, clays and feldspars) along with an indication of their density and hardness, and it will be referred to throughout the following section (7.2.3) on terrigenous environmental interpretations.

Mineral	Chemical formula	Density	Hardness
Quartz	SiO ₂	2.65	7
Zircon	Zr (SiO ₄)	4.65	7.5
Ilmenite	FeTiO ₃	4.74	5.5
Rutile	TiO ₂	4.8	6
Anatase	TiO ₂	3.9	5.5
Magnetite	Fe ₃ O ₄	5.2	7.5
Haematite	Fe ₂ O ₃	5.25	5.5
Alkali feldspar	(K,Na) (AlSi ₃ O ₈)	2.6	6
Plagioclase feldspar	Na (AlSi ₃ O ₈) - Ca (Al ₂ Si ₂ O ₈)	2.6	6
Illite	K _{1-1.5} Al ₄ [(Si,Al) ₈ O ₂₀] (OH) ₄	2.75	1.5
Chlorite	(Mg,Al,Fe) ₁₂ [(Si,Al) ₈ O ₂₀] (OH) ₁₆	3.0	2.5
Smectite	(0.5Ca,Na) _{0.7} (Al,Mg,Fe) ₄ [(Si,Al) ₈ O ₂₀] (OH) ₄ .nH ₂ O	2.5	1.5

Table 7.2. Terrigenous mineral composition, density and hardness (Deer *et al.*, 1966).

Terrigenous element fluxes

In order to examine the true variation of a particular sediment component and then to interpret the reasons for its temporal variation of input to the sediment, mass accumulation rate (MAR) fluxes need to be calculated. In this study, only piston cores CD38-02 and CD38-11 have been designated accurate age models and therefore flux data can only be calculated for these two cores (2.4.2). In this section the MAR fluxes of Al and Si_{terr} will be used to display quantitative differences of terrigenous input both between the two cores (which are situated in contrasting depositional environments) and within the cores, in terms of glacial/interglacial variability.

The use of MAR fluxes does not completely solve the problem of correctly quantifying the amount of input of a particular geochemical component over time.

The method of calculation of fluxes (i.e. multiplication of the sediment accumulation rate by the dry bulk density and then by the component weight percentage) renders the result susceptible to potentially large and accumulative errors. The flux data is dependant on correct sediment accumulation rates, which in turn relies on an accurate age model. If there are any errors in the designation of the depth of the stage boundaries then the sedimentation rates (which are assumed to be linear between these points) can be significantly increased or decreased. A second problem can arise if there are errors in the dry bulk density measurement which was calculated directly from the wt.% water content of the sediment (Eqn 2.4., 2.2.1) and assumed a constant grain density of 2.6 g cm⁻³. If, for example, one particular section of the core suffered from evaporation loss during transport and/or sampling then the dry bulk density calculated may be anomalously high. Unreliable flux data can also occur if the component of interest is only present as a small percentage compared with a second, more dominant component. Small variations in the abundance of the dominant component can significantly affect the concentration and flux measurement of the minor component even though the input of the latter may not have varied by much, if at all.

As a result of these problems, MAR flux data has to be interpreted with these possible errors in mind and corroborative evidence of component input variation should be looked for.

The terrigenous MAR flux data was calculated by multiplying the salt-free concentrations of Al and Si_{terr} by the MAR for each sample (Eqn 7.2) and the complete dataset for cores CD38-02 and CD38-11 is listed in Appendix C.19.

Equation 7.2. Mass accumulation rate flux calculation

$$\text{MAR flux (mg/cm}^2\text{/kyr)} = \text{Element conc.} \times [\text{MAR (g/cm}^2\text{/kyr)} \times 1000]$$

where, MAR flux = mass accumulation rate flux of element,
 Element conc. = concentration of element, expressed as a
 weight fraction of total sediment,
 MAR = mass accumulation rate (from Eqn 2.5).

The range and mean of the Al and Si_{terr} MAR fluxes are shown in Table 7.2, along with similar data from the Eastern Equatorial Pacific (Patience, 1992) for comparison. Figure 7.8 displays the fluxes as down-core age profiles for both CD38-02 and CD38-11.

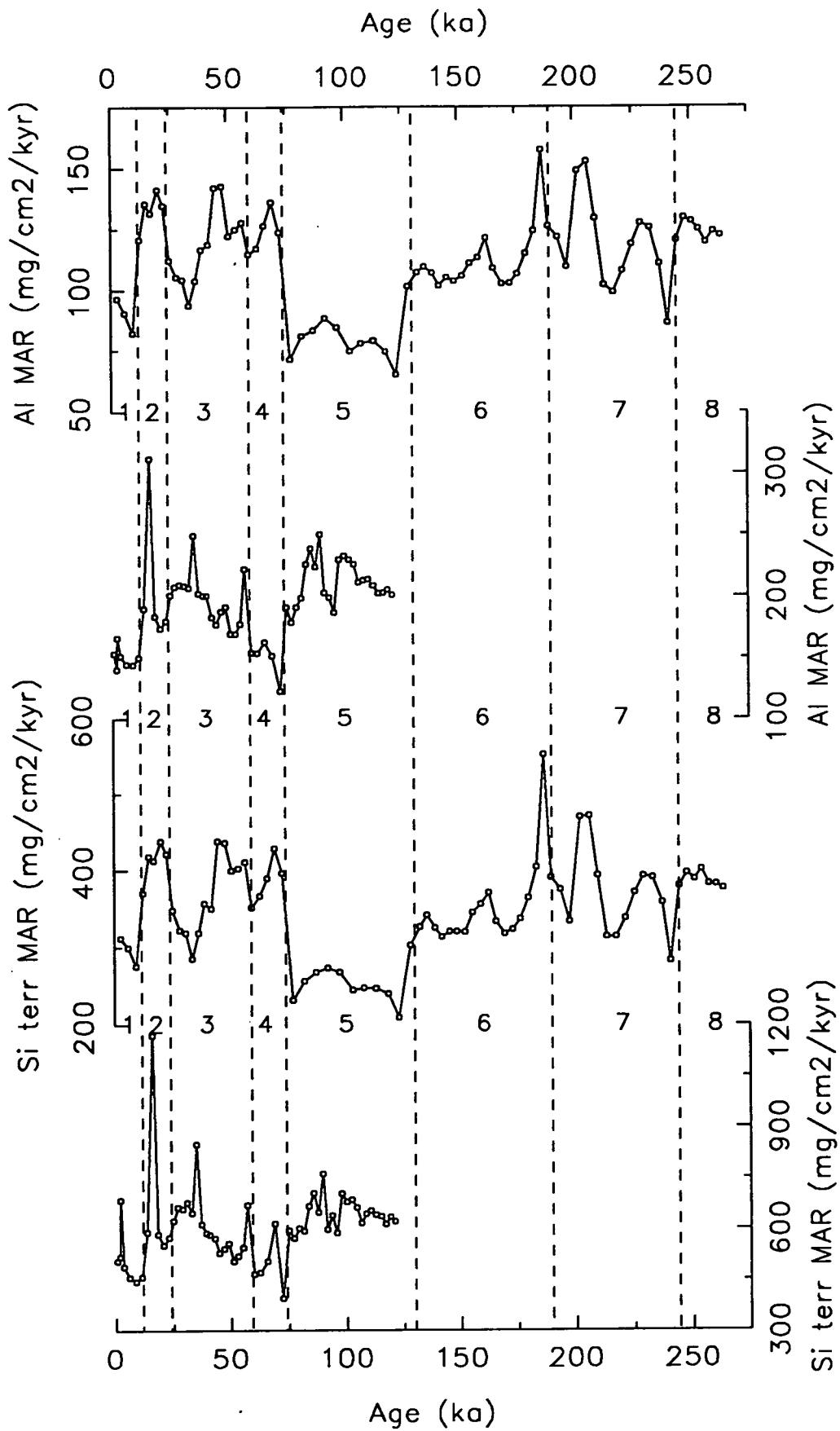


Figure 7.8. Terrigenous component Al and Si_{terr} mass accumulation rate fluxes: A) and C) CD38-02, B) and D) CD38-11.

Table 7.3 reveals the basic fact that core CD38-11 has received a higher average flux of both Al and Si_{terr} when compared with core CD38-02. It also shows that, as expected from the average deep-sea Si_{terr}/Al ratio (Table 7.1, Turekian and Wedepohl, 1961) the Si_{terr} MAR is approximately three times the Al MAR. The average flux data for both cores fall within the range measured by Patience (1992) which implies that over the Late Quaternary, similar volumes of terrigenous material have been introduced to the marine sediments accumulating on the Peru margin and the Eastern Equatorial Pacific (Panama Basin).

		Al MAR ($mg\ cm^{-2}\ kyr^{-1}$)	Si_{terr} MAR ($mg\ cm^{-2}\ kyr^{-1}$)
CD38-02 (2525m)	Range	65.0-157.5	208.5-551.7
	Mean	112.0	349.7
CD38-11 (3835m)	Range	122.0-312.0	393.7-1169
	Mean	193.7	605.4
Patience (1992)		15.2-292.1	85.3-754.0

Table 7.3. Range and mean of the mass accumulation rates of Al and Si_{terr} ($mg\ cm^{-2}\ kyr^{-1}$) for cores CD38-02 and CD38-11.

Data from Patience (1992) is a range of the mean values for five cores from the Eastern Equatorial Pacific (water depth range, 1540-3225m).

The co-variation of both the fluxes of Al and Si_{terr} over the past 265ka for CD38-02 and 120ka for CD38-11 is illustrated in Fig. 7.8. In the case of core CD38-02, the terrigenous fluxes are, on average, higher during glacial stages than during interglacial ones. However, high fluxes do occur during stages 3 and 7 which distort the glacial/interglacial cyclicality. No simple climatic pattern exists for core CD38-11, where interglacial stage 5 is a period of relatively high terrigenous flux, the Holocene (stage 1) contains a low flux and the period in between (from 75 to 12ka) shows a general trend of increasing flux over time. The highest fluxes of Al ($312\ mg\ cm^{-2}\ kyr^{-1}$) and Si_{terr} ($1169\ mg\ cm^{-2}\ kyr^{-1}$) measured in this study occur in core CD38-11 during glacial stage 2 at 16.5ka.

7.2.3. Terrigenous environmental interpretations

This section is divided into sub-sections, each of which will discuss a particular environmental control on the deposition of terrigenous material along the Peru continental margin by interpretation of the geochemical data described above.

Continental landmass proximity

As stated in the introduction to this terrigenous input study (7.2.1), the terrigenous material which is found within the marine sediments in this study originates from the continental landmass of South America. Whatever the mode of transport of this material (wind-blown or fluvial input to the ocean) it is probable that the proximity of a particular core site to the continent (i.e. source area) will be the dominant control on the volume of material reaching that site. Measurement of the Al/MAR and Si_{terr} /MAR fluxes showed that core CD38-11 has received an average of nearly twice the volume of terrigenous material compared with core CD38-02 (Table 7.3) and since the former core is situated closer to the continental landmass then this fact could be taken as evidence of the above statement. It is unfortunate that no mass accumulation rates could be calculated for cores CD38-09 and CD38-10, which are the closest sites in this study to the Peruvian coast, because it is likely that the terrigenous fluxes for these two sites would exceed those for CD38-11 by an order of magnitude or more.

However, the measured flux of terrigenous input is by no means linearly correlated with the distance from the continent. Factors such as latitudinal source differences, ocean currents and the actual oceanographic setting of the core on the continental slope, shelf or ridge, both on a regional and local scale, (all of which will be discussed fully below) can all affect the concentration of the terrigenous component in marine sediments (Scheidegger and Krissek, 1982; Clayton and Kemp, 1990).

Compositional, rather than abundance, differences in the terrigenous component of all six cores can, however, be examined and it is possible that the proximity of each site to the continent may play a role in such spatial variations. Cores CD38-09, CD38-10 and CD38-11 form a transect of increasing distance from South America at approximately 11°S and so any source-derived compositional differences will be minimal between the three sites. Therefore, the fact that the two near-shore cores contain much higher average Si_{terr}/Al ratios compared with CD38-11 (3.85 and 4.02 compared with 2.32, Table 7.1) may be interpreted as a proximity-controlled compositional difference. Increased Si_{terr}/Al ratios can be obtained by a higher than average quartz concentration compared to clays (Table 7.2, Shimmiel and Mowbray, 1991; Patience, 1992). The Si_{terr}/Al data from this study imply that

cores CD38-09 and CD38-10 are accumulating greater quantities of quartz detritus, relative to aluminosilicate clays, due to their proximity to the continental margin.

In a study of the distribution of opal and quartz in the southeastern Pacific, Molina-Cruz and Price (1977) found that along the Peruvian and northern Chilean coast, quartz distribution (principally controlled by aeolian transport) decreased rapidly seaward and quartz/feldspar ratios measured by Scheidegger and Krissek (1982) confirmed this finding. The source of the quartz is thought to be the arid coastal plains of Peru and Chile, including the Atacama desert (Prospero and Bonatti, 1969; Molina-Cruz and Price, 1977).

If the enrichment of quartz within the terrestrial-derived assemblage at near-shore sites is due to shorter transport times for larger quartz grains compared to fine-grained clays, then any indicator of sediment grain-size (physical or geochemical) should also show differences between sediments deposited at different distances from the continental landmass. In marine sediments zirconium (Zr) occurs almost exclusively in zircon; a mineral which is highly resistant to weathering upon erosion of continental rocks and therefore tends to occur in the coarse-grained fraction of the sediment (Table 7.2, Hill and Parker, 1970). On the other hand, rubidium (Rb) is found associated mainly with the fine-grained fraction of marine sediments (Calvert, 1976) since it can easily substitute for potassium (ionic radius of $Rb^+ = 1.47\text{\AA}$ and $K^+ = 1.33\text{\AA}$, Ahrens, 1952) in clays, such as illite (potassic-mica), and feldspars (Pedersen, 1979). Therefore, the ratio of Zr/Rb can be used as an indication of the average sediment grain-size, where the higher the Zr/Rb ratio, the coarser-grained the sediment (compare Fig. 7.7 with the % sediment $> 63\mu\text{m}$ profiles in Figs 2.1 and 2.2).

It was highlighted in the results of this terrigenous input study (Table 7.1) that the only sites with an average Zr/Rb ratio appreciably enriched compared with the average deep-sea clay (Turekian and Wedepohl, 1961) were the near-shore cores, CD38-09 and CD38-10. This indication that coarser (and denser) grained terrigenous material is more abundant in samples from close to the Peruvian coast supports the Si_{terr}/Al results and implies that the proximity to the continental margin (i.e. source of terrigenous material) is a controlling influence on the geochemical and sedimentological composition of the total sediment.

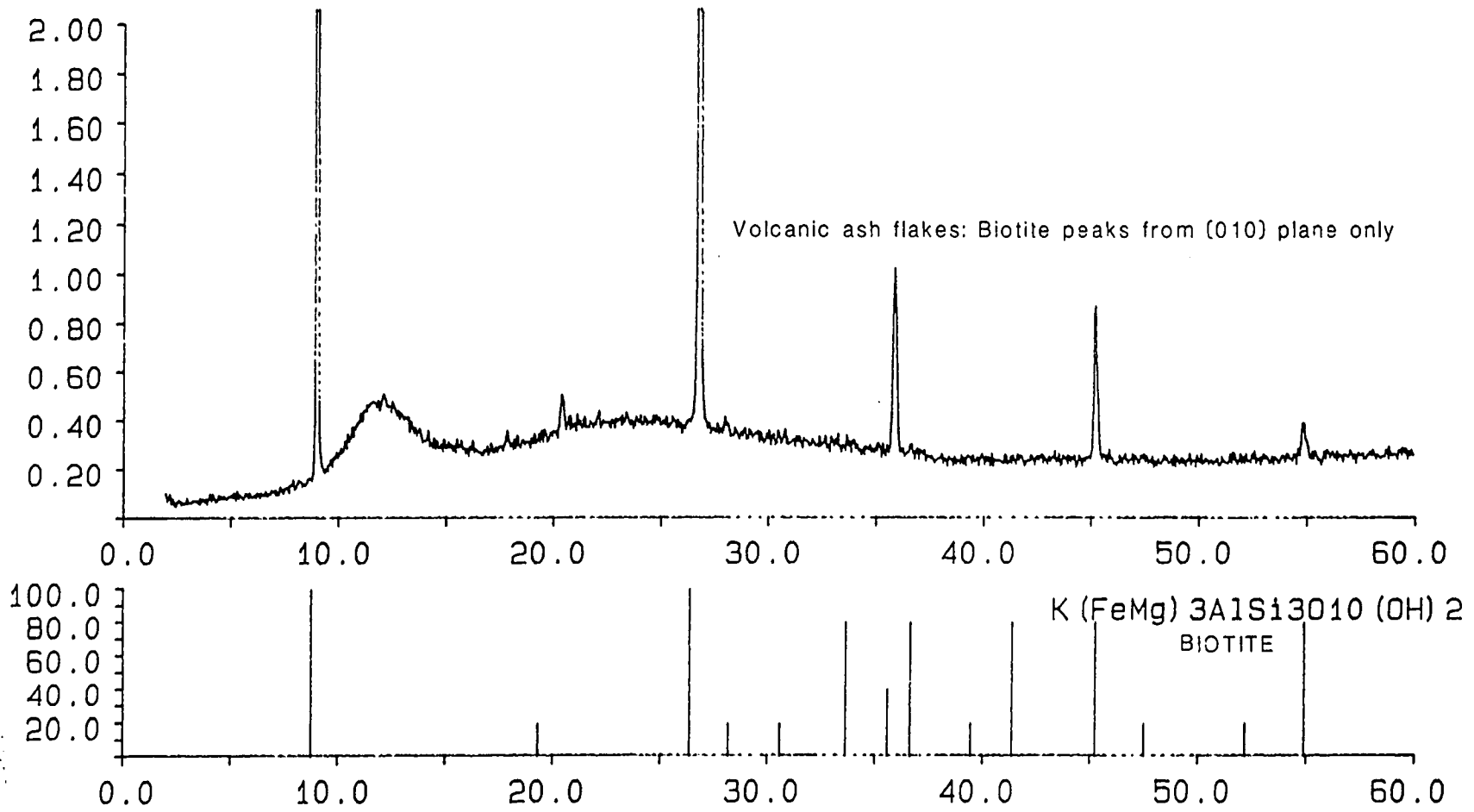
Volcanic activity

The only sedimentary component which originates from the terrestrial environment but which has not been produced by continuous weathering of

continental rocks is tephra. Volcanic ash deposits in the eastern Pacific, transported to the ocean by atmospheric winds, are the result of andesitic to rhyolitic continental volcanism associated with the subduction of the oceanic Nazca and Cocos plates under the central and south American continent (Rose *et al.*, 1979; Wright, 1981; Pouclet *et al.*, 1990). Kennett and Thunell (1975) evaluated the distribution of ash layers contained within the deep-drilled cores of the Deep Sea Drilling Project from throughout the world's oceans and their results indicated a global increase of explosive volcanism within the Quaternary (over the last 2 million years) compared with the previous 20 million years. In a study of the distribution and age of ash layer "L" (Bowles *et al.*, 1973) in the Panama Basin region, Ninkovich and Shackleton (1975) also found the layer present in core V15-39 (4cm thick), located at 10°S at 2545m off the Peru margin. From its geochemical composition, the source of this particular ash deposit was interpreted as the andesitic volcanoes between 5°N and 2°S (i.e. Colombia and Ecuador) and the extreme southerly distribution was thought to be controlled initially by high-altitude winds which deposited the ash in the ocean between 5°N and 5°S, followed by ocean current transport (i.e. the Peru poleward undercurrent, 3.1.1).

Many authors have used volcanic ash layers as stratigraphic markers (Ninkovich and Shackleton, 1975; Drexler *et al.*, 1980, Ledbetter, 1982, Patience, 1992) and a study by Ledbetter (1985) attempted to integrate the tephrochronology of the eastern Pacific with microprobe geochemical analyses, which designated particular tephra layers using their characteristic chemical compositions. In terms of the recognition of ash layers using bulk-sediment geochemical analysis, the most striking characteristic is a low Ti/Al ratio compared with the surrounding aluminosilicate clays (Finney *et al.*, 1988; Patience, 1992). The only sample in all of the cores from this study to contain an anomalously low Ti/Al ratio is in core CD38-02 at an age of 186ka ($38.5 \times E^{-3}$, Fig. 7.2). During the process of foraminifera picking (Appendix A.2) by microscopic study of the > 63µm fraction of the sediment, the sample from this depth in core CD38-02 was found to contain abundant small, dark brown crystals. These were subsequently picked out of the sample, analysed by X-ray diffraction (Appendix A.9) and found to be biotite minerals (Fig. 7.9). The interpretation that the biotite flakes at 186ka in core CD38-02 are part of a volcanic ash deposit (with a low Ti/Al ratio) is supported by the evidence of the tephra study of the ODP Leg 112 (Pouclet *et al.*, 1990) which found biotite flakes present in Quaternary andesitic-ash layers in core 687A.

Figure 7.9. X-ray diffraction spectrum of biotite flakes of the ash layer at 186ka in core CD38-02.



The presence of a volcanic ash layer in the Nazca ridge site at 186ka leads to the question of the timing and origin of the volcanic activity that produced it, with respect to the regional temporal and spatial pattern of central and south American volcanism. Ash layer "G" was dated by Ledbetter (1985) at 190 ± 11 ka but was only seen in cores to the north of 10°N . It is possible that, by atmospheric wind and then sea current transport, the ash layer seen at 16°S in core CD38-02 was erupted from the same central American volcanoes. However, it is more likely that there was an eruption within the Central Andean volcanic arc of Peru (Poulet *et al.*, 1990) at a similar time to the ash layer G eruption event, which produced this andesitic, biotite-rich ash deposit.

Wind strength/continental aridity variations

Throughout the Late Quaternary, climatic conditions have fluctuated relatively rapidly between glacial and interglacial periods and environmental factors such as wind strength and continental aridity have varied accordingly. During glacial periods it is thought that stronger atmospheric winds were produced by the growth of ice caps and latitudinal shrinking of the pressure cells in the Pacific and Atlantic oceans (Sarnthein *et al.*, 1988) around which the wind-systems move (anti-clockwise around the S. Pacific and therefore equator-ward up the western coast of S. America, 3.1.1). In addition to stronger glacial winds eroding more terrigenous detritus and transporting it to the oceans, the tropical regions were apparently more arid during glacial periods (and the sea-level dropped) and therefore, the source regions should have expanded (Sarnthein, 1978; Boyle, 1983).

The record of depositional variation of the terrigenous input contained within the Peru margin cores should therefore illustrate this glacial/interglacial periodicity of wind strength and aridity. There are two geochemical methods available in order to study such fluctuations; measurement of either the flux of the total terrigenous component (Al MAR and $\text{Si}_{\text{terr}} \text{MAR}$) or the ratio of two particular elements which can indicate terrigenous grain-density/size and may be dependant on wind strength.

The terrigenous mass accumulation rate fluxes for cores CD38-02 and CD38-11 show quite large variations in their down-core age profiles (Fig. 7.8). For CD38-02, the cyclic pattern of low Al and Si_{terr} fluxes during stages 5 and 1 compared with higher (about a 50% increase) fluxes during stages 2, 4, 6 and 8 could be interpreted as a climatic control on the volume of terrigenous material deposition on the Nazca ridge, where stronger winds during glacial stages have brought more clay, quartz and

feldspar detritus to this area of the Pacific Ocean. Although the highest terrigenous flux in core CD38-11 is seen during a glacial period, there seems to be no particular cyclic pattern and it is interpreted that this continental slope site receives a high input of terrigenous material from further up the slope and shelf which is not controlled simply by wind strength or aridity. At this site there is a more complex interplay of the above factors and also fluvial-transport input, sea-level eustatic variations and ocean current direction/strength need to be considered; all of which vary on different scales of glacial/interglacial change.

In his work on sediment accumulation off Peru, Boyle (1983) developed the use of high precision Ti/Al ratios as an indicator of climate change and attributed "fluctuations of Ti/Al in core V19-29 to changes in the intensity of aeolian transport associated with glacial/interglacial climate oscillations". His reasons for this are that the occurrence of Ti in the terrigenous component is principally in coarse-grained, dense minerals such as anatase, rutile and ilmenite (Table 7.2, Chester and Aston, 1976) and therefore the Ti/Al ratio of a sediment should increase if stronger winds are carrying more coarse grains to a particular depositional location (Shimmiel and Mowbray, 1991). Boyle (1983) measured Ti/Al ratios which varied between 44 and 46 x E⁻³ with higher ratios associated with glacial periods, and in this study the Ti/Al ratios show strong down-core variations between 44 and 55 x E⁻³ (Fig. 7.2). The exceptionally low Ti/Al ratio in core CD38-02 at 186ka has been interpreted as a volcanic ash deposit and the anomalous peak in core CD38-11 occurs within the turbidite zone (a deposit of sediment washed down from the continental slope which is enriched in coarse-grained material) and therefore these two horizons can be excluded from this wind strength interpretation. For these two cores (in which the Ti/Al signal is plotted against age) CD38-11 shows no obvious glacial/interglacial pattern and CD38-02 varies on a sub-stage scale which is characterised by a drop in Ti/Al at the end of each glacial stage. This latter feature could be interpreted as an indication of a reduction in wind strength and/or continental aridity during the change from glacial to interglacial climatic conditions.

Of the four other cores (Ti/Al plotted against depth), the two box cores contain increasing ratios with depth (most noticeable in CD38-03) which may imply that both contain sediments which represent Holocene deposition at the surface down to the last glacial stage at the base of the cores. This would give these two sites an average sediment accumulation rate of about 3cm kyr⁻¹ (55cm in approximately 18kyr) which is roughly similar to the average SAR for piston core CD38-02 (Table 2.2).

There is also a marked variation in the Ti/Al record of the two near-shore cores on a fairly rapid scale and on a longer time-scale in core CD38-10, where lower Ti/Al ratios below 500cm, compared with those above this depth (where phosphorite enrichment occurs), may represent deposition of terrigenous matter during an interglacial stage. Interpretations of this nature are prone to errors because of the lack of an accurate age model (2.3.2) and, as will be discussed later, the influence of sea-level variations at such a shallow-water site.

It should be noted here that if both the Ti/Al ratio and the Zr/Rb ratio are indicators of sediment grain-size then, in these Peruvian continental margin sediments, they must be representative of different fractions of the grain-size (i.e. Zr-rich coarse-grained minerals are not the same as the Ti-rich ones) because the down-core profiles (compare Figs 7.2 and 7.7) are not very similar (except perhaps for box core CD38-03). One reason for this difference between Ti/Al and Zr/Rb may be that the Ti-rich minerals are dominated by aeolian transport (Parkin and Shackleton, 1973; Boyle, 1983) whereas the input of zircon to the oceans is principally by fluvial transport.

Terrigenous source variation

The six cores in this study can be split on a geographical basis into a northerly group at about 11°S (CD38-09, CD38-10 and CD38-11) and a southerly group between 14 and 16°S (piston and box cores CD38-02 and CD38-03). There is a strong possibility that compositional differences in the terrigenous components between these two locations will be influenced by variations in the original composition of the source rocks from which the quartz, clay, feldspar and other minerals have been eroded. In order to examine this spatial variability in the composition of the sediments, the geochemical signal will have to be one which is not strongly affected by grain-size variations and/or mode of transport to the ocean. If the ratios of two elements which occur predominantly in fine-grained clays display inter-core and down-core variation, then it is possible that such geochemical variation is caused by differences in the ratio of one clay to another which, in turn, may give an indication of spatial and temporal source variations.

Both iron (Fe) and potassium (K) are mostly contained within aluminosilicate clays and can be strongly controlled by the illite/chlorite/smectite mineralogy of the terrigenous component of the sediment (Table 7.2, Boyle, 1983; Shankar *et al.*, 1987;

Shimmiel and Mowbray, 1991). Boyle (1983) measured an average Fe/Al ratio in core V19-29 (at 3°S) of about 0.45 and concluded that this value was probably representative of aluminosilicate material in the region of the Peru margin. If the average Fe/Al ratios of the cores in this study are examined, with respect to their northerly/southerly groupings, it can be seen that the cores located around 11°S have ratios around 0.45 or less, but the southerly group have higher ratios (0.47-0.55, Table 7.1) and this may be an indication of clay variation between the two groups. However, all the Fe/Al data show a depletion of iron (7.2.2) when compared to the average deep-sea clay (Turekian and Wedepohl, 1961) and Patience (1992) interpreted similar, low Fe/Al ratios in Panama Basin sediments as representing higher feldspar content in the terrigenous component relative to ferro-magnesium minerals.

It can be seen from the mineralogical composition data (Table 7.2) that Fe in terrigenous-derived sediments is present in dense minerals such as haematite, ilmenite, pyrite and magnetite as well as the fine-grained clays (mainly chlorite and perhaps nontronite). Therefore, the apparent spatial difference in Fe/Al ratios could be due to either one of two environmental influences (or a mixture of both). If the variation is due solely to the contrast in the source of the terrestrial detritus then, perhaps there is an increase in the illite/chlorite clay ratio from south to north along the Peruvian continent. However, if the variation is simply controlled by the relative concentrations of Fe-rich, dense minerals (compared to feldspars) then, perhaps the north/south variation is simply caused by grain-size differences due to the contrasting proximity to the continent and/or mode of transport of sediment to the cores.

One further interesting feature of the Fe/Al ratios is seen in the shallow-water core CD38-09, where there is a marked difference between the average Fe/Al ratio above and below the phosphorite-rich zone at 273cm. As with the spatial differences described above, this temporal difference could be caused by either a change in the source of the terrigenous matter (over a glacial/interglacial boundary) or a change in the average grain-size of sediment deposited at this site (due to sea-level increase since the last glacial maximum).

The Fe/Al ratio does not give conclusive evidence of north/south source variation along the Peru margin but the K/Al and K/Rb ratios can perhaps act as indicators of clay composition variation contained within the marine sediments. Whilst Al is present in all clay minerals (as suggested by the name, aluminosilicates) K occurs mainly in illite (Table 7.2) and it is therefore likely that variations in K/Al reflect the abundance of illite compared with other clay minerals (Boyle, 1983).

Rubidium can substitute for K in illite and the K/Rb ratio may also indicate differences in clay composition along the Peru margin.

There is a north/south difference present in the average K/Al ratios of the six cores but no such variation is shown by the K/Rb ratios (Table 7.1). The northerly group have a K/Al range from 0.226 to 0.254 and the southerly group from 0.266 to 0.278, which may be an indication of a source clay variation with increased illite concentrations (relative to chlorite and smectite) to the south. However, Scheidegger and Krissek (1983) undertook a comprehensive study of the clay mineralogy of fluvial sediments from 41 rivers along the Peruvian coastline from 3°S down to 17°S, which showed that illite was generally more abundant towards the north with relative increases of smectite south of 14°S. The explanation for this difference was related to the continental geology of the area resulting in latitudinal source variation of the clay composition. On the western slopes of the Andes and the coastal cordillera of Peru, the igneous rocks vary from gabbroic batholiths and basaltic volcanics south of approximately 14°S to more granitic igneous complexes and less-basic to intermediate volcanics to the north (Noble *et al.*, 1974; Pitcher, 1974). As well as influencing the clay composition, erosion of the northern province produces sediments which are two or three times more quartz-rich than those from the southern province (Scheidegger and Krissek, 1983) which may explain the very high Si_{terr}/Al ratios measured in cores CD38-09 and CD38-10.

The clay mineralogy work of ODP Leg 112 sediments (Clayton and Kemp, 1991) found Quaternary assemblages in the Salaverry, Lima and Trujillo basins (all between 6 and 12°S) which contained abundant illite compared to expandable clay minerals (smectite and vermiculite) and the opposite relative concentrations in core 686 located in the West Pisco basin at 13.5°S, and this supports the source variation control theory of Scheidegger and Krissek (1983).

The north/south variation measured in the K/Al ratio of the marine sediments in this study, therefore, contradicts the clay composition variation of the above authors. This is possibly due to a north/south source change in the feldspar content of the terrigenous component, with the more northerly group containing a lower alkali/plagioclase feldspar ratio compared with the southerly group (being more dominant than a clay variation). There are down-core variations of K/Al present in the sediments (Fig. 7.5) which may result from localised changes in either the clay and/or the feldspar composition over time. There is no glacial/interglacial cyclicality seen in this geochemical signal in cores CD38-02 and CD38-11 but in the box core CD38-03 there is a general increase in K/Al with depth which may be caused by decreased illite concentrations at this site since the last glacial stage. This interpretation is very

speculative because the sediments in CD38-03 have not been dated, as is the interpretation (for similar reasons) that the K/Al profiles of CD38-09 and CD38-10 represent increasing illite concentrations from the present day composition (surface sediments) down to a phosphorite concentration horizon (glacial stage?) where the K/Al (and K/Rb) is at a maximum. This is followed by a change in the clay composition (sharp decrease in illite in CD38-09, gentler in CD38-10) which once again becomes enriched in illite towards the base of each core.

This section about terrigenous source variations has shown that the geochemical signals of Fe/Al, K/Al and K/Rb are all, to varying degrees, controlled by the north/south variation in the igneous rock composition of the South American continent. However, the geochemical results are of limited use because of the multi-phase mineralogical composition of the above elements (Table 7.2). A purely mineralogical study of cores from a wider distribution along the continental shelf and slope would be required for a more detailed and accurate interpretation of source differences in the Peru margin sediments.

Sea-level, ocean currents and other oceanographic influences

The actual oceanographic setting of each of the sediment cores can strongly influence the volume and composition of the terrigenous component present (Rosato and Kulm, 1981; Scheidegger and Krissek, 1983). In near-shore locations, the supply of terrigenous material over time may be dependant on the eustatic variation of the global sea-level during glacial/interglacial periods. In contrast, the terrigenous component input to deeper-water sites will not be strongly influenced by such sea-level changes, but may be dependant on the precise location and environment within the continental margin.

The Zr/Rb ratio can be used as an indicator of average sediment grain-size because of the contrasting affinity of the two trace elements for coarse- and fine-grained minerals. The down-core profiles of Zr/Rb for cores CD38-09 and CD38-10 (both extremely shallow-water sites) illustrate a pattern of variation which can be interpreted by sea-level variations. The broad peak in CD38-09 and the five sharp peaks in CD38-10 of Zr/Rb all correspond to zones of phosphorite enrichment (compare Fig. 7.7 with Fig. 4.5). These are thought to be periods of lower sea-level on the Peru margin which resulted in stronger bottom-water currents sweeping the continental shelf and, therefore, fine-grained clays (Rb-rich) were winnowed off down

the continental slope leaving behind a lag deposit, which includes a concentration of heavy minerals (Zr-rich) and phosphorite pellets and nodules. If the sea-level drop in this area during maximum glacial periods of the Late Quaternary was as much as estimated by Fairbanks (1989) who analysed submerged coral terraces on Barbados (i.e. 100-120m) then this would give core CD38-10 a glacial water depth of about 150m and CD38-09 only about 30-50m. The drop in sea-level would expose a large area of freshly-deposited marine sediments along the Peru coast and cores CD38-09 and CD38-10 would be sites for increased terrigenous input of a preferentially clay-depleted composition during glacial periods.

Rosato and Kulm (1981) carried out factor analysis on the clay mineralogy of surface sediments from the Nazca plate and concluded that various environments of terrigenous-sediment deposition existed, whose spatial distribution could be characterised by the degree of mixing between two continental-factor assemblages and an oceanic-factor assemblage. More detailed examination of the clay mineral assemblages on either side of the Peru-Chile Trench was undertaken by Scheidegger and Krissek (1983) who concluded that the trench was "an imposing physiographic barrier to the seaward near-bottom advection of suspended particulates". This limits the influence of hemipelagic sedimentation to the relatively narrow continental margin and therefore, on the seaward side of the trench the deposition of terrigenous material is dominated by aeolian (rather than fluvial) transport.

It is highly probable, therefore, that the Peru-Chile Trench has a very strong influence on the differences between cores CD38-11 and CD38-03 (located on the continental slope) and CD38-02 (located on the seaward side of the trench) both in the volume (Al and Si_{terr} MAR fluxes) and in the composition (Fe/Al, K/Al and Zr/Rb) of the terrigenous material being deposited at each site.

Sediment redox potential

Both iron (Fe) and manganese (Mn) can be incorporated into marine sediments by a variety of pathways. Initial introduction to the ocean from a terrigenous source can be fluvial (Sholkovitz, 1978; Martin and Whitfield, 1983), aeolian (Hodge *et al.*, 1978) or from hydrothermal/volcanic activity (Klinkhammer *et al.*, 1985). Deposition of these two redox-sensitive metals can occur by either direct clay mineral accumulation or, after desorption from clays in sea-water, the dissolved metals are re-adsorbed by biogenic and faecal particles or form oxyhydroxide coatings on particle surfaces (Shimmield and Pedersen, 1990). Patience (1992) states that these latter

methods of Fe and Mn accumulation in continental margin sediments are quantitatively less important relative to the input from terrigenous clay minerals. However, the latter Fe- and Mn-oxyhydroxide formation is sensitive to the redox potential of the sediments and surrounding pore-waters and has, therefore, been the focus of attention for many marine geochemical studies (e.g. Calvert and Price, 1977; Heath and Lyle, 1981; Graybeal and Heath, 1984; Thomson *et al.*, 1990).

The complex chemical processes between dissolved and particulate Fe and Mn under oxic or reduced conditions have been extensively reviewed in Shimmield and Pedersen (1990) and involve the following redox-controlled cyclic process. The oxyhydroxide minerals are stable in surface, oxic sediments and upon burial into a reduced-sediment zone, the metals are preferentially reduced to their dissolved-phase within the pore-waters. Upward migration of these pore-waters, upon compaction of the sediment, transports the metals back into the oxic-sediment zone and reprecipitation of solid-phase oxyhydroxide minerals occurs.

This natural, recycling process results in an enrichment in surficial sediments of solid-phase Mn and Fe, which decreases with depth across the redox boundary layer, and the pore-water concentrations of the dissolved metals display the opposite profile (Lynn and Bonatti, 1965). The driving forces for such cyclic processes are the continuous accumulation of fresh sediments and the diagenetic breakdown of organic matter (Patience, 1992). Therefore, the controlling factors on the extent of surface Fe and Mn enrichment are the sediment accumulation rate and the input flux of organic matter.

The data from the six cores on the Peru margin show a depletion of both average Fe/Al and Mn/Al ratios, relative to the average deep-sea clay which must be the result of Turekian and Wedepohl (1961) analysing only surface (oxic) sediment samples compared with the down-core samples measured in this study. When interpreting surface redox processes, it is vital that the true sediment/water interface is sampled and therefore, only the down-core Fe/Al and Mn/Al profiles of the box cores CD38-02 and CD38-03 (Figs 7.3 and 7.4) can be used to study Fe and Mn redox recycling.

It was shown in the halogen/ C_{org} interpretation (6.2.3) that these two cores are accumulating under surface-oxic conditions and the Mn/Al and Fe/Al profiles display strong surface enrichments, which are up to three times that of the ratio for the reduced-sediments which lie below the redox boundary layer. In both cores, the depth of the enrichment is shallower for Mn/Al compared to Fe/Al indicating that, although the processes of Fe and Mn redox-cycling are essentially similar for the two metals,

they do occur at slightly different Eh levels (Shimmield and Pedersen, 1990). There are also oxic-layer depth differences between the two cores (shallower for CD38-03) that may be related to different rates of sediment accumulation and/or organic matter flux between the Nazca ridge site and the continental slope site.

The Fe/Al enrichment in both cores (Fig. 7.3) displays a maximum which is below the actual sediment/water interface (at about 12cm in CD38-02 and 3cm in CD38-03) and this can be interpreted as resulting from the fact that precipitation of Fe is occurring from both above (from fresh terrigenous deposition) and below (from upward migration of dissolved-Fe) the oxic zone, which produces the maximum concentration of solid-phase Fe (relative to Al) towards the base of the oxic layer rather than at the top of it.

7.3. THE BIOGENIC INPUT

7.3.1. Introduction

Marine sediments, deposited in a range of environments along the Peru continental margin, can contain a relatively high concentration of material which originated from a biogenic source. In terms of wt.%, the biogenic component measured by multi-component analysis (Table 5.1) constitutes an average of 25.8% in the piston core sediments of this study, and can be as high as 47%. The biogenic component is composed of:

- 1) organic matter from the decaying remains of phytoplankton, zooplankton and other marine life (as well as their faecal pellets) - represented by organic carbon (C_{org}),
- 2) skeletal remains of diatoms, radiolaria and silicoflagellates which consist of amorphous silica - represented by biogenic silica (bio.sil),
- 3) skeletal remains of foraminifera and coccoliths which consist of hard, carbonate shells - represented by calcium carbonate ($CaCO_3$),
- 4) fish remains which are highly resistant to decomposition, i.e. scales and bones.

The first three of the above biogenic components are present in most marine sediments and have often been interpreted in marine geochemical studies as tracers of oceanic palæo-productivity (Arrhenius, 1952; Molina-Cruz and Price, 1977; Müller and Suess, 1979). The actual concentrations of C_{org} , bio.sil and $CaCO_3$, and the relative concentrations to each other, can vary considerably and depend on the

complex interplay between a number of factors and, therefore, the spatial and temporal variation of the biogenic input to the sediment can be interpreted in terms of the environment of biogenic production, transport and deposition.

This section will present the biogenic component data from all six cores along the Peru margin as individual concentrations of C_{org} , bio.sil and $CaCO_3$ and as mass accumulation rate fluxes for the two cores with accurate age models. The interpretations of this data will then be given, with respect to the following environmental factors which control the composition and the volume of biogenic input to continental margin sediments.

- 1) Primary productivity in the overlying water column which, in turn, is dependant on the location and strength of the coastal upwelling zone off Peru (3.1.1).
- 2) Faunal variations of the marine biomass which can fluctuate on many time scales from seasonal up to glacial/interglacial periodicity.
- 3) Decomposition of organic matter and dissolution of silica and carbonate, as the biogenic material falls to the sea-floor and within the sediment column, which is dependant on ocean chemistry, redox environment and water mass circulation. This results in the recycling of most of the elements vital to further marine life and the preservation of only a small fraction of the original biogenic signal.
- 4) Dilution by non-biogenic material, which is principally the terrigenous component along the continental margin.

7.3.2. Analyses and results

The concentration of organic carbon, biogenic silica and calcium carbonate have been analytically determined using the techniques detailed in Appendices A.3, A.4 and A.5 (and $CaCO_3$ calculated using the equation in Appendix B.1), respectively.

Biogenic component concentrations

The biogenic component dataset, presented on a salt-free basis, is tabulated in full in Appendix C.12 and is summarised in Table 7.4, which lists the range, mean and surface values of C_{org} , bio.sil and $CaCO_3$ (all wt.%) for all six cores in this study.

		C _{org} (wt.%)	Bio.Sil (wt.%)	CaCO ₃ (wt.%)
CD38-09 (148m)	Range	1.59-8.26	3.10-25.82	0-6.40
	Mean	4.38	15.45	2.93
	Surface	6.70	16.85	2.16
CD38-10 (257m)	Range	0.79-11.92	0.48-28.61	0-25.71
	Mean	5.37	13.37	8.25
	Surface	9.21	9.38	10.58
CD38-02 (Box, 2530m)	Range	0.86-1.83	4.58-8.90	11.58-36.15
	Mean	1.20	6.53	24.75
	Surface	1.02	8.48	12.34
CD38-02 (2525m)	Range	0.82-2.67	3.52-9.83	0.60-37.54
	Mean	1.48	6.28	22.25
	Surface	1.49	9.54	16.84
CD38-11 (3835m)	Range	1.62-4.55	3.46-18.09	0-20.92
	Mean	3.31	10.59	5.42
	Surface	3.87	7.99	2.19
CD38-03 (Box, 4289m)	Range	1.46-2.48	11.97-17.86	0-0.94
	Mean	1.76	14.80	0.38
	Surface	1.72	17.86	0.04

Table 7.4. Range, mean and surface values of organic carbon, biogenic silica and calcium carbonate (all wt.%) in Peru margin cores.

There are a number of features of the data in Table 7.4, which will be fully interpreted in the following section (7.3.3).

- a) The mean C_{org} concentrations of the two near-shore, shallow-water cores (CD38-09 and CD38-10) are two to three times higher than those of the deeper-water cores.
- b) The Nazca ridge site (box and piston cores CD38-02) contains sediment with the largest mean and individual CaCO₃ concentrations of all the cores in this study.
- c) The deepest-water core at 4289m (CD38-03) contains negligible quantities of CaCO₃ but has a bio.sil content which is consistently above 10wt.% of the total sediment.

- d) All the sediments contain reasonable concentrations of bio.sil (> 3wt.%) except for within core CD38-10, which has a minimum of only 0.5wt.% (due to strong terrigenous dilution).

Included in Table 7.4 are the surface-sediment biogenic concentrations but, as was explained in the halogen section (6.2.2), care must be taken in the interpretation of this surface data because it is only the two box cores which are from true surface samples. The piston core surface samples are actually from up to 10cm depth in the core but they may still be useful in the interpretation of spatial variance of the three biogenic components along the Peru margin.

Figure 7.10 illustrates this variation by graphically representing the water depth of each core site plotted against the surface wt.% of the biogenic components. It can be seen that the maximum surface sediment concentrations of C_{org} are found in the shallow-water sites (CD38-09 and CD38-10), that the surface bio.sil concentration is high in both the shallowest (CD38-09) and the deepest (CD38-03) sites and that the intermediate water core (CD38-02) contains the highest concentration of surface $CaCO_3$. These surface-sediment concentrations are similar to the overall mean sediment contents of the Peru cores, however, none of the plots (Fig. 7.10) display a simple concentration pattern with respect to the depth of water through which the C_{org} , bio.sil and $CaCO_3$ biogenic-remains have fallen before reaching the accumulating sediment. This implies that, as well as water depth, there are a number of other factors influencing the spatial pattern of biogenic input to marine sediments.

The down-core, temporal variation of the total biogenic input was demonstrated by the MCA results (Figs 5.6 to 5.9) for the four piston cores. Here, the individual down-core profiles of C_{org} , bio.sil and $CaCO_3$ are illustrated for all six cores in Figs 7.11, 7.12 and 7.13 respectively. Each of the biogenic components, when expressed as a wt.%, is susceptible to down-core fluctuations in its concentration as a result of dilution effects either from another of the biogenic components or from a non-biogenic component. Therefore, it will be impossible to be certain of any environmental interpretations made from the profiles in Figs 7.11 to 7.13. However, the following features are of interest and the biological/oceanographic factors controlling them need to be examined (7.3.3).

- a) Of the two near-shore cores, CD38-10 demonstrates a possible down-core correlation between the three biogenic components; characterised by low concentrations at 30, 80-110 and 500cm and decreasing concentrations with

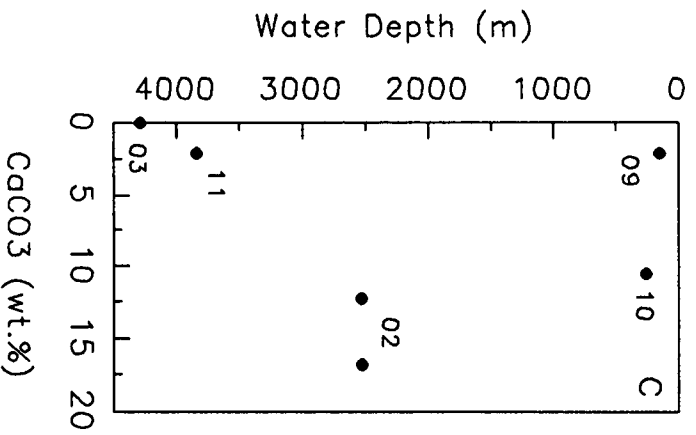
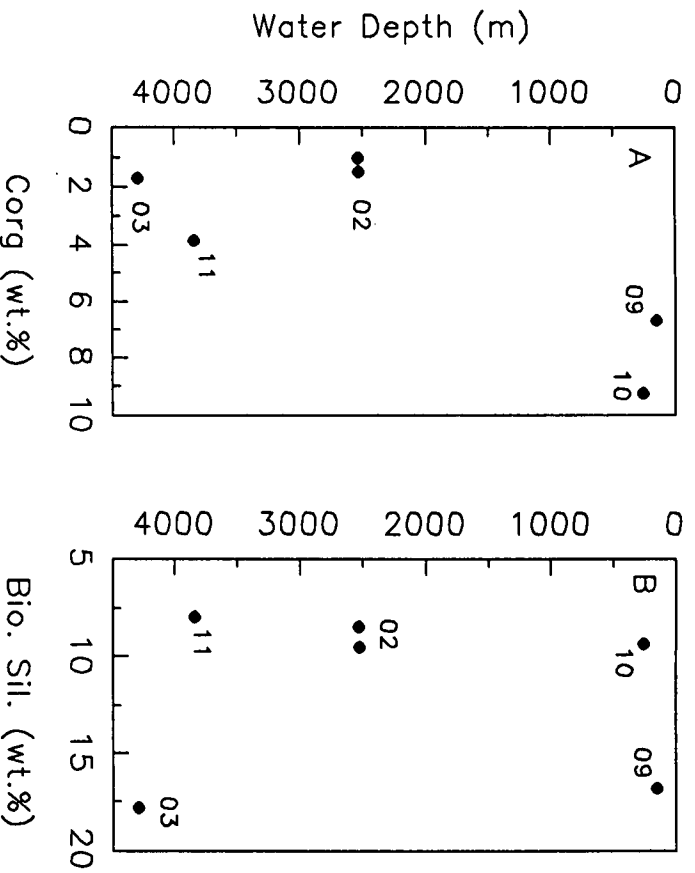


Figure 7.10. Core site water depth against the concentrations of A) organic carbon, B) biogenic silica and C) calcium carbonate of the surface samples from cores CD38-09, CD38-10, CD38-02 (piston and box), CD38-11 and CD38-03 (box).

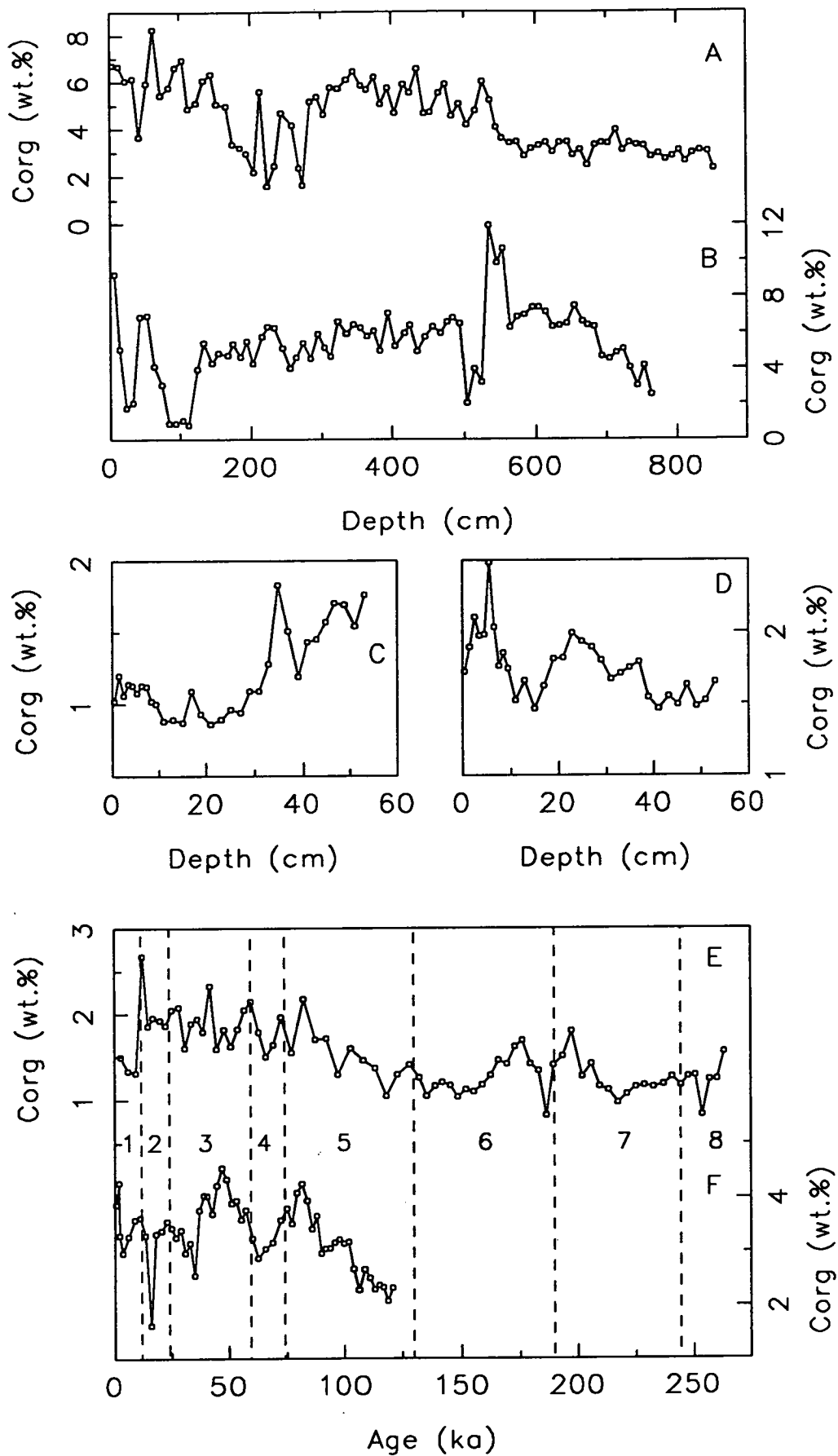


Figure 7.11. Organic carbon (wt.%) down-core profiles: A) CD38-09, B) CD38-10, C) box core CD38-02, D) box core CD38-03, E) CD38-02 and F) CD38-11.

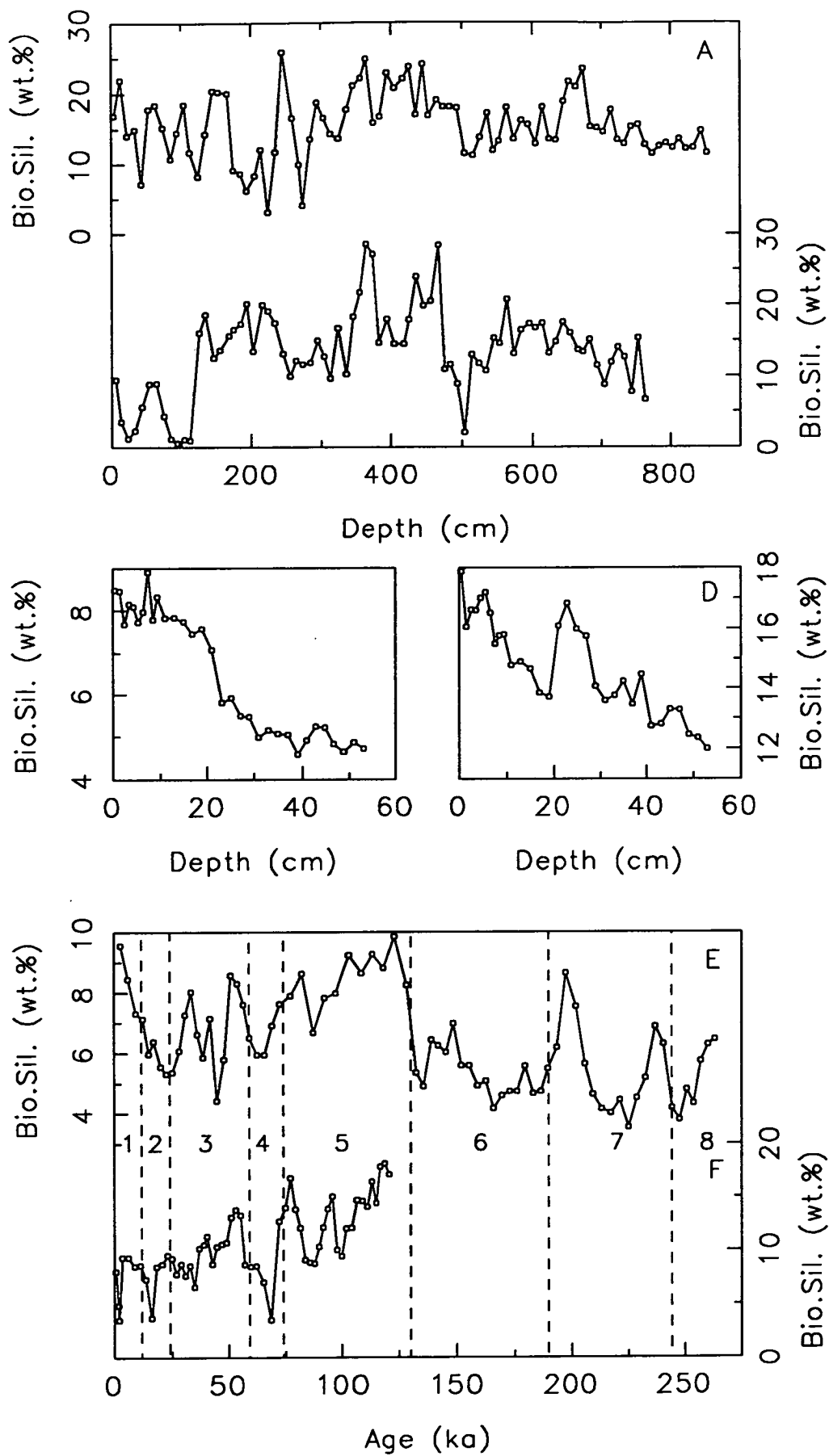


Figure 7.12. Biogenic silica (wt.%) down-core profiles: A) CD38-09, B) CD38-10, C) box core CD38-02, D) box core CD38-03, E) CD38-02 and F) CD38-11.

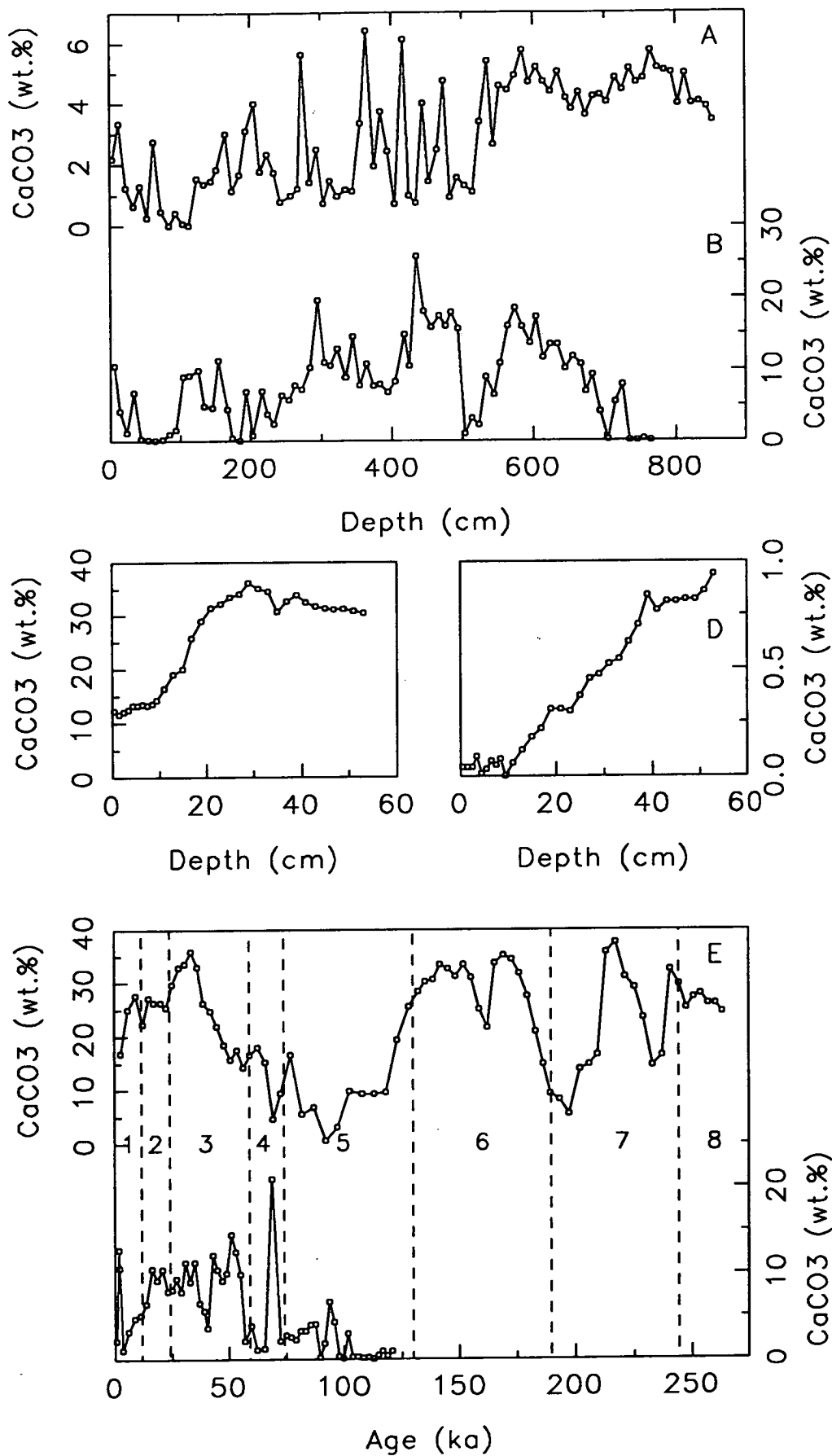


Figure 7.13. Calcium carbonate (wt.%) down-core profiles: A) CD38-09, B) CD38-10, C) box core CD38-02, D) box core CD38-03, E) CD38-02 and F) CD38-11.

- depth from 550cm to the base of the core (most pronounced in C_{org} and CaCO_3). In contrast, CD38-09 demonstrates very little correlation between C_{org} , bio.sil and CaCO_3 and, in fact, by comparing the average concentrations both above and below a transition zone about 530cm, it can be seen that the C_{org} and CaCO_3 contents in CD38-09 are possibly inversely correlated.
- b) In the box cores, there is a noticeable inverse relationship between the bio.sil and CaCO_3 concentrations, with the former showing a generally decreasing trend with depth whilst the latter increases. The reason for this variation is unlikely to be simply caused by dilution because core CD38-02 has a dramatically higher CaCO_3 content (and slightly lower bio.sil) compared with CD38-03.
 - c) More accurate temporal fluctuation interpretations can be made for piston cores CD38-02 and CD38-11, which have their biogenic concentrations plotted against age (ka) in Figs 7.11 to 7.13. The general trend of decreasing C_{org} contents with increasing sediment age, due to decomposition of organic matter upon burial, does not show a smooth exponential profile in cores CD38-02 or CD38-11 but is distorted by peaks and troughs. These show no obvious glacial/interglacial pattern except for the general increase of C_{org} (wt.%) from the earlier to the later parts of interglacial stage 5.
 - d) The bio.sil and CaCO_3 signals in core CD38-02 are, at first sight, inversely related with relatively higher bio.sil during interglacial stages 1, 3, 5 and 7 and higher CaCO_3 during glacial stages 2, 6 and 8. However, closer examination of the down-core profiles (Figs 7.12 and 7.13) shows that the magnitude and timing of each of the glacial/interglacial cycles of bio.sil and CaCO_3 are not exactly similar. This indicates that the concentration of the biogenic components are controlled by factors which affect the amplitude of variation and the relative lag of each individual component to different degrees, which may, or may not, be related to global climatic changes.
 - e) Core CD38-11 contains approximately half the CaCO_3 , but double the bio.sil, content when compared with CD38-02. Although there are spatial differences in the biogenic input to the sediment at these two sites (Fig. 7.10), the temporal variations shown within CD38-11 are coincident with those in CD38-02, with generally higher interglacial bio.sil and glacial CaCO_3 .
 - f) The ash band found at 186ka in core CD38-02 (7.2.3) is characterised by a low C_{org} concentration but by normal levels of bio.sil and CaCO_3 . In contrast, the turbidite zone in core CD38-11 at about 2-3ka contains an enrichment

(compared with the surrounding sediments) of C_{org} and $CaCO_3$ but a depletion of bio.sil.

Biogenic component fluxes

The problem of dilution which affects the above down-core profiles of the biogenic components expressed as a wt.%, can be removed by the calculation of mass accumulation rate (MAR) fluxes. As was the case in the terrigenous input section (7.2), the MAR fluxes of C_{org} , bio.sil and $CaCO_3$ have only be calculated for cores CD38-02 and CD38-11. The fluxes have been calculated using Eqn 7.2, and it must be remembered that, because of the possible errors involved (7.2.2), MAR fluxes are not the perfect solution to the representation of the true biogenic flux input.

The biogenic flux data is presented in full in Appendix C.19 and summarised below in Table 7.5, giving the range and mean values of C_{org} , bio.sil and $CaCO_3$ MAR fluxes. The average fluxes for four piston cores from the Eastern Equatorial Pacific (Patience, 1992) are also given in Table 7.5, for comparison with the Peru margin cores.

(MAR = mg cm ⁻² kyr ⁻¹)		C _{org} MAR	Bio.Sil MAR	CaCO ₃ MAR
CD38-02	Range	11.8-59.0	75.0-179.8	7.0-781.7
(2525m)	Mean	29.2	119.7	457.1
CD38-11	Range	57.3-127.2	94.3-530.6	0-586.0
(3835m)	Mean	91.4	295.7	154.5
Patience (1992)		60	133	1948

Table 7.5. Biogenic component mass accumulation rate fluxes (all in mg cm⁻² kyr⁻¹) for the Peru margin cores CD38-02 and CD38-11 and an average for four cores from the Eastern Equatorial Pacific (Patience, 1992).

From the data in Table 7.5, it can be seen that both CD38-02 and CD38-11 display large fluctuations in the flux of all three of the biogenic component inputs, with mean values which are higher in C_{org} and bio.sil for CD38-11 but higher in $CaCO_3$ for CD38-02. Comparisons between the Peru margin and E. Equatorial Pacific (Patience, 1992) show rough agreement for the flux of organic carbon to the sediments but contrasting fluxes for the other two biogenic components, with core CD38-11 receiving over double the flux of bio.sil and the mean $CaCO_3$ flux of the E. Equatorial Pacific being four times that of core CD38-02.

The down-core profiles of the above biogenic MAR fluxes plotted against age (ka) are illustrated in Fig. 7.14 for cores CD38-02 and CD38-11. The C_{org} MAR at the Nazca ridge site (CD38-02) is relatively stable during stages 6, 7 and 8 at about 20-30 $mg\ cm^{-2}\ kyr^{-1}$ followed by a drop at the beginning of interglacial stage 5 to only 12 $mg\ cm^{-2}\ kyr^{-1}$, which steadily rises up to a maximum of 60 $mg\ cm^{-2}\ kyr^{-1}$ during glacial stage 2. This glacial maximum, however, is not seen in the C_{org} MAR flux of the Peru continental slope (CD38-11) where maxima are seen during interglacial stages 3 and 5.

The bio.sil MAR profiles also contrast between the two cores, where from stage 5 up to the present Holocene, core CD38-02 displays a generally increasing trend and core CD38-11, a generally decreasing trend. The actual pattern of $CaCO_3$ variation has not been affected by the change from wt.% to MAR fluxes (compare Figs 7.13 and 7.14) especially for CD38-02. The glacial/interglacial cyclicity of relatively higher glacial flux to the sediment of $CaCO_3$ shells (complicated by the peaks during stages 3 and 7) gives rise to the question of whether this signal is produced by surface-water productivity variations or by preservation changes (dissolution effects) or by a complex interplay of both environmental factors (7.3.3).

7.3.3. Biogenic environmental interpretations

This section will discuss the biological and oceanographic environmental controls on the deposition of biogenic material along the Peru continental margin by interpretation of the geochemical data described above (7.3.2). Since the concentration of each component is critically dependant on the complex (and ever changing) interactions of the four factors described in the introduction above (7.3.1), this discussion section cannot be easily split into separate sections which will each interpret one particular environmental condition (as was done for 7.2.3). Therefore, the organic carbon, biogenic silica and calcium carbonate geochemical data will each be interpreted in turn and then, in the conclusions the overall palæo-oceanographic history of the Peru margin will be discussed.

Organic carbon

This thesis has already shown that the upwelling movement of nutrient-rich water (which replaces the nutrient-poor surface water pushed off-shore by Ekman transport) helps to sustain high levels of biological productivity, resulting in an

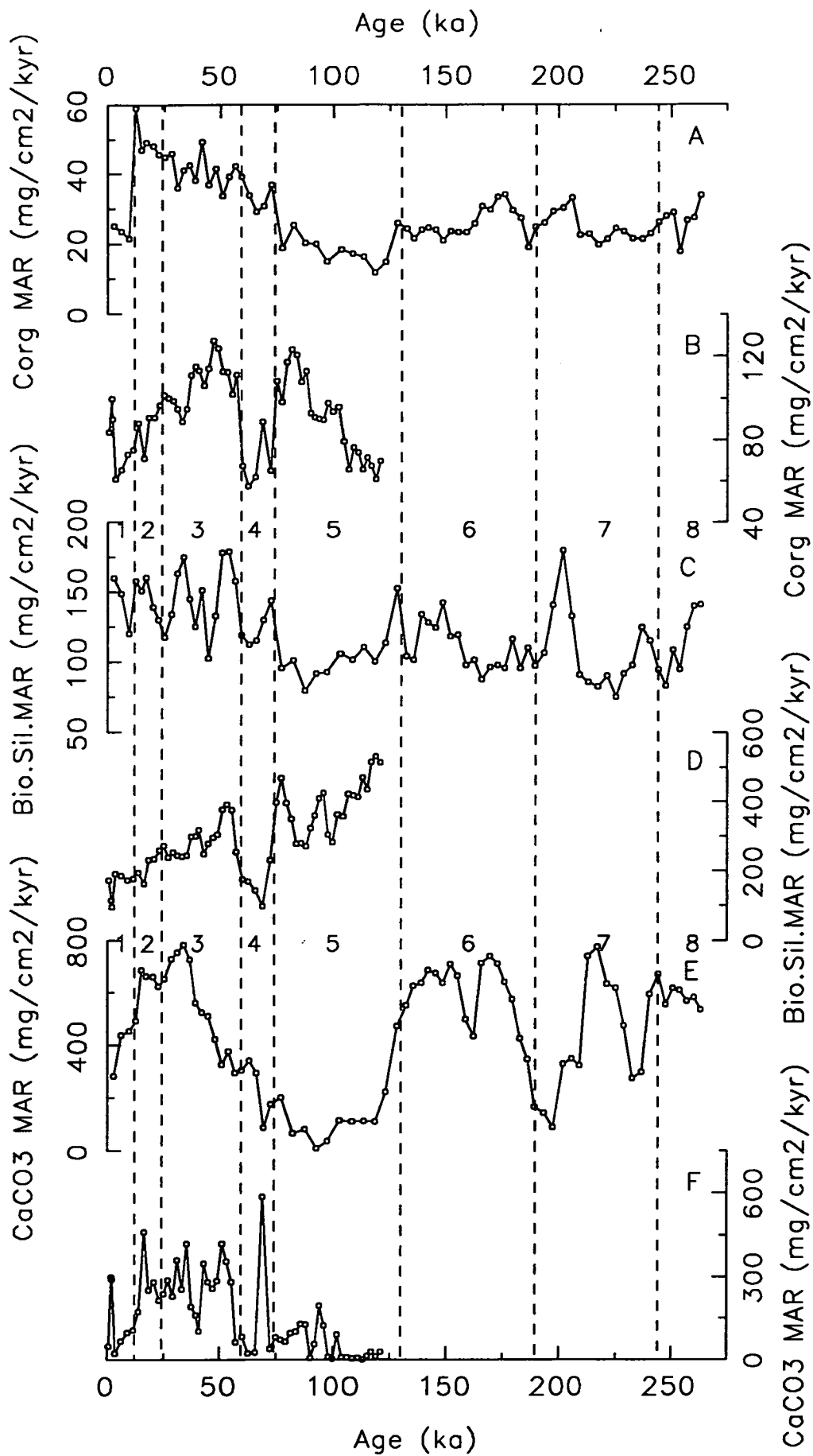


Figure 7.14. Organic carbon, biogenic silica and calcium carbonate flux ($\text{mg cm}^{-2} \text{kyr}^{-1}$) profiles against age for cores CD38-02 (A, C and E) and CD38-11 (B, D and F).

anomalously high flux of organic matter in the water column and high concentrations of C_{org} in the sediment below (Chapter 3; Reimers and Suess, 1983A; Henrichs and Farrington, 1984).

Thus, the productivity control of coastal upwelling is the initial environmental factor which influences the concentrations of C_{org} measured in these marine sediments. Its dominance over other possible factors, in terms of the spatial variance of the C_{org} concentrations along the Peru margin, is supported by the mean and surface data for the sediments in this study (Table 7.4) which shows higher C_{org} contents in the two near-shore core sites (CD38-09 and CD38-10) which are located within the main coastal upwelling zone, compared to the other sites which occur either seaward or at a more southerly location from the upwelling zone.

The plot of water depth against C_{org} (Fig. 7.10) which indicates a decrease in the C_{org} concentration of surface sediments with increasing water depth is, therefore, showing the near-shore proximity to the coastal upwelling zone rather than a pattern of equal C_{org} surface-water levels with the degree of organic matter decomposition dependant on the depth of water through which it falls.

This simple spatial control on the depositional differences in the input of organic matter between the core sites does not explain the temporal variation of C_{org} (wt.%) seen within each core (Fig. 7.11). If a particular sediment site was receiving a constant flux of organic matter over a period of time (and all the other component inputs remained constant as well) then the level of organic matter (measured as C_{org}) would not be at a constant concentration but would exponentially decrease with depth/age due to the natural decomposition of the organic matter upon burial (Reimers and Suess, 1983B; Calvert, 1987). Of course, this ideal scenario is unlikely to exist in the marine environment due to one or more of the following factors:

- 1) changes in the surface-water productivity levels on a range of time scales from seasonal to glacial/interglacial periodicity,
- 2) variations in the degree of organic matter recycling in the water column,
- 3) changes in the strength of the dilution effects from one or more components, mainly terrigenous and other biogenic inputs,
- 4) differences in the redox environment at the sediment/water interface and the depth of the oxic layer within the sediment column,
- 5) variations in the sediment accumulation rate over time.

The down-core profiles of C_{org} for the six cores all show a large degree of variation over time; very little of which can be easily explained by only one of the above and most of which is open to the question of a productivity and/or preservation control (Shimmield, 1992).

In core CD38-10, the prominent depletions of C_{org} coincide exactly with the zones of phosphorite concentration (4.3.3), increased terrigenous input (7.2.3) and coarser sediment grain-size (Fig. 7.7). It is possible that this dilution control has occurred because of a decrease in the organic matter input relative to the authigenic and terrigenous component inputs to the sediment. However, it is far more likely that these phosphorite-rich zones correspond to periods of erosion of the sediment column by bottom-water currents, which have resuspended the organic matter (along with the fine-grained clays) and swept it down the continental slope to be redeposited at greater water depths. This theory is supported Walsh (1981) who studied the influence of modern-day Peru margin bottom-water currents on C_{org} transport in relation to the Peruvian anchovy fishery, and can also explain the broad band of low C_{org} contents found in core CD38-09 between 190 and 270cm.

The preservation and accumulation of C_{org} was originally thought to have been strongly influenced by the redox environment of deposition, which allowed for faster decomposition of organic matter within oxic sediments compared with suboxic or anoxic sediments due to the differing pathways of degradation utilised (following the equations set out in Froelich *et al.*, 1979, Emerson, 1985). However, recent work has shown that organic matter decomposes as readily under anoxic as oxic conditions as a result of bacterial activity (Canfield, 1989; Pedersen and Calvert, 1990; Lee, 1992; Pedersen *et al.*, 1992).

The increase in C_{org} concentration seen in core CD38-09 from about 3wt.% below 530cm to nearly 6wt.% above this zone may, a few years ago, have been interpreted as relating to the movement of this core site from above the oxygen minimum zone (OMZ) during a glacial stage to within the OMZ as the sea-level rose during an interglacial stage, producing increased preservation of organic matter under stronger anoxic conditions (Emerson, 1985). However, this cannot be the correct explanation because it was shown by using the halogen/ C_{org} ratios (6.2.3) that the sediment in CD38-09 has accumulated under continuous suboxic/anoxic conditions and also it is now generally believed that the OMZ plays only a small part in the preferential preservation of a high C_{org} concentration record. In fact the opposite occurs, with the high rates of primary productivity in the surface waters off Peru producing the low benthic oxygen levels (Pedersen and Calvert, 1990).

The C_{org} biogenic component input is therefore dominantly controlled by the rate of primary productivity (Pedersen *et al.*, 1992) along the Peru continental margin and, in order to avoid the effects of non-biogenic dilution, the C_{org} MAR flux data can be interpreted to study possible palæo-productivity signals.

The average C_{org} MAR flux at CD38-11 is approximately three times that of CD38-02 (Table 7.5) simply because of the position of the upwelling zone with respect to the two core sites. If it had been possible to calculate MAR flux data for cores CD38-09 and CD38-10, then the C_{org} MAR would probably have needed to be expressed as $\text{g cm}^{-2} \text{ kyr}^{-1}$ instead of only $\text{mg cm}^{-2} \text{ kyr}^{-1}$ (Henrichs and Farrington, 1984).

Sarnthein *et al.* (1988) observed a marked increase in biological productivity at low- and mid-latitude upwelling zones during the last glacial maximum. This conforms to the hypothesis that polar ice-sheet growth reduced the latitudinal-size of the atmospheric pressure cells which increased the wind strength during glacial periods, causing more coastal and equatorial upwelling and thereby increasing the productivity of the marine biomass (Müller *et al.*, 1983; Pedersen, 1983; Lyle *et al.*, 1988). The C_{org} MAR flux profile of CD38-02 (Fig. 7.14) does possibly show this glacial/interglacial pattern with relatively high C_{org} input during glacial stages 2, 4 and 6 compared with the interglacial stages 1 and 5. However, core CD38-11 does not conform to the above hypothesis since it displays considerably higher C_{org} MAR flux during stages 3 and 5 compared with stage 4. It is quite possible that the coastal upwelling off Peru has varied in its strength in time with the global climatic changes. However, these two core sites have received contrasting C_{org} flux inputs over time, which is possibly due to the movement of the main upwelling zone along-shore and/or off-shore caused by sea-level and wind strength variations over glacial/interglacial periods.

The flux of biogenic barium to the sediment has already been used (for core CD38-02) to calculate a palæo-productivity signal of new production (P_{new}) levels in the surface-waters during the Late Quaternary (6.3.4, Dymond *et al.*, 1992). If the flux of organic carbon to the sediment can be used to estimate the levels of ocean productivity in the past, does it compare or contrast with the Ba calculations? In order to answer this question, the level of surface productivity must firstly be calculated and this can be done using the formula shown in Eqn 7.3, which is taken from the work by Müller and Suess (1979).

The relationship between C_{org} and palæo-productivity (R) was thought to be dependant on the sediment accumulation rate, sediment porosity and dry bulk density (Müller and Suess, 1979) and although future studies tried to improve the equation (e.g. incorporation of a water depth factor, Sarnthein *et al.*, 1987) the original equation is still used to calculate palæo-productivity for cores CD38-02 and CD38-11.

Equation 7.3. Palæo-productivity from C_{org} concentrations (Müller and Suess, 1979)

$$R = [C_{\text{org}} \times fs \times (1 - \phi)] / [0.0030 \times S^{0.30}]$$

where, R = Palæo-productivity ($\text{gC m}^{-2} \text{ yr}^{-1}$),
 C_{org} = organic carbon (wt.%),
 fs = sediment density (g cm^{-2}),
 ϕ = sediment porosity (% water / 100),
 S = sediment accumulation rate (cm kyr^{-1}).

The results of this palæo-productivity calculation are presented in Appendix C.19, and Fig. 7.15 displays the down-core profiles of R against age for both cores. It is apparent from the results that, even once the differences in sedimentation rate and the physical properties of the sediments between the two cores sites (Chapter 2) have been taken into account, core CD38-11 still contains a higher palæo-productivity record compared with core CD38-02. However, neither cores achieve the levels of productivity that were measured by Müller and Suess (1979) at two sites on the Peru margin ($330 \text{ gC m}^{-2} \text{ yr}^{-1}$) but this is simply due to the fact that these levels were measured at shallow water sites within the coastal upwelling zone, whereas cores CD38-11 and CD38-02 are located at some distance from this very high productivity zone.

The down-core profiles of palæo-productivity (Fig. 7.15) show no obvious glacial/interglacial pattern as would be expected if the high glacial productivity scenario of Sarnthein *et al.* (1988) was operating. However, the limitations of the calculation of R must be remembered, i.e. there is no mention in Eqn 7.3 of the depth/age of each sample which therefore ignores the effects of the natural decomposition of organic matter upon burial. The only similarity between the two core sites is the shape of the profile during interglacial stage 5, which displays a generally increasing level of R from 120ka up to 80ka, followed by a sharp drop over the transition from stage 5 into stage 4. This implies that after glacial stage 6, the productivity of the surface waters along the Peru margin dropped to a minimum and

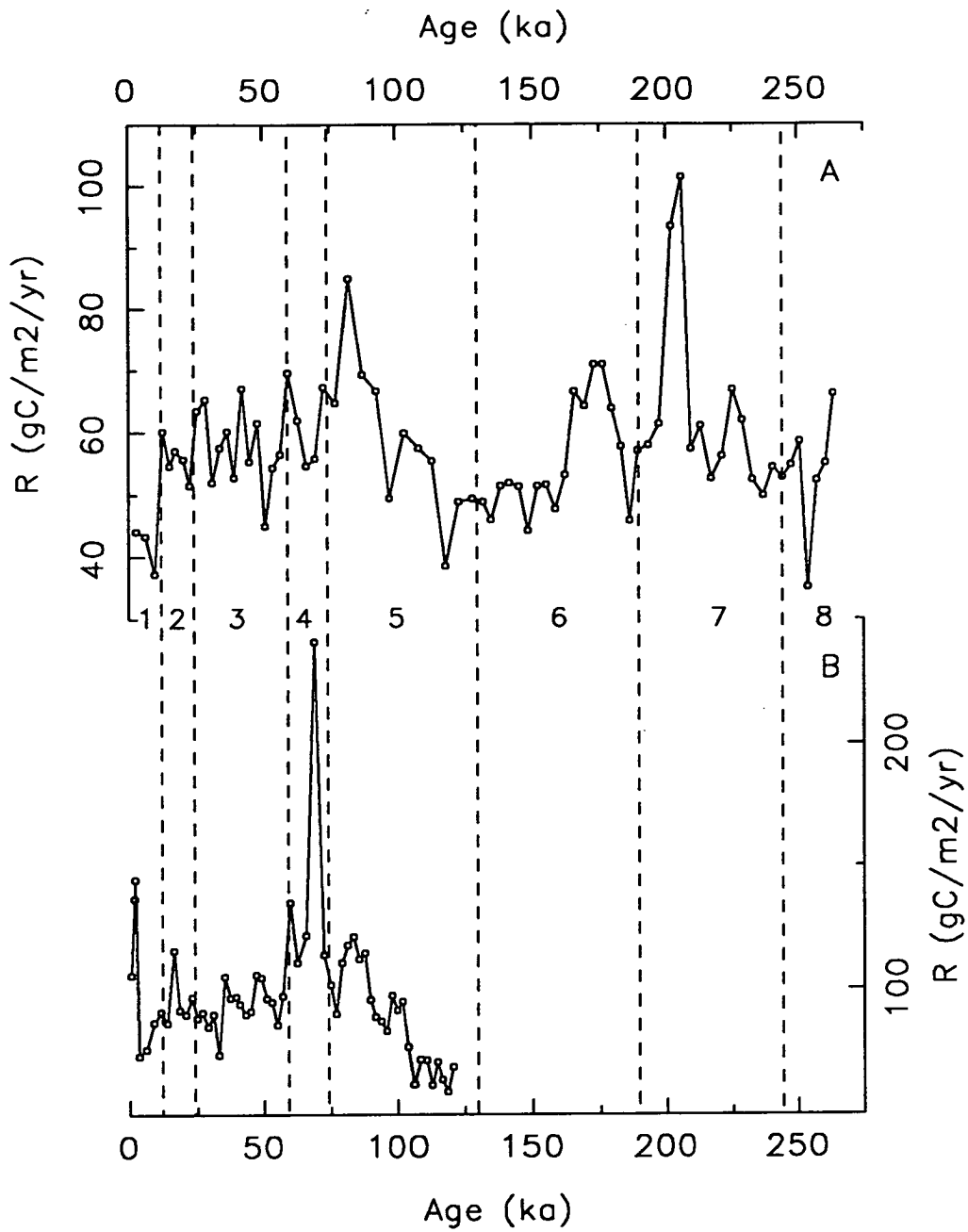


Figure 7.15. Palaeo-productivity measurements calculated from Equation 7.3 (Müller and Suess, 1979) for cores CD38-02 (A) and CD38-11 (B).

then gradually (as the warm, interglacial stage continued) the productivity increased until it reached maximum levels, after which the productivity levels crashed with the onset of glacial climatic conditions. Perhaps the same scenario is occurring at both core sites during interglacial stage 1, which sees a drop from high, glacial stage 2 levels and shows signs of the start of an increase up to the present-day productivity levels.

The palæo-productivity profile of CD38-02 (Fig. 7.15) can be compared with the P_{new} profile calculated from the Ba content of the same core (Fig. 6.10.C). The latter productivity record is a signal of new production in the water column, i.e. the amount of organic matter falling out of the euphotic zone (Dymond *et al.*, 1992). This is perhaps the reason why the levels of P_{new} are considerably lower than those of R, which is an indicator of the surface-water levels of primary productivity. However, the two profiles do not really match in terms of the timing and magnitude of variations in productivity, except perhaps for the peak during stage 7 (about 200ka) and the trough during stage 4 (about 65ka). The reasons for the differences must be either due to the errors involved in the two palæo-productivity calculations (Eqns 6.2 and 7.3) or, more likely, caused by the contrasting geochemical behaviours of C_{org} and Ba upon burial in the sediment column, i.e. the degradation of the former compared with the residual nature of the latter.

Biogenic Silica

The planktonic organisms which form their skeletons from silica (diatoms, radiolaria and silicoflagellates; Diester-Haass, 1988) are primary producers and their productivity should increase dramatically in fertile, upwelling areas (Chapter 3). If the record of their existence in marine sediments as biogenic silica, was controlled purely by the level of primary productivity in the overlying surface-waters, then the pattern of highest productivity above core sites CD38-09 and CD38-10 compared with the other sites in this study would be expected to show a similar surface-sediment wt.% bio.sil distribution to the one seen for organic carbon. However, in the plot of water depth against bio.sil (Fig. 7.10) the cores with the highest concentration are CD38-09 and CD38-03 and therefore the spatial distribution of bio.sil along the Peru margin must be controlled by more than one of the environmental factors listed in the introduction to this biogenic input section (7.3.1).

Sea-water and interstitial pore-waters are undersaturated with respect to silica (Wollast, 1974) and therefore the siliceous parts of marine organisms will be susceptible to dissolution as soon as they die. This recycles most of the silica within the euphotic zone (Calvert, 1968; Berger, 1976) as dissolved silicate; an essential nutrient for marine life. Murray (1987) estimated that, in the Pacific, only 8-11% of the biogenic silica which actually escapes from the euphotic zone survives to be incorporated into marine sediments. This dissolution means that under normal primary productivity levels all, or nearly all, the bio.sil is dissolved before reaching the sediment column (Diester-Haass, 1988) and so the very high mean bio.sil concentrations measured in the Peru cores (> 6wt.%, Table 7.4) can only be produced as a result of high productivity from coastal upwelling.

Other environmental factors to be considered include dilution effects by the CaCO₃ content of the sediment. This is probably dominating the variation in the down-core wt.% bio.sil profile of the box and piston cores CD38-02 (Fig. 7.12) but is definitely absent in the box core CD38-03, resulting in the high bio.sil concentration at this deep-water site (Table 7.4).

Dilution by terrigenous material is possibly the cause of the extreme fluctuations in the concentration of bio.sil seen in core CD38-10 (Fig. 7.12) which ranges from virtually zero up to nearly 30wt.% of the total sediment. The erosion and winnowing which explained the very low C_{org} contents at certain horizons in this core has also produced the lowest bio.sil concentrations. The high energy environment of strong bottom-water currents along the continental shelf will tend to fragment the fragile diatom and radiolarian skeletons with the result that a greater surface area of bio.sil will be exposed to the undersaturated waters and will cause greater dissolution (Patience, 1992).

However, despite these environmental influences affecting the original bio.sil signal, many authors have considered the bio.sil concentration in marine sediments to be a rough reflection of the levels of primary productivity and upwelling (e.g. Molina-Cruz and Price, 1977; Broecker and Peng, 1982; Leinen *et al.*, 1986). As for the C_{org} discussion above, it is easier to remove the influence of dilution caused by other sediment components and study the MAR flux of bio.sil, when interpreting the possible palæo-productivity signal.

The weight of bio.sil input which has been deposited at sites CD38-02 and CD38-11 is, on average, four to five times that of C_{org} (Table 7.5) and its down-core profile (Fig. 7.14) has varied considerably over (although not exactly in phase with) the interglacial/glacial cycles of the Late Quaternary. Generally higher bio.sil fluxes

are associated with the interglacial periods (stages 3 and 7 in CD38-02 and stages 3 and 5 in CD38-11) but the timing and magnitude of these peaks are not consistent. If this is a purely productivity controlled signal then the bio.sil MAR broadly agrees with the Ba flux data (6.3.4) and implies that the palæo-productivity signals from bio.sil and C_{org} are perhaps representing relative changes in the faunal composition of the marine biomass over time periods which are longer than just a simple seasonal fluctuation (Lyle *et al.*, 1988; Rea *et al.*, 1991). If, for example, the organic matter flux resulting from a predominantly diatom-based plankton biomass is considerably different from that of a predominantly foram-based biomass than the signal recorded in the sediment column would display contrasting bio.sil and C_{org} MAR flux patterns (Patience, 1992).

Some marine sediment studies have examined the varying species-assemblage of the diatoms found in coastal sediments as a function of the levels of primary productivity and, hence, the strength of coastal upwelling (Abrantes, 1988; Schrader and Sorkness, 1991; Schrader, 1992). However, the changes in diatom assemblage over time are not reflected in the overall total bio.sil abundance measured in a sediment (pers. comm., H. Schrader, 1991) and therefore the results found by the above authors in terms of the palæo-productivity of the Peru and other upwelling ecosystems can not be directly compared with the bio.sil wt.% and MAR flux records presented in this thesis.

Calcium Carbonate

The carbonate shell-remains of foraminifera and coccoliths which are incorporated into marine sediments, have been measured in many cores as variations in the wt.% $CaCO_3$ which form cycles relating to the glacial/interglacial periodicity of the Late Quaternary (e.g. Pisias and Rea, 1988; Farrell and Prell, 1989, 1991; Rea *et al.*, 1991; Patience, 1992). Originally a relationship between the $CaCO_3$ content of oceanic sediments and climate was established by Murray and Philippi (1908) and this theory was supported by Arrhenius (1952) who concluded that Pleistocene climate changes increased the glacial trade winds and upwelling strength which was recorded by higher glacial $CaCO_3$ concentrations. It is possible that, as with the C_{org} and bio.sil contents, the $CaCO_3$ input to a sediment is controlled by variations of palæo-productivity but there is also the environmental factors of faunal variations, dilution effects from the terrigenous detritus and dissolution of the carbonate shells within the water column to be considered.

Of the above, the latter is now generally accepted as being the most important factor in the variation of CaCO_3 content measured in marine sediments. The dissolution of CaCO_3 is thoroughly reviewed by Volat *et al.* (1980) but before the carbonate record of the Peru margin cores can be interpreted, the following brief explanation of carbonate dissolution is required.

Berger (1971) proposed a carbonate-solution ocean model which requires an equilibrium between the amount of carbonate being supplied to the oceans (from terrestrial weathering) and the amount taken out by organisms. If the latter exceeds the former, dissolution of carbonate is required to return the dissolved carbonate levels to equilibrium. Dissolution of CaCO_3 generally increases with water depth due to the thermodynamic effects at lower temperature and higher hydrostatic pressure which both increase the solubility of carbonate in water.

Therefore a simple model of carbonate dissolution can be envisaged within which a number of depth-boundaries have been defined. Dissolution increases dramatically below the "lysocline" (Berger, 1971), a depth defined as where the *in situ* carbonate ion concentration of the water is equal to the saturation level (Broecker and Takahashi, 1978). Below the lysocline lies a transition zone within which the majority of all dissolution occurs, down to the "calcite critical depth" (CCrD, Farrell and Prell, 1989) which is the shallowest pelagic depth where the sediments contain <10wt.% CaCO_3 (Lisitzin and Peltelin, 1967). The actual depth at which sediments contain no CaCO_3 because the rate of dissolution equals the rate of deposition (Farrell and Prell, 1989) is termed the calcite compensation depth (CCD) and although this lies only slightly deeper than the CCrD, the two should not be confused.

The above theory of increasing dissolution with water depth can explain the contrasting mean and surface CaCO_3 concentrations measured in cores CD38-02, CD38-11 and CD38-03 (Table 7.4 and Fig. 7.10). Core CD38-02 at less than 2500m water depth must lie above or very close to the lysocline in order to receive its high carbonate input.* In contrast, core CD38-11 at 3835m lies towards the lower end of the transition zone, possibly at the CCrD, resulting in much lower CaCO_3 levels and core CD38-03 at 4289m lies on or below the CCD resulting in minimal carbonate

*It should be noted that the high terrigenous flux along a continental margin (7.2.3) will prevent the CaCO_3 concentration from achieving the levels (up to 90wt.%) measured in cores at similar water depths but away from a strong terrigenous source.

deposition (the less than 1% CaCO₃ measured in this core may just be the result of errors in the Ca/Al ratio used in the calculation of wt.% CaCO₃, Appendix B.1).

However, if the CaCO₃ concentration was controlled only by the above dissolution theory then it would be expected that the shallow-water core sites would contain the highest wt.% CaCO₃ content. The data in Table 7.4 and Figs 7.10 and 7.13 show that this is not the case and cores CD38-09 and CD38-10 are sites of lower CaCO₃ concentration than site CD38-02. There are a few possible reasons for this anomaly. Firstly, the low carbonate concentrations may just be the result of dilution by the strong terrigenous input in these near-shore sediments. There may also be a preferential winnowing effect on the foraminifera and coccolith shells, which means they are swept down the continental slope by bottom-water current activity. This is illustrated in core CD38-10 as the virtual lack of carbonate content within the phosphorite-rich horizons. One final explanation could be that the presence of the oxygen minimum zone, impinging on the continental shelf at water depths within which CD38-09 and CD38-10 are located, lowers the pH of the water which increases the solubility of carbonate and, therefore increases the carbonate dissolution at these very shallow water depths (Steens *et al.*, 1991).

Thus, the spatial variance of carbonate concentrations in the Peru margin sediments can be explained as a function of the water depth of each core site influencing the degree of dissolution affecting the original productivity levels of calcium carbonate (Volat *et al.*, 1980). Does the same oceanographic process control the temporal fluctuations of CaCO₃ wt.% (Fig. 7.13) and MAR flux (Fig. 7.14) seen in the down-core profiles or do productivity and/or dilution variations play a more dominant role?

In sediments above the lysocline and under zones of high primary production, it is thought that variation in the volume of biogenic carbonate from the euphotic zone will be represented by similar changes in the input of carbonate to the sediment and recorded in the sediment column. Unfortunately, the two cores which could be examined to study this hypothesis (CD38-09 and CD38-10) because they are shallow-water cores located under the coastal upwelling zone are the ones for which MAR fluxes cannot be calculated (2.3.2). Therefore, their down-core signal (Fig. 7.13) is susceptible to an interpretation of variation in the strength of the terrigenous-dilution effect.

Recalculation of CaCO₃ wt.% into CaCO₃ MAR flux, in order to avoid these dilution effects, is possible for cores CD38-02 and CD38-11. The similarity of the profiles in Figs 7.13 and 7.14 for these two cores implies that dilution effects are, in

fact, minimal and that the variation in the bulk-sediment MAR is being principally controlled by the carbonate flux to the sediment and its variation over time. This interpretation is supported by comparison of the carbonate MAR down-core profile (Fig. 7.14) and the bulk-sediment MAR profile (Fig. 2.10).

The variations of CaCO_3 MAR flux during the Late Quaternary are quite smooth for core CD38-02 but very erratic for core CD38-11 (Fig. 7.14). This may be due to the fact that CD38-11 is located well within the carbonate transition zone and is therefore susceptible to changes in the degree of carbonate dissolution over shorter time scales than core CD38-02, which changes gradually over glacial/interglacial periods. This points towards a possible dissolution control on the temporal fluctuations of CaCO_3 flux in both these cores and leads on to the question of how the depth positions of the lysocline, CCrD and CCD have varied over time.

The depth of the lysocline is thought to have changed markedly during the global climatic cycles (shallowing by up to 800m in the central Pacific during interglacials) whilst the CCrD has remained relatively constant (Farrell and Prell, 1989). Therefore, significant variations in the thickness of the transition zone between the lysocline and the CCrD are envisaged over this time (Farrell and Prell, 1989, 1991; Rea *et al.*, 1991). The reasons for this variation are thought to be linked to circulation patterns of the ocean water masses (Berger, 1968; Broecker, 1971; Farrell and Prell, 1991) which brought more "corrosive" water to shallower depths during interglacial periods and increased the dissolution of carbonate material (Luz and Shackleton, 1975; Farrell and Prell, 1989). Therefore, if core CD38-02 on the Nazca ridge lies at the present day, and during previous interglacial periods, somewhere about the lysocline depth but well above it during glacial periods, this environmental fluctuation could produce the CaCO_3 MAR flux pattern displayed in Fig. 7.14. This interpretation is not ideal because it does not explain the peaks of carbonate input (lower dissolution periods?) during interglacial stages 3 and 7. It is possible that the strong down-core dissolution pattern is being overprinted on top of fluctuations of CaCO_3 input caused by changes in the primary production of carbonate microfossils over time.

7.4. OVERALL PALÆO-ENVIRONMENTAL CONCLUSIONS

This chapter has examined the deposition of the terrigenous and biogenic components on the Peruvian continental margin in terms of the spatial and temporal environmental parameters, which are recorded in the bulk geochemical signals of the

four piston and two box cores in this study. It would be more constructive to conclude and summarise the findings of this chapter by bringing together the various processes (climatic, oceanographic and biological) into an overall palæo-environmental picture of sediment deposition on the margin, rather than just simply summarise the results of each section above (7.2.3 and 7.3.3) individually.

The quote which began this chapter (7.1) has been shown to be quite true because, although the many processes which can control and affect the chemical composition of the various sediment components can be easily described, the correct interpretation of the strength and influence of each individual component is "difficult to induce because the [element] distributions are frequently the result of non-equilibrium processes" (Spencer *et al.*, 1968). However, it is safe to conclude that the two most important factors which affect the composition of these Peru margin sediments are the extreme closeness of the core sites to the continent and the high surface-water biological productivity which results from coastal upwelling.

The two environmental features above manifest themselves in the following geochemical signals:

A) Continental proximity

1) High mass accumulation rates of terrigenous derived clay and quartz detritus, seen in cores CD38-02 and CD38-11 as Al and Si_{terr} MAR fluxes which are consistently above 75 and 200 mg cm⁻² kyr⁻¹ respectively (Table 7.2 and Fig. 7.8).

2) Terrigenous elemental ratios which are anomalously high compared with the average deep-sea clay (Turekian and Wedepohl, 1961), e.g. Si/Al and Zr/Rb in the two near-shore cores CD38-09 and CD38-10 indicate very high quartz and heavy mineral deposition compared with clays. These minerals tend to be coarse-grained and denser than alumino-silicate clays (Table 7.3) and therefore have a shorter history of transport from source (Andes and Peru coastal plain) to depositional environment.

3) The generally high terrigenous component input can produce strong dilution-effects when examining other geochemical records on a wt.% basis.

B) Coastal upwelling

1) High mass accumulation rates of organic carbon, biogenic silica and calcium carbonate calculated for cores CD38-02 and CD38-11 (Table 7.5 and Fig. 7.14) which are situated south and sea-ward from the strong upwelling zone respectively.

2) Anomalously high organic carbon concentrations (on average >5 times the normal for marine sediments) in cores CD38-09 and CD38-10, which are located directly under the main upwelling zone and at shallow-water depths. These cores are situated within the water-depth boundaries (100-400m; Veeh *et al.*, 1973) of the oxygen-minimum zone, which results from the intense bottom-water microbial decomposition of the high organic matter input (Pedersen and Calvert, 1990; Pedersen *et al.*, 1992).

3) The high biogenic component input can also produce strong dilution-effects (especially from CaCO₃) when examining other geochemical signals on a wt.% basis.

The spatial and oceanographic location of each core produce latitudinal and water-depth variations in the terrigenous and biogenic inputs and are highlighted by:

1) Possible source rock compositional differences in the Fe/Al and K/Al ratios measured in the northerly group of cores compared to the southerly ones.

2) The degree of dissolution of carbonate- and silicate-shelled planktonic organisms within the water column indicated by the water-depth against surface sediment CaCO₃ and bio.sil concentration plots (Fig. 7.10).

3) Differences between the fluvial- and aeolian-dominated transport on the landward and sea-ward sides of the Peru-Chile Trench respectively, as shown by both the volumetric (Al and Si_{terr} MAR fluxes) and compositional (Fe/Al, Ti/Al and Zr/Rb) variation in the terrigenous components of cores CD38-03, CD38-11 and CD38-02.

On a temporal basis, the global climatic variations of the Late Quaternary have influenced the sediment terrigenous and biogenic compositional input over time. The following are just a few environmental factors which have affected the Peru margin during glacial/interglacial periodicity.

1) Sea-level change, caused by polar ice-sheet growth, results in extreme shallowing of the water-depths at CD38-09 and CD38-10 during glacial periods, which altered the terrigenous supply to these sites (Si/Al ratio; Fig. 7.1) and may have produced stronger bottom-water current activity and preferential erosion of fine-grained clays compared with heavy minerals (Zr/Rb ratio; Fig. 7.7). The strong coastal upwelling zone may also have moved off-shore and/or along-shore due to sea-level fluctuation which may, in turn, have altered the palæo-productivity pattern of the region and produced the C_{org} , bio.sil and $CaCO_3$ variation seen in the above two cores (Figs 7.11 to 7.13).

2) Movement of $CaCO_3$ dissolution depths occurs as a result of variation in the circulation pattern of the oceanic water masses in the Pacific (Farrell and Prell, 1989). This environmental process is probably the controlling factor on the carbonate profile (wt.% and MAR flux) of core CD38-02 (Figs 7.13 and 7.14). This site lies at 2525m at the present day on the Nazca Ridge which is probably just below the lysocline. However, during glacial periods, the depth of the lysocline deepened in the Pacific Ocean (Farrell and Prell, 1989) and CD38-02 would have sat well above the lysocline. In terms of carbonate dissolution and preservation, the $CaCO_3$ record of CD38-02 can be explained by interglacial stages as periods of relatively higher dissolution of $CaCO_3$ microfossils and hence lower preservation of the carbonate production signal compared with glacial periods, without the need for any significant variation in the surface-water production levels.

3) Fluctuations in the average wind strength during global climate change is caused by ice-sheet growth and latitudinal shrinking of the atmospheric pressure cells during glacial periods, resulting in stronger glacial winds (Sarnthein *et al.*, 1988). This natural process can significantly affect the strength of coastal upwelling and hence an increase of biological productivity along the Peru margin during the glacial periods is displayed in the sediment record as higher concentrations of the biogenic components (Fig. 7.11 and 7.12). Stronger winds can also transport greater volumes of terrigenous debris as airborne dust to the oceans and deposit it further from the continental source area. For this reason, and because the continents were more arid during the cold climatic stages, the glacial signal of terrigenous input shows higher mass accumulation rates (Fig. 7.8) and variation in some of the terrigenous element/Al ratios (Si/Al and Ti/Al; Figs 7.1 and 7.2).

However, the complex interplay of the climatic, oceanographic and biological systems results in marine sediment geochemical records which do not simply automatically switch between glacial and interglacial global conditions, and therefore they do not display down-core profiles which fluctuate in perfect timing with the stage boundaries.* There is a general tendency for the environmental processes to increase and/or decrease their influences and strengths to varying degrees within the climatic stages and to do so with differing lengths of lag or lead in relation to the glacial/interglacial periods. This results in terrigenous and biogenic component inputs which vary with non-linear relationships to time, such as seen in the Peru margin cores studied in this thesis.

*Of course, the global climate does not switch between the two extremes of glacial and interglacial stages instantly, but can take thousands of years to build up or remove glacial conditions. It is a gradual process over time, upon which the lines of stage boundaries have been placed as indicators of movement from a dominantly glacial period into a dominantly interglacial period, or vice versa.

CHAPTER 8

CONCLUSIONS

8.1. SCIENTIFIC RELEVANCE OF MARINE SEDIMENT STUDIES

"Nothing is rich but the inexhaustible wealth of nature.

She shows us only surfaces, but she is a million fathoms deep."

Ralph Waldo Emerson (1957)

The above quote brings to mind some aspects of this marine sediment geochemical study in terms of its scientific relevance. Firstly, there is the implication that nature is an extremely complex system, which depends on the interplay between marine life, terrestrial life, meteorology, climate conditions, ocean water movement and many other parameters. No science-based, environmental project is able to study all aspects of these processes, let alone interpret and understand all of them, and therefore each study must be biased towards attempting to understand just one small part of the "wealth of nature". This thesis has concentrated on the interpretation of the oceanographic conditions (biological, chemical and physical) which occurred along the Peruvian continental margin over the latter stages of the Quaternary period.

The second part of the quote could be interpreted as man's view of the oceans. From the land we can see only the surface of the sea but we know that it is within the deep, ocean waters and on the sea-floor that some of the most important natural processes occur, e.g. photosynthesis by marine phytoplankton, CO₂ uptake from the atmosphere and storage of the carbon (as C_{org}) in marine sediments below. It is only relatively recently that man has been able to study the deep-sea environment and to collect marine sediment cores, in order to analyse the important historical records contained within them. However, it must be remembered that in a study of such sediments, the cores analysed represent only a minute fraction of the total area of sea-floor in the region of interest. Therefore, any interpretations and conclusions made from cores (such as the CD38 ones) may be representative of only localised features and not of the overall regional palæo-environmental picture.

Finally, the quote is a reminder of the fact that nature supplies man with many resources, some of which are regarded as riches, e.g. gold and diamonds. Natural oil and gas could nowadays be included in the above category and this study has concentrated on a particular type of marine sediment which can be a precursor, source-rock to these important fossil fuels. The coastal upwelling region of Peru supplies a high flux of biogenic debris to the accumulating sediment column which, under the correct geological conditions, may be regenerated as an oil or gas deposit in the future (Calvert, 1987). Unfortunately, the petroleum-forming process takes millions of years to occur, but if studies, such as this, can lead to a greater

understanding of the environmental controls on the formation of organic-rich sediments, then perhaps this will result in the location and recovery of further fossil fuel deposits at the present day. Another natural resource studied in this thesis is the mineral phosphorite, found as hardgrounds, nodules and pellets within the sediments of the Peru margin. Phosphorites are formed by a complex series of diagenetic processes at the sediment/water interface (Froelich *et al.*, 1988). Present-day formation occurs along continental margins under zones of strong coastal upwelling and, in time, may produce large phosphate ore deposits such as those of economic importance in the agricultural fertiliser industry today (Cook *et al.*, 1990).

8.2. THE GEOCHEMICAL PALÆO-OCEANOGRAPHY AND MINERALOGY OF MARINE SEDIMENTS FROM THE PERUVIAN CONTINENTAL MARGIN

Each of the preceding chapters has sections contained within it (2.5, 3.4, 4.4, 5.3.3, 5.4.3, 6.6 and 7.4) in which the main conclusions of this study are individually presented. However, by bringing together the interpretations and hypotheses that have been drawn from this geochemical analysis of the Peru margin sediments, it is possible to present the following general statements regarding the palæo-environmental and palæo-oceanographic features of the area and their influence upon the sediment composition.

Oceanographic setting

The specific location of the CD38 cores, on the shelf and slope of the Peruvian continental margin, has produced marine sediments which can be distinguished from deep-sea sediments by the following features.

- 1) The proximity of the continental land-mass of South America results in a strong, but highly variable, input of terrigenous, detrital material. The terrigenous component supplies up to 90 wt.% of the total sediment composition. This results in high concentrations of elements such as Si, Al, Fe, Ti and K, from quartz, clays, feldspars and heavy minerals.
- 2) The high rate of sediment accumulation along the Peru margin produces sediment cores which preserve a high resolution signal of sediment input. Cores CD38-02 and CD38-11 have sediment accumulation rates which have been measured

at between 2 and 5 cm kyr⁻¹ and it is expected that the shallower-water cores, CD38-09 and CD38-10, have accumulated at faster rates. Unfortunately, these near-shore sediments have suffered from periods of sediment erosion and/or turbidite deposition resulting in depth/age models which are distorted and susceptible to errors in their interpretation.

3) A wide range of water-depths and environments of sediment deposition can be achieved for cores taken on a continental margin from a relatively small area, compared with the deep-ocean floor. This allows for inter-core comparison of the effects of many geochemical processes, such as carbonate dissolution and terrigenous transport patterns, to be examined. The carbonate profile of core CD38-02 from an intermediate water-depth has been interpreted as representing its position relative to variation of the lysoclinical-depth at the Nazca Ridge. This same core was shown to have a terrigenous component which varies in its Fe/Al, K/Al, Ti/Al and Zr/Rb element ratios compared with cores CD38-03 and CD38-11. The oceanic setting of the Nazca Ridge (on the sea-ward side of the Peru-Chile Trench) limits its terrigenous input to only that from aeolian transport, in comparison with the latter cores (on the land-ward side of the trench) which receive a mixture of fluvial- and aeolian-transported terrigenous material.

Coastal upwelling

The continental margin of Peru is a region of the Pacific Ocean which is strongly influenced by the physical phenomena of persistent coastal upwelling of cold, nutrient-rich water into the euphotic zone and the resultant high marine biological productivity (Suess and Thiede, 1983). Even though the majority of the organic matter and other biogenic-remains is recycled within the water column, an enhanced flux of this material reaches the sediment/water interface for incorporation into the sediment column. This manifests itself as an enrichment of the following geochemical components.

1) Organic carbon: within cores CD38-09 and CD38-10, the C_{org} concentration was measured as over an order of magnitude greater than that found in deep-sea sediments. Down-core variation of the organic matter concentration may be a result of off-shore and/or along-shore movement of the main coastal upwelling zone in response to shifting wind patterns (the atmospheric driving-force behind upwelling).

2) Biogenic-remains: the hard-part shells of plankton which survive water-column dissolution were measured geochemically as enrichments of biogenic silica and calcium carbonate. During the microscopic examination of the $>63\mu\text{m}$ sediment fraction of cores CD38-09 and CD38-10, strong preservation of fish bones and scales was also recorded.

3) Barium: this trace element is associated with biogenic productivity within the water column but survives dissolution to be measured as a residual component in oxic, marine sediments. By using the present-day relationship between Ba and organic matter (Dymond *et al.*, 1992) palæo-productivity levels at core site CD38-02 were calculated, which suggest that intense surface-water biological production occurred during interglacial periods.

4) Halogens: uptake of iodine by organic matter occurs at a rate which is dependent on the redox state at the sediment/water interface. Anoxic (lack of oxygen) conditions exist at sites CD38-09 and CD38-10, resulting in lower I/C_{org} compared with the other oxic cores in this study. Organic matter flux changes may be recorded by I/Br ratio variations in oxic environments (CD38-02) though the exact chemical mechanisms of the halogen-organic carbon relationships are still poorly understood (Shimmiel and Pedersen, 1990).

5) Trace metals: within the water column, the high flux of organic matter along the Peru margin can scavenge large quantities of metals, such as Mo, U, Cr, V, Cu and Ni, and incorporate them in the sediment column. In cores CD38-09 and CD38-10, the down-core profiles of the metal enrichment factors resemble the respective C_{org} profile, supporting a hypothesis of strong organo-metallic relationships in anoxic marine sediments (McNeill and Shimmiel, 1991). The metal/ C_{org} ratios show good agreement between the two shallow-water cores and may be useful in future studies of an anthropogenic, metal-polluted environment.

Chemical diagenesis

The concentration of organic matter, which was introduced to the Peru margin sediments as a direct result of coastal upwelling, is the main reason for the following chemical conditions and diagenetic processes.

1) Redox environment: bottom-water dissolved oxygen levels are reduced to a minimum in zones where the high flux of organic matter produces intense benthic activity by microbial bacteria, which utilise oxygen in decompositional processes. An oxygen minimum zone (OMZ) exists between 100 and 400m water-depth off Peru under coastal upwelling zones (Veeh *et al.*, 1971) and impinges on the sea-floor at sites CD38-09 and CD38-10. As a result, these sediments are accumulating under a reduced, anoxic environment, which is geochemically represented by low I/C_{org} and Ba/Al ratios compared with the oxic cores of CD38-02 and CD38-11. The Mo/U ratios from the CD38 cores contradict the established palæo-redox theory of Bertine and Turekian (1973) due to their complex organo-metallic relationships and diagenetic mobility.

2) Phosphorite pellets: carbonate fluorapatite (CFA) mineral growth occurs as a result of the release of phosphorus from decaying organic matter into near-surface pore-waters in a suboxic/anoxic environment. Authigenic precipitation of CFA is a two-stage process from the pore-water phosphate onto the surfaces of other mineral grains and diatom/foraminifera shells (Froelich *et al.*, 1988). This formation of phosphorite pellets can incorporate many elements into its crystal lattice, including U, Sr, Ba and Y. The presence of disseminated phosphorite pellets throughout the sediments of cores CD38-09, CD38-10 and CD38-11 has been demonstrated using pore-water phosphate profiles and sediment phosphorus partitioning equations.

3) Trace element partitioning: the concentrations of multi-phase elements (U, Sr and Y) are partitioned into their organic, terrigenous, phosphorite and/or carbonate phases using a series of geochemical-relationship equations. The trace element/ P_{phos} ratios in the Peru margin phosphorites are quantified to allow for the calculation of the U_{org} , $Sr_{calcite}$ and Y_{terr} concentrations in the CD38 piston cores.

Climate change

The period of time during which the cores studied in this thesis accumulated on the Peru margin, was one of relatively intense and frequent variation between glacial and interglacial conditions of the global climate. These Late Quaternary climate changes are due to the orbital position of the Earth relative to the Sun (Imbrie *et al.*, 1984) and have resulted in polar and continental ice-sheet growth during glacial periods. Glacial/interglacial periodicity has affected the Peru margin in the following manner.

1) Wind-strength variation: latitudinal shrinking of the pressure-cells around which the Pacific wind-systems move resulted in stronger glacial winds. This may have induced more intense coastal upwelling off Peru and increased the biological production of the area and/or moved the main zone of primary productivity off-shore and along-shore. Both of the above scenarios could be responsible for the variation of the biogenic components recorded in the Peruvian marine sediment cores. Stronger winds and continental aridity during glacial periods (Sarnthein *et al.*, 1984) may also have blown more terrigenous detritus into the ocean, to produce the increased terrigenous mass accumulation rates (Al and Si_{terr}) measured in cores CD38-02 and CD38-11.

2) Eustatic variation: the global sea-level has fluctuated by about 50-100m in response to ice-sheet growth/decay during the glacial/interglacial stages of the Late Quaternary (Fairbanks, 1989). A drop in glacial sea-level of this magnitude at the near-shore core sites, CD38-09 and CD38-10, is thought to be responsible for the zones of sediment erosion, when stronger bottom-water currents winnowed down-slope the fine-grained clays, leaving behind a concentration of phosphorite pellets and other heavy minerals. The phosphorite formed hardground beds which subsequently broke up into flat nodules. Such nodules have been found in a position in the sediment column (273cm in CD38-09) which indicates a younger age than their actual U/Th radiochemical age of formation (114ka) suggests. The contrasting geochemical behaviour of Rb (in fine-grained clays) and Zr (in coarse-grained zircon) results in a Zr/Rb ratio, whose down-core profile displays peaks during these glacial, erosion events, illustrating its use as a sediment grain-size indicator.

3) Water mass circulation: glacial/interglacial variation in the pattern of water mass movement around the Pacific can alter the water-depth of the lysocline, below which the majority of carbonate dissolution occurs (Farrell and Prell, 1989). Strong variation in the concentration and flux of CaCO₃ presented for the Nazca Ridge site, CD38-02, can be explained by dissolution variation due to lysocline-depth movement resulting in a glacial/interglacial preservation signal rather than a productivity one (better preservation during glacial periods).

The hypothesis above of stronger upwelling during glacial periods contradicts the results from the barium-productivity calculations for CD38-02 (which peaked during interglacials) and therefore, further and more detailed work is required in order

to solve this enigma. It is thought that the impact of wind strength variation on productivity in the oceans is probably decoupled over the 100,000 year glacial/interglacial periodicity. The barium signal is probably also affected by changes in the deep-ocean circulation (Lea and Boyle, 1990B, Dymond *et al.*, 1992) over this long term climate change. However, at this moment not enough is known about the exact mechanisms and strengths of these complex palæo-oceanographic processes.

8.3. SUGGESTED FUTURE WORK

This geochemical study has measured the concentrations and fluxes of many elements and sediment components from the marine sediments of the Peruvian continental margin. However, there are some geochemical parameters whose results and down-core profiles merit a more thorough examination. The following could be studied in the future in order to expand on the hypotheses presented and/or to determine the exact causes of various marine geochemical relationships.

1) **Organo-metallic ratios:** organic matter has been shown to have a strong relationship with particular metals. The exact mechanisms/bonding structures of organo-metallic scavenging in sea-water could be examined by a detailed organic geochemical study of the sediments from cores CD38-09 and CD38-10.

2) **Barium and palæo-productivity relationship:** core CD38-02 contains a Ba flux signal which matches that of the glacial/interglacial oxygen isotope profile from foraminifera microfossils. It would be interesting to measure closely the timing of these profiles with respect to each other in order to determine if there is a consistent lead or lag of the increased productivity in the surface waters around the Nazca Ridge relative to the onset of an interglacial period. This future work could closely examine a glacial/interglacial stage boundary using very high resolution Ba and oxygen isotope analyses from closely-spaced (every 1-2cm) sub-samples from core CD38-02.

3) **I/Br and Sr/Ca ratios:** these two geochemical ratios show down-core variation (in cores CD38-02 and CD38-11) which may be linked to changes in the structure of the marine biomass over glacial/interglacial periodicity. The sediments of the Peruvian margin could be used in an in-depth study of the close, but highly variable, relationship between various types of organic matter and the halogens; which is known to be dependant on both the redox environment of deposition and the depth of sediment burial. Inductively-coupled plasma mass spectrometry (ICP-MS) could

possibly be used to examine any differences in the Sr/Ca ratio of foraminifera microfossils compared with that of coccoliths, and to determine if this signal changes over time.

4) U/Th radiochemistry of phosphorites: the average age of 114ka for the phosphorite material of the nodule in CD38-09 supported the prevailing hypothesis of initial pellet formation during an interglacial period under a coastal upwelling zone followed by concentration and conglomeration into a hardground nodule during a glacial period. However, more evidence for this theory could be gained by carrying out further U-series disequilibrium radiochemical measurements of the Peruvian phosphorites. Such work may also help in the calculation of sedimentation rates for the two near-shore cores, if the phosphorite zones at 273cm in CD38-09 and at about 90cm in CD38-10 are shown to contain phosphatic material of the same age.

The following are possible future areas of study which would be able to use some of the results and interpretations presented in this thesis.

1) Time-series spectral analysis of the geochemical signals (such as Ba/Al, CaCO₃, Ti/Al, Si_{terr}/Al) measured in core CD38-02 may generate results which would demonstrate which of the Milankovitch orbital frequencies (eccentricity, tilt or precession) is dominating the variation in input of the biogenic and terrigenous components to the sediment at the Nazca Ridge. This core would need to be used because, of the four piston cores in this study, CD38-02 has the most accurate age model.

2) A more detailed mineralogical examination of the down-core changes in both terrigenous and authigenic minerals in cores CD38-09 and CD38-10 may reveal more evidence of continental margin erosion events. Of most interest would be the diagenetic formation of phosphorite pellets and the mineralogical associations of the nodules in the phosphorite-rich zones. This work could involve both thin-section studies and scanning electron microscopy.

3) The Zr/Rb ratio has been used in this thesis as a trace element indicator of the average grain-size of marine sediments. Detailed particle size profiles of the terrigenous component in cores CD38-09 and CD38-10 could be obtained using a laser particle size analyser. This would provide a means of proving the existence of

(and perhaps allow for the quantification of) such a geochemical/physical sediment relationship.

Finally, now that most of the co-workers (1.5) in this multi-disciplined study have completed their respective projects, there is a need for all the results, interpretations and conclusions to be drawn together. The process of scientific discussion between geochemists, sedimentologists and micro-palæontologists may lead to a greater understanding of each individual's results, regarding the marine sediments recovered by *R.R.S. Charles Darwin Leg 38* from the Peruvian continental margin.

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APPENDIX A

ANALYTICAL METHODS

APPENDIX A.1. SEDIMENT COLLECTION AND SAMPLING

Four piston cores and two box cores recovered from the Peruvian continental margin during the *R.R.S. Charles Darwin Leg 38* cruise (April-May 1989) were selected and sampled for analysis (Table 1.1).

The piston cores (in sections of about 1m in length) and the box cores (sliced at 1-2cm intervals onboard ship and stored in sealed polythene bags) were transported in a sealed container at 4°C to the Grant Institute, University of Edinburgh.

Sub-sampling of the piston cores was carried out after the sections had been sliced in half lengthwise and one half stored for archive. Using 10cm³ polythene plugs (2cm diameter), samples were taken at approximately 10cm intervals down to the base of each core. The intervals varied slightly due to irregularities in the core and also due to the fact that, for some of the cores, S. King from Southampton University was also taking samples.

The wet sediment samples (from both piston and box cores) were placed on watchglasses, weighed and then dried in an oven at 50°C for up to 5 days. Reweighing after drying allowed for calculation of the sample water content, and from this value the sample salt content was also calculated (Appendix A.6). Water and salt content data are tabulated in Appendix C.1.

Dried sediment samples were ground to a very fine powder (<2µm) using a tungsten-carbide TEMA mill for 1 minute. These samples are the dried bulk sediment samples used for XRF and other geochemical analyses.

APPENDIX A.2.

SAMPLING, CLEANING AND ANALYSIS OF FORAMINIFERA

A.2.1. Sample Preparation

The four piston cores (Table 1.1) were resampled at about 10cm intervals using the same techniques as for the bulk sediment samples (Appendix A.1). However, instead of being dried after weighing, the samples were sieved through a 63µm mesh using a fine spray of warm tap water. The >63µm fraction remaining contained foraminifera, radiolaria, diatoms, fish bones and coarse-grained material, and this was dried overnight at 40°C in an oven and then reweighed. This enabled

determination of the weight percent $>63\mu\text{m}$ fraction for each sample (data are given in Appendix C.2).

Under a microscope and using a very fine paintbrush, up to 40 individual and intact tests of particular foraminifera species were picked from each sample; species, numbers and size fractions are detailed in Appendix C.2. The foraminifera were placed in labelled plastic vials, ultrasonicated in methanol for up to 1 min and dried prior to analysis of their stable isotope ratios at the Scottish Universities' Research and Reactor Centre (SURRC), East Kilbride. During foraminifera picking, each sample was semi-quantitatively examined for the presence of diatom frustules, fish remains and quartz and clay grains using a simple scaling of : 0 = absent, 1 = rare, 2 = common and 3 = abundant. The results of this examination are detailed in Appendix C.2.

A.2.2. Stable Isotope Analysis

Determination of the carbon and oxygen stable isotope ratios of the foraminifera CaCO_3 tests was carried out on a VG Isotech PRISM isotope mass spectrometer, under the supervision of A.E. Fallick and T. Donnelly. Between 3 and 20 individual tests per sample (depending on size and species) were weighed into tiny buckets. The optimum weight for analysis was about 0.1mg. Both SM calcite and MBL1 standards were run with each autorun batch of samples.

The mass spectrometer autorun procedure was as follows: the sample is dropped from the rotating carousel into the reaction vessel containing 10ml phosphoric acid (at 90°C and continuously stirred). The CO_2 gas given off from the reaction between the calcium carbonate and the acid, is pumped via a water trap (at -100°C) over to a cold finger (at -196°C) under high vacuum. The cold finger is then heated back to room temperature and the CO_2 gas moved through a series of valves and a second cold finger, until it reaches the mass spectrometer. The reference ion beam current is matched to that of the sample ion beam by the use of variable-volume bellows. The mass spectrometer then measures the difference between the $^{13}\text{C}/^{12}\text{C}$ and the $^{18}\text{O}/^{16}\text{O}$ ratios of the sample and those of the reference gas, and gives the results as $\delta 1$ and $\delta 2$ values (Eqn A.2.1).

These values are then recalculated into $\delta^{13}\text{C}$ (‰) and $\delta^{18}\text{O}$ (‰) by comparison with the average $\delta 1$ and $\delta 2$ values for the SM calcite standards in the autorun and then, using Eqn A.2.2, converted into the standard nomenclature for

foraminifera isotope results. Results of $\delta^{13}\text{C}$ (PDB, ‰) and $\delta^{18}\text{O}$ (PDB, ‰) for all the foraminifera samples are tabulated in Appendix C.2.

Equation A.2.1. Delta Calculation

$$\delta 1 (\text{‰}) = ((^{13}\text{C}/^{12}\text{C}_{\text{sam}} - ^{13}\text{C}/^{12}\text{C}_{\text{ref}}) / ^{13}\text{C}/^{12}\text{C}_{\text{ref}}) \times 1000$$

$$\delta 2 (\text{‰}) = ((^{18}\text{O}/^{16}\text{O}_{\text{sam}} - ^{18}\text{O}/^{16}\text{O}_{\text{ref}}) / ^{18}\text{O}/^{16}\text{O}_{\text{ref}}) \times 1000$$

where, sam = sample gas
ref = reference gas

Equation A.2.2. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ calculations

$$\delta^{13}\text{C} (\text{PDB, ‰}) = (\delta^{13}\text{C}_{\text{sample}} - \delta^{13}\text{C}_{\text{PDB standard}}) / \delta^{13}\text{C}_{\text{PDB standard}} \times 1000$$

$$\delta^{18}\text{O} (\text{PDB, ‰}) = (\delta^{18}\text{O}_{\text{sample}} - \delta^{18}\text{O}_{\text{PDB standard}}) / \delta^{18}\text{O}_{\text{PDB standard}} \times 1000$$

Target major ion beam	6.00 x 10 ⁻⁹ A	
Maximum reference ion beam	1.64 x 10 ⁻⁸ A	
Minimum reference ion beam	2.49 x 10 ⁻⁹ A	
Ion gauge base pressure	7.60 x 10 ⁻¹⁰ Torr	
Cold finger ambient temperature	25°C	
	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$
Std. dev. for SM1 standard (n = 100)	0.085%	0.115%

Table A.2.1. Normal operating conditions of the PRISM mass spectrometer and the typical standard deviation values for the SM calcite standard.

APPENDIX A.3. ORGANIC CARBON

Carbon occurs in marine sediments from two main sources; carbonate carbon (CaCO_3 shells of zooplankton) and organic carbon (from the remains of marine organisms). Before the concentration of organic carbon (C_{org}) can be measured, the carbonate carbon within the sample must be preferentially removed. Acid digestion of the carbonate is the common way to remove this phase. Care must be taken to avoid

loss of C_{org} by hydrolysis if the sample is washed after acid attack, and so the entire analytical procedure is carried out with the sample in a LECO ceramic crucible.

The dried bulk sediment sample was accurately weighed (0.2-0.5g \pm 0.01mg) into a LECO crucible and dampened with deionised water. This ensured no loss of sample from splashing, upon addition of the first few drops of 50% solution HCl (aq). The strength of effervescence was dependant upon the concentration of carbonate and so extra care was taken with carbonate-rich samples. Further drops of acid were added only once the fizzing had ceased each time, and then when no more effervescence occurred the crucible was placed on a hotplate set at about 60°C for 2 hours to allow for evaporation of the excess water. After cooling, more acid was added and the sample stirred with a glass rod to ensure complete digestion of the carbonate. The glass rod was washed with deionised water into the crucible after each stirring. All work was carried out in a fume cupboard.

Samples were evaporated to dryness on the hotplate overnight before analysis. C_{org} concentration was analysed by combustion in an induction furnace, in an oxygen atmosphere, followed by potassium hydroxide absorption of the CO_2 produced. Combustion of the sample was performed using a LECO 521-200 induction furnace fitted with a dust trap, sulphur trap (MnO_2 powder) and catalyst furnace. The sample crucible was put into the furnace straight from the hotplate (to minimise loss of $CaCl_2$), with tin and iron chip accelerators and at an oxygen flow rate of 1.5 l min^{-1} .

The furnace was connected to a LECO 572-100 carbon analyser which has a glass burette to measure the change in volume that results when the CO_2 - O_2 mixture from combustion is flushed through the CO_2 -absorbing KOH solution. The burette reading was then corrected for air pressure, temperature and the original weight of sample to calculate the percentage weight of organic carbon.

These values were then corrected for salt dilution (see Appendix A.6) and the results are tabulated in Appendix C.12.

Steel rings were run as standards after every fifth sample and one (high carbonate) sample was replicated to assess analytical precision.

Sample 3803-29 : $n = 48$, mean = 1.50 wt.% C_{org}
 $\sigma = 0.07$, standard deviation = 4.66%.

APPENDIX A.4. BIOGENIC SILICA

Analytical determination of the concentration of biogenic silica was based on a wet chemical leaching technique (Eggimann *et al.*, 1980) which is more sensitive than

other methods, e.g. X-ray diffraction or infra-red spectroscopy. Exact procedures follow the work by Dobbie (1988) and involve initial digestion of the sample in sodium carbonate, and then colorimetric spectrophotometry of both silica and alumina in the filtered solution.

A.4.1. Sample Digestion

Into a PTFE beaker, approximately 50mg of bulk sediment sample was accurately weighed, 20ml of 2M NaCO₃ (aq) was added and the beaker sealed in a steel bomb. The bomb was then placed in an oven at 90-100°C for 4 hours; leaching conditions which are sufficient to allow for complete digestion of biogenic, amorphous silica whilst keeping aluminosilicate (clays) and quartz attack to a minimum. The increase in pressure with heating raised the boiling point of the solution and ensured no loss of solution at the lid, and the closed-system reaction required no stirring and prevented evaporation and concentration of the sodium carbonate solution.

After cooling, the contents of the beaker were vacuum filtered through a 0.4µm polycarbonate membrane filter, using a plastic filtering system. Plastic apparatus was used to prevent contamination caused by silica leaching from glassware. The filtrate and washings (always using deionised water) were diluted to 100ml in a volumetric flask and then the solution was stored in a plastic bottle, prior to silica and alumina analysis.

A.4.2. Silica Determination

Measurement of the silica content of the filtrate by colorimetric analysis depends on the formation of yellow, unreduced silicomolybdate acid, followed by selective reduction to molybdate blue using excess molybdate (Strickland and Parsons, 1968). Methods of reagent preparation follow those of Dobbie (1988).

The procedure was carried out in a 100ml glass volumetric flask and silica contamination was avoided by initially adding dilute HCl (aq) : enough to neutralise the sodium carbonate plus 1ml in excess to obtain the correct pH (1.0-1.4). The aliquot of sample (or standard or blank) that was added depended on the rough percentage of biogenic silica, and this was followed by deionised water to make the volume up to 15ml. After addition of 1ml ammonium molybdate reagent the flask was shaken and left for exactly 10 min to allow the colour to develop. Then 5ml oxalic acid (which decomposes any yellow phosphomolybdate and prevents iron

interference) and 2ml reducing solution were added in quick succession along with deionised water to make up to the 100ml mark.

After 1 hour, the absorption of the solution was measured at 812nm using 2cm cells in a Perkin Elmer 550 spectrophotometer.

A calibration graph of absorption against concentration gave a linear correlation for a range of standards and so with each batch of samples only one standard needed to be measured. One blank per batch was also required to allow for interference from NaCl in solution.

Silica concentration of the sample was calculated by direct comparison with the known standard and then weight percent from the known weight of sample digested (Eqn A.4.1.). This weight % silica is termed apparent biogenic silica because some of the silica in solution may be derived from non-amorphous sources. The final stage of the analytical procedure is therefore to measure the alumina content of the sample solution so that corrections can be made to allow for any digestion of aluminosilicates. The presence of quartz-derived silica is thought to be negligible and is ignored because it would require a second-order correction.

Equation A.4.1. Apparent Biogenic Silica Calculation

$$\text{App. Bio. Sil. (wt.\%)} = [(R-B) \times k] / [(S-B) \times \text{wt.}]$$

where, R = Absorption of sample
 B = Absorption of blank
 S = Absorption of standard
 wt. = Sample weight (mg)
 k = [(No. of ml standard in 100ml) x (100%)
 x (wt. of Specpure SiO₂ in standard stock solution)].

A.4.3. Alumina Determination

This colorimetric method (Dougan and Wilson, 1974) involved the formation of an aluminium catechol violet complex. All standards and reagents were stored in plastic bottles to avoid leaching of Al₂O₃ from Pyrex glassware. Once again, the methods of reagent preparation follow those of Dobbie (1988).

A 5ml aliquot of sample, standard or blank was added to a 50ml plastic volumetric flask, followed by dilute HCl (enough to neutralise the sodium carbonate

plus 1.24ml in excess) and dilution to 35ml with deionised water. Then 1ml of 10% phenanthroline solution was added to prevent iron interference, followed by 2ml of the catechol violet reagent and 10ml hexamine solution (this acts as a buffer to obtain pH = 5.9-6.2). The flask was shaken after each addition and the solution made up to the 50ml mark with deionised water.

After 10 min, the absorption of the solution was measured at 585nm using 1cm cells in a Perkin Elmer 550 spectrophotometer.

The standard calibration graph (absorption against concentration) was linear and so only one standard (and one blank) was measured per batch of samples. The calculation of Al₂O₃ content of the sample solutions was by comparison with the standard and use of the known sample weight (Eqn A.4.2.).

Equation A.4.2. Alumina Calculation

$$\text{Al}_2\text{O}_3 \text{ (wt.\%)} = [(R-B) \times k] / [(S-B) \times \text{wt.}]$$

where, R = Absorption of sample
 B = Absorption of blank
 S = Absorption of standard
 wt. = Weight of sample (mg)
 k = [(No. of ml of standard in 100ml) x (No. of ml Al₂O₃ standard) x (weight of Al₂O₃ in stock standard) x (100%)].

Equation A.4.3. was used to calculate the weight percent biogenic silica, and then these values were corrected for salt dilution (Appendix A.6.) and the results are tabulated in Appendix C.12.

Equation A.4.3. Biogenic Silica Calculation

$$\text{Biogenic Silica (wt.\%)} = \text{Apparent Biogenic Silica (wt.\%)} - [2 \times \text{Al}_2\text{O}_3 \text{ (wt.\%)}]$$

where, 2 = SiO₂ / Al₂O₃ ratio of marine clays (Dobbie, 1988).

A.4.4. Analytical Precision

One sediment sample was replicated to assess analytical precision.

Sample BC 3803-32 : n = 7, mean = 11.25 wt.% biogenic silica
 $\sigma = 0.193$, standard deviation = 1.71%.

APPENDIX A.5.

X-RAY FLUORESCENCE (XRF) SPECTROMETRY

XRF spectrometry was used to measure a wide range of major and minor (trace) elements in the sediment samples, using a Phillips PW 1480 sequential automatic X-ray spectrometer and a PW 1510 sample changer.

A.5.1. Major Element Disc Preparation

Fused glass discs (45mm diameter) were prepared following methods similar to those of Norrish and Hutton (1969). Approximately 1.5g of dried bulk sediment sample was dried overnight at 50°C in an oven and then about 0.9g of the sample was accurately weighed (± 0.0001 g) into a platinum crucible. The crucible, with Pt lid, was then placed in a muffle furnace at 1100°C for 5 min ignition. This length of time was chosen after a test was run to examine the loss of volatile alkali metals (K and Na) with varying ignition times (Table A.5.1.). Over five minutes ignition resulted in loss of Na and K but at less than 5 min. ignition time, the furnace did not return to 1100°C.

Ignition time (mins)	Na ₂ O (wt.%)	K ₂ O (wt.%)
0	3.08	1.775
0	3.00	1.761
2	3.25	1.794
5	2.92	1.680
10	2.75	1.501
15	2.69	1.402
20	2.49	1.115
60	2.32	0.934

Table A.5.1. Loss of Na and K upon increasing ignition times.

After cooling and reweighing, to calculate a loss on ignition percentage, an ultrapure flux (Spectroflux 105, Johnson Matthey Chemicals Ltd.) was added in a ratio to the pre-ignited sample weight of exactly 5:1. The crucible was covered again

and placed back in the furnace to fuse the sample and flux for 20 min. Working with batches of four crucibles was most suitable.

The flux is composed of $\text{Li}_2\text{B}_4\text{O}_7$, La_2O_3 and Li_2CO_3 ; the tetraborate helps to dissolve the sediment and the lanthanum acts as a heavy absorber of the X-rays and helps to minimise matrix effects. The effect of the matrix differences between samples and standards is also corrected for by using theoretical absorption coefficients (Theisen and Vollach, 1967).

Once the crucible had cooled back to room temperature, it was reweighed. A small amount of flux was added to make up to the correct total weight ($\pm 0.0002\text{g}$) and the sample was fused again over a Meker burner. The molten glass was then poured into a disc-shaped graphite mould, placed in a brass sleeve and on a hot-plate at 220°C . With an aluminium plunger, also at 220°C , the glass was quickly pressed into a 1mm thick disc, the upper surface of which had an "orange peel" texture. The disc was allowed to anneal on the hot-plate, cooled slowly and then stored in a sealed polythene bag in a desiccator prior to analysis.

A.5.2. Major Element Analysis

International rock and sediment standards which cover the wide range in composition of major elements found in marine sediments were used for calibration of the X-ray spectrometer (Table A.5.2). For all the major elements (Si, Al, Fe, K, P, Na, Ti, Mn, Mg and Ca) measured, calibration lines were found to be linear.

Analytical conditions for the XRF major element analysis are given in Table A.5.3 and the precision and accuracy for each element in Table A.5.4. The raw data in the form of major element oxides (Appendix C.5) were then recalculated into major element concentrations (Appendix C.6) and corrected for the effects of the presence of salt (Appendix A.6) and the resulting data are tabulated in Appendix C.7.

Standards
Ba-1 (I-III), Ba-2 (I-III), Ba-3 (I-III), Ba-4 (I-III), Ba-5 (I-III), Ba-6 (I-III)
BRIMO-1 (I-III), BRIMO-2 (I-III), BRIMO-3 (I-III), BRIMO-4 (I-III)
BRIMO-5 (I-III), BRIMO-6 (I-III), BRIMO-7 (I-III)
MAG-1, BCR-1, AGV-1, GA, BR, GH, SY-2, SY-3, JB-1, PCC-1, SGR-1, GSP-1

Table A.5.2. Internal and international rock standards used in XRF calibration.

Ba- and BRIMO- standards are a synthetic dilution series made from the following SPECPURE compounds: $\text{Ba}(\text{IO}_3)_2$, KBrO_3 , $(\text{NH}_4)\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and

Table A.5.4. XRF analytical precision and accuracy									
Oxide	Mean	S.D.	% S.D.	Accuracy	Element	Mean	S.D.	% S.D.	Accuracy
	(n=8)					(n=8)			
SiO ₂	52.137	0.061	0.117	0.147	Ba	2615.1	11.1	0.4	27.66
Al ₂ O ₃	15.619	0.033	0.211	0.124	Br	160.1	1.7	1.1	2.4
Fe ₂ O ₃	8.894	0.021	0.236	0.157	Ce	26.4	3.5	13.4	7.89
MgO	3.407	0.02	0.582	0.037	Cr	71.8	1	1.4	55.48
CaO	1.852	0.01	0.523	0.086	Cu	89.9	0.7	0.8	5.69
Na ₂ O	3.111	0.031	0.996	0.062	I	84.9	3.5	4.1	3.7
K ₂ O	1.439	0.007	0.486	0.017	La	13.9	2.2	15.9	4.3
TiO ₂	0.824	0.003	0.314	0.017	Mo	4.4	0.3	6.4	0.6
MnO	0.054	0.002	4.444	0.01	Nb	3.5	0.2	6.4	2.42
P ₂ O ₅	0.11	0.003	2.573	0.014	Nd	19.5	2.3	11.7	3.14
					Ni	153.4	0.9	0.6	4.45
					Pb	7	0.8	11.4	2.02
					Rb	26.7	0.2	0.7	3.08
					Sc	16.7	1.5	9	3.19
					Sr	528.2	3.2	0.6	8.46
					Th	0.4	0.4	100	1.77
					U	10.2	0.9	9.2	4.73
					V	198.4	1.2	0.6	6.37
					Y	23.7	0.5	2.3	1.28
					Zn	285.2	1.2	0.4	3.27
					Zr	58.8	0.5	0.8	10.49
Major element oxides measured in wt. %									
Minor elements measured in ppm									
% S.D. is total precision including counting error, disc reproducibility, error.									
in regression line and error in matrix mass absorption determinations.									
Accuracy determined from r.m.s.d. of international standards about the regression line.									
Repeat analysis carried out by A.J. Patience on a marine sediment sample									
from the Eastern Equatorial Pacific (Patience, 1992),									
who ran XRF samples at same time as the CD38 samples in this study.									

BaCO₃. Each was prepared using CaCO₃ (I), Salisbury Crag Dolomite (II) and Shap Granite (III) matrices, to represent a wide range of possible sediment compositions and mass absorption effects. Calibration lines were periodically revised and some standards changed, depending on what concentrations of each element were required.

A.5.3. Minor Element Disc Preparation

Pressed powder discs (32mm diameter) were used for minor element analysis. Approximately 3g (± 0.1 g) of dried bulk sediment sample was placed onto a polished tungsten carbide disc, enclosed in a stainless steel inner sleeve (which itself was enclosed in a larger cylinder). A perspex plunger was inserted down the inner sleeve, carefully compacting the sediment under hand pressure. After removal of both the plunger and inner sleeve, boric acid powder was added to cover the sample disc. Then a large, stainless steel plunger was lowered onto the boric acid and, using a hydraulic press at 10 tons for 1 min, the disc was fully compacted. The pressed powder disc was then stored in a sealed polythene bag and within a desiccator prior to analysis (this prevented loss of halogens and movement of salt to the surface).

A.5.4. Minor Element Analysis

The international rock and sediment standards used gave linear calibration lines for all the minor elements (Ba, Sc, V, Ni, Cu, Zn, Sr, Nb, Cr, Zr, Pb, Th, U, Rb, Mo, I, Br, Y, La, Ce and Nd) measured over their wide range in concentrations (Table A.5.2). Analytical conditions for XRF minor element analysis are given in Table A.5.3, with the precision and accuracy for each element in Table A.5.4. Minor element raw data (Appendix C.9) was then corrected for salt dilution (Appendix A.6) and the results are tabulated in Appendix C.10.

APPENDIX A.6. SALT CORRECTIONS

Upon drying the bulk sediment samples (Appendix A.1) the sea salt that is contained within the pore-waters is incorporated within the sediment. This salt contains significant amounts of Na, Mg, Ca, K and Br and thus the measured concentration of these elements needs to be corrected for the contribution that the salt makes to the sample. All XRF elemental, C_{org} and biogenic silica measurements of the bulk sediment sample must then be corrected for the dilution effect of the salt.

The salinity of pore-waters is assumed to be constant and the same as that of normal sea-water, i.e. about 35 parts per thousand. Using this assumed value and the water contents measured for each sample (Appendix C.1), the salt content in the sediment was calculated using Eqn A.6.1.

Equation A.6.1. Salt Content

$$\text{Salt} = (3.513 \times W) / (100 - W)$$

where, W = Water content (% wet weight).

Salt contribution corrections for Na, Mg, Ca, K and Br were calculated using the following equations:

$$\begin{aligned} \text{Na}_{\text{sed}} (\text{wt.}\%) &= \text{Total Na}_{\text{sed}} (\text{wt.}\%) - (0.306 \times \text{Salt}) \\ \text{Mg}_{\text{sed}} (\text{wt.}\%) &= \text{Total Mg}_{\text{sed}} (\text{wt.}\%) - (0.037 \times \text{Salt}) \\ \text{Ca}_{\text{sed}} (\text{wt.}\%) &= \text{Total Ca}_{\text{sed}} (\text{wt.}\%) - (0.012 \times \text{Salt}) \\ \text{K}_{\text{sed}} (\text{wt.}\%) &= \text{Total K}_{\text{sed}} (\text{wt.}\%) - (0.011 \times \text{Salt}) \\ \text{Br}_{\text{sed}} (\text{ppm}) &= \text{Total Br}_{\text{sed}} (\text{ppm}) - (19 \times \text{Salt}) \end{aligned}$$

where, Total wt.% or ppm are from XRF raw data,
Salt is from Eqn A.6.1,
Multiplication factors are from Horne (1969).

Then, all elemental concentrations were corrected for salt dilution using Eqn A.6.2 to obtain salt-free values.

Equation A.6.2. Salt dilution correction

$$\text{Element (salt-free)} = \text{Element}_{\text{meas}} \times (100 / (100 \times \text{Salt}))$$

where, Element_{meas} is from XRF, C_{org} and biogenic silica raw data or from above for Na, Mg, Ca, K and Br,
Salt is from Eqn A.6.1.

APPENDIX A.7. PORE-WATER PHOSPHATE

Pore-water phosphate concentrations were measured on samples from thin slices of box core material which had been centrifuged and filtered through 0.4 μ m membrane filters into acid-washed vials. Analyses were carried out using a FIATRON flow injection analysis system following methods based on Strickland and Parsons (1968) and results were found to be very precise but may contain ± 5 -10% errors in accuracy due to matrix interference. Analysis was carried out onboard the *R.R.S. Charles Darwin* by G.B. Shimmiel, T. Shimmiel and A.J. Patience. The results for cores CD38-09, CD38-10 and CD38-11 are listed in Appendix C.4.

APPENDIX A.8. URANIUM-SERIES DISEQUILIBRIUM METHODS

The uranium-series dating of the large phosphorite nodule from core CD38-09 was carried out under the supervision of Dr G.B. Shimmiel. Although I carried out a large number of test samples to try to increase the efficiency of the procedure, the actual phosphorite sample determination was done by Colin Chilcott, a research assistant, in the new clean laboratory at the Department of Geology and Geophysics. The data of the count rates and activities of the U and Th isotopes can be seen in Appendix C.15.

The following is a short description of the analytical methods used. Full details can be found in Poole (1992).

- 1) The sample was ground to a fine powder using a TEMA mill and then divided into two duplicate samples of between 0.3 and 0.4g in weight. Both samples were then run in parallel to check for precision of results.
- 2) The sample was transferred to a PTFE crucible and completely digested in conc. HNO₃ and conc. HF acids, then fumed to dryness.
- 3) In order to allow the yield of the procedure to be deduced, a mixed spike of ²²⁸Th and ²³²U was added using an Eppendorf pipette.
- 4) ²³⁰Th and ²³⁴U have very similar peak α -particle energies and therefore the U and Th radionuclides were chemically separated using an anion exchange column filled with Bio-Rad AG1-X8 resin.
- 5) Once separated, the U and Th solutions were electroplated onto different stainless steel planchets, in order to obtain a mono-atomic layer suitable for counting.

- 6) Samples were counted using α -spectrometry on a silicon surface barrier counter for about 10^4 counts or a time equivalent to the background counting time (measured for 2 days prior to the sample and used to correct for detector contamination).
- 7) ^{238}U , ^{234}U , ^{232}Th and ^{230}Th activity rates were calculated using knowledge of sample weight, unknown isotope corrected-counts, spike corrected-counts and spike activity.
- 8) $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ ratios were then calculated, along with their errors, and from an isochron plot and the formula in Appendix B.5, the (maximum) age of the sample was calculated.

APPENDIX A.9. X-RAY DIFFRACTION ANALYSIS

Sample preparation for X-ray diffraction analysis involved placing a small amount (about 0.1g) of the bulk-sediment sample in a mortar, adding a few drops of acetone and gently grinding with a pestle.

Generator settings	40kV, 50mA
Cu $k\alpha$ 1,2 wavelengths	1.54060, 1.554439
Step size, sample time	15 sec / °
Monochromator used	Yes
Divergence slit	Automatic
Analysis program number	8
Peak angle range	2° to 60° (2 θ)
Range in D-spacing	2.25221 to 44.1372 Å
Crystal peak width range	0 to 2°
Minimum peak significance	0.75

Table A.9.1. X-ray diffraction analytical conditions

The resulting solution was drawn up in a pipette and dispersed onto a 2cm diameter glass slide. The acetone was allowed to evaporate off, leaving a thin, even film of the sample on the glass disc. The mineral identification analysis was carried out using a Phillips PW 1011/1050 diffractometer, under the analytical conditions set out in Table A.9.1.

APPENDIX B

CALCULATION OF SEDIMENT PARAMETERS

APPENDIX B.1. Calcium carbonate

$$\text{CaCO}_3 \text{ (wt.\%)} = [\text{Ca} - \{(\text{Ca}/\text{Al}^* \times \text{Al}) + (\text{Ca}/\text{P} \times \text{P}_{\text{phos}})\}] \times (100/40)$$

where, Ca, Al and P are XRF data (salt corrected and in wt.%),
Ca/Al* = Ca/Al ratio from average shale (Turekian and Wedepohl, 1961) or minimum Ca/Al ratio for core,
Ca/P = Ca/P ratio in phosphorite nodule :CD38-09 (273cm),
(100/40) = molecular weight conversion factor.

APPENDIX B.2. Enrichment factors of metals

$$\text{E.F.}_{\text{metal}} = [\text{Metal}_{\text{sample}}/\text{Al}_{\text{sample}}] / [\text{Metal}_{\text{clay}}/\text{Al}_{\text{clay}}]$$

where values from Turekian and Wedepohl (1961) for deep-sea clay are as follows (all in ppm):

$$\text{Al} = 84,000, \text{Mo} = 27, \text{U} = 1.3, \text{Ni} = 225, \text{Cr} = 90, \text{V} = 120 \text{ and } \text{Cu} = 250.$$

$\text{E.F.}_{\text{metal}} > 1.0$ = Enrichment above that expected from terrigenous input

$\text{E.F.}_{\text{metal}} < 1.0$ = Depletion below that expected from terrigenous input.

APPENDIX B.3. Phosphorite mineral composition calculation

Algorithm for calculation of mineral composition in phosphorite nodules (uses end-member compositions from Table B.1.)

Step 1. Recalculate XRF major element oxides to total 100%.

Step 2. Put all P_2O_5 available into CFA
 $(\text{P}_2\text{O}_5 / 39.85) \times 100 = \text{CFA} (\%)$

Step 3. Put all MgO available into dolomite
 $(\text{MgO} / 42.0) \times 100 = \text{Dolomite} (\%)$

Step 4. Calculate how much CaO is left over from CFA and dolomite
 $\text{CaO} - ((\text{CFA} / 100) \times 58.77) - ((\text{Dolomite} / 100) \times 58.0) = \text{CaO left}$

- Step 5. Put all CaO left into calcite
 $(\text{CaO left} / 100) \times 100 = \text{Calcite (\%)}$
- Step 6. Put all Fe₂O₃ available into pyrite
 $(\text{Fe}_2\text{O}_3 / 100) \times 100 = \text{Pyrite (\%)}$
- Step 7. Put all K₂O available into orthoclase
 $(\text{K}_2\text{O} / 15.16) \times 100 = \text{Orthoclase (\%)}$
- Step 8. Calculate how much Al₂O₃ is left over from orthoclase
 $\text{Al}_2\text{O}_3 - ((\text{Orthoclase} / 100) \times 26.74) = \text{Al}_2\text{O}_3 \text{ left}$
- Step 9. Put all Al₂O₃ left into plagioclase
 $(\text{Al}_2\text{O}_3 \text{ left} / 25.26) \times 100 = \text{Plagioclase (\%)}$
- Step 10. Calculate how much SiO₂ is left over from orthoclase and plagioclase
 $\text{SiO}_2 - ((\text{Orthoclase} / 100) \times 59.6) - ((\text{Plagioclase} / 100) \times 62.38) = \text{SiO}_2 \text{ left}$
- Step 11. Put all SiO₂ left into opal/quartz
 $(\text{SiO}_2 \text{ left} / 100) \times 100 = \text{Opal/Quartz (\%)}$

	CFA	Dolom.	Calcite	Pyrite	Orth.	Plag.	Opal/Qtz
SiO ₂	0	0	0	0	59.60	62.38	100
Al ₂ O ₃	0	0	0	0	25.26	26.74	0
Fe ₂ O ₃	0	0	0	100	0	0	0
MgO	0	42.0	0	0	0	0	0
CaO	58.77	58.0	100	0	0	0	0
Na ₂ O	1.00	0	0	0	0	10.90	0
K ₂ O	0	0	0	0	15.16	0	0
P ₂ O ₅	39.85	0	0	0	0	0	0

Table B.1. End-member mineral compositions (Glenn and Arthur, 1988)

APPENDIX B.4. Partitioning Equations

B.4.1. Phosphorus

$$P_{\text{phos}} = P_{\text{total}} - (P_{\text{terr}} + P_{\text{org}})$$

where, P_{total} = salt-corrected XRF data,
 $P_{terr} = Al \times 0.00875$ (Turekian and Wedepohl, 1961),
 $P_{org} = C_{org} \times 0.0053$ (Mach *et al.*, 1987)

and, phosphorite concentration,

$$\text{Phosphorite} = P_{phos} \times (100 / 8.29)$$

B.4.2. Uranium

$$U_{org} = U_{total} - (U_{terr} + U_{phos})$$

where, U_{total} = salt-corrected XRF data,
 $U_{terr} = Al \times 0.4625$ (Turekian and Wedepohl, 1961),
 $U_{phos} = P_{phos} \times 14.1$ (Fig. 3.8).

B.4.3. Strontium

$$Sr_{calcite} = Sr_{total} - (Sr_{terr} + Sr_{phos})$$

where, Sr_{total} = salt-corrected XRF data,
 $Sr_{terr} = Al \times 21.43$ (Turekian and Wedepohl, 1961),
 $Sr_{phos} = P_{phos} \times 186$ (Fig. 3.10).

B.4.4. Yttrium

$$Y_{terr} = Y_{total} - Y_{phos}$$

where, Y_{total} = salt-corrected XRF data,
 $Y_{phos} = P_{phos} \times 12.1$ (Fig. 3.12).

B.4.5. Silicon

$$Si_{terr} = Si_{total} - [\text{Bio. Sil.} \times 0.466]$$

where, Si_{terr} = terrigenous silicon (wt.%),
 Si_{total} = XRF Si concentration (wt.%),
 Bio. Sil. = biogenic silica concentration (wt.%),
 0.466 = atomic weight conversion from silica to silicon.

APPENDIX B.5. U-series disequilibrium age and initial $^{234}\text{U}/^{238}\text{U}$ calculation

Using the measured $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ ratios, the age of the sample can either be graphically estimated using a U/Th isochron plot or accurately calculated using the equation below (Ivanovich and Harmon, 1982).

B.5.1. Age calculation

$$\begin{aligned} ^{230}\text{Th}/^{234}\text{U} = & \left[\left\{ 1 - \exp - (\lambda^{230}\text{Th} \times t) \right\} / ^{234}\text{U}/^{238}\text{U} \right] \\ & + \left[\left\{ 1 - (1 / ^{234}\text{U}/^{238}\text{U}) \right\} \times \left\{ \lambda^{230}\text{Th} / (\lambda^{230}\text{Th} - \lambda^{234}\text{U}) \right\} \right] \\ & \times \left\{ 1 - \exp - (\lambda^{230}\text{Th} - \lambda^{234}\text{U}) \times t \right\} \end{aligned}$$

where,

$$\begin{aligned} ^{234}\text{U}/^{238}\text{U} &= \text{ratio calculated from } \alpha\text{-spectrometry results,} \\ ^{230}\text{Th}/^{234}\text{U} &= \text{ratio calculated from } \alpha\text{-spectrometry results,} \\ \lambda^{230}\text{Th} &= 9.2154 \times \text{E}^{-6} = 0.693 / ^{230}\text{Th}_{\text{half-life}}, \\ \lambda^{234}\text{U} &= 2.7943 \times \text{E}^{-6} = 0.693 / ^{234}\text{U}_{\text{half-life}}, \\ t &= \text{age of sample (years).} \end{aligned}$$

B.5.2. Initial $^{234}\text{U}/^{238}\text{U}$ calculation

$$^{234}\text{U}/^{238}\text{U}_{\text{initial}} = (^{234}\text{U}/^{238}\text{U}_t - 1) / \exp - (\lambda^{234}\text{U} \times t)$$

where,

$$\begin{aligned} ^{234}\text{U}/^{238}\text{U}_{\text{initial}} &= \text{initial ratio (as incorporated from sea-water),} \\ ^{234}\text{U}/^{238}\text{U}_t &= \text{ratio at time (t),} \\ \lambda^{234}\text{U} &= 2.7943 \times \text{E}^{-6}, \\ t &= \text{age of sample (years).} \end{aligned}$$

APPENDIX B.6. Multi-component analysis (MCA) algorithm

Algorithm for calculation of relative concentrations of 5 components (terrigenous, biogenic, authigenic, residual and hydrothermal) in marine sediments. Adapted from Dymond and Heath (1979) and Dymond (1981).

Step 1. Assume all Al (wt.%) is present only in the terrigenous component. Calculate TERR using the Al content of average clay composition (Turekian and Wedepohl, 1961).

$$\text{TERR} = (\text{Al} / \text{Al}_{\text{clay}}) \times 100 \quad \text{where, } \text{Al}_{\text{clay}} = 8.40$$

Step 2. Calculate biogenic component by adding calcium carbonate, biogenic silica and organic carbon concentrations (all wt.%).

$$\text{BIOG} = \text{CaCO}_3 + \text{Bio.Sil.} + \text{C}_{\text{org}}$$

Step 3. Phosphorite is the dominant authigenic mineral in Peru margin sediments and therefore, calculate authigenic component as equal to wt.% phosphorite.

$$\text{AUTH} = (\text{P}_{\text{phos}} / \text{P}_{\text{nodule}}) \times 100$$

where, P_{phos} = calculated from Eqn 4.1,
 P_{nodule} = average P concentration of phosphorite nodule in core CD38-09 = 8.29 wt.% (Table 4.1).

Step 4. Calculate the concentration of Ba (ppm) in excess to that required by the TERR, BIOG and AUTH components.

$$\text{Ba}_{\text{xs}} = \text{Ba}_{\text{total}} - (\text{Ba}_{\text{TERR}} + \text{Ba}_{\text{BIOG}} + \text{Ba}_{\text{AUTH}})$$

where, $\text{Ba}_{\text{TERR}} = \text{Al (wt.\%)} \times \text{Ba}/\text{Al}_{\text{clay}} = \text{Al} \times 273.41$,
 $\text{Ba}_{\text{BIOG}} = \text{CaCO}_3 \text{ (wt.\%)} \times (40/100) \times \text{Ba}/\text{Ca}_{\text{carbonate}}$
 $= \text{CaCO}_3 \times 0.4 \times 6.082$,
 $\text{Ba}_{\text{AUTH}} = \text{P}_{\text{phos}} \text{ (wt.\%)} \times \text{Ba}/\text{P}_{\text{nodule}} = \text{P}_{\text{phos}} \times 10.133$.
 ($\text{Ba}/\text{Al}_{\text{clay}}$ and $\text{Ba}/\text{Ca}_{\text{carbonate}}$ from Turekian and Wedepohl, 1961. $\text{Ba}/\text{P}_{\text{nodule}}$ from Table 4.1)

Step 5. Calculate the concentration of Fe (wt.%) in excess to that required by the TERR component.

$$\text{Fe}_{\text{xs}} = \text{Fe}_{\text{total}} - [\text{Al (wt.\%)} \times \text{Fe}/\text{Al}_{\text{clay}}]$$

where, $\text{Fe}/\text{Al}_{\text{clay}} = 0.774$ (Turekian and Wedepohl, 1961)

Step 6. If Ba_{xs} is non-negative, calculate the residual component by assuming concentration of pure residual phase = 270,000 ppm Ba (Dymond, 1981).

$$RESID = (Ba_{xs} / 270,000) \times 100$$

Step 7. If Fe_{xs} is non-negative, calculate the hydrothermal component by assuming concentration of pure hydrothermal phase = 34.8 wt.% Fe (Dymond, 1981).

$$HYDRO = (Fe_{xs} / 34.8) \times 100$$

Step 8. Recalculate all five components to % by dividing by the sum of components and multiplying by 100.

$$\text{e.g. } TERR \% = [TERR / (TERR + BIOG + AUTH + RESID + HYDRO)] \times 100$$

APPENDIX C

DATA TABLES

APPENDIX C.1. SEDIMENT PHYSICAL PARAMETERS											
CD38-03						CD38-02					
Sample	Depth	Water	Salt	Porosity	D.B.D.	Sample	Depth	Water	Salt	Porosity	D.B.D.
	(cm.)	(%)					(cm.)	(%)			
BC3803-01	0.5	81.6	15.58	0.921	0.218	BC3802-01	0.5	72.1	9.08	0.872	0.351
BC3803-02	1.5	77.0	11.76	0.898	0.281	BC3802-02	1.5	73.0	9.50	0.877	0.338
BC3803-03	2.5	78.1	12.53	0.904	0.264	BC3802-03	2.5	67.4	7.26	0.845	0.427
BC3803-04	3.5	72.7	9.36	0.875	0.358	BC3802-04	3.5	67.4	7.26	0.845	0.426
BC3803-05	4.5	73.9	9.95	0.882	0.325	BC3802-05	4.5	68.4	7.60	0.851	0.411
BC3803-06	5.5	73.1	9.55	0.877	0.338	BC3802-06	5.5	64.7	6.44	0.828	0.470
BC3803-07	6.5	68.7	7.71	0.853	0.405	BC3802-07	6.5	61.5	5.61	0.808	0.527
BC3803-08	7.5	69.1	7.86	0.855	0.399	BC3802-08	7.5	59.7	5.20	0.796	0.559
BC3803-09	8.5	70.9	8.56	0.865	0.370	BC3802-09	8.5	59.6	5.18	0.795	0.562
BC3803-10	9.5	68.6	7.67	0.852	0.407	BC3802-10	9.5	59.4	5.14	0.794	0.564
BC3803-11	11.0	68.9	7.78	0.854	0.411	BC3802-11	11.0	59.7	5.20	0.796	0.559
BC3803-12	13.0	68.6	7.67	0.852	0.406	BC3802-12	13.0	59.5	5.16	0.795	0.562
BC3803-13	15.0	66.6	7.00	0.840	0.447	BC3802-13	15.0	58.8	5.01	0.790	0.576
BC3803-14	17.0	66.8	7.07	0.841	0.436	BC3802-13A	17.0	57.2	4.69	0.779	0.606
BC3803-15	19.0	65.6	6.70	0.834	0.463	BC3802-14	19.0	54.9	4.28	0.762	0.649
BC3803-16	21.0	64.5	6.38	0.827	0.474	BC3802-15	21.0	54.5	4.21	0.759	0.658
BC3803-17	23.0	65.8	6.76	0.835	0.456	BC3802-16	23.0	54.7	4.24	0.761	0.655
BC3803-18	25.0	65.1	6.55	0.831	0.463	BC3802-17	25.0	54.4	4.19	0.759	0.661
BC3803-19	27.0	63.9	6.22	0.823	0.487	BC3802-18	27.0	54.1	4.14	0.756	0.667
BC3803-20	29.0	63.7	6.16	0.822	0.488	BC3802-19	29.0	55.4	4.36	0.766	0.642
BC3803-21	31.0	63.6	6.14	0.822	0.499	BC3802-20	31.0	55.1	4.31	0.764	0.645
BC3803-22	33.0	62.3	5.81	0.813	0.512	BC3802-21	33.0	55.9	4.45	0.770	0.630
BC3803-23	35.0	62.6	5.88	0.815	0.510	BC3802-21A	35.0	56.4	4.54	0.773	0.621
BC3803-24	37.0	60.9	5.47	0.804	0.538	BC3802-22	37.0	56.1	4.49	0.771	0.644
BC3803-25	39.0	64.5	6.38	0.827	0.478	BC3802-23	39.0	56.6	4.58	0.775	0.616
BC3803-26	41.0	63.7	6.16	0.822	0.488	BC3802-24	41.0	56.0	4.47	0.770	0.638
BC3803-27	43.0	61.4	5.59	0.807	0.528	BC3802-25	43.0	56.3	4.53	0.772	0.631
BC3803-28	45.0	61.6	5.64	0.809	0.525	BC3802-26	45.0	56.6	4.58	0.775	0.618
BC3803-29	47.0	62.3	5.81	0.813	0.515	BC3802-27	47.0	56.4	4.54	0.773	0.621
BC3803-30	49.0	62.3	5.81	0.813	0.512	BC3802-28	49.0	56.0	4.47	0.770	0.630
BC3803-31	51.0	63.5	6.11	0.821	0.496	BC3802-29	51.0	55.7	4.42	0.768	0.635
BC3803-32	53.0	62.9	5.96	0.817	0.502	BC3802-30	53.0	56.5	4.56	0.774	0.620

APPENDIX C.1. SEDIMENT PHYSICAL PARAMETERS

CD38-09						CD38-09					
Sample	Depth (cm.)	Water (%)	Salt	Porosity	D.B.D.	Sample	Depth (cm.)	Water (%)	Salt	Porosity	D.B.D.
PC3809G01	4.0	67.7	7.36	0.847	0.421	PC3809G33	324.0	59.8	5.23	0.797	0.556
PC3809G02	13.0	74.7	10.37	0.886	0.323	PC3809G34	335.0	65.0	6.52	0.830	0.465
PC3809G03	23.0	65.2	6.58	0.832	0.462	PC3809G35	344.0	66.9	7.10	0.842	0.433
PC3809G04	34.0	66.1	6.85	0.837	0.448	PC3809G36	355.0	71.5	8.81	0.869	0.360
PC3809G05	43.0	54.3	4.17	0.758	0.662	PC3809G37	364.0	71.0	8.60	0.866	0.369
PC3809G06	53.0	68.4	7.60	0.851	0.410	PC3809G38	375.0	65.3	6.61	0.832	0.461
PC3809G07	62.0	69.8	8.12	0.859	0.386	PC3809G39	384.0	58.5	4.95	0.788	0.581
PC3809G08	73.0	68.3	7.57	0.850	0.412	PC3809G40	394.0	64.9	6.50	0.830	0.468
PC3809G09	84.0	64.2	6.30	0.825	0.480	PC3809G41	404.0	61.3	5.56	0.807	0.530
PC3809G10	94.0	66.9	7.10	0.842	0.433	PC3809G42	416.0	66.0	6.82	0.836	0.449
PC3809G11	104.0	69.7	8.08	0.858	0.388	PC3809G43	424.0	66.2	6.88	0.838	0.446
PC3809G12	113.0	59.4	5.14	0.794	0.564	PC3809G44	434.0	60.5	5.38	0.801	0.544
PC3809G13	124.0	58.1	4.87	0.785	0.589	PC3809G45	444.0	66.0	6.82	0.836	0.448
PC3809G14	134.0	66.3	6.91	0.838	0.445	PC3809G46	453.0	58.6	4.97	0.789	0.578
PC3809G15	144.0	68.7	7.71	0.853	0.404	PC3809G47	465.0	63.4	6.09	0.820	0.493
PC3809G16	152.0	68.2	7.53	0.850	0.413	PC3809G48	474.0	64.7	6.44	0.828	0.470
PC3809G17	165.0	68.8	7.75	0.853	0.403	PC3809G49	483.0	58.9	5.03	0.791	0.574
PC3809G18	174.0	53.8	4.09	0.754	0.672	PC3809G50	493.0	61.6	5.64	0.809	0.524
PC3809G19	185.0	55.3	4.35	0.765	0.642	PC3809G51	504.0	54.3	4.17	0.758	0.661
PC3809G20	194.0	46.8	3.09	0.699	0.783	PC3809G52	515.0	52.8	3.93	0.747	0.692
PC3809G21	205.0	53.0	3.96	0.748	0.687	PC3809G53	525.0	61.7	5.66	0.809	0.522
PC3809G22	214.0	60.9	5.47	0.804	0.537	PC3809G54	536.0	64.1	6.27	0.825	0.481
PC3809G23	224.0	36.9	2.05	0.606	1.070	PC3809G55	544.0	56.2	4.51	0.772	0.625
PC3809G24	234.0	55.6	4.40	0.767	0.636	PC3809G56	553.0	63.0	5.98	0.818	0.500
PC3809G25	243.0	70.3	8.32	0.862	0.379	PC3809G57	564.0	67.3	7.23	0.844	0.427
PC3809G26	257.0	63.8	6.19	0.823	0.486	PC3809G58	574.0	64.5	6.38	0.827	0.473
PC3809G27	267.0	52.7	3.91	0.746	0.695	PC3809G59	585.0	65.5	6.67	0.833	0.456
PC3809G28	273.0	43.3	2.68	0.668	0.903	PC3809G60	594.0	67.0	7.13	0.842	0.432
PC3809G29	284.0	62.4	5.83	0.814	0.510	PC3809G61	605.0	59.3	5.12	0.793	0.565
PC3809G30	294.0	66.9	7.10	0.842	0.433	PC3809G62	615.0	66.5	6.97	0.839	0.441
PC3809G31	304.0	62.4	5.83	0.814	0.510	PC3809G63	625.0	61.9	5.71	0.811	0.518
PC3809G32	314.0	64.4	6.35	0.827	0.476	PC3809G64	635.0	60.0	5.27	0.798	0.554

APPENDIX C.1. SEDIMENT PHYSICAL PARAMETERS											
CD38-09						CD38-10					
Sample	Depth (cm.)	Water (%)	Salt	Porosity	D.B.D.	Sample	Depth (cm.)	Water (%)	Salt	Porosity	D.B.D.
PC3809G65	646.0	68.8	7.75	0.853	0.402	PC3810A08	74.0	50.1	3.53	0.726	0.748
PC3809G66	654.0	68.2	7.53	0.850	0.413	PC3810A09	84.0	25.6	1.21	0.475	1.415
PC3809G67	664.0	68.9	7.78	0.854	0.401	PC3810A10	94.0	26.2	1.25	0.483	1.396
PC3809G68	674.0	69.3	7.93	0.856	0.394	PC3810A11	104.0	31.5	1.62	0.548	1.225
PC3809G69	684.0	63.8	6.19	0.823	0.485	PC3810A12	113.0	26.5	1.27	0.487	1.386
PC3809G70	694.0	62.8	5.93	0.816	0.503	PC3810A13	126.0	62.8	5.93	0.816	0.502
PC3809G71	703.0	63.8	6.19	0.823	0.485	PC3810A14	134.0	62.7	5.91	0.816	0.505
PC3809G72	714.0	64.4	6.35	0.827	0.476	PC3810A15	146.0	56.3	4.53	0.772	0.623
PC3809G73	724.0	60.7	5.43	0.803	0.541	PC3810A16	154.0	58.6	4.97	0.789	0.578
PC3809G74	734.0	60.3	5.34	0.800	0.548	PC3810A17	167.0	63.1	6.01	0.818	0.499
PC3809G75	744.0	65.5	6.67	0.833	0.457	PC3810A18	174.0	60.6	5.40	0.802	0.542
PC3809G76	754.0	66.4	6.94	0.839	0.442	PC3810A19	185.0	59.1	5.08	0.792	0.570
PC3809G77	764.0	59.7	5.20	0.796	0.558	PC3810A20	194.0	66.5	6.97	0.839	0.440
PC3809G78	774.0	56.8	4.62	0.776	0.613	PC3810A21	203.0	57.3	4.71	0.779	0.603
PC3809G79	784.0	59.8	5.23	0.797	0.557	PC3810A22	216.0	66.1	6.85	0.837	0.447
PC3809G80	794.0	58.5	4.95	0.788	0.581	PC3810A23	224.0	66.3	6.91	0.838	0.444
PC3809G81	804.0	59.3	5.12	0.793	0.567	PC3810A24	233.0	63.9	6.22	0.823	0.485
PC3809G82	813.0	56.4	4.54	0.773	0.621	PC3810A25	244.0	60.2	5.31	0.799	0.551
PC3809G83	823.0	57.1	4.68	0.778	0.608	PC3810A26	254.0	60.7	5.43	0.803	0.541
PC3809G84	834.0	57.1	4.68	0.778	0.606	PC3810A27	263.0	63.5	6.11	0.821	0.490
PC3809G85	845.0	58.7	4.99	0.789	0.577	PC3810A28	273.0	59.4	5.14	0.794	0.565
PC3809G86	854.0	56.1	4.49	0.771	0.626	PC3810A29	284.0	56.7	4.60	0.775	0.615
						PC3810A30	295.0	64.1	6.27	0.825	0.480
CD38-10						PC3810A31	305.0	59.2	5.10	0.793	0.568
						PC3810A32	314.0	55.3	4.35	0.765	0.642
PC3810A01	6.0	69.1	7.86	0.855	0.398	PC3810A33	324.0	65.7	6.73	0.835	0.454
PC3810A02	14.0	52.7	3.91	0.746	0.695	PC3810A34	335.0	58.3	4.91	0.786	0.585
PC3810A03	24.0	32.1	1.66	0.555	1.207	PC3810A35	344.0	66.9	7.10	0.842	0.433
PC3810A04	34.0	39.0	2.25	0.627	1.013	PC3810A36	354.0	70.4	8.36	0.862	0.378
PC3810A05	44.0	59.6	5.18	0.795	0.561	PC3810A37	364.0	70.4	8.36	0.862	0.378
PC3810A06	54.0	63.3	6.06	0.820	0.494	PC3810A38	374.0	69.6	8.04	0.858	0.392
PC3810A07	64.0	57.7	4.79	0.782	0.596	PC3810A39	383.0	59.5	5.16	0.795	0.561

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APPENDIX C.1. SEDIMENT PHYSICAL PARAMETERS											
CD38-10						CD38-10					
Sample	Depth (cm.)	Water (%)	Salt	Porosity	D.B.D.	Sample	Depth (cm.)	Water (%)	Salt	Porosity	D.B.D.
PC3810A40	394.0	63.9	6.22	0.823	0.483	PC3810A72	714.0	58.5	4.95	0.788	0.580
PC3810A41	404.0	58.5	4.95	0.788	0.581	PC3810A73	724.0	60.3	5.34	0.800	0.548
PC3810A42	417.0	61.1	5.52	0.805	0.533	PC3810A74	734.0	57.8	4.81	0.783	0.594
PC3810A43	424.0	62.6	5.88	0.815	0.506	PC3810A75	745.0	52.6	3.90	0.745	0.698
PC3810A44	434.0	70.7	8.48	0.864	0.373	PC3810A76	754.0	59.4	5.14	0.794	0.564
PC3810A45	445.0	64.5	6.38	0.827	0.475	PC3810A77	764.0	46.4	3.04	0.695	0.833
PC3810A46	456.0	67.2	7.20	0.844	0.429						
PC3810A47	467.0	73.3	9.64	0.879	0.481	CD38-02					
PC3810A48	476.0	57.5	4.75	0.781	0.600						
PC3810A49	484.0	55.9	4.45	0.770	0.631	PC3802P01	8.0	58.71	4.99	0.79	0.58
PC3810A50	494.0	50.8	3.63	0.731	0.733	PC3802P02	18.0	57.20	4.69	0.78	0.61
PC3810A51	504.0	31.5	1.62	0.548	1.227	PC3802P03	28.0	59.27	5.11	0.79	0.57
PC3810A52	514.0	58.9	5.03	0.791	0.574	PC3802P04	38.0	61.14	5.53	0.81	0.53
PC3810A53	524.0	55.7	4.42	0.768	0.633	PC3802P05	48.0	57.06	4.67	0.78	0.61
PC3810A54	534.0	64.9	6.50	0.830	0.468	PC3802P06	57.5	57.18	4.69	0.78	0.61
PC3810A55	545.0	63.9	6.22	0.823	0.485	PC3802P07	70.0	57.30	4.71	0.78	0.60
PC3810A56	554.0	67.9	7.43	0.848	0.418	PC3802P08	79.0	58.02	4.86	0.78	0.59
PC3810A57	564.0	70.1	8.24	0.861	0.384	PC3802P09	89.0	56.92	4.64	0.78	0.61
PC3810A58	574.0	64.8	6.47	0.829	0.469	PC3802P10	100.0	56.70	4.60	0.78	0.62
PC3810A59	584.0	66.9	7.10	0.842	0.434	PC3802P11	110.0	56.21	4.51	0.77	0.63
PC3810A60	596.0	67.3	7.23	0.844	0.428	PC3802P12	120.0	57.20	4.70	0.78	0.61
PC3810A61	604.0	66.3	6.91	0.838	0.444	PC3802P13	130.0	56.92	4.64	0.78	0.61
PC3810A62	614.0	66.6	7.00	0.840	0.440	PC3802P14	139.0	57.68	4.79	0.78	0.60
PC3810A63	624.0	62.0	5.73	0.811	0.517	PC3802P15	150.0	58.05	4.86	0.78	0.59
PC3810A64	634.0	62.0	5.73	0.811	0.518	PC3802P16	160.0	55.08	4.31	0.76	0.65
PC3810A65	645.0	66.0	6.82	0.836	0.449	PC3802P17	171.0	55.45	4.37	0.77	0.64
PC3810A66	655.0	66.8	7.07	0.841	0.436	PC3802P18	181.0	58.67	4.99	0.79	0.58
PC3810A67	667.0	64.0	6.25	0.824	0.471	PC3802P19	191.0	57.51	4.75	0.78	0.60
PC3810A68	674.0	62.8	5.93	0.816	0.504	PC3802P20	201.0	58.71	4.99	0.79	0.58
PC3810A69	683.0	63.3	6.06	0.820	0.494	PC3802P21	211.0	57.01	4.66	0.78	0.61
PC3810A70	694.0	57.2	4.69	0.779	0.605	PC3802P22	221.0	55.94	4.46	0.77	0.63
PC3810A71	704.0	54.4	4.19	0.759	0.659	PC3802P23	231.0	55.12	4.32	0.76	0.65

APPENDIX C.1. SEDIMENT PHYSICAL PARAMETERS											
CD38-02						CD38-02					
Sample	Depth	Water	Salt	Porosity	D.B.D.	Sample	Depth	Water	Salt	Porosity	D.B.D.
	(cm.)	(%)					(cm.)	(%)			
PC3802P24	241.0	56.23	4.51	0.77	0.62	PC3802P56	560.0	56.79	4.62	0.78	0.61
PC3802P25	251.0	56.13	4.50	0.77	0.63	PC3802P57	572.0	43.54	2.71	0.67	0.90
PC3802P26	261.0	55.22	4.33	0.76	0.64	PC3802P58	582.0	44.01	2.76	0.67	0.89
PC3802P27	271.0	56.30	4.53	0.77	0.62	PC3802P59	591.0	50.57	3.59	0.73	0.74
PC3802P28	281.0	55.60	4.40	0.77	0.64	PC3802P60	601.0	48.79	3.35	0.72	0.78
PC3802P29	291.0	56.35	4.53	0.77	0.62	PC3802P61	611.0	48.96	3.37	0.72	0.77
PC3802P30	301.0	56.62	4.58	0.77	0.62	PC3802P62	621.0	49.42	3.43	0.72	0.76
PC3802P31	312.0	56.97	4.65	0.78	0.61	PC3802P63	631.0	47.80	3.22	0.71	0.80
PC3802P32	322.0	56.17	4.50	0.77	0.63	PC3802P64	641.0	49.36	3.42	0.72	0.77
PC3802P33	332.0	55.67	4.41	0.77	0.64	PC3802P65	651.0	51.99	3.80	0.74	0.71
PC3802P34	342.0	57.20	4.70	0.78	0.61	PC3802P66	662.0	53.32	4.01	0.75	0.68
PC3802P35	352.0	56.82	4.62	0.78	0.61	PC3802P67	671.0	53.02	3.96	0.75	0.69
PC3802P36	362.0	55.88	4.45	0.77	0.63	PC3802P68	681.0	51.33	3.71	0.74	0.72
PC3802P37	372.0	54.20	4.16	0.76	0.66	PC3802P69	691.0	52.22	3.84	0.74	0.71
PC3802P38	381.0	52.13	3.82	0.74	0.71	PC3802P70	701.0	51.17	3.68	0.73	0.73
PC3802P39	391.0	51.99	3.80	0.74	0.71	PC3802P71	711.0	52.40	3.87	0.74	0.70
PC3802P40	400.0	52.43	3.87	0.74	0.70	PC3802P72	721.0	52.42	3.87	0.74	0.70
PC3802P41	410.0	52.16	3.83	0.74	0.71	PC3802P73	731.0	51.69	3.76	0.74	0.72
PC3802P42	420.0	52.61	3.90	0.75	0.70	PC3802P74	741.0	52.37	3.86	0.74	0.70
PC3802P43	430.0	51.33	3.71	0.74	0.72						
PC3802P44	440.0	50.94	3.65	0.73	0.73	CD38-11					
PC3802P45	450.0	53.44	4.03	0.75	0.68						
PC3802P46	460.0	53.19	3.99	0.75	0.69	PC3811P01	3.0	58.76	5.01	0.79	0.58
PC3802P47	470.0	51.51	3.73	0.74	0.72	PC3811P02	13.0	56.25	4.52	0.77	0.62
PC3802P48	481.0	51.64	3.75	0.74	0.72	PC3811P03	23.0	51.05	3.66	0.73	0.73
PC3802P49	491.0	52.18	3.83	0.74	0.71	PC3811P04	33.0	60.27	5.33	0.80	0.55
PC3802P50	501.0	52.94	3.95	0.75	0.69	PC3811P05	43.0	61.22	5.55	0.81	0.53
PC3802P51	511.0	51.75	3.77	0.74	0.71	PC3811P06	53.0	60.62	5.41	0.80	0.54
PC3802P52	521.0	52.43	3.87	0.74	0.70	PC3811P07	63.0	60.08	5.29	0.80	0.55
PC3802P53	531.0	47.96	3.24	0.71	0.80	PC3811P08	73.0	58.45	4.94	0.79	0.58
PC3802P54	540.0	53.93	4.11	0.76	0.67	PC3811P09	85.0	41.18	2.46	0.65	0.96
PC3802P55	550.0	54.90	4.28	0.76	0.65	PC3811P10	95.0	57.70	4.79	0.78	0.60

APPENDIX C.1. SEDIMENT PHYSICAL PARAMETERS

CD38-11						CD38-11					
Sample	Depth (cm.)	Water (%)	Salt	Porosity	D.B.D.	Sample	Depth (cm.)	Water (%)	Salt	Porosity	D.B.D.
PC3811P11	105.0	58.22	4.90	0.79	0.59	PC3811P43	425.0	56.53	4.57	0.77	0.62
PC3811P12	116.0	57.88	4.83	0.78	0.59	PC3811P44	435.0	56.88	4.63	0.78	0.61
PC3811P13	125.0	58.28	4.91	0.79	0.59	PC3811P45	445.0	58.14	4.88	0.79	0.59
PC3811P14	135.0	57.07	4.67	0.78	0.61	PC3811P46	455.0	55.95	4.46	0.77	0.63
PC3811P15	145.0	58.71	4.99	0.79	0.58	PC3811P47	465.0	56.51	4.57	0.77	0.62
PC3811P16	155.0	55.71	4.42	0.77	0.63	PC3811P48	475.0	56.09	4.49	0.77	0.63
PC3811P17	165.0	59.75	5.21	0.80	0.56	PC3811P49	485.0	56.71	4.60	0.78	0.62
PC3811P18	175.0	50.60	3.60	0.73	0.74	PC3811P50	495.0	57.64	4.78	0.78	0.60
PC3811P19	186.0	58.33	4.92	0.79	0.58	PC3811P51	505.0	57.70	4.79	0.78	0.60
PC3811P20	197.0	59.33	5.13	0.79	0.57	PC3811P52	515.0	56.85	4.63	0.78	0.61
PC3811P21	204.0	59.77	5.22	0.80	0.56	PC3811P53	525.0	57.80	4.81	0.78	0.59
PC3811P22	215.0	59.15	5.09	0.79	0.57	PC3811P54	535.0	56.07	4.48	0.77	0.63
PC3811P23	225.0	60.95	5.48	0.80	0.54	PC3811P55	545.0	57.49	4.75	0.78	0.60
PC3811P24	235.0	59.82	5.23	0.80	0.56	PC3811P56	555.0	56.94	4.64	0.78	0.61
PC3811P25	245.0	59.30	5.12	0.79	0.57	PC3811P57	565.0	56.18	4.50	0.77	0.63
PC3811P26	255.0	58.90	5.03	0.79	0.57						
PC3811P27	265.0	59.31	5.12	0.79	0.57						
PC3811P28	275.0	59.47	5.15	0.79	0.56						
PC3811P29	285.0	58.23	4.90	0.79	0.59						
PC3811P30	297.0	52.97	3.96	0.75	0.69						
PC3811P31	305.0	54.28	4.17	0.76	0.66						
PC3811P32	315.0	53.70	4.07	0.75	0.67						
PC3811P33	325.0	42.27	2.57	0.66	0.93						
PC3811P34	335.0	57.38	4.73	0.78	0.60						
PC3811P35	345.0	57.86	4.82	0.78	0.59						
PC3811P36	355.0	58.54	4.96	0.79	0.58						
PC3811P37	365.0	57.68	4.79	0.78	0.60						
PC3811P38	375.0	57.34	4.72	0.78	0.60						
PC3811P39	385.0	55.68	4.41	0.77	0.64						
PC3811P40	395.0	54.63	4.23	0.76	0.66						
PC3811P41	405.0	55.38	4.36	0.77	0.64						
PC3811P42	415.0	54.82	4.26	0.76	0.65						

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APPENDIX C.2 SEDIMENT >63µm DESCRIPTION AND FORAMINIFERA STABLE ISOTOPES														
CD38-02			Description (0=absent, 1=rare, 2=common, 3=abundant)					Number of forams picked			Isotopic composition of Uvigerina			
Sample	Depth	Sed.>63µm	Forams	Qtz.	Clays	Diatoms	Fish bits	Uvig.	Cibicid.	Glob.	Sample	Depth	d18O	d13C
	(cm)	(%)	(0-10)	(0-3)	(0-3)	(0-3)	(0-3)					(cm)	(PDB)	(PDB)
3802F1	5.0	0.64	9	0	0	0	1	24	2	18	3802F1	5.0	2.833	-0.827
3802F2	14.0	0.72	9	0	1	1	1	26	5	22	3802F2	14.0	3.004	-0.960
3802F3	24.0	1.39	10	0	0	2	1	22	10	22	3802F3	24.0	3.770	-1.065
3802F4	35.0	1.10	7	0	2	1	0	21	11	33	3802F4	35.0	3.955	-1.293
3802F5	45.0	1.25	8	0	1	1	1	33	9	31	3802F5	45.0	4.921	-1.217
3802F6	54.0	1.08	8	0	1	2	1	29	5	26	3802F6	54.0	4.924	-1.275
3802F7	67.0	1.49	9	0	1	1	1	31	21	30	3802F7	67.0	4.939	-1.379
3802F8	76.0	1.03	7	0	1	1	2	25	19	26	3802F8	76.0	4.586	-1.423
3802F9	86.0	1.34	9	0	1	1	1	28	15	30	3802F9	86.0	4.997	-1.179
3802F10	96.0	1.48	10	0	1	1	0	28	9	25	3802F10	96.0	3.694	-1.265
3802F11	106.0	1.91	8	0	1	3	0	22	8	33	3802F11	106.0	4.689	-1.302
3802F12	116.0	1.68	9	0	1	2	0	26	9	28	3802F12	116.0	4.695	-1.440
3802F13	126.0	1.77	6	0	1	3	1	29	15	38	3802F13	126.0	4.746	-1.499
3802F14	136.0	1.50	7	0	1	2	1	29	10	26	3802F14	136.0	4.403	-1.284
3802F15	146.0	1.91	7	0	1	2	1	24	5	28	3802F15	146.0	4.463	-1.272
3802F16	156.0	1.20	9	0	1	1	1	28	10	34	3802F16	156.0	4.471	-1.263
3802F17	164.5	1.05	8	0	1	2	1	36	15	23	3802F17	164.5	4.460	-1.252
3802F18	178.0	0.86	9	0	0	3	0	32	14	22	3802F18	178.0	4.402	-1.159
3802F19	188.0	0.69	9	0	1	2	0	29	7	23	3802F19	188.0	4.516	-1.228
3802F20	198.0	0.73	6	0	2	3	0	30	4	26	3802F20	198.0	4.350	-1.260
3802F21	208.0	0.70	7	0	1	2	0	34	7	20	3802F21	208.0	4.583	-1.197
3802F22	218.0	0.90	9	0	1	1	0	38	5	26	3802F22	218.0	4.630	-1.407
3802F23	228.0	0.68	9	0	1	0	0	33	11	30	3802F23	228.0	4.634	-1.329
3802F24	238.0	0.80	8	2	2	0	0	35	17	22	3802F24	238.0	4.272	-1.175
3802F25	248.0	0.58	8	2	1	1	1	26	2	16	3802F25	248.0	4.418	-0.559
3802F26	258.0	0.69	9	0	1	2	1	36	15	23	3802F26	258.0	4.122	-0.946
3802F27	268.0	0.62	9	1	1	2	0	33	7	24	3802F27	268.0	4.059	-0.992
3802F28	278.0	0.64	8	1	2	1	0	35	1	11	3802F28	278.0	4.281	-1.223
3802F29	288.0	0.79	7	1	1	2	1	38	3	26	3802F29	288.0	4.417	-1.040
3802F30	299.0	0.35	6	2	3	1	0	33	0	0	3802F30	299.0	4.082	-0.998
3802F31	309.0	0.57	8	0	2	2	0	34	5	12	3802F31	309.0	4.228	-0.958
3802F32	319.0	0.73	8	1	1	1	1	25	7	17	3802F32	319.0	4.437	-0.994
3802F33	329.0	0.82	8	1	1	1	2	37	4	29	3802F33	329.0	4.480	-0.998
3802F34	339.0	0.63	7	0	1	2	1	33	5	19	3802F34	339.0	4.025	-0.943
3802F35	349.0	0.93	5	0	1	3	0	23	5	23	3802F35	349.0	3.728	-0.981
3802F36	359.0	1.38	5	0	1	3	0	23	5	27	3802F36	359.0	4.051	-1.048
3802F37	369.0	0.94	8	0	1	0	1	20	15	37	3802F37	369.0	5.038	-0.758
3808F38	378.0	1.16	9	0	1	0	0	29	16	46	3808F38	378.0	4.636	-1.083

APPENDIX C.2 SEDIMENT >63µm DESCRIPTION AND FORAMINIFERA STABLE ISOTOPEs														
CD38-02		Description (0=absent, 1=rare, 2=common, 3=abundant)						Number of forams picked			Isotopic composition of Uvigerina			
Sample	Depth	Sed.>63µm	Forams	Qtz.	Clays	Diatoms	Fish bits	Uvig.	Cibicid.	Glob.	Sample	Depth	d18O	d13C
	(cm)	(%)	(0-10)	(0-3)	(0-3)	(0-3)	(0-3)					(cm)	(PDB)	(PDB)
3802F39	388.0	1.43	9	0	1	0	0	27	21	45	3802F39	388.0	5.049	-1.350
3802F40	398.0	1.76	9	0	1	0	0	34	26	32	3802F40	398.0	4.876	-1.412
3802F41	407.0	0.94	9	0	1	0	1	20	3	25	3802F41	407.0	4.863	-1.295
3802F42	417.0	0.96	10	0	1	0	0	24	12	44	3802F42	417.0	4.930	-1.464
3802F43	427.0	1.77	10	0	1	0	0	23	13	45	3802F43	427.0	4.632	-1.554
3802F44	437.0	1.39	10	0	1	0	0	29	7	38	3802F44	437.0	4.772	-1.351
3802F45	447.0	0.76	9	0	1	0	1	29	9	37	3802F45	447.0	4.739	-1.318
3802F46	457.0	0.95	8	0	2	0	1	19	13	30	3802F46	457.0	4.826	-1.301
3802F47	468.0	0.82	8	0	2	0	1	20	6	28	3802F47	468.0	4.779	-1.513
3802F48	478.0	1.30	10	0	1	1	0	19	12	39	3802F48	478.0	4.642	-1.407
3802F49	488.0	0.99	8	0	1	1	0	22	10	37	3802F49	488.0	4.449	-1.268
3802F50	498.0	0.88	9	0	1	1	1	22	9	29	3802F50	498.0	4.618	-1.573
3802F51	508.0	1.09	10	0	1	1	0	22	22	39	3802F51	508.0	4.664	-1.282
3802F52	518.0	1.15	9	0	1	1	1	19	6	28	3802F52	518.0	4.582	-1.779
3802F53	528.0	2.01	6	2	1	0	1	16	8	28	3802F53	528.0	4.615	-1.191
3802F54	537.0	1.28	7	2	2	0	1	19	3	24	3802F54	537.0	4.527	-1.370
3802F55	547.0	0.75	7	3	2	0	0	23	0	37	3802F55	547.0	3.510	-1.266
3802F56	557.0	0.53	6	1	2	1	0	15	1	20	3802F56	557.0	4.075	-1.209
3802F57	568.0	0.64	8	0	1	1	0	20	3	19	3802F57	568.0	3.538	-1.107
3802F58	578.0	0.77	8	0	2	1	1	30	3	26	3802F58	578.0	3.468	-1.013
3802F59	588.0	1.00	9	0	2	1	1	28	5	27	3802F59	588.0	3.518	-1.253
3802F60	598.0	1.03	10	0	2	1	1	33	10	36	3802F60	598.0	3.549	-1.112
3802F61	608.0	0.85	9	0	1	1	0	20	2	34	3802F61	608.0	3.123	-1.095
3802F62	618.0	1.08	10	0	1	0	0	34	8	24	3802F62	618.0	4.167	-1.636
3802F63	628.0	0.85	10	0	1	0	0	27	15	32	3802F63	628.0	4.260	-1.483
3802F64	638.0	1.01	10	1	1	0	0	33	22	34	3802F64	638.0	4.818	-1.373
3802F65	648.0	0.86	9	0	1	1	1	31	10	22	3802F65	648.0	4.348	-1.238
3802F66	660.0	0.79	7	1	2	1	1	32	12	22	3802F66	660.0	4.055	-1.310
3802F67	668.0	0.93	8	0	2	1	1	30	8	26	3802F67	668.0	4.149	-1.263
3802F68	678.0	0.94	10	0	1	0	0	25	15	37	3802F68	678.0	4.333	-1.360
3802F69	688.0	1.67	9	1	2	0	1	26	14	30	3802F69	688.0	4.459	-1.351
3802F70	698.0	1.38	10	0	1	1	1	30	8	44	3802F70	698.0	4.804	-1.423
3802F71	708.0	0.83	9	0	3	0	1	19	8	36	3802F71	708.0	4.927	-1.297
3802F72	718.0	0.84	8	1	2	0	0	27	9	45	3802F72	718.0	4.744	-1.426
3802F73	728.0	1.07	8	1	3	1	1	23	10	41	3802F73	728.0	4.272	-1.519
3802F74	738.0	1.20	7	1	3	1	1	21	7	33	3802F74	738.0	4.850	-1.720
3802F75	748.0	1.13	8	0	2	1	0	18	2	34	3802F75	748.0	4.653	-1.708

APPENDIX C.2 SEDIMENT >63µm DESCRIPTION AND FORAMINIFERA STABLE ISOTOPES														
CD38-09		Description (0=absent, 1=rare, 2=common, 3=abundant)						Number of forams picked			Isotopic composition of B.sem.			
Sample	Depth (cm)	Sed.>63µm (%)	Forams (0-10)	Qtz. (0-3)	Clays (0-3)	Diatoms (0-3)	Fish bits (0-3)	Bolivina seminuda			Sample	Depth (cm)	d180 (PDB)	d13C (PDB)
3809F1	7.5	0.69	0	2	3	2	1			0	3809F2	18.0	0.568	-0.962
3809F2	18.0	0.22	1	0	0	3	1			24	3809F19	199.0	0.993	-1.547
3809F3	28.0	0.27	1	2	2	2	2			17	3809F20	208.0	0.928	-1.006
3809F4	38.0	0.39	0	1	2	3	1			0	3809F29	297.0	1.004	-4.556
3809F5	47.5	0.58	1	2	3	2	2			20	09-349SK	349.0	0.719	-1.863
3809F6	57.0	0.30	3	2	3	2	2			31	3809F35	358.5	1.543	-1.676
3809F7	67.0	0.18	0	2	2	3	1			0	3809F37	379.0	1.153	-3.661
3809F8	77.5	0.35	1	3	2	2	2			11	3809F42	428.0	1.287	-2.005
3809F9	87.0	0.16	0	2	3	3	2			0	3809F43	438.0	1.278	-6.562
3809F10	98.0	0.32	3	2	3	2	2			26	3809F47	476.5	1.369	-4.453
3809F11	106.5	0.35	0	2	2	2	3			0	3809F52	523.0	1.056	-1.188
3809F12	118.0	0.61	0	3	2	1	2			0	09-530SK	530.0	0.533	-1.902
3809F13	128.0	0.72	0	3	2	1	2			0	3809F54	539.0	1.046	-3.652
3809F14	137.5	0.45	2	1	2	2	2			26	09-540SK	540.0	1.145	-4.434
3809F15	149.5	0.43	4	1	2	2	1			23	3809F55	547.0	1.223	-4.081
3809F16	167.0	1.69	0	2	2	2	2			0	09-550SK	550.0	1.099	-2.344
3809F17	177.5	4.47	0	3	2	1	0			0	3809F63	631.5	1.248	-2.634
3809F18	189.0	1.85	0	3	2	2	2			0	3809F68	688.0	0.640	-3.526
3809F19	199.0	1.68	4	2	3	2	2			26	09-740SK	740.0	1.137	-3.755
3809F20	208.0	2.86	6	2	2	1	2			31	3809F74	747.0	1.810	-2.580
3809F21	218.0	8.47	3	3	3	1	1			22	09-750SK	750.0	1.123	-2.718
3809F22	228.0	18.94	0	3	2	1	2			0	3809F76	768.0	1.315	-1.394
3809F23	236.0	8.21	0	3	2	1	3			0	09-780SK	780.0	0.944	-3.374
3809F24	241.0	1.89	0	2	2	3	2			0	3809F79	797.0	1.464	-3.268
3809F25	249.5	0.27	0	1	1	3	1			0	09-800SK	800.0	1.097	-3.441
3809F26	260.5	0.33	0	1	1	3	2			0	3809F82	827.5	1.434	-3.268
3809F27	267.0	9.80	0	2	3	2	3			0				
3809F28	287.0	0.28	0	0	1	3	1			0	(SK samples from S.King - Southampton)			
3809F29	297.0	0.06	2	0	2	2	1			23				
3809F30	308.0	0.26	0	0	2	2	2			0				
3809F31	317.5	0.13	2	0	2	2	1			25				
3809F32	326.0	0.13	1	0	2	2	1			13				
3809F33	337.5	0.14	0	0	1	3	0			0				
3809F34	347.0	0.14	1	0	2	3	0			22				
3809F35	358.5	0.29	6	0	1	3	1			35				
3809F36	369.0	0.62	2	0	0	3	0			22				
3809F37	379.0	0.33	7	1	2	2	1			33				
3809F38	388.0	0.17	2	0	2	2	1			27				

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APPENDIX C.2 SEDIMENT >63 μ m DESCRIPTION AND FORAMINIFERA STABLE ISOTOPES									
CD38-09									
Sample	Depth (cm)	Sed. >63 μ m (%)	Description (0=absent, 1=rare, 2=common, 3=abundant)					Number of forams picked	
			Forams (0-10)	Qtz. (0-3)	Clays (0-3)	Diatoms (0-3)	Fish bits (0-3)	Bolivina seminuda	
3809F39	398.0	0.11	0	1	2	2	2	0	
3809F40	410.0	0.19	1	0	2	3	1	20	
3809F41	416.5	0.33	2	0	1	3	0	23	
3809F42	428.0	0.25	6	0	1	3	0	35	
3809F43	438.0	0.33	8	0	2	1	1	37	
3809F44	448.0	0.34	2	0	2	2	1	20	
3809F45	458.0	0.12	1	0	2	2	1	20	
3809F46	468.0	0.06	4	0	2	2	2	25	
3809F47	476.5	0.13	5	0	2	2	3	31	
3809F48	487.0	0.14	3	1	2	1	2	17	
3809F49	498.0	0.18	1	1	3	1	2	16	
3809F50	506.5	0.23	0	1	3	1	1	0	
3809F51	518.0	0.12	0	0	2	2	1	0	
3809F52	523.0	0.22	5	0	2	2	1	30	
3809F53	534.0	0.12	5	0	2	1	2	27	
3809F54	539.0	0.18	9	0	1	1	0	30	
3809F55	547.0	0.15	5	0	2	2	1	29	
3809F56	558.0	0.72	3	0	1	3	0	15	
3809F57	568.0	0.44	1	0	2	3	0	12	
3809F58	579.0	0.14	3	0	1	3	0	27	
3809F59	591.0	0.19	1	0	1	3	0	20	
3809F60	599.0	0.45	5	0	2	2	1	23	
3809F61	608.0	0.61	4	0	2	2	0	22	
3809F62	618.5	0.44	1	0	1	3	0	0	
3809F63	631.5	0.86	2	0	2	3	0	22	
3809F64	642.0	0.39	1	0	2	3	0	0	
3809F65	656.5	1.10	1	0	2	3	0	10	
3809F66	668.0	0.65	1	0	1	3	0	0	
3809F67	678.5	0.27	1	0	2	3	0	0	
3809F68	688.0	0.23	4	0	2	2	0	34	
3809F69	701.0	0.57	1	0	1	3	0	0	
3809F70	707.0	0.27	5	0	2	2	1	25	
3809F71	717.5	0.31	2	0	2	2	0	0	
3809F72	727.5	0.50	2	0	2	2	0	27	
3809F73	737.0	0.63	1	0	1	3	0	13	
3809F74	747.0	0.20	2	0	2	2	0	28	
3809F75	757.0	0.24	6	0	2	2	0	24	
3809F76	768.0	0.37	4	0	2	2	1	26	

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APPENDIX C.2 SEDIMENT >63µm DESCRIPTION AND FORAMINIFERA STABLE ISOTOPIES																
CD38-09																
Sample	Depth (cm)	Sed. >63µm (%)	Description (0=absent, 1=rare, 2=common, 3=abundant)					Number of forams picked								
			Forams (0-10)	Qtz. (0-3)	Clays (0-3)	Diatoms (0-3)	Fish bits (0-3)	Bolivina seminuda								
3809F77	778.0	0.45	2	0	2	2	0					22				
3809F78	787.0	0.63	2	0	2	2	1					10				
3809F79	797.0	0.21	7	0	2	2	1					34				
3809F80	807.5	0.35	3	0	2	3	1					24				
3809F81	819.5	0.44	2	0	2	3	1					22				
3809F82	827.5	0.47	4	0	2	3	0					30				
3809F83	836.0	0.41	2	0	2	3	0					20				
3809F84	855.0	0.75	3	0	2	2	0					24				
										Isotopic composition of B.sem.						
										Sample	Depth (cm)	d18O (PDB)	d13C (PDB)			
CD38-10																
3810F1	9.0	1.64	4	1	3	2	2					19	3810F1	9.0	1.809	-0.455
3810F2	18.0	4.81	2	2	2	0	2					9	3810F4	42.0	1.262	-2.645
3810F3	29.0	5.08	3	3	1	0	2					5	3810F11	108.0	1.687	-1.903
3810F4	42.0	0.82	8	2	1	0	1					17	3810F12	122.0	2.503	-1.646
3810F5	49.0	1.66	0	2	3	2	2					0	3810F13	128.0	2.148	-1.394
3810F6	58.0	1.88	0	2	3	2	3					0	3810F14	138.0	2.028	-1.461
3810F7	68.0	4.07	0	1	3	2	2					0	3810F15	148.0	1.795	-0.812
3810F8	78.5	33.62	0	2	2	0	1					0	3810F16	157.0	2.013	-1.268
3810F9	88.0	54.40	0	2	2	0	2					0	3810F17	165.0	2.048	-2.168
3810F10	97.0	19.17	6	3	1	0	1					16	3810F18	176.0	2.048	-1.055
3810F11	108.0	20.88	7	2	2	0	1					21	3810F19	190.5	2.440	-1.186
3810F12	122.0	6.80	8	2	1	0	2					26	3810F20	197.0	1.984	-1.880
3810F13	128.0	1.76	9	2	2	1	1					29	3810F21	207.0	1.612	-1.821
3810F14	138.0	0.72	6	2	1	3	1					33	3810F22	219.0	1.845	-1.035
3810F15	148.0	0.68	6	2	2	1	1					26	3810F25	250.0	1.710	-1.050
3810F16	157.0	0.61	5	2	1	2	3					33	3810F26	259.0	1.456	-1.026
3810F17	165.0	0.63	10	0	0	1	1					35	3810F27	266.5	2.011	-1.204
3810F18	176.0	0.36	4	3	0	3	1					23	3810F29	289.0	1.788	-1.598
3810F19	190.5	0.20	6	2	2	2	1					37	3810F30	299.0	1.989	-1.949
3810F20	197.0	0.54	10	0	0	1	1					31	3810F31	308.0	2.143	-1.589
3810F21	207.0	0.32	5	2	1	2	1					20	3810F32	316.0	2.159	-1.872
3810F22	219.0	0.19	4	2	1	2	1					19	3810F33	320.5	2.009	-1.589
3810F23	226.5	0.66	2	1	2	3	2					13	3810F34	329.0	2.140	-1.924
3810F24	238.0	0.39	1	3	1	2	2					2	3810F36	346.0	2.014	-2.331
3810F25	250.0	0.29	3	3	1	1	1					21	3810F37	356.0	0.863	-2.074
3810F26	259.0	0.41	7	3	0	1	1					36	3810F38	367.0	1.948	-1.805
3810F27	266.5	0.53	9	2	0	0	1					31	3810F39	376.0	1.849	-1.755

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APPENDIX C.2 SEDIMENT >63µm DESCRIPTION AND FORAMINIFERA STABLE ISOTOPES														
CD38-10		Description (0=absent, 1=rare, 2=common, 3=abundant)						Number of forams picked			Isotopic composition of B.sem.			
Sample	Depth	Sed.>63µm	Forams	Qtz.	Clays	Diatoms	Fish bits	Bolivina seminuda			Sample	Depth	d18O	d13C
	(cm)	(%)	(0-10)	(0-3)	(0-3)	(0-3)	(0-3)					(cm)	(PDB)	(PDB)
3810F28	278.0	0.53	7	1	1	1	2			23	3810F41	397.0	1.645	-1.393
3810F29	289.0	0.13	5	2	2	1	1			32	3810F42	407.0	1.371	-1.497
3810F30	299.0	0.53	10	0	1	0	1			30	3810F43	415.0	1.903	-1.640
3810F31	308.0	0.20	4	2	2	2	2			24	3810F44	427.0	1.677	-1.962
3810F32	316.0	0.17	9	0	2	0	1			29	3810F45	436.0	1.930	-2.110
3810F33	320.5	0.36	10	1	1	0	2			30	3810F47	452.0	1.837	-2.064
3810F34	329.0	0.45	10	1	1	0	1			28	3810F48	459.0	1.662	-1.481
3810F35	338.0	0.29	4	2	2	0	2			23	3810F49	469.0	1.530	-1.987
3810F36	346.0	0.40	8	0	1	2	1			25	3810F50	478.0	1.392	-1.831
3810F37	356.0	0.87	8	0	1	2	1			27	3810F51	486.0	1.427	-1.814
3810F38	367.0	0.76	9	0	2	1	1			26	3810F52	497.0	0.876	-1.223
3810F39	376.0	0.56	8	0	2	1	2			21	3810F53	507.0	1.333	-1.863
3810F40	386.0	0.13	5	1	2	0	1			24	3810F54	517.0	0.829	-2.003
3810F41	397.0	0.65	6	1	2	0	1			29	3810F55	525.0	1.066	-2.106
3810F42	407.0	0.19	4	2	3	0	1			22	3810F56	537.5	0.999	-3.045
3810F43	415.0	0.29	10	1	0	0	1			27	3810F57	547.0	-0.296	-1.988
3810F44	427.0	0.56	8	1	1	1	1			22	3810F58	557.0	1.551	-5.166
3810F45	436.0	0.66	9	1	1	1	1			25	3810F59	565.5	1.516	-3.176
3810F46	446.0	0.63	8	1	2	2	0			26	3810F60	570.0	1.644	-7.899
3810F47	452.0	0.33	9	0	1	3	0			32	3810F61	579.0	1.468	-3.313
3810F48	459.0	2.20	10	0	1	1	1			33	3810F62	587.5	1.454	-3.066
3810F49	469.0	0.82	9	0	1	2	1			34	3810F63	593.5	1.432	-3.943
3810F50	478.0	0.75	4	2	2	1	2			24	3810F64	607.0	1.676	-3.331
3810F51	486.0	0.84	4	2	2	1	2			25	3810F65	616.0	1.657	-2.958
3810F52	497.0	1.71	2	3	3	0	2			22	3810F66	627.0	1.653	-3.495
3810F53	507.0	6.74	7	2	2	0	1			29	3810F67	637.0	2.022	-2.969
3810F54	517.0	0.81	4	1	1	3	0			20	3810F68	649.0	1.891	-2.693
3810F55	525.0	0.54	4	1	1	3	0			22	3810F69	660.0	2.081	-2.618
3810F56	537.5	0.75	9	0	2	0	1			29	3810F70	678.0	2.210	-2.095
3810F57	547.0	0.29	7	0	2	0	1			26	3810F71	689.0	2.304	-1.983
3810F58	557.0	1.20	7	0	1	2	0			27	3810F72	698.0	2.587	-1.921
3810F59	565.5	0.54	7	0	1	2	0			28	3810F73	708.0	2.453	-2.538
3810F60	570.0	2.40	9	0	1	2	1			32	3810F74	718.0	2.412	-2.068
3810F61	579.0	0.92	8	0	1	2	1			23	3810F75	728.0	2.519	-1.899
3810F62	587.5	1.12	8	0	1	2	1			26	3810F76	737.0	2.761	-1.330
3810F63	593.5	0.63	5	0	1	3	0			23				
3810F64	607.0	1.18	8	0	2	1	2			24				
3810F65	616.0	0.87	6	0	1	2	1			24				

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APPENDIX C.2 SEDIMENT >63µm DESCRIPTION AND FORAMINIFERA STABLE ISOTOPES									
CD38-10		Description (0=absent, 1=rare, 2=common, 3=abundant)						Number of forams picked	
Sample	Depth (cm)	Sed.>63µm (%)	Forams (0-10)	Qtz. (0-3)	Clays (0-3)	Diatoms (0-3)	Fish bits (0-3)	Bolivina seminuda	
3810F66	627.0	0.64	9	0	2	2	1	26	
3810F67	637.0	1.36	7	0	2	3	1	26	
3810F68	649.0	1.47	9	0	1	1	1	37	
3810F69	660.0	0.52	3	0	3	3	1	22	
3810F70	678.0	0.59	10	0	1	1	1	39	
3810F71	689.0	0.61	7	0	2	1	1	40	
3810F72	698.0	0.36	6	0	2	1	2	37	
3810F73	708.0	0.52	8	0	2	1	2	39	
3810F74	718.0	4.27	7	0	2	2	3	45	
3810F75	728.0	0.44	5	0	3	2	2	33	
3810F76	737.0	0.48	5	0	3	3	2	32	
3810F77	748.0	0.70	0	2	2	2	2	0	
3810F78	758.0	1.02	0	2	2	1	3	0	
3810F79	766.0	14.53	0	3	2	1	2	0	
									Isotopic composition of Uvigerina
									Sample
									Depth (cm)
									d180 (PDB)
									d13C (PDB)
CD38-11								Uvigerina	
3811F01	6.0	1.37	1	3	2	1	1	1	3811F01 6.0 4.762 -1.338
3811F02	16.0	0.88	3	3	2	1	1	0	3811F05 46.0 4.913 -1.243
3811F03	26.0	0.77	0	2	1	1	3	0	3811F06 56.0 5.189 -1.210
3811F04	36.0	0.40	1	2	1	1	3	0	3811F07 66.0 5.254 -1.184
3811F05	46.0	0.44	4	2	1	1	2	17	3811F08 76.0 5.006 -1.284
3811F06	56.0	0.21	5	2	1	2	2	21	3811F09 88.0 5.326 -1.467
3811F07	66.0	0.32	4	2	1	2	3	23	3811F10 102.0 5.336 -1.534
3811F08	76.0	1.95	5	2	1	2	2	29	3811F11 111.0 5.283 -1.360
3811F09	88.0	2.65	6	3	1	1	1	34	3811F12 121.0 5.386 -1.259
3811F10	102.0	0.90	6	3	2	2	2	36	3811F13 131.0 5.358 -1.451
3811F11	111.0	0.53	4	3	2	2	2	20	3811F14 141.0 5.261 -1.388
3811F12	121.0	0.31	6	3	1	1	2	22	3811F15 151.0 5.303 -1.397
3811F13	131.0	1.93	7	3	2	1	1	37	3811F16 161.0 5.213 -1.418
3811F14	141.0	1.80	3	2	1	2	1	14	3811F17 171.0 5.348 -1.481
3811F15	151.0	1.43	7	3	1	2	2	29	3811F18 181.0 5.327 -1.323
3811F16	161.0	1.16	5	3	2	1	2	31	3811F19 191.0 5.332 -1.322
3811F17	171.0	2.66	5	3	2	1	2	30	3811F20 200.0 5.066 -1.350
3811F18	181.0	0.68	7	3	1	1	2	30	3811F21 211.0 5.085 -1.463
3811F19	191.0	0.41	4	2	2	1	2	20	3811F22 222.0 5.176 -1.498
3811F20	200.0	0.60	6	2	2	1	2	31	3811F23 231.0 5.083 -1.405
3811F21	211.0	3.44	4	2	2	1	2	21	3811F24 241.0 5.115 -1.326

APPENDIX C.2 SEDIMENT >63µm DESCRIPTION AND FORAMINIFERA STABLE ISOTOPES													
CD38-11		Description (0=absent, 1=rare, 2=common, 3=abundant)						Number of forams picked		Isotopic composition of Uvigerina			
Sample	Depth (cm)	Sed.>63µm (%)	Forams (0-10)	Qtz. (0-3)	Clays (0-3)	Diatoms (0-3)	Fish bits (0-3)	Uvigerina		Sample	Depth (cm)	d18O (PDB)	d13C (PDB)
3811F22	222.0	1.02	4	2	2	1	2	23		3811F26	261.0	4.723	-1.216
3811F23	231.0	0.27	6	2	2	1	3	25		3811F27	271.0	4.701	-1.345
3811F24	241.0	0.26	8	2	1	1	3	33		3811F28	281.0	4.794	-1.299
3811F25	251.0	0.28	7	1	1	2	3	21		3811F29	291.0	4.589	-1.361
3811F26	261.0	0.24	6	1	1	2	3	22		3811F30	301.0	4.432	-1.379
3811F27	271.0	0.31	7	1	2	2	3	27		3811F33	331.0	4.692	-1.175
3811F28	281.0	0.28	5	2	2	1	3	26		3811F35	351.0	3.659	-1.483
3811F29	291.0	0.37	5	2	2	2	3	17		3811F36	361.0	4.459	-1.351
3811F30	301.0	0.46	4	2	2	1	3	20		3811F37	371.0	4.715	-1.316
3811F31	311.0	0.68	2	2	2	1	3	0		3811F38	381.0	4.752	-1.470
3811F32	321.0	2.76	3	2	2	1	3	0		3811F39	391.0	4.708	-1.480
3811F33	331.0	0.32	2	2	2	2	3	5		3811F40	401.0	4.549	-1.521
3811F34	341.0	0.25	2	1	2	1	3	1		3811F41	411.0	4.533	-1.298
3811F35	351.0	0.17	1	2	2	1	3	9		3811F42	421.0	4.201	-1.278
3811F36	361.0	0.19	2	2	1	1	3	11		3811F43	431.0	4.138	-1.285
3811F37	371.0	0.11	2	2	2	1	3	8		3811F44	441.0	4.190	-1.315
3811F38	381.0	0.08	3	2	1	1	3	9		3811F45	451.0	3.673	
3811F39	391.0	0.22	5	2	2	1	3	26		3811F47	471.0	4.411	-1.256
3811F40	401.0	0.12	4	1	2	1	3	16		3811F48	481.0	4.762	-0.996
3811F41	411.0	0.17	3	1	1	1	3	16		3811F50	501.0	4.276	-0.923
3811F42	421.0	0.24	2	1	2	1	2	20		3811F51	511.0	4.150	-0.729
3811F43	431.0	0.23	5	1	1	1	3	21		3811F57	571.0	3.639	-1.164
3811F44	441.0	0.27	3	1	1	1	3	12					
3811F45	451.0	0.13	1	1	1	1	3	1					
3811F46	461.0	0.08	1	1	1	1	3	2					
3811F47	471.0	0.17	4	0	1	1	3	24					
3811F48	481.0	0.20	2	1	2	1	3	8					
3811F49	491.0	0.10	0	1	2	1	3	0					
3811F50	501.0	0.14	1	1	1	1	3	3					
3811F51	511.0	0.10	1	1	2	1	3	2					
3811F52	521.0	0.18	0	0	2	1	3	0					
3811F53	531.0	0.25	0	0	2	1	3	0					
3811F54	541.0	0.15	0	0	2	1	3	0					
3811F55	551.0	0.38	1	1	1	1	3	0					
3811F56	561.0	0.33	1	1	1	1	3	2					
3811F57	571.0	0.20	2	1	1	1	3	7					

APPENDIX C.3. SEDIMENT ACCUMULATION RATES, DRY BULK DENSITIES, MASS ACCUMULATION RATES AND DEPTH/AGE CORRELATION										
CD38-02 2525m					CD38-11 3835m					
Depth	SAR	DBD	MAR	Age	Depth	SAR	DBD	MAR	Age	
(cm)	(cm/kyr)	(g/cm ²)	(g/cm ² /kyr)	(ka)	(cm)	(cm/kyr)	(g/cm ²)	(g/cm ² /kyr)	(ka)	
8.0	2.90	0.58	1.67	2.76	3.0	3.73	0.68	2.15	0.80	
18.0	2.90	0.61	1.76	6.21	13.0	3.73	0.62	2.33	2.00	
28.0	2.90	0.57	1.64	9.66	23.0	3.73	0.73	2.72	2.20	
38.0	4.15	0.53	2.21	12.77	33.0	3.73	0.55	2.05	3.49	
48.0	4.15	0.61	2.53	15.18	43.0	3.73	0.53	1.98	6.17	
57.5	4.15	0.61	2.52	17.47	53.0	3.73	0.54	2.02	8.85	
70.0	4.15	0.60	2.51	20.48	63.0	3.73	0.55	2.06	11.53	
79.0	4.15	0.59	2.45	22.65	73.0	4.56	0.58	2.66	13.80	
89.0	3.59	0.61	2.19	25.22	85.0	4.56	0.96	4.37	16.44	
100.0	3.59	0.62	2.21	28.29	95.0	4.56	0.60	2.72	18.63	
110.0	3.59	0.63	2.24	31.07	105.0	4.56	0.59	2.67	20.82	
120.0	3.59	0.61	2.18	33.86	116.0	4.56	0.59	2.70	23.23	
130.0	3.59	0.61	2.19	36.64	125.0	5.02	0.59	2.94	25.11	
139.0	3.59	0.60	2.14	39.15	135.0	5.02	0.61	3.05	27.10	
150.0	3.59	0.59	2.12	42.22	145.0	5.02	0.58	2.90	29.09	
160.0	3.59	0.65	2.32	45.00	155.0	5.02	0.63	3.19	31.08	
171.0	3.59	0.64	2.30	48.07	165.0	5.02	0.56	2.80	33.07	
181.0	3.59	0.58	2.08	50.85	175.0	5.02	0.74	3.71	35.07	
191.0	3.59	0.60	2.15	53.64	186.0	5.02	0.58	2.93	37.26	
201.0	3.59	0.58	2.07	56.42	197.0	5.02	0.57	2.84	39.45	
211.0	3.01	0.61	1.83	59.29	204.0	5.02	0.56	2.80	40.84	
221.0	3.01	0.63	1.90	62.61	215.0	5.02	0.57	2.86	43.03	
231.0	3.01	0.65	1.95	65.94	225.0	5.02	0.54	2.69	45.03	
241.0	3.01	0.62	1.88	69.26	235.0	5.02	0.56	2.80	47.02	
251.0	3.01	0.63	1.89	72.58	245.0	5.02	0.57	2.84	49.01	
261.0	1.88	0.64	1.21	76.96	255.0	5.02	0.57	2.88	51.00	
271.0	1.88	0.62	1.17	82.03	265.0	5.02	0.57	2.84	52.99	
281.0	1.88	0.64	1.20	87.11	275.0	5.02	0.56	2.83	54.99	
291.0	1.88	0.62	1.17	92.18	285.0	5.02	0.59	2.94	56.98	
301.0	1.88	0.62	1.16	97.26	297.0	3.01	0.69	2.08	59.62	
312.0	1.88	0.61	1.15	102.84	305.0	3.01	0.66	2.00	62.28	
322.0	1.88	0.63	1.18	107.92	315.0	3.01	0.67	2.03	65.60	
332.0	1.88	0.64	1.19	113.00	325.0	3.01	0.93	2.80	68.93	
342.0	1.88	0.61	1.14	118.07	335.0	3.01	0.60	1.81	72.25	
352.0	1.88	0.61	1.15	123.15	345.0	4.80	0.59	2.85	74.95	
362.0	2.93	0.63	1.85	128.22	355.0	4.80	0.58	2.79	77.04	
372.0	2.93	0.66	1.95	132.23	365.0	4.80	0.60	2.86	79.12	
381.0	2.93	0.71	2.07	135.30	375.0	4.80	0.60	2.90	81.20	
391.0	2.93	0.71	2.08	138.71	385.0	4.80	0.64	3.05	83.29	
400.0	2.93	0.70	2.05	141.79	395.0	4.80	0.66	3.15	85.37	
410.0	2.93	0.71	2.07	145.20	405.0	4.80	0.64	3.08	87.45	
420.0	2.93	0.70	2.04	148.61	415.0	4.80	0.65	3.13	89.54	
430.0	2.93	0.72	2.12	152.02	425.0	4.80	0.62	2.97	91.62	
440.0	2.93	0.73	2.14	155.44	435.0	4.80	0.61	2.94	93.70	
450.0	2.93	0.68	1.99	158.85	445.0	4.80	0.59	2.82	95.79	
460.0	2.93	0.69	2.01	162.26	455.0	4.80	0.63	3.02	97.87	
470.0	2.93	0.72	2.11	165.68	465.0	4.80	0.62	2.97	99.95	
481.0	2.93	0.72	2.10	169.43	475.0	4.80	0.63	3.01	102.04	
491.0	2.93	0.71	2.07	172.84	485.0	4.80	0.62	2.95	104.12	
501.0	2.93	0.69	2.02	176.26	495.0	4.80	0.60	2.87	106.20	
511.0	2.93	0.71	2.09	179.67	505.0	4.80	0.60	2.86	108.29	
521.0	2.93	0.70	2.05	183.08	515.0	4.80	0.61	2.94	110.37	
531.0	2.93	0.80	2.33	186.50	525.0	4.80	0.59	2.85	112.45	
540.0	2.66	0.67	1.78	189.57	535.0	4.80	0.63	3.01	114.54	
550.0	2.66	0.65	1.73	193.52	545.0	4.80	0.60	2.88	116.62	
560.0	2.66	0.61	1.63	197.42	555.0	4.80	0.61	2.93	118.70	
572.0	2.66	0.90	2.39	202.11	565.0	4.80	0.63	3.00	120.79	
582.0	2.66	0.89	2.36	206.02						
591.0	2.66	0.74	1.97	209.53						
601.0	2.66	0.78	2.07	213.44						
611.0	2.66	0.77	2.06	217.34						
621.0	2.66	0.76	2.03	221.25						
631.0	2.66	0.80	2.13	225.16						
641.0	2.66	0.77	2.04	229.06						
651.0	2.66	0.71	1.89	232.97						
662.0	2.66	0.68	1.82	237.27						
671.0	2.66	0.69	1.83	240.78						
681.0	3.12	0.72	2.26	244.50						
691.0	3.12	0.71	2.20	247.71						
701.0	3.12	0.73	2.27	250.91						
711.0	3.12	0.70	2.19	254.12						
721.0	3.12	0.70	2.19	257.32						
731.0	3.12	0.72	2.23	260.53						
741.0	3.12	0.70	2.19	263.73						

APPENDIX C.5. UNCORRECTED MAJOR ELEMENT DATA : OXIDES (XRF)

Sample	Depth (cm)	SiO2 (wt.%)	Al2O3 (wt.%)	Fe2O3 (wt.%)	MgO (wt.%)	CaO (wt.%)	Na2O (wt.%)	K2O (wt.%)	TiO2 (wt.%)	MnO2 (wt.%)	P2O5 (wt.%)	LOI (%)	Total (%)
BC38-03	4289m												
BC3803-01	0.5	57.53	11.45	5.27	0.25	1.44	5.47	2.039	0.466	0.098	0.251	10.13	94.39
BC3803-02	1.5	58.48	11.60	5.57	0.24	1.41	4.86	2.074	0.478	0.081	0.257	10.74	95.80
BC3803-03	2.5	57.99	11.52	5.57	0.25	1.41	4.92	2.079	0.476	0.056	0.252	10.73	95.25
BC3803-04	3.5	58.62	11.64	5.23	0.24	1.41	4.89	2.057	0.479	0.034	0.233	10.95	95.79
BC3803-05	4.5	60.20	12.25	4.68	0.26	1.44	5.03	2.193	0.496	0.029	0.210	10.81	97.60
BC3803-06	5.5	59.08	12.03	3.85	0.24	1.42	4.83	2.179	0.495	0.033	0.205	11.00	95.36
BC3803-07	6.5	59.67	12.15	3.88	0.24	1.42	4.65	2.211	0.505	0.031	0.203	10.65	95.61
BC3803-08	7.5	59.81	12.34	4.05	0.24	1.44	4.74	2.224	0.509	0.027	0.198	10.93	96.51
BC3803-09	8.5	59.66	12.30	4.15	0.24	1.46	4.68	2.236	0.508	0.030	0.199	10.78	96.26
BC3803-10	9.5	62.22	13.17	4.42	0.26	1.50	4.76	2.279	0.528	0.037	0.205	10.68	100.07
BC3803-11	11.0	60.09	12.77	4.29	0.26	1.49	4.90	2.274	0.526	0.035	0.207	10.32	97.17
BC3803-12	13.0	60.36	12.89	4.00	0.25	1.53	4.30	2.305	0.542	0.035	0.205	10.27	96.69
BC3803-13	15.0	59.57	12.65	4.40	0.25	1.53	4.72	2.312	0.532	0.038	0.211	9.54	95.74
BC3803-14	17.0	61.07	12.92	4.17	0.25	1.58	4.15	2.339	0.552	0.035	0.219	10.13	97.42
BC3803-15	19.0	60.42	12.92	4.05	0.27	1.62	4.55	2.316	0.546	0.039	0.227	10.49	97.44
BC3803-16	21.0	61.13	12.38	3.81	0.25	1.56	4.14	2.229	0.526	0.029	0.217	10.82	97.08
BC3803-17	23.0	60.74	12.38	4.21	0.25	1.55	4.52	2.243	0.521	0.032	0.220	10.36	97.03
BC3803-18	25.0	60.68	12.53	3.90	0.25	1.61	4.09	2.262	0.536	0.036	0.227	10.62	96.73
BC3803-19	27.0	59.99	12.24	4.03	0.25	1.62	4.54	2.221	0.527	0.035	0.226	10.26	95.94
BC3803-20	29.0	61.25	12.76	4.21	0.25	1.67	4.02	2.311	0.546	0.041	0.234	10.00	97.30
BC3803-21	31.0	60.28	12.48	4.36	0.26	1.67	4.70	2.330	0.535	0.044	0.228	9.75	96.64
BC3803-22	33.0	60.91	12.61	4.09	0.26	1.70	4.22	2.293	0.539	0.036	0.235	9.86	96.76
BC3803-23	35.0	60.43	12.43	3.99	0.26	1.71	4.40	2.297	0.534	0.036	0.231	9.60	95.91
BC3803-24	37.0	62.43	13.00	4.42	0.27	1.82	4.22	2.361	0.547	0.040	0.240	9.75	99.10
BC3803-25	39.0	63.03	12.96	4.43	0.28	1.90	4.51	2.377	0.542	0.044	0.319	9.57	99.96
BC3803-26	41.0	60.95	12.46	4.32	0.26	1.81	4.02	2.343	0.540	0.040	0.230	9.72	96.68
BC3803-27	43.0	61.12	12.64	4.49	0.27	1.85	4.38	2.362	0.542	0.039	0.234	9.65	97.57
BC3803-28	45.0	60.90	12.44	4.23	0.26	1.82	4.03	2.334	0.535	0.034	0.233	9.70	96.52
BC3803-29	47.0	60.57	12.37	4.44	0.26	1.82	4.30	2.358	0.534	0.040	0.233	9.34	96.26
BC3803-30	49.0	61.18	12.53	4.43	0.26	1.85	3.92	2.365	0.537	0.038	0.237	9.20	96.53
BC3803-31	51.0	61.38	12.80	4.72	0.27	1.88	4.30	2.423	0.550	0.038	0.249	8.92	97.55
BC3803-32	53.0	60.03	12.59	4.42	0.27	1.91	4.39	2.371	0.544	0.039	0.241	9.91	96.73

APPENDIX C.5. UNCORRECTED MAJOR ELEMENT DATA : OXIDES (XRF)

Sample	Depth (cm)	SiO2 (wt.%)	Al2O3 (wt.%)	Fe2O3 (wt.%)	MgO (wt.%)	CaO (wt.%)	Na2O (wt.%)	K2O (wt.%)	TiO2 (wt.%)	MnO2 (wt.%)	P2O5 (wt.%)	LOI (%)	Total (%)
BC38-02	2530m												
BC3802-01	0.5	50.36	11.15	5.22	0.24	8.71	4.29	2.021	0.450	0.050	0.306	12.10	94.89
BC3802-02	1.5	50.65	11.25	5.24	0.25	8.32	4.14	2.055	0.451	0.049	0.290	12.07	94.76
BC3802-03	2.5	50.58	11.18	5.22	0.24	8.70	3.95	2.042	0.453	0.048	0.285	12.15	94.84
BC3802-04	3.5	50.14	11.12	5.19	0.24	8.92	3.81	1.980	0.447	0.036	0.289	13.02	95.20
BC3802-05	4.5	50.15	11.08	5.16	0.24	9.24	3.88	2.081	0.449	0.033	0.286	12.22	94.82
BC3802-06	5.5	49.84	11.03	5.05	0.24	9.34	3.86	2.084	0.442	0.035	0.298	12.62	94.84
BC3802-07	6.5	49.72	11.46	5.14	0.25	9.56	3.99	2.096	0.450	0.033	0.275	12.93	95.91
BC3802-08	7.5	49.81	11.12	5.17	0.25	9.39	3.81	2.068	0.444	0.032	0.282	12.83	95.20
BC3802-09	8.5	49.54	11.34	5.13	0.26	9.61	3.80	2.140	0.460	0.038	0.293	12.45	95.06
BC3802-10	9.5	49.15	11.27	5.03	0.25	9.94	3.61	2.085	0.462	0.036	0.276	12.71	94.81
BC3802-11	11.0	51.13	11.84	5.15	0.28	11.22	3.58	2.152	0.465	0.038	0.282	13.28	99.40
BC3802-12	13.0	46.80	10.50	4.93	0.24	12.32	3.21	1.988	0.438	0.032	0.269	14.24	94.98
BC3802-13	15.0	45.82	10.39	4.49	0.25	12.85	3.86	1.983	0.423	0.034	0.270	14.32	94.68
BC3802-13A	17.0	42.56	9.92	3.96	0.23	15.82	3.50	1.827	0.394	0.031	0.253	16.58	95.08
BC3802-14	19.0	41.33	9.15	3.72	0.21	17.44	3.25	1.724	0.375	0.030	0.254	17.67	95.15
BC3802-15	21.0	40.68	9.03	3.64	0.21	18.78	2.81	1.728	0.374	0.032	0.252	18.56	96.09
BC3802-16	23.0	39.58	8.75	3.58	0.21	19.12	3.20	1.631	0.364	0.026	0.250	19.00	95.72
BC3802-17	25.0	39.21	8.76	3.54	0.20	19.83	2.69	1.664	0.361	0.027	0.252	19.24	95.78
BC3802-18	27.0	37.92	8.60	3.48	0.20	20.12	3.06	1.586	0.353	0.030	0.244	20.05	95.64
BC3802-19	29.0	37.48	8.47	3.40	0.20	21.19	2.65	1.591	0.351	0.026	0.245	20.74	96.34
BC3802-20	31.0	36.91	8.40	3.34	0.20	20.62	3.12	1.510	0.348	0.028	0.243	20.88	95.60
BC3802-21	33.0	37.37	8.72	3.40	0.20	20.34	2.73	1.714	0.359	0.031	0.236	20.52	95.61
BC3802-21A	35.0	37.50	9.09	3.45	0.21	18.61	3.18	1.705	0.377	0.023	0.201	19.85	94.18
BC3802-22	37.0	37.68	8.95	3.47	0.20	19.38	2.73	1.641	0.368	0.021	0.214	20.54	95.19
BC3802-23	39.0	36.95	8.62	3.38	0.21	19.91	3.29	1.637	0.355	0.027	0.234	20.20	94.81
BC3802-24	41.0	37.46	9.11	3.52	0.20	19.33	3.00	1.696	0.374	0.030	0.203	20.45	95.38
BC3802-25	43.0	37.70	9.25	3.60	0.21	18.91	3.24	1.813	0.382	0.025	0.203	19.64	94.97
BC3802-26	45.0	37.11	9.08	3.57	0.20	18.67	2.91	1.789	0.387	0.030	0.203	19.77	93.73
BC3802-27	47.0	37.64	9.32	3.52	0.22	18.64	3.27	1.805	0.387	0.023	0.208	19.61	94.63
BC3802-28	49.0	38.03	9.37	3.56	0.21	18.69	3.05	1.816	0.394	0.027	0.208	19.62	94.98
BC3802-29	51.0	38.05	9.37	3.55	0.21	18.47	3.16	1.783	0.394	0.028	0.208	19.64	94.87
BC3802-30	53.0	38.02	9.45	3.52	0.22	18.26	3.16	1.761	0.393	0.031	0.221	19.38	94.41

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APPENDIX C.5. UNCORRECTED MAJOR ELEMENT DATA : OXIDES (XRF)

PC38-09	148m													
Sample	Depth	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	MnO2	P2O5	LOI	Total	
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(%)	(%)	
PC3809-01	4.0	53.88	10.29	3.44	0.19	2.84	4.52	1.573	0.498	0.028	0.509	15.62	93.38	
PC3809-02	13.0	53.45	10.01	2.97	0.18	3.17	5.02	1.476	0.450	0.028	0.361	16.58	93.69	
PC3809-03	23.0	53.91	13.31	3.66	0.20	2.48	4.49	1.821	0.544	0.037	0.430	14.63	95.50	
PC3809-04	34.0	54.53	12.21	3.38	0.20	2.08	4.68	1.735	0.536	0.032	0.425	15.87	95.68	
PC3809-05	43.0	60.09	12.65	3.55	0.17	2.68	3.69	1.890	0.625	0.045	0.549	10.46	96.39	
PC3809-06	53.0	54.01	11.24	3.55	0.20	2.06	4.55	1.669	0.521	0.036	0.576	15.68	94.10	
PC3809-07	62.0	50.42	10.24	3.07	0.20	3.07	4.97	1.414	0.438	0.024	0.486	19.56	93.90	
PC3809-08	73.0	57.12	12.33	3.46	0.18	2.05	3.86	1.784	0.583	0.041	0.440	13.84	95.68	
PC3809-09	84.0	52.41	14.30	4.18	0.20	1.57	4.05	2.038	0.644	0.037	0.354	15.14	94.91	
PC3809-10	94.0	51.04	13.20	4.47	0.19	1.94	4.25	1.913	0.567	0.038	0.370	15.73	93.71	
PC3809-11	104.0	52.73	11.74	3.31	0.19	1.59	4.51	1.710	0.503	0.028	0.333	16.98	93.63	
PC3809-12	113.0	55.39	14.85	4.39	0.25	1.73	3.94	2.151	0.679	0.043	0.350	14.81	98.59	
PC3809-13	124.0	55.12	13.17	3.53	0.18	2.79	3.56	1.895	0.643	0.039	0.521	14.71	96.17	
PC3809-14	134.0	55.10	11.29	3.30	0.18	2.71	4.55	1.633	0.512	0.031	0.631	14.61	94.54	
PC3809-15	144.0	56.01	9.95	3.02	0.17	2.32	4.54	1.497	0.457	0.026	0.429	15.34	93.76	
PC3809-16	152.0	58.75	9.90	3.17	0.17	2.33	4.37	1.518	0.455	0.025	0.311	12.35	93.36	
PC3809-17	165.0	58.45	9.58	2.97	0.16	3.25	4.54	1.445	0.457	0.029	0.509	13.01	94.40	
PC3809-18	174.0	61.99	12.12	3.22	0.15	2.62	3.53	1.817	0.579	0.037	0.587	10.18	96.83	
PC3809-19	185.0	64.17	10.77	2.88	0.13	3.38	3.78	1.634	0.525	0.036	0.935	9.24	97.49	
PC3809-20	194.0	63.09	11.18	2.89	0.14	4.15	3.40	1.668	0.559	0.044	0.908	8.87	96.90	
PC3809-21	205.0	60.83	12.30	4.28	0.21	3.79	3.90	1.859	0.614	0.061	0.341	8.62	96.80	
PC3809-22	214.0	59.43	10.09	2.66	0.15	3.21	3.98	1.534	0.486	0.029	0.862	13.87	96.31	
PC3809-23	224.0	69.26	11.06	2.45	0.10	4.08	3.20	1.706	0.516	0.035	1.108	5.20	98.73	
PC3809-24	234.0	65.55	9.70	2.76	0.12	3.95	3.76	1.471	0.462	0.028	1.296	8.64	97.74	
PC3809-25	243.0	63.40	7.53	2.53	0.16	2.30	4.80	1.212	0.344	0.027	0.729	11.21	94.24	
PC3809-26	257.0	63.02	9.05	2.95	0.15	2.38	4.06	1.423	0.432	0.028	0.647	12.32	96.47	
PC3809-27	267.0	64.45	9.24	2.54	0.12	5.28	3.52	1.482	0.438	0.033	2.280	6.34	95.72	
PC3809-28	273.0	29.70	4.74	4.07	0.28	25.20	2.48	0.831	0.227	0.023	12.921	13.71	94.18	
PC3809-29	284.0	57.65	10.71	3.86	0.21	2.78	4.08	1.591	0.531	0.043	0.677	13.27	95.40	
PC3809-30	294.0	59.40	8.48	2.96	0.17	2.61	4.66	1.328	0.386	0.025	0.351	13.96	94.33	
PC3809-31	304.0	58.76	11.01	3.93	0.21	1.92	4.14	1.620	0.544	0.045	0.362	12.80	95.35	
PC3809-32	314.0	52.86	10.74	3.67	0.22	2.17	4.09	1.568	0.467	0.035	0.300	15.55	91.66	

APPENDIX C.5. UNCORRECTED MAJOR ELEMENT DATA : OXIDES (XRF)													
PC38-09	148m												
Sample	Depth	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	MnO2	P2O5	LOI	Total
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(%)	(%)
PC3809-33	324.0	56.60	11.28	4.29	0.21	2.25	3.79	1.640	0.547	0.040	0.482	14.55	95.67
PC3809-34	335.0	57.77	9.59	3.55	0.18	1.99	4.15	1.416	0.444	0.036	0.343	15.39	94.86
PC3809-35	344.0	58.45	8.70	3.57	0.19	1.88	4.36	1.302	0.431	0.028	0.340	14.34	93.59
PC3809-36	355.0	59.19	7.23	2.53	0.17	2.71	5.23	1.144	0.310	0.026	0.219	13.88	92.65
PC3809-37	364.0	57.90	7.10	2.68	0.17	4.27	4.68	1.110	0.302	0.024	0.214	14.53	92.96
PC3809-38	375.0	57.27	9.83	3.43	0.19	2.23	4.42	1.514	0.419	0.034	0.240	15.24	94.82
PC3809-39	384.0	57.07	10.54	4.02	0.19	3.63	3.72	1.533	0.509	0.043	0.459	13.77	95.49
PC3809-40	394.0	59.37	8.94	3.06	0.17	2.59	4.21	1.377	0.402	0.033	0.340	14.89	95.37
PC3809-41	404.0	61.24	10.03	3.44	0.18	1.66	3.96	1.547	0.452	0.038	0.264	12.73	95.54
PC3809-42	416.0	56.31	8.43	2.97	0.18	4.42	4.25	1.274	0.373	0.023	0.309	16.40	94.94
PC3809-43	424.0	59.98	9.22	3.05	0.17	1.66	4.36	1.458	0.399	0.032	0.215	13.31	93.85
PC3809-44	434.0	57.66	10.62	3.70	0.19	1.71	3.99	1.653	0.453	0.035	0.275	15.74	96.04
PC3809-45	444.0	60.16	8.62	3.26	0.17	3.34	4.34	1.329	0.382	0.032	0.299	12.80	94.75
PC3809-46	453.0	59.22	10.72	3.79	0.19	2.27	3.72	1.575	0.518	0.036	0.363	13.62	96.02
PC3809-47	465.0	57.31	9.99	3.74	0.19	2.73	3.90	1.503	0.457	0.038	0.351	15.28	95.49
PC3809-48	474.0	56.14	9.35	3.15	0.18	3.79	4.14	1.480	0.387	0.027	0.311	15.39	94.35
PC3809-49	483.0	61.15	10.37	3.77	0.18	2.01	3.83	1.607	0.496	0.036	0.383	13.00	96.83
PC3809-50	493.0	58.68	10.25	3.75	0.18	2.24	3.98	1.657	0.455	0.046	0.335	13.33	94.90
PC3809-51	504.0	61.28	10.93	3.93	0.18	2.28	3.50	1.705	0.534	0.041	0.399	12.53	97.31
PC3809-52	515.0	60.46	10.96	3.88	0.19	2.03	3.63	1.751	0.513	0.040	0.319	12.70	96.47
PC3809-53	525.0	57.15	10.07	3.45	0.18	3.05	4.10	1.603	0.426	0.037	0.255	15.37	95.69
PC3809-54	536.0	59.25	9.12	3.20	0.19	4.02	4.24	1.448	0.394	0.036	0.247	14.12	96.27
PC3809-55	544.0	59.18	11.00	4.09	0.20	2.91	3.67	1.708	0.524	0.042	0.339	13.11	96.77
PC3809-56	553.0	58.33	10.18	3.92	0.20	3.66	4.08	1.560	0.452	0.045	0.215	11.98	94.62
PC3809-57	564.0	59.48	9.29	3.58	0.20	3.52	4.48	1.409	0.430	0.041	0.221	12.62	95.26
PC3809-58	574.0	58.74	9.34	3.66	0.18	3.84	4.31	1.515	0.428	0.042	0.257	12.07	94.38
PC3809-59	585.0	58.96	8.97	3.45	0.18	4.97	4.23	1.418	0.417	0.040	0.682	12.64	95.95
PC3809-60	594.0	60.50	8.95	3.34	0.17	3.73	4.51	1.465	0.415	0.040	0.281	11.09	94.49
PC3809-61	605.0	58.19	10.25	4.01	0.18	4.33	3.70	1.613	0.481	0.047	0.409	13.18	96.40
PC3809-62	615.0	60.34	8.89	3.26	0.17	4.06	4.35	1.491	0.410	0.042	0.477	10.75	94.24
PC3809-63	625.0	59.73	9.99	3.80	0.18	3.95	4.08	1.580	0.470	0.047	0.443	11.85	96.11
PC3809-64	635.0	58.69	10.24	3.94	0.18	4.30	3.82	1.598	0.487	0.049	0.440	12.87	96.61

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APPENDIX C.5. UNCORRECTED MAJOR ELEMENT DATA : OXIDES (XRF)														
PC38-09	148m													
Sample	Depth	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	MnO2	P2O5	LOI	Total	
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(%)	(%)	
PC3809-65	646.0	60.63	8.76	3.16	0.17	3.45	4.60	1.378	0.399	0.037	0.294	12.97	95.85	
PC3809-66	654.0	62.06	8.38	3.04	0.17	3.13	4.44	1.318	0.396	0.039	0.231	12.35	95.56	
PC3809-67	664.0	62.23	8.41	3.03	0.16	3.36	4.61	1.345	0.378	0.032	0.199	12.37	96.13	
PC3809-68	674.0	60.23	7.32	2.92	0.16	2.86	4.35	1.243	0.353	0.032	0.177	11.32	90.96	
PC3809-69	684.0	60.25	9.99	3.74	0.18	3.53	4.19	1.641	0.452	0.038	0.254	12.52	96.78	
PC3809-70	694.0	59.57	10.73	3.99	0.19	3.62	4.09	1.639	0.488	0.050	0.256	13.23	97.86	
PC3809-71	703.0	58.08	10.60	4.10	0.19	3.41	4.22	1.717	0.469	0.047	0.211	10.27	93.30	
PC3809-72	714.0	58.86	9.64	3.68	0.18	3.88	4.32	1.559	0.445	0.039	0.296	11.90	94.80	
PC3809-73	724.0	59.68	10.63	4.16	0.20	3.99	3.99	1.695	0.500	0.049	0.420	9.91	95.22	
PC3809-74	734.0	57.40	10.73	4.11	0.19	4.38	3.87	1.703	0.504	0.046	0.429	11.50	94.87	
PC3809-75	744.0	61.74	10.31	4.07	0.18	3.95	4.47	1.696	0.459	0.049	0.346	11.44	98.71	
PC3809-76	754.0	59.60	9.46	3.66	0.17	3.73	4.34	1.545	0.432	0.043	0.222	11.87	95.08	
PC3809-77	764.0	57.79	10.76	4.01	0.18	4.48	3.72	1.830	0.490	0.051	0.289	11.03	94.63	
PC3809-78	774.0	58.54	11.03	4.25	0.18	4.21	3.57	1.776	0.528	0.052	0.301	12.09	96.52	
PC3809-79	784.0	59.42	10.51	4.13	0.18	4.09	3.69	1.755	0.495	0.045	0.282	10.76	95.36	
PC3809-80	794.0	59.86	10.57	3.90	0.18	4.14	3.63	1.787	0.498	0.044	0.327	10.99	95.92	
PC3809-81	804.0	61.03	10.11	3.74	0.17	3.67	3.73	1.650	0.486	0.043	0.406	10.28	95.32	
PC3809-82	813.0	60.10	10.49	4.28	0.19	4.68	3.63	1.622	0.510	0.048	0.665	11.23	97.45	
PC3809-83	823.0	61.09	10.24	3.99	0.17	3.76	3.61	1.667	0.493	0.049	0.443	10.40	95.92	
PC3809-84	834.0	60.01	10.62	3.91	0.17	3.68	3.57	1.701	0.509	0.046	0.360	11.32	95.90	
PC3809-85	845.0	62.58	10.71	3.88	0.18	3.70	3.84	1.767	0.488	0.047	0.424	10.34	97.96	
PC3809-86	854.0	60.05	12.11	4.50	0.20	3.25	3.70	2.019	0.548	0.060	0.221	10.37	97.03	
PC38-10	257m													
PC3810-01	6.0	42.71	9.10	2.63	0.17	8.25	4.60	1.421	0.400	0.021	0.990	22.15	92.45	
PC3810-02	14.0	53.31	9.93	2.57	0.14	7.45	3.58	1.545	0.476	0.032	2.337	14.52	95.89	
PC3810-03	24.0	60.10	10.27	2.22	0.11	9.36	3.06	1.652	0.458	0.034	4.412	5.98	97.66	
PC3810-04	34.0	59.93	10.21	2.07	0.11	8.92	3.13	1.606	0.453	0.026	2.299	8.80	97.55	
PC3810-05	44.0	56.40	10.48	2.86	0.16	3.04	4.02	1.786	0.498	0.038	0.945	15.00	95.23	
PC3810-06	54.0	57.61	10.59	2.86	0.16	2.45	4.35	1.767	0.473	0.025	0.633	15.52	96.44	
PC3810-07	64.0	60.10	11.01	3.26	0.15	3.16	3.99	1.877	0.508	0.031	1.007	11.19	96.28	

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APPENDIX C.5. UNCORRECTED MAJOR ELEMENT DATA : OXIDES (XRF)													
PC38-10	257m												
Sample	Depth	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	MnO2	P2O5	LOI	Total
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(%)	(%)
PC3810-08	74.0	61.67	11.52	3.13	0.14	4.20	3.64	1.946	0.526	0.037	1.558	9.90	98.26
PC3810-09	84.0	67.40	10.10	2.47	0.10	5.95	2.69	1.801	0.440	0.034	2.457	3.92	97.36
PC3810-10	94.0	64.41	10.71	2.54	0.10	7.96	2.88	1.747	0.437	0.034	3.404	4.17	98.39
PC3810-10	104.0	62.17	10.09	2.11	0.10	9.59	2.94	1.692	0.420	0.032	1.954	6.74	97.82
PC3810-11	113.0	64.27	10.41	2.07	0.09	8.63	2.82	1.659	0.417	0.034	1.309	6.33	98.04
PC3810-12	126.0	56.08	8.53	2.61	0.14	8.25	3.83	1.418	0.384	0.024	1.129	13.40	95.80
PC3810-13	134.0	56.43	8.41	2.69	0.15	5.65	3.74	1.397	0.381	0.024	1.205	14.82	94.90
PC3810-14	146.0	57.92	9.88	3.04	0.15	5.33	3.59	1.635	0.459	0.028	0.936	12.71	95.67
PC3810-15	154.0	52.76	9.10	2.86	0.15	8.77	3.43	1.482	0.415	0.031	0.942	16.27	96.22
PC3810-16	167.0	57.44	9.55	2.91	0.17	4.71	3.85	1.608	0.447	0.024	0.685	13.58	94.98
PC3810-17	174.0	60.19	10.22	2.85	0.17	2.80	3.82	1.718	0.459	0.029	0.789	13.03	96.07
PC3810-18	185.0	61.53	10.22	3.04	0.17	2.05	3.51	1.751	0.472	0.033	0.650	13.31	96.73
PC3810-19	194.0	55.26	8.51	2.74	0.16	5.67	3.99	1.464	0.371	0.025	0.582	15.25	94.02
PC3810-20	203.0	59.87	10.71	3.02	0.17	3.16	3.58	1.782	0.498	0.031	0.832	12.50	96.15
PC3810-21	216.0	54.65	8.04	2.55	0.15	5.91	4.08	1.369	0.365	0.022	0.728	16.11	93.98
PC3810-22	224.0	56.33	8.51	2.74	0.16	3.99	3.98	1.404	0.380	0.022	0.580	15.60	93.71
PC3810-23	233.0	55.56	9.81	3.03	0.18	3.55	3.96	1.662	0.451	0.031	0.644	14.64	93.52
PC3810-24	244.0	54.50	10.03	3.10	0.17	6.04	3.68	1.639	0.461	0.028	0.811	14.65	95.11
PC3810-25	254.0	57.13	9.38	2.43	0.14	6.81	3.94	1.573	0.415	0.027	1.512	11.65	95.01
PC3810-26	263.0	54.42	8.74	2.43	0.14	7.30	4.06	1.450	0.390	0.023	1.228	14.14	94.33
PC3810-27	273.0	52.71	9.94	3.12	0.16	6.28	3.57	1.654	0.456	0.032	0.700	15.41	94.04
PC3810-28	284.0	53.19	9.50	2.81	0.15	8.05	3.24	1.542	0.449	0.030	0.802	15.76	95.52
PC3810-29	295.0	44.97	7.15	2.37	0.15	12.32	3.46	1.190	0.313	0.021	0.661	21.67	94.27
PC3810-30	305.0	51.35	9.79	3.20	0.17	8.09	3.34	1.533	0.459	0.032	0.602	16.64	95.20
PC3810-31	314.0	52.57	10.33	2.95	0.16	8.17	3.24	1.622	0.488	0.027	0.712	15.57	95.85
PC3810-32	324.0	49.03	7.82	2.57	0.16	8.79	3.77	1.277	0.344	0.026	0.637	19.65	94.07
PC3810-33	335.0	51.53	9.79	2.93	0.17	7.07	3.44	1.604	0.447	0.029	0.673	16.77	94.45
PC3810-34	344.0	49.97	6.74	2.27	0.15	9.58	3.87	1.096	0.294	0.019	0.677	20.70	95.36
PC3810-35	354.0	56.32	6.16	1.90	0.14	5.66	4.36	1.047	0.269	0.009	0.504	17.04	93.40
PC3810-36	364.0	55.97	5.42	1.73	0.13	7.17	4.28	0.939	0.235	0.013	0.550	17.48	93.91
PC3810-37	374.0	58.01	5.70	1.66	0.13	5.48	4.07	0.942	0.245	0.009	0.463	17.66	94.36
PC3810-38	383.0	52.03	10.48	3.09	0.18	6.44	3.35	1.604	0.471	0.031	0.521	17.29	95.49

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APPENDIX C.5. UNCORRECTED MAJOR ELEMENT DATA : OXIDES (XRF)														
PC38-10	257m													
Sample	Depth	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	MnO2	P2O5	LOI	Total	
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(%)	(%)	
PC3810-39	394.0	52.69	8.41	2.33	0.15	5.70	3.68	1.334	0.382	0.021	0.638	18.66	94.01	
PC3810-40	404.0	53.38	9.86	2.65	0.16	6.71	3.34	1.536	0.471	0.029	0.627	16.66	95.41	
PC3810-41	417.0	47.62	8.33	2.44	0.15	10.17	3.31	1.278	0.386	0.020	0.751	20.45	94.90	
PC3810-42	424.0	50.40	8.69	2.45	0.15	7.75	3.59	1.388	0.391	0.030	0.677	18.87	94.39	
PC3810-43	434.0	45.20	3.99	1.24	0.12	15.07	4.01	0.708	0.179	0.009	0.797	22.17	93.51	
PC3810-44	445.0	47.81	6.84	2.02	0.14	11.31	3.51	1.108	0.297	0.013	0.573	20.45	94.07	
PC3810-45	456.0	48.86	6.21	1.86	0.14	10.04	3.76	0.993	0.272	0.014	0.587	21.55	94.27	
PC3810-46	467.0	50.87	4.16	1.29	0.12	10.11	4.47	0.755	0.181	0.003	0.445	20.14	92.55	
PC3810-47	476.0	44.62	8.51	2.45	0.15	11.41	3.14	1.336	0.394	0.025	1.080	21.95	95.06	
PC3810-48	484.0	43.73	8.05	2.38	0.14	12.27	2.90	1.254	0.368	0.019	1.015	22.67	94.80	
PC3810-49	494.0	45.25	7.70	2.04	0.13	12.69	2.85	1.164	0.365	0.022	1.969	20.86	95.02	
PC3810-50	504.0	57.32	9.72	2.25	0.11	10.88	2.88	1.554	0.435	0.025	5.417	7.34	97.94	
PC3810-51	514.0	59.81	9.97	3.73	0.18	3.39	3.75	1.543	0.486	0.038	0.254	11.97	95.13	
PC3810-52	524.0	62.78	10.90	3.92	0.19	2.97	3.69	1.677	0.531	0.047	0.236	10.50	97.45	
PC3810-53	534.0	44.04	7.91	2.36	0.17	6.54	3.97	1.236	0.315	0.019	0.565	23.30	90.43	
PC3810-54	545.0	50.08	7.99	2.33	0.16	5.07	4.01	1.315	0.325	0.021	0.438	21.45	93.19	
PC3810-55	554.0	45.78	7.20	2.17	0.17	7.17	4.22	1.157	0.286	0.019	0.422	24.40	93.00	
PC3810-56	564.0	47.96	6.12	2.01	0.17	10.08	4.37	1.014	0.257	0.023	0.628	20.08	92.71	
PC3810-57	574.0	43.79	7.10	2.26	0.18	11.47	3.69	1.111	0.298	0.022	0.538	23.60	94.06	
PC3810-58	584.0	47.08	6.95	2.23	0.17	9.84	4.09	1.180	0.291	0.025	0.409	21.12	93.38	
PC3810-59	596.0	48.35	6.87	2.19	0.16	8.68	4.22	1.164	0.285	0.018	0.429	20.85	93.21	
PC3810-60	604.0	46.00	7.02	2.29	0.17	10.60	4.15	1.198	0.289	0.023	0.437	20.35	92.51	
PC3810-61	614.0	50.02	7.76	2.48	0.16	7.57	4.01	1.273	0.316	0.020	0.313	20.32	94.26	
PC3810-62	624.0	48.46	8.49	2.65	0.17	8.92	3.52	1.439	0.363	0.027	0.440	19.73	94.22	
PC3810-63	634.0	49.29	8.33	2.56	0.16	8.93	4.50	1.400	0.343	0.026	0.466	20.13	96.14	
PC3810-64	645.0	50.90	8.08	2.66	0.17	6.84	4.04	1.318	0.328	0.032	0.312	19.30	93.97	
PC3810-65	655.0	48.55	7.76	2.51	0.16	7.60	4.16	1.284	0.308	0.020	0.289	20.21	92.86	
PC3810-66	667.0	50.10	8.61	2.75	0.16	7.32	3.92	1.459	0.344	0.025	0.378	18.29	93.35	
PC3810-67	674.0	51.44	10.04	3.10	0.18	5.59	3.68	1.685	0.406	0.033	0.394	18.17	94.72	
PC3810-68	683.0	51.25	9.21	2.82	0.17	6.51	3.73	1.578	0.357	0.027	0.299	14.98	90.94	
PC3810-69	694.0	53.53	12.19	3.72	0.20	4.48	3.44	2.070	0.499	0.034	0.450	18.24	98.84	
PC3810-70	704.0	55.29	13.57	3.61	0.22	2.52	3.23	2.376	0.582	0.043	0.424	14.24	96.11	

APPENDIX C.5. UNCORRECTED MAJOR ELEMENT DATA : OXIDES (XRF)														
PC38-10	257m													
Sample	Depth	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	MnO2	P2O5	LOI	Total	
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(%)	(%)	
PC3810-71	714.0	52.24	12.08	3.54	0.21	5.24	3.41	2.133	0.477	0.036	0.468	14.81	94.66	
PC3810-72	724.0	52.66	10.64	3.15	0.19	6.23	3.35	1.813	0.409	0.038	0.418	16.42	95.32	
PC3810-74	734.0	57.18	12.89	3.33	0.21	2.16	3.52	2.253	0.538	0.031	0.469	13.87	96.44	
PC3810-75	745.0	57.89	14.38	3.94	0.22	2.18	3.45	2.484	0.612	0.046	0.445	10.99	96.63	
PC3810-76	754.0	58.32	11.52	3.29	0.19	2.54	3.67	1.988	0.494	0.036	0.552	13.03	95.64	
PC3810-77	764.0	60.88	12.95	3.34	0.18	3.61	3.24	2.200	0.607	0.041	1.197	9.53	97.76	
PC38-02	2525m													
PC3802-01	8.0	46.91	10.31	4.13	2.31	11.68	3.70	1.76	0.447	0.034	0.254	15.75	97.29	
PC3802-02	18.0	42.77	9.25	3.62	2.14	15.75	3.41	1.62	0.393	0.035	0.246	15.66	94.90	
PC3802-03	28.0	40.99	8.95	3.51	2.09	17.04	3.49	1.50	0.387	0.029	0.228	19.06	97.27	
PC3802-04	38.0	40.57	9.75	3.66	2.20	14.35	3.70	1.73	0.404	0.030	0.207	19.64	96.22	
PC3802-05	48.0	39.45	9.66	3.58	2.11	17.02	3.29	1.66	0.422	0.030	0.200	19.72	97.15	
PC3802-06	57.5	39.51	9.42	3.77	2.07	16.51	3.37	1.67	0.406	0.032	0.198	19.53	96.49	
PC3802-07	70.0	40.91	10.14	3.71	2.15	16.69	2.61	1.67	0.452	0.033	0.212	19.62	98.18	
PC3802-08	79.0	40.10	9.89	3.79	2.22	16.15	3.19	1.70	0.436	0.028	0.207	19.08	96.80	
PC3802-09	89.0	37.47	9.21	3.53	2.09	18.26	3.18	1.57	0.427	0.030	0.211	20.71	96.68	
PC3802-10	100.0	35.55	8.58	3.29	1.97	19.83	3.19	1.47	0.403	0.029	0.208	22.04	96.55	
PC3802-11	110.0	35.99	8.38	3.20	1.94	20.15	3.11	1.45	0.392	0.034	0.205	21.83	96.68	
PC3802-12	120.0	34.41	7.74	3.19	1.81	21.22	3.15	1.39	0.367	0.027	0.195	22.71	96.20	
PC3802-13	130.0	35.92	8.51	3.51	1.93	19.87	3.08	1.42	0.384	0.030	0.200	23.21	98.08	
PC3802-14	139.0	39.47	9.81	3.53	2.14	16.52	3.42	1.69	0.432	0.035	0.211	19.80	97.06	
PC3802-15	150.0	40.46	10.10	3.78	2.20	15.82	3.55	1.77	0.441	0.033	0.214	19.55	97.92	
PC3802-16	160.0	42.84	11.06	4.07	2.30	14.64	3.09	1.93	0.491	0.037	0.226	16.86	97.54	
PC3802-17	171.0	44.39	11.23	4.10	2.37	12.79	3.43	2.01	0.494	0.035	0.224	15.80	96.87	
PC3802-18	181.0	47.29	10.57	4.50	2.34	11.10	3.70	1.96	0.486	0.039	0.225	15.39	97.60	
PC3802-19	191.0	45.98	10.44	4.29	2.33	12.02	3.54	1.88	0.474	0.037	0.224	16.33	97.54	
PC3802-20	201.0	47.47	11.06	4.28	2.44	10.45	3.73	1.99	0.507	0.036	0.225	15.86	98.03	
PC3802-21	211.0	45.29	11.27	4.30	2.40	11.78	3.50	1.98	0.503	0.038	0.225	16.58	97.87	
PC3802-22	221.0	45.14	11.16	4.27	2.42	12.52	3.50	1.96	0.496	0.037	0.225	15.77	97.50	
PC3802-23	231.0	46.68	11.75	4.40	2.50	11.19	3.55	2.07	0.531	0.041	0.231	14.49	97.45	

APPENDIX C.5. UNCORRECTED MAJOR ELEMENT DATA : OXIDES (XRF)													
PC38-02	2525m												
Sample	Depth	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	MnO2	P2O5	LOI	Total
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(%)	(%)
PC3802-24	241.0	53.18	13.05	4.89	2.79	5.85	3.92	2.39	0.592	0.042	0.243	11.85	98.79
PC3802-25	251.0	50.22	11.84	4.62	2.58	8.07	3.74	2.11	0.552	0.039	0.257	13.92	97.95
PC3802-26	261.0	46.62	10.61	4.24	2.34	11.65	3.55	1.90	0.495	0.036	0.261	15.95	97.66
PC3802-27	271.0	52.91	12.45	4.77	2.64	6.18	3.90	2.31	0.556	0.041	0.254	13.08	99.08
PC3802-28	281.0	52.08	12.53	4.75	2.57	6.89	3.73	2.35	0.546	0.036	0.247	12.94	98.66
PC3802-29	291.0	55.20	13.59	5.00	2.75	3.87	3.84	2.52	0.590	0.040	0.246	11.26	98.91
PC3802-30	301.0	54.72	13.13	5.03	2.74	5.03	3.78	2.41	0.592	0.042	0.286	10.85	98.62
PC3802-31	312.0	52.29	11.71	4.59	2.56	8.29	3.68	2.10	0.535	0.038	0.283	12.52	98.60
PC3802-32	322.0	51.18	11.94	4.70	2.66	8.08	3.65	2.17	0.535	0.041	0.271	12.89	98.11
PC3802-33	332.0	51.11	11.93	5.01	2.57	8.05	3.56	2.18	0.523	0.043	0.239	13.10	98.32
PC3802-34	342.0	51.30	11.75	4.99	2.62	8.17	3.70	2.12	0.505	0.036	0.249	12.52	97.95
PC3802-35	352.0	46.33	10.17	3.87	2.21	12.94	3.49	1.84	0.416	0.035	0.221	15.61	97.13
PC3802-36	362.0	41.28	9.89	3.81	2.14	16.24	3.25	1.70	0.402	0.036	0.195	18.37	97.32
PC3802-37	372.0	39.50	9.96	3.79	2.12	17.80	3.15	1.69	0.411	0.034	0.182	19.34	97.97
PC3802-38	381.0	38.59	9.60	3.74	2.10	18.73	2.94	1.73	0.418	0.032	0.181	19.26	97.32
PC3802-39	391.0	38.38	9.34	3.62	2.06	18.90	2.89	1.65	0.413	0.030	0.184	20.41	97.87
PC3802-40	400.0	37.34	8.99	3.45	2.01	20.33	2.98	1.61	0.399	0.032	0.191	20.92	98.25
PC3802-41	410.0	37.65	9.22	3.43	1.95	19.95	3.05	1.65	0.400	0.033	0.189	20.18	97.71
PC3802-42	420.0	38.90	9.20	3.49	1.95	19.16	3.10	1.67	0.397	0.031	0.183	18.72	96.79
PC3802-43	430.0	36.41	9.07	3.43	1.97	20.37	2.88	1.56	0.399	0.033	0.183	19.53	95.82
PC3802-44	440.0	38.52	9.42	3.51	2.04	19.16	2.98	1.71	0.423	0.031	0.192	19.74	97.73
PC3802-45	450.0	41.35	10.31	3.98	2.24	16.14	3.16	1.76	0.450	0.035	0.194	17.86	97.49
PC3802-46	460.0	42.75	10.97	4.12	2.32	14.48	3.42	2.00	0.481	0.038	0.202	16.23	97.03
PC3802-47	470.0	36.54	9.39	3.61	2.02	20.62	2.87	1.52	0.406	0.031	0.201	21.37	98.57
PC3802-48	481.0	35.55	8.87	3.48	1.94	21.27	2.56	1.15	0.405	0.032	0.198	23.37	98.82
PC3802-49	491.0	36.66	9.03	3.52	1.95	20.87	2.82	1.63	0.401	0.027	0.199	20.79	97.90
PC3802-50	501.0	38.72	9.56	3.89	2.05	19.53	3.04	1.72	0.411	0.038	0.215	21.11	100.28
PC3802-51	511.0	41.09	9.98	3.69	2.06	17.38	3.03	1.76	0.439	0.035	0.207	18.25	97.93
PC3802-52	521.0	44.92	11.01	4.11	2.15	14.06	3.38	2.12	0.443	0.037	0.212	15.00	97.45
PC3802-53	531.0	53.57	12.33	3.54	1.84	11.23	3.80	2.77	0.419	0.037	0.195	12.26	101.99
PC3802-54	540.0	50.17	12.84	4.88	2.65	8.33	3.56	2.38	0.563	0.044	0.249	13.03	98.70
PC3802-55	550.0	50.24	12.73	5.11	2.69	7.71	3.53	2.30	0.564	0.042	0.253	13.75	98.92

APPENDIX C.5. UNCORRECTED MAJOR ELEMENT DATA : OXIDES (XRF)

Sample	Depth (cm)	SiO2 (wt.%)	Al2O3 (wt.%)	Fe2O3 (wt.%)	MgO (wt.%)	CaO (wt.%)	Na2O (wt.%)	K2O (wt.%)	TiO2 (wt.%)	MnO2 (wt.%)	P2O5 (wt.%)	LOI (%)	Total (%)
PC38-02	2525m												
PC3802-56	560.0	49.85	12.09	5.69	2.65	6.06	3.55	2.25	0.556	0.041	0.252	13.69	96.67
PC3802-57	572.0	48.13	11.43	4.83	2.62	10.47	3.93	2.10	0.485	0.037	0.247	14.00	98.28
PC3802-58	582.0	46.92	11.87	4.73	2.49	11.09	3.46	2.16	0.490	0.040	0.230	13.95	97.42
PC3802-59	591.0	45.66	11.98	4.79	2.51	12.00	3.33	2.12	0.490	0.039	0.221	14.43	97.55
PC3802-60	601.0	35.32	8.98	3.72	1.97	21.65	2.69	1.47	0.396	0.030	0.212	21.32	97.76
PC3802-61	611.0	35.30	8.76	3.57	2.01	22.61	2.86	1.61	0.378	0.033	0.209	21.69	99.03
PC3802-62	621.0	38.56	9.68	3.92	2.16	19.32	2.89	1.75	0.441	0.036	0.209	19.00	97.98
PC3802-63	631.0	39.45	10.22	3.98	2.21	18.36	2.88	1.79	0.455	0.037	0.208	18.49	98.09
PC3802-64	641.0	44.11	11.42	4.35	2.41	15.58	3.04	2.01	0.487	0.039	0.225	16.10	99.77
PC3802-65	651.0	47.51	12.09	4.48	2.53	10.96	3.30	2.26	0.506	0.037	0.225	13.65	97.55
PC3802-66	662.0	47.04	11.08	4.45	2.44	11.70	3.59	2.09	0.473	0.038	0.247	13.99	97.14
PC3802-67	671.0	37.64	8.54	3.22	1.92	19.64	3.09	1.57	0.348	0.031	0.206	19.46	95.66
PC3802-68	681.0	38.64	9.72	3.56	2.06	18.54	2.98	1.80	0.404	0.034	0.187	17.95	95.87
PC3802-69	691.0	40.74	10.71	3.78	2.14	16.37	3.11	1.94	0.445	0.036	0.173	17.50	96.93
PC3802-70	701.0	39.93	10.28	3.55	2.09	17.34	2.92	1.86	0.433	0.034	0.170	18.25	96.86
PC3802-71	711.0	41.87	10.37	3.91	2.34	17.69	3.17	1.85	0.427	0.034	0.174	18.34	100.18
PC3802-72	721.0	41.43	9.95	3.61	2.14	16.59	3.07	1.86	0.429	0.034	0.178	17.72	97.02
PC3802-73	731.0	41.21	10.10	3.60	2.13	16.65	3.01	1.88	0.435	0.038	0.184	17.90	97.14
PC3802-74	741.0	41.54	10.16	3.66	2.17	15.79	3.04	1.85	0.450	0.037	0.193	17.97	96.85
PC38-11	3835m												
PC3811-01	3.0	55.33	12.78	3.31	2.11	2.59	3.61	2.040	0.596	0.036	0.682	14.35	97.43
PC3811-02	13.0	50.01	10.84	3.48	1.75	8.07	3.35	1.591	0.539	0.041	0.827	16.67	97.17
PC3811-03	23.0	55.25	11.09	3.39	1.63	7.00	3.21	1.704	0.591	0.045	0.800	12.63	97.34
PC3811-04	33.0	57.24	13.20	3.62	2.45	2.04	3.77	2.237	0.581	0.034	0.428	12.51	98.10
PC3811-05	43.0	55.37	12.97	3.31	2.40	3.18	3.83	2.195	0.566	0.037	0.366	13.70	97.92
PC3811-06	53.0	52.50	12.70	3.91	2.23	3.96	3.59	2.143	0.555	0.035	0.289	14.81	96.73
PC3811-07	63.0	53.17	13.01	3.78	2.28	4.18	3.69	2.200	0.553	0.041	0.280	14.86	98.04
PC3811-08	73.0	52.14	12.83	3.90	2.24	4.89	3.52	2.149	0.551	0.039	0.304	15.77	98.34
PC3811-09	85.0	59.53	13.16	3.74	1.90	7.19	3.60	2.182	0.517	0.048	0.606	9.13	101.61
PC3811-10	95.0	51.70	12.13	3.83	2.32	6.28	3.52	2.100	0.538	0.040	0.304	16.47	99.23

APPENDIX C.5. UNCORRECTED MAJOR ELEMENT DATA : OXIDES (XRF)													
PC38-11	3835m												
Sample	Depth	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	MnO2	P2O5	LOI	Total
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(%)	(%)
PC3811-11	105.0	50.24	11.65	3.88	2.25	6.90	3.46	1.979	0.522	0.039	0.293	16.01	97.24
PC3811-12	116.0	52.28	11.94	4.03	2.28	5.56	3.49	2.022	0.525	0.036	0.306	15.47	97.93
PC3811-13	125.0	51.98	12.27	3.94	2.35	5.70	3.55	2.149	0.537	0.038	0.291	14.90	97.72
PC3811-14	135.0	51.69	12.23	3.90	2.27	6.38	3.48	2.030	0.543	0.038	0.334	15.51	98.39
PC3811-15	145.0	54.47	12.96	3.89	2.54	5.64	3.81	2.154	0.552	0.041	0.330	15.95	102.34
PC3811-16	155.0	50.72	11.82	3.75	2.16	7.36	3.36	1.944	0.531	0.045	0.359	15.07	97.12
PC3811-17	165.0	54.89	13.21	4.06	2.58	6.28	3.94	2.195	0.539	0.042	0.329	14.81	102.87
PC3811-18	175.0	53.48	12.23	3.86	2.07	7.43	3.41	2.104	0.526	0.043	0.493	12.89	98.54
PC3811-19	186.0	52.08	12.36	3.51	2.26	4.85	3.50	2.170	0.534	0.044	0.328	17.87	99.52
PC3811-20	197.0	51.91	12.63	4.05	2.35	4.42	3.51	2.133	0.548	0.036	0.316	11.87	93.77
PC3811-21	204.0	52.79	12.80	3.99	2.32	3.37	3.64	2.251	0.540	0.036	0.301	14.46	96.51
PC3811-22	215.0	48.83	11.43	3.91	2.13	7.73	3.53	1.948	0.502	0.039	0.402	16.93	97.38
PC3811-23	225.0	49.40	11.71	4.04	2.28	6.84	3.68	1.975	0.499	0.038	0.328	17.09	97.87
PC3811-24	235.0	49.15	11.97	3.99	2.20	6.21	3.38	1.995	0.513	0.035	0.329	18.43	98.21
PC3811-25	245.0	49.80	12.03	3.96	2.33	6.65	3.55	2.011	0.497	0.036	0.337	17.34	98.54
PC3811-26	255.0	47.98	10.52	3.97	1.96	8.90	3.26	1.753	0.455	0.031	0.322	18.76	97.92
PC3811-27	265.0	50.17	10.64	3.69	2.04	7.83	3.30	1.791	0.457	0.030	0.325	18.77	99.04
PC3811-28	275.0	51.64	11.21	3.79	2.04	6.52	3.29	1.848	0.488	0.032	0.334	17.31	98.52
PC3811-29	285.0	54.44	13.54	3.77	2.23	2.63	3.50	2.427	0.587	0.033	0.336	13.97	97.47
PC3811-30	297.0	54.20	13.41	4.05	2.20	3.57	3.19	2.309	0.589	0.036	0.352	14.21	98.12
PC3811-31	305.0	56.41	13.90	3.85	2.25	2.12	3.34	2.487	0.613	0.035	0.341	12.81	98.17
PC3811-32	315.0	57.61	14.46	3.77	2.33	2.24	3.41	2.487	0.621	0.039	0.440	15.39	102.80
PC3811-33	325.0	49.08	9.92	3.07	1.57	12.50	2.52	1.616	0.456	0.032	0.980	16.57	98.32
PC3811-34	335.0	56.38	12.10	3.74	2.10	2.48	3.35	2.160	0.536	0.031	0.332	14.39	97.59
PC3811-35	345.0	55.73	12.04	3.76	2.13	2.83	3.45	2.115	0.521	0.032	0.330	14.90	97.83
PC3811-36	355.0	57.63	11.48	3.22	2.08	2.63	3.61	1.996	0.496	0.029	0.335	14.59	98.09
PC3811-37	365.0	55.80	11.97	3.50	2.11	2.53	3.59	2.047	0.517	0.028	0.342	15.15	97.58
PC3811-38	375.0	53.19	12.31	4.25	2.12	3.10	3.33	2.107	0.540	0.029	0.303	16.37	97.64
PC3811-39	385.0	53.40	13.37	3.99	2.30	3.22	3.30	2.318	0.594	0.039	0.335	15.75	98.61
PC3811-40	395.0	54.31	13.70	4.34	2.46	3.66	3.34	2.331	0.599	0.039	0.346	14.84	99.96
PC3811-41	405.0	51.42	13.13	4.24	2.39	3.62	3.26	2.259	0.580	0.038	0.335	15.71	96.99
PC3811-42	415.0	59.64	14.45	4.40	2.54	1.68	3.56	2.498	0.609	0.034	0.353	13.52	103.30

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APPENDIX C.6. UNCORRECTED MAJOR ELEMENTS											
BC38-03	4289m										
Sample	Depth	Si	Al	Fe	Mg	Ca	Na	K	Ti	Mn	P
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
BC3803-01	0.5	26.85	6.06	3.69	0.15	1.03	4.06	1.657	0.279	0.076	0.110
BC3803-02	1.5	27.29	6.14	3.90	0.15	1.01	3.61	1.686	0.287	0.063	0.112
BC3803-03	2.5	27.06	6.10	3.90	0.15	1.01	3.65	1.690	0.285	0.044	0.110
BC3803-04	3.5	27.36	6.16	3.66	0.15	1.01	3.63	1.672	0.287	0.026	0.102
BC3803-05	4.5	28.10	6.48	3.28	0.15	1.03	3.73	1.782	0.297	0.023	0.092
BC3803-06	5.5	27.57	6.37	2.70	0.14	1.02	3.58	1.771	0.297	0.025	0.090
BC3803-07	6.5	27.84	6.43	2.71	0.15	1.02	3.45	1.798	0.303	0.024	0.089
BC3803-08	7.5	27.91	6.53	2.84	0.15	1.03	3.52	1.808	0.305	0.021	0.087
BC3803-09	8.5	27.84	6.51	2.91	0.15	1.04	3.47	1.818	0.304	0.023	0.087
BC3803-10	9.5	29.04	6.97	3.09	0.16	1.07	3.53	1.852	0.317	0.029	0.090
BC3803-11	11.0	28.04	6.76	3.01	0.16	1.06	3.63	1.849	0.315	0.027	0.090
BC3803-12	13.0	28.17	6.82	2.80	0.15	1.09	3.19	1.874	0.325	0.027	0.090
BC3803-13	15.0	27.80	6.70	3.08	0.15	1.09	3.50	1.880	0.319	0.030	0.092
BC3803-14	17.0	28.50	6.84	2.92	0.15	1.13	3.08	1.901	0.331	0.027	0.096
BC3803-15	19.0	28.20	6.84	2.84	0.16	1.16	3.38	1.883	0.327	0.030	0.099
BC3803-16	21.0	28.53	6.55	2.67	0.15	1.11	3.07	1.812	0.315	0.022	0.095
BC3803-17	23.0	28.34	6.55	2.95	0.15	1.11	3.36	1.823	0.312	0.025	0.096
BC3803-18	25.0	28.32	6.63	2.73	0.15	1.15	3.03	1.839	0.321	0.028	0.099
BC3803-19	27.0	27.99	6.48	2.82	0.15	1.16	3.37	1.806	0.316	0.027	0.098
BC3803-20	29.0	28.58	6.76	2.95	0.15	1.20	2.98	1.878	0.328	0.032	0.102
BC3803-21	31.0	28.13	6.61	3.05	0.15	1.20	3.49	1.894	0.321	0.034	0.099
BC3803-22	33.0	28.43	6.68	2.86	0.15	1.21	3.13	1.864	0.323	0.028	0.103
BC3803-23	35.0	28.20	6.58	2.80	0.15	1.22	3.27	1.867	0.320	0.028	0.101
BC3803-24	37.0	29.13	6.88	3.09	0.16	1.30	3.13	1.919	0.328	0.031	0.105
BC3803-25	39.0	29.42	6.86	3.10	0.17	1.35	3.34	1.932	0.325	0.034	0.139
BC3803-26	41.0	28.44	6.60	3.02	0.15	1.29	2.98	1.905	0.324	0.031	0.100
BC3803-27	43.0	28.52	6.69	3.14	0.16	1.32	3.25	1.920	0.325	0.030	0.102
BC3803-28	45.0	28.42	6.59	2.96	0.16	1.30	2.99	1.898	0.321	0.026	0.102
BC3803-29	47.0	28.27	6.55	3.11	0.16	1.30	3.19	1.917	0.320	0.031	0.102
BC3803-30	49.0	28.55	6.63	3.10	0.16	1.32	2.91	1.922	0.322	0.029	0.104
BC3803-31	51.0	28.65	6.78	3.30	0.16	1.35	3.19	1.970	0.330	0.029	0.109
BC3803-32	53.0	28.01	6.67	3.09	0.17	1.37	3.26	1.927	0.326	0.030	0.105
BC38-02	2530m										
BC3802-01	0.5	23.50	5.90	3.65	0.15	6.22	3.18	1.643	0.270	0.039	0.134
BC3802-02	1.5	23.64	5.95	3.67	0.15	5.94	3.07	1.670	0.271	0.038	0.127
BC3802-03	2.5	23.60	5.92	3.65	0.15	6.21	2.93	1.660	0.272	0.037	0.124
BC3802-04	3.5	23.40	5.89	3.64	0.14	6.37	2.83	1.610	0.268	0.028	0.126
BC3802-05	4.5	23.40	5.87	3.61	0.14	6.60	2.88	1.691	0.269	0.026	0.125
BC3802-06	5.5	23.26	5.84	3.54	0.15	6.67	2.86	1.694	0.265	0.027	0.130
BC3802-07	6.5	23.20	6.07	3.60	0.15	6.83	2.96	1.703	0.270	0.025	0.120
BC3802-08	7.5	23.24	5.89	3.62	0.15	6.70	2.83	1.681	0.266	0.025	0.123
BC3802-09	8.5	23.12	6.00	3.59	0.15	6.87	2.82	1.740	0.276	0.029	0.128
BC3802-10	9.5	22.94	5.97	3.52	0.15	7.10	2.68	1.695	0.277	0.028	0.120
BC3802-11	11.0	23.86	6.27	3.60	0.17	8.01	2.66	1.749	0.279	0.029	0.123
BC3802-12	13.0	21.84	5.56	3.45	0.15	8.80	2.38	1.616	0.263	0.025	0.118
BC3802-13	15.0	21.38	5.50	3.14	0.15	9.18	2.86	1.612	0.254	0.027	0.118
BC3802-13A	17.0	19.86	5.25	2.77	0.14	11.30	2.60	1.485	0.236	0.024	0.111
BC3802-14	19.0	19.29	4.84	2.60	0.13	12.45	2.41	1.401	0.225	0.023	0.111
BC3802-15	21.0	18.99	4.78	2.55	0.12	13.41	2.09	1.405	0.224	0.025	0.110
BC3802-16	23.0	18.47	4.63	2.51	0.13	13.66	2.37	1.326	0.218	0.020	0.109
BC3802-17	25.0	18.30	4.64	2.48	0.12	14.16	1.99	1.353	0.217	0.021	0.110
BC3802-18	27.0	17.70	4.55	2.43	0.12	14.37	2.27	1.289	0.212	0.023	0.106
BC3802-19	29.0	17.49	4.49	2.38	0.12	15.13	1.96	1.293	0.210	0.020	0.107
BC3802-20	31.0	17.22	4.45	2.33	0.12	14.73	2.31	1.227	0.209	0.022	0.106
BC3802-21	33.0	17.44	4.62	2.38	0.12	14.53	2.03	1.393	0.215	0.024	0.103
BC3802-21A	35.0	17.50	4.81	2.42	0.13	13.29	2.36	1.386	0.226	0.018	0.088
BC3802-22	37.0	17.58	4.74	2.43	0.12	13.84	2.03	1.334	0.221	0.016	0.094
BC3802-23	39.0	17.24	4.56	2.37	0.12	14.22	2.44	1.331	0.213	0.021	0.102
BC3802-24	41.0	17.48	4.82	2.46	0.12	13.81	2.22	1.379	0.224	0.023	0.089
BC3802-25	43.0	17.60	4.90	2.52	0.13	13.50	2.40	1.474	0.229	0.019	0.089
BC3802-26	45.0	17.32	4.81	2.50	0.12	13.33	2.16	1.455	0.232	0.023	0.089
BC3802-27	47.0	17.56	4.94	2.46	0.13	13.31	2.42	1.467	0.232	0.018	0.091
BC3802-28	49.0	17.75	4.96	2.49	0.13	13.35	2.26	1.476	0.236	0.021	0.091
BC3802-29	51.0	17.76	4.96	2.49	0.13	13.19	2.34	1.450	0.236	0.022	0.091
BC3802-30	53.0	17.74	5.00	2.46	0.13	13.04	2.34	1.432	0.236	0.024	0.096

APPENDIX C.6. UNCORRECTED MAJOR ELEMENTS											
PC38-09	148m										
Sample	Depth	Si	Al	Fe	Mg	Ca	Na	K	Ti	Mn	P
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
PC3809-01	4.0	25.14	5.45	2.41	0.11	2.03	3.36	1.278	0.298	0.021	0.222
PC3809-02	13.0	24.94	5.30	2.08	0.11	2.26	3.72	1.200	0.270	0.022	0.158
PC3809-03	23.0	25.16	7.04	2.56	0.12	1.77	3.33	1.480	0.326	0.029	0.188
PC3809-04	34.0	25.45	6.46	2.37	0.12	1.48	3.47	1.411	0.321	0.025	0.185
PC3809-05	43.0	28.04	6.70	2.48	0.10	1.92	2.74	1.536	0.375	0.034	0.240
PC3809-06	53.0	25.21	5.95	2.49	0.12	1.47	3.38	1.357	0.312	0.028	0.251
PC3809-07	62.0	23.53	5.42	2.15	0.12	2.19	3.69	1.150	0.263	0.018	0.212
PC3809-08	73.0	26.66	6.53	2.42	0.11	1.46	2.86	1.450	0.349	0.031	0.192
PC3809-09	84.0	24.46	7.57	2.92	0.12	1.12	3.01	1.657	0.386	0.029	0.155
PC3809-10	94.0	23.82	6.99	3.13	0.12	1.39	3.15	1.555	0.340	0.030	0.162
PC3809-11	104.0	24.61	6.21	2.32	0.12	1.14	3.35	1.390	0.301	0.022	0.145
PC3809-12	113.0	25.85	7.86	3.07	0.15	1.23	2.92	1.749	0.407	0.033	0.153
PC3809-13	124.0	25.72	6.97	2.47	0.11	2.00	2.64	1.541	0.385	0.030	0.227
PC3809-14	134.0	25.71	5.98	2.31	0.11	1.94	3.37	1.327	0.307	0.024	0.276
PC3809-15	144.0	26.14	5.27	2.11	0.10	1.65	3.37	1.217	0.274	0.020	0.187
PC3809-16	152.0	27.42	5.24	2.22	0.10	1.66	3.24	1.234	0.273	0.019	0.136
PC3809-17	165.0	27.28	5.07	2.08	0.10	2.32	3.37	1.175	0.274	0.022	0.222
PC3809-18	174.0	28.93	6.42	2.25	0.09	1.87	2.62	1.477	0.347	0.029	0.256
PC3809-19	185.0	29.95	5.70	2.02	0.08	2.41	2.80	1.328	0.315	0.028	0.408
PC3809-20	194.0	29.44	5.92	2.03	0.08	2.96	2.53	1.356	0.335	0.034	0.396
PC3809-21	205.0	28.39	6.51	3.00	0.12	2.71	2.89	1.511	0.368	0.047	0.149
PC3809-22	214.0	27.74	5.34	1.86	0.09	2.29	2.95	1.247	0.291	0.023	0.376
PC3809-23	224.0	32.32	5.86	1.71	0.06	2.91	2.38	1.387	0.310	0.027	0.484
PC3809-24	234.0	30.59	5.13	1.93	0.07	2.82	2.79	1.195	0.277	0.022	0.566
PC3809-25	243.0	29.59	3.99	1.77	0.10	1.64	3.56	0.985	0.206	0.021	0.318
PC3809-26	257.0	29.41	4.79	2.06	0.09	1.70	3.02	1.157	0.259	0.022	0.282
PC3809-27	267.0	30.08	4.89	1.78	0.07	3.77	2.61	1.205	0.262	0.026	0.995
PC3809-28	273.0	13.86	2.51	2.85	0.17	18.00	1.84	0.676	0.136	0.018	5.642
PC3809-29	284.0	26.90	5.67	2.70	0.12	1.99	3.03	1.293	0.318	0.033	0.296
PC3809-30	294.0	27.72	4.49	2.07	0.10	1.86	3.46	1.080	0.231	0.020	0.153
PC3809-31	304.0	27.42	5.83	2.75	0.12	1.37	3.07	1.317	0.326	0.035	0.158
PC3809-32	314.0	24.67	5.68	2.57	0.13	1.55	3.04	1.274	0.280	0.027	0.131
PC3809-33	324.0	26.41	5.97	3.00	0.12	1.60	2.82	1.333	0.328	0.031	0.210
PC3809-34	335.0	26.96	5.08	2.49	0.11	1.42	3.08	1.151	0.266	0.028	0.150
PC3809-35	344.0	27.28	4.61	2.50	0.11	1.34	3.24	1.058	0.258	0.021	0.149
PC3809-36	355.0	27.62	3.83	1.77	0.10	1.94	3.88	0.930	0.186	0.020	0.096
PC3809-37	364.0	27.02	3.76	1.87	0.10	3.05	3.47	0.903	0.181	0.018	0.093
PC3809-38	375.0	26.73	5.20	2.40	0.11	1.60	3.28	1.231	0.251	0.026	0.105
PC3809-39	384.0	26.63	5.58	2.81	0.12	2.59	2.76	1.247	0.305	0.033	0.201
PC3809-40	394.0	27.70	4.73	2.14	0.10	1.85	3.12	1.120	0.241	0.025	0.149
PC3809-41	404.0	28.58	5.31	2.41	0.11	1.19	2.94	1.257	0.271	0.029	0.115
PC3809-42	416.0	26.28	4.46	2.08	0.11	3.16	3.16	1.035	0.224	0.018	0.135
PC3809-43	424.0	27.99	4.88	2.13	0.10	1.19	3.24	1.185	0.239	0.025	0.094
PC3809-44	434.0	26.91	5.62	2.59	0.12	1.22	2.96	1.344	0.272	0.027	0.120
PC3809-45	444.0	28.08	4.57	2.28	0.10	2.39	3.22	1.080	0.229	0.025	0.130
PC3809-46	453.0	27.63	5.67	2.65	0.11	1.62	2.76	1.281	0.311	0.028	0.159
PC3809-47	465.0	26.75	5.29	2.62	0.11	1.95	2.90	1.222	0.274	0.029	0.153
PC3809-48	474.0	26.20	4.95	2.21	0.11	2.71	3.07	1.203	0.232	0.021	0.136
PC3809-49	483.0	28.54	5.49	2.64	0.11	1.43	2.84	1.306	0.297	0.028	0.167
PC3809-50	493.0	27.38	5.43	2.62	0.11	1.60	2.95	1.347	0.273	0.036	0.146
PC3809-51	504.0	28.60	5.79	2.75	0.11	1.63	2.59	1.386	0.320	0.032	0.174
PC3809-52	515.0	28.22	5.80	2.72	0.11	1.45	2.69	1.423	0.307	0.031	0.139
PC3809-53	525.0	26.67	5.33	2.42	0.11	2.18	3.04	1.303	0.256	0.028	0.111
PC3809-54	536.0	27.65	4.83	2.24	0.11	2.87	3.15	1.177	0.236	0.028	0.108
PC3809-55	544.0	27.62	5.82	2.86	0.12	2.08	2.72	1.388	0.314	0.032	0.148
PC3809-56	553.0	27.22	5.39	2.75	0.12	2.62	3.03	1.268	0.271	0.035	0.094
PC3809-57	564.0	27.76	4.92	2.50	0.12	2.51	3.32	1.145	0.258	0.032	0.096
PC3809-58	574.0	27.41	4.94	2.57	0.11	2.74	3.19	1.231	0.257	0.033	0.112
PC3809-59	585.0	27.51	4.75	2.42	0.11	3.55	3.14	1.153	0.250	0.031	0.298
PC3809-60	594.0	28.23	4.74	2.34	0.10	2.66	3.34	1.191	0.249	0.031	0.123
PC3809-61	605.0	27.15	5.43	2.81	0.11	3.09	2.75	1.312	0.288	0.036	0.178
PC3809-62	615.0	28.16	4.71	2.28	0.10	2.90	3.23	1.212	0.246	0.033	0.208
PC3809-63	625.0	27.87	5.29	2.66	0.11	2.82	3.02	1.284	0.282	0.037	0.193
PC3809-64	635.0	27.39	5.42	2.76	0.11	3.07	2.83	1.299	0.292	0.038	0.192
PC3809-65	646.0	28.29	4.64	2.21	0.10	2.47	3.41	1.120	0.239	0.029	0.128
PC3809-66	654.0	28.96	4.44	2.13	0.10	2.24	3.30	1.072	0.238	0.031	0.101
PC3809-67	664.0	29.04	4.45	2.12	0.10	2.40	3.42	1.093	0.227	0.025	0.087

APPENDIX C.6. UNCORRECTED MAJOR ELEMENTS											
Sample	Depth (cm)	Si (wt.%)	Al (wt.%)	Fe (wt.%)	Mg (wt.%)	Ca (wt.%)	Na (wt.%)	K (wt.%)	Ti (wt.%)	Mn (wt.%)	P (wt.%)
PC38-09	148m										
PC3809-68	674.0	28.11	3.88	2.04	0.09	2.04	3.23	1.010	0.212	0.025	0.077
PC3809-69	684.0	28.11	5.29	2.62	0.11	2.52	3.11	1.334	0.271	0.029	0.111
PC3809-70	694.0	27.80	5.68	2.79	0.12	2.59	3.03	1.332	0.293	0.039	0.112
PC3809-71	703.0	27.10	5.61	2.87	0.12	2.43	3.13	1.396	0.281	0.037	0.092
PC3809-72	714.0	27.47	5.10	2.58	0.11	2.77	3.21	1.267	0.267	0.030	0.129
PC3809-73	724.0	27.85	5.63	2.91	0.12	2.85	2.96	1.378	0.300	0.038	0.183
PC3809-74	734.0	26.79	5.68	2.88	0.12	3.13	2.87	1.385	0.302	0.036	0.187
PC3809-75	744.0	28.81	5.46	2.85	0.11	2.82	3.31	1.379	0.275	0.038	0.151
PC3809-76	754.0	27.82	5.01	2.56	0.10	2.66	3.22	1.256	0.259	0.034	0.097
PC3809-77	764.0	26.97	5.70	2.81	0.11	3.20	2.76	1.488	0.294	0.040	0.126
PC3809-78	774.0	27.32	5.84	2.98	0.11	3.01	2.65	1.444	0.317	0.040	0.132
PC3809-79	784.0	27.73	5.56	2.89	0.11	2.92	2.74	1.427	0.297	0.035	0.123
PC3809-80	794.0	27.94	5.60	2.73	0.11	2.96	2.69	1.453	0.298	0.034	0.143
PC3809-81	804.0	28.48	5.35	2.62	0.10	2.62	2.77	1.341	0.291	0.033	0.177
PC3809-82	813.0	28.05	5.56	3.00	0.12	3.35	2.69	1.318	0.305	0.037	0.290
PC3809-83	823.0	28.51	5.42	2.79	0.10	2.68	2.68	1.355	0.295	0.038	0.193
PC3809-84	834.0	28.01	5.62	2.74	0.10	2.63	2.65	1.383	0.305	0.035	0.157
PC3809-85	845.0	29.21	5.67	2.72	0.11	2.64	2.85	1.436	0.293	0.036	0.185
PC3809-86	854.0	28.02	6.41	3.15	0.12	2.32	2.74	1.641	0.329	0.047	0.096
PC38-10	257m										
PC3810-01	6.0	19.93	4.82	1.84	0.10	5.89	3.41	1.155	0.240	0.017	0.432
PC3810-02	14.0	24.88	5.26	1.80	0.09	5.32	2.66	1.256	0.285	0.025	1.020
PC3810-03	24.0	28.05	5.44	1.55	0.07	6.69	2.27	1.343	0.274	0.027	1.926
PC3810-04	34.0	27.97	5.41	1.45	0.07	6.37	2.32	1.306	0.272	0.021	1.004
PC3810-05	44.0	26.32	5.55	2.00	0.10	2.17	2.98	1.452	0.299	0.029	0.412
PC3810-06	54.0	26.89	5.61	2.00	0.10	1.75	3.23	1.436	0.284	0.020	0.276
PC3810-07	64.0	28.05	5.83	2.29	0.09	2.25	2.96	1.526	0.305	0.024	0.440
PC3810-08	74.0	28.78	6.10	2.19	0.08	3.00	2.70	1.582	0.315	0.029	0.680
PC3810-09	84.0	31.45	5.34	1.73	0.06	4.25	2.00	1.464	0.264	0.027	1.073
PC3810-10	94.0	30.06	5.67	1.78	0.06	5.68	2.14	1.420	0.262	0.027	1.486
PC3810-10	104.0	29.01	5.34	1.48	0.06	6.85	2.18	1.375	0.252	0.025	0.853
PC3810-11	113.0	29.99	5.51	1.45	0.05	6.17	2.09	1.349	0.250	0.027	0.572
PC3810-12	126.0	26.17	4.52	1.82	0.09	5.89	2.85	1.153	0.230	0.019	0.493
PC3810-13	134.0	26.34	4.45	1.88	0.09	4.04	2.77	1.136	0.229	0.019	0.526
PC3810-14	146.0	27.03	5.23	2.13	0.09	3.80	2.66	1.329	0.275	0.022	0.409
PC3810-15	154.0	24.62	4.82	2.01	0.09	6.26	2.55	1.205	0.249	0.024	0.411
PC3810-16	167.0	26.81	5.06	2.04	0.10	3.37	2.86	1.308	0.268	0.019	0.299
PC3810-17	174.0	28.09	5.41	2.00	0.10	2.00	2.83	1.397	0.275	0.023	0.344
PC3810-18	185.0	28.71	5.41	2.13	0.10	1.46	2.61	1.424	0.283	0.026	0.284
PC3810-19	194.0	25.79	4.50	1.92	0.10	4.05	2.96	1.190	0.222	0.020	0.254
PC3810-20	203.0	27.94	5.67	2.12	0.10	2.26	2.66	1.448	0.298	0.024	0.363
PC3810-21	216.0	25.50	4.26	1.79	0.09	4.22	3.02	1.113	0.219	0.017	0.318
PC3810-22	224.0	26.29	4.51	1.92	0.10	2.85	2.96	1.141	0.228	0.017	0.253
PC3810-23	233.0	25.93	5.20	2.12	0.11	2.54	2.94	1.351	0.270	0.024	0.281
PC3810-24	244.0	25.43	5.31	2.17	0.10	4.31	2.73	1.333	0.276	0.022	0.354
PC3810-25	254.0	26.66	4.96	1.70	0.08	4.87	2.92	1.278	0.249	0.021	0.660
PC3810-26	263.0	25.40	4.63	1.70	0.09	5.21	3.01	1.179	0.234	0.018	0.536
PC3810-27	273.0	24.60	5.26	2.18	0.10	4.49	2.65	1.345	0.273	0.025	0.305
PC3810-28	284.0	24.82	5.03	1.97	0.09	5.75	2.40	1.253	0.269	0.023	0.350
PC3810-29	295.0	20.99	3.79	1.66	0.09	8.80	2.57	0.967	0.187	0.016	0.289
PC3810-30	305.0	23.96	5.18	2.24	0.10	5.78	2.48	1.246	0.275	0.025	0.263
PC3810-31	314.0	24.53	5.47	2.07	0.10	5.84	2.40	1.319	0.293	0.021	0.311
PC3810-32	324.0	22.88	4.14	1.80	0.09	6.28	2.80	1.038	0.206	0.021	0.278
PC3810-33	335.0	24.05	5.18	2.05	0.10	5.05	2.55	1.304	0.268	0.023	0.294
PC3810-34	344.0	23.32	3.57	1.59	0.09	6.84	2.87	0.891	0.177	0.015	0.295
PC3810-35	354.0	26.28	3.26	1.33	0.08	4.04	3.23	0.851	0.161	0.007	0.220
PC3810-36	364.0	26.12	2.87	1.21	0.08	5.12	3.18	0.763	0.141	0.010	0.240
PC3810-37	374.0	27.07	3.02	1.16	0.08	3.91	3.02	0.766	0.147	0.007	0.202
PC3810-38	383.0	24.28	5.55	2.16	0.11	4.60	2.48	1.304	0.283	0.024	0.228
PC3810-39	394.0	24.59	4.45	1.63	0.09	4.07	2.73	1.084	0.229	0.016	0.279
PC3810-40	404.0	24.91	5.22	1.85	0.10	4.79	2.48	1.248	0.282	0.023	0.274
PC3810-41	417.0	22.22	4.41	1.71	0.09	7.26	2.46	1.039	0.231	0.015	0.328
PC3810-42	424.0	23.52	4.60	1.71	0.09	5.53	2.66	1.128	0.234	0.024	0.296
PC3810-43	434.0	21.10	2.11	0.87	0.07	10.76	2.98	0.576	0.107	0.007	0.348
PC3810-44	445.0	22.31	3.62	1.41	0.08	8.08	2.60	0.901	0.178	0.010	0.250

APPENDIX C.6. UNCORRECTED MAJOR ELEMENTS											
PC38-10	257m										
Sample	Depth	Si	Al	Fe	Mg	Ca	Na	K	Ti	Mn	P
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
PC3810-45	456.0	22.80	3.29	1.30	0.08	7.17	2.79	0.808	0.163	0.011	0.256
PC3810-46	467.0	23.74	2.20	0.90	0.07	7.22	3.32	0.614	0.108	0.003	0.194
PC3810-47	476.0	20.82	4.51	1.71	0.09	8.15	2.33	1.086	0.236	0.019	0.471
PC3810-48	484.0	20.41	4.26	1.66	0.09	8.77	2.15	1.019	0.221	0.014	0.443
PC3810-49	494.0	21.11	4.08	1.43	0.08	9.06	2.11	0.946	0.219	0.017	0.860
PC3810-50	504.0	26.75	5.15	1.57	0.07	7.77	2.14	1.263	0.261	0.020	2.365
PC3810-51	514.0	27.91	5.28	2.61	0.11	2.42	2.78	1.254	0.292	0.029	0.111
PC3810-52	524.0	29.30	5.77	2.74	0.12	2.12	2.74	1.364	0.318	0.036	0.103
PC3810-53	534.0	20.55	4.19	1.65	0.10	4.67	2.94	1.005	0.189	0.015	0.247
PC3810-54	545.0	23.37	4.23	1.63	0.10	3.62	2.98	1.069	0.195	0.016	0.191
PC3810-55	554.0	21.37	3.81	1.52	0.10	5.12	3.13	0.940	0.171	0.015	0.184
PC3810-56	564.0	22.38	3.24	1.40	0.10	7.20	3.24	0.825	0.154	0.017	0.274
PC3810-57	574.0	20.44	3.76	1.58	0.11	8.19	2.74	0.903	0.179	0.017	0.235
PC3810-58	584.0	21.97	3.68	1.56	0.10	7.03	3.03	0.959	0.175	0.020	0.178
PC3810-59	596.0	22.56	3.64	1.53	0.10	6.20	3.13	0.946	0.171	0.014	0.187
PC3810-60	604.0	21.47	3.71	1.60	0.10	7.57	3.08	0.974	0.173	0.018	0.191
PC3810-61	614.0	23.34	4.11	1.74	0.10	5.41	2.98	1.035	0.190	0.016	0.137
PC3810-62	624.0	22.62	4.50	1.86	0.10	6.37	2.61	1.170	0.218	0.021	0.192
PC3810-63	634.0	23.00	4.41	1.79	0.10	6.38	3.34	1.138	0.206	0.020	0.204
PC3810-64	645.0	23.75	4.28	1.86	0.10	4.88	3.00	1.072	0.197	0.025	0.136
PC3810-65	655.0	22.66	4.11	1.76	0.10	5.43	3.09	1.043	0.185	0.016	0.126
PC3810-66	667.0	23.38	4.56	1.92	0.10	5.23	2.91	1.186	0.206	0.020	0.165
PC3810-67	674.0	24.01	5.31	2.17	0.11	3.99	2.73	1.370	0.244	0.025	0.172
PC3810-68	683.0	23.92	4.88	1.97	0.10	4.65	2.77	1.283	0.214	0.021	0.131
PC3810-69	694.0	24.98	6.45	2.60	0.12	3.20	2.55	1.683	0.299	0.027	0.196
PC3810-70	704.0	25.80	7.19	2.53	0.13	1.80	2.40	1.932	0.349	0.034	0.185
PC3810-71	714.0	24.38	6.40	2.48	0.13	3.74	2.53	1.734	0.286	0.028	0.204
PC3810-72	724.0	24.57	5.63	2.21	0.12	4.45	2.48	1.474	0.245	0.029	0.183
PC3810-74	734.0	26.68	6.83	2.33	0.13	1.54	2.61	1.831	0.323	0.024	0.205
PC3810-75	745.0	27.01	7.61	2.76	0.13	1.55	2.56	2.019	0.367	0.036	0.194
PC3810-76	754.0	27.22	6.10	2.31	0.12	1.81	2.73	1.616	0.296	0.028	0.241
PC3810-77	764.0	28.41	6.86	2.34	0.11	2.58	2.40	1.788	0.364	0.032	0.523
PC38-02	2525m										
PC3802-01	8.0	21.89	5.46	2.89	1.39	8.34	2.75	1.428	0.268	0.026	0.111
PC3802-02	18.0	19.96	4.90	2.53	1.29	11.25	2.53	1.316	0.236	0.027	0.107
PC3802-03	28.0	19.13	4.74	2.46	1.26	12.17	2.59	1.223	0.232	0.022	0.100
PC3802-04	38.0	18.93	5.16	2.56	1.33	10.25	2.75	1.404	0.242	0.023	0.090
PC3802-05	48.0	18.41	5.11	2.51	1.27	12.16	2.44	1.349	0.253	0.023	0.087
PC3802-06	57.5	18.44	4.99	2.64	1.25	11.79	2.50	1.358	0.243	0.025	0.086
PC3802-07	70.0	19.09	5.37	2.60	1.30	11.92	1.94	1.360	0.271	0.026	0.093
PC3802-08	79.0	18.71	5.24	2.65	1.34	11.54	2.37	1.384	0.261	0.022	0.090
PC3802-09	89.0	17.49	4.88	2.47	1.26	13.04	2.36	1.277	0.256	0.023	0.092
PC3802-10	100.0	16.59	4.54	2.30	1.19	14.16	2.37	1.191	0.242	0.022	0.091
PC3802-11	110.0	16.80	4.44	2.24	1.17	14.39	2.31	1.181	0.235	0.026	0.090
PC3802-12	120.0	16.06	4.10	2.23	1.09	15.16	2.34	1.129	0.220	0.021	0.085
PC3802-13	130.0	16.76	4.51	2.46	1.16	14.19	2.29	1.158	0.230	0.023	0.087
PC3802-14	139.0	18.42	5.19	2.47	1.29	11.80	2.54	1.376	0.259	0.027	0.092
PC3802-15	150.0	18.88	5.35	2.65	1.33	11.30	2.63	1.436	0.264	0.026	0.093
PC3802-16	160.0	19.99	5.86	2.85	1.39	10.46	2.29	1.570	0.294	0.029	0.099
PC3802-17	171.0	20.72	5.95	2.87	1.43	9.14	2.54	1.631	0.296	0.027	0.098
PC3802-18	181.0	22.07	5.60	3.15	1.41	7.93	2.75	1.595	0.291	0.030	0.098
PC3802-19	191.0	21.46	5.53	3.00	1.40	8.59	2.63	1.528	0.284	0.029	0.098
PC3802-20	201.0	22.15	5.86	3.00	1.47	7.46	2.77	1.616	0.304	0.028	0.098
PC3802-21	211.0	21.14	5.97	3.01	1.45	8.41	2.60	1.606	0.302	0.029	0.098
PC3802-22	221.0	21.07	5.91	2.99	1.46	8.94	2.60	1.597	0.297	0.029	0.098
PC3802-23	231.0	21.78	6.22	3.08	1.51	7.99	2.63	1.686	0.318	0.032	0.101
PC3802-24	241.0	24.82	6.91	3.42	1.68	4.18	2.91	1.942	0.355	0.033	0.106
PC3802-25	251.0	23.44	6.27	3.23	1.56	5.76	2.77	1.716	0.331	0.030	0.112
PC3802-26	261.0	21.76	5.62	2.97	1.41	8.32	2.63	1.547	0.297	0.028	0.114
PC3802-27	271.0	24.69	6.59	3.34	1.59	4.41	2.89	1.875	0.333	0.032	0.111
PC3802-28	281.0	24.30	6.63	3.33	1.55	4.92	2.77	1.907	0.327	0.028	0.108
PC3802-29	291.0	25.76	7.19	3.50	1.66	2.76	2.85	2.048	0.354	0.031	0.107
PC3802-30	301.0	25.54	6.95	3.52	1.65	3.59	2.80	1.962	0.355	0.033	0.125
PC3802-31	312.0	24.40	6.20	3.21	1.54	5.92	2.73	1.705	0.321	0.029	0.124
PC3802-32	322.0	23.88	6.32	3.29	1.60	5.77	2.71	1.766	0.321	0.032	0.118

APPENDIX C.6. UNCORRECTED MAJOR ELEMENTS											
PC38-02	2525m										
Sample	Depth	Si	Al	Fe	Mg	Ca	Na	K	Ti	Mn	P
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
PC3802-33	332.0	23.85	6.32	3.51	1.55	5.75	2.64	1.771	0.314	0.033	0.104
PC3802-34	342.0	23.94	6.22	3.49	1.58	5.84	2.75	1.720	0.303	0.028	0.109
PC3802-35	352.0	21.62	5.38	2.71	1.33	9.24	2.59	1.492	0.249	0.027	0.096
PC3802-36	362.0	19.26	5.24	2.67	1.29	11.60	2.41	1.384	0.241	0.028	0.085
PC3802-37	372.0	18.43	5.27	2.65	1.28	12.71	2.34	1.374	0.246	0.026	0.079
PC3802-38	381.0	18.01	5.08	2.62	1.27	13.38	2.18	1.406	0.251	0.025	0.079
PC3802-39	391.0	17.91	4.94	2.53	1.24	13.50	2.14	1.342	0.248	0.023	0.080
PC3802-40	400.0	17.43	4.76	2.42	1.21	14.52	2.21	1.311	0.239	0.025	0.083
PC3802-41	410.0	17.57	4.88	2.40	1.18	14.25	2.26	1.344	0.240	0.026	0.083
PC3802-42	420.0	18.15	4.87	2.44	1.18	13.69	2.30	1.355	0.238	0.024	0.080
PC3802-43	430.0	16.99	4.80	2.40	1.19	14.55	2.14	1.265	0.239	0.026	0.080
PC3802-44	440.0	17.98	4.99	2.46	1.23	13.69	2.21	1.392	0.254	0.024	0.084
PC3802-45	450.0	19.30	5.46	2.79	1.35	11.53	2.34	1.434	0.270	0.027	0.085
PC3802-46	460.0	19.95	5.81	2.88	1.40	10.34	2.54	1.629	0.288	0.029	0.088
PC3802-47	470.0	17.05	4.97	2.53	1.22	14.73	2.13	1.232	0.243	0.024	0.088
PC3802-48	481.0	16.59	4.70	2.44	1.17	15.19	1.90	0.932	0.243	0.025	0.086
PC3802-49	491.0	17.11	4.78	2.46	1.18	14.91	2.09	1.328	0.240	0.021	0.087
PC3802-50	501.0	18.07	5.06	2.72	1.24	13.95	2.26	1.396	0.246	0.029	0.094
PC3802-51	511.0	19.18	5.28	2.58	1.24	12.41	2.25	1.434	0.263	0.027	0.090
PC3802-52	521.0	20.96	5.83	2.88	1.30	10.04	2.51	1.727	0.266	0.029	0.093
PC3802-53	531.0	25.00	6.53	2.48	1.11	8.02	2.82	2.248	0.251	0.029	0.085
PC3802-54	540.0	23.41	6.80	3.42	1.60	5.95	2.64	1.938	0.338	0.034	0.109
PC3802-55	550.0	23.45	6.74	3.58	1.62	5.51	2.62	1.872	0.338	0.033	0.110
PC3802-56	560.0	23.26	6.40	3.98	1.60	4.33	2.63	1.829	0.333	0.032	0.110
PC3802-57	572.0	22.46	6.05	3.38	1.58	7.48	2.92	1.704	0.291	0.029	0.108
PC3802-58	582.0	21.90	6.28	3.31	1.50	7.92	2.57	1.753	0.294	0.031	0.100
PC3802-59	591.0	21.31	6.34	3.35	1.51	8.57	2.47	1.720	0.294	0.030	0.096
PC3802-60	601.0	16.48	4.75	2.60	1.19	15.46	2.00	1.196	0.237	0.023	0.093
PC3802-61	611.0	16.47	4.64	2.50	1.21	16.15	2.12	1.310	0.227	0.026	0.091
PC3802-62	621.0	17.99	5.12	2.74	1.30	13.80	2.14	1.424	0.264	0.028	0.091
PC3802-63	631.0	18.41	5.41	2.79	1.33	13.11	2.14	1.453	0.273	0.029	0.091
PC3802-64	641.0	20.58	6.05	3.05	1.45	11.13	2.26	1.631	0.292	0.030	0.098
PC3802-65	651.0	22.17	6.40	3.14	1.53	7.83	2.45	1.836	0.303	0.029	0.098
PC3802-66	662.0	21.95	5.87	3.12	1.47	8.36	2.66	1.698	0.284	0.029	0.108
PC3802-67	671.0	17.57	4.52	2.25	1.16	14.03	2.29	1.273	0.209	0.024	0.090
PC3802-68	681.0	18.03	5.15	2.49	1.24	13.24	2.21	1.466	0.242	0.026	0.082
PC3802-69	691.0	19.01	5.67	2.65	1.29	11.69	2.31	1.573	0.267	0.028	0.076
PC3802-70	701.0	18.63	5.44	2.49	1.26	12.39	2.17	1.514	0.260	0.026	0.074
PC3802-71	711.0	19.54	5.49	2.74	1.41	12.64	2.35	1.503	0.256	0.026	0.076
PC3802-72	721.0	19.33	5.27	2.53	1.29	11.85	2.28	1.514	0.257	0.026	0.078
PC3802-73	731.0	19.23	5.35	2.52	1.28	11.89	2.23	1.528	0.261	0.029	0.080
PC3802-74	741.0	19.39	5.38	2.56	1.31	11.28	2.26	1.505	0.270	0.029	0.084
PC38-11	3835m										
PC3811-01	3.0	25.82	6.77	2.32	1.27	1.85	2.68	1.66	0.36	0.03	0.30
PC3811-02	13.0	23.34	5.74	2.44	1.06	5.76	2.49	1.29	0.32	0.03	0.36
PC3811-03	23.0	25.78	5.87	2.37	0.98	5.00	2.38	1.39	0.35	0.03	0.35
PC3811-04	33.0	26.71	6.99	2.53	1.48	1.46	2.80	1.82	0.35	0.03	0.19
PC3811-05	43.0	25.84	6.87	2.32	1.45	2.27	2.84	1.78	0.34	0.03	0.16
PC3811-06	53.0	24.50	6.72	2.74	1.34	2.83	2.66	1.74	0.33	0.03	0.13
PC3811-07	63.0	24.81	6.89	2.65	1.37	2.99	2.74	1.79	0.33	0.03	0.12
PC3811-08	73.0	24.33	6.79	2.73	1.35	3.49	2.61	1.75	0.33	0.03	0.13
PC3811-09	85.0	27.78	6.97	2.62	1.15	5.14	2.67	1.77	0.31	0.04	0.26
PC3811-10	95.0	24.13	6.42	2.68	1.40	4.49	2.61	1.71	0.32	0.03	0.13
PC3811-11	105.0	23.45	6.17	2.72	1.36	4.93	2.57	1.61	0.31	0.03	0.13
PC3811-12	116.0	24.40	6.32	2.82	1.37	3.97	2.59	1.64	0.31	0.03	0.13
PC3811-13	125.0	24.26	6.50	2.76	1.42	4.07	2.63	1.75	0.32	0.03	0.13
PC3811-14	135.0	24.12	6.47	2.73	1.37	4.56	2.58	1.65	0.33	0.03	0.15
PC3811-15	145.0	25.42	6.86	2.72	1.53	4.03	2.83	1.75	0.33	0.03	0.14
PC3811-16	155.0	23.67	6.26	2.63	1.30	5.26	2.49	1.58	0.32	0.03	0.16
PC3811-17	165.0	25.62	6.99	2.84	1.56	4.49	2.92	1.78	0.32	0.03	0.14
PC3811-18	175.0	24.96	6.47	2.70	1.25	5.31	2.53	1.71	0.32	0.03	0.22
PC3811-19	186.0	24.30	6.54	2.46	1.36	3.46	2.60	1.76	0.32	0.03	0.14
PC3811-20	197.0	24.22	6.69	2.84	1.42	3.16	2.60	1.73	0.33	0.03	0.14
PC3811-21	204.0	24.64	6.78	2.79	1.40	2.41	2.70	1.83	0.32	0.03	0.13
PC3811-22	215.0	22.79	6.05	2.74	1.28	5.52	2.62	1.58	0.30	0.03	0.18

APPENDIX C.7. SALT-CORRECTED MAJOR ELEMENTS										
BC38-02	2530m									
Sample	Depth	Al	Si	Fe	Ca	Na	K	P	Mn	Ti
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
BC3802-01	0.5	6.49	25.85	4.02	6.73	0.72	1.707	0.147	0.043	0.297
BC3802-02	1.5	6.58	26.12	4.05	6.45	0.49	1.741	0.140	0.042	0.299
BC3802-03	2.5	6.38	25.45	3.94	6.61	0.94	1.710	0.134	0.040	0.293
BC3802-04	3.5	6.35	25.23	3.92	6.78	0.83	1.656	0.136	0.030	0.289
BC3802-05	4.5	6.35	25.33	3.91	7.05	0.79	1.747	0.135	0.028	0.291
BC3802-06	5.5	6.24	24.86	3.78	7.05	1.09	1.740	0.139	0.029	0.283
BC3802-07	6.5	6.43	24.58	3.81	7.17	1.42	1.743	0.127	0.027	0.286
BC3802-08	7.5	6.21	24.52	3.82	7.01	1.39	1.716	0.130	0.026	0.281
BC3802-09	8.5	6.33	24.38	3.79	7.18	1.39	1.778	0.135	0.031	0.291
BC3802-10	9.5	6.29	24.18	3.71	7.42	1.25	1.730	0.127	0.029	0.292
BC3802-11	11.0	6.61	25.17	3.80	8.39	1.21	1.788	0.130	0.031	0.294
BC3802-12	13.0	5.86	23.03	3.64	9.22	0.93	1.647	0.124	0.026	0.277
BC3802-13	15.0	5.79	22.51	3.31	9.60	1.48	1.642	0.124	0.028	0.267
BC3802-13A	17.0	5.51	20.84	2.91	11.80	1.29	1.507	0.116	0.025	0.248
BC3802-14	19.0	5.06	20.15	2.72	12.96	1.21	1.417	0.116	0.024	0.235
BC3802-15	21.0	4.99	19.82	2.66	13.95	0.89	1.420	0.115	0.026	0.234
BC3802-16	23.0	4.84	19.29	2.62	14.21	1.18	1.338	0.114	0.021	0.228
BC3802-17	25.0	4.84	19.10	2.59	14.73	0.80	1.366	0.115	0.022	0.226
BC3802-18	27.0	4.75	18.46	2.54	14.94	1.10	1.299	0.111	0.024	0.221
BC3802-19	29.0	4.69	18.29	2.49	15.77	0.72	1.304	0.112	0.021	0.220
BC3802-20	31.0	4.65	18.00	2.44	15.34	1.10	1.235	0.111	0.023	0.218
BC3802-21	33.0	4.83	18.25	2.49	15.15	0.76	1.409	0.108	0.025	0.225
BC3802-21A	35.0	5.04	18.33	2.53	13.87	1.08	1.402	0.092	0.019	0.237
BC3802-22	37.0	4.96	18.41	2.54	14.44	0.75	1.347	0.098	0.017	0.231
BC3802-23	39.0	4.78	18.07	2.48	14.85	1.16	1.344	0.107	0.022	0.223
BC3802-24	41.0	5.05	18.30	2.58	14.40	0.96	1.394	0.093	0.024	0.235
BC3802-25	43.0	5.13	18.43	2.64	14.09	1.13	1.494	0.093	0.020	0.240
BC3802-26	45.0	5.04	18.15	2.62	13.92	0.86	1.474	0.093	0.024	0.243
BC3802-27	47.0	5.17	18.40	2.58	13.89	1.15	1.487	0.095	0.019	0.243
BC3802-28	49.0	5.19	18.58	2.61	13.92	1.00	1.496	0.095	0.022	0.247
BC3802-29	51.0	5.19	18.58	2.60	13.75	1.10	1.468	0.095	0.023	0.247
BC3802-30	53.0	5.24	18.59	2.58	13.61	1.06	1.450	0.101	0.025	0.247
BC38-03	4289m									
BC3803-01	0.5	7.18	31.80	4.37	1.03	0.04	1.792	0.130	0.090	0.331
BC3803-02	1.5	6.96	30.93	4.42	1.00	0.49	1.781	0.127	0.071	0.325
BC3803-03	2.5	6.97	30.94	4.46	1.00	0.34	1.794	0.126	0.050	0.326
BC3803-04	3.5	6.80	30.18	4.04	1.00	1.14	1.742	0.112	0.029	0.317
BC3803-05	4.5	7.20	31.20	3.64	1.02	1.10	1.870	0.102	0.025	0.330
BC3803-06	5.5	7.04	30.48	2.98	1.01	1.04	1.853	0.099	0.028	0.328
BC3803-07	6.5	6.97	30.17	2.94	1.01	1.38	1.863	0.096	0.026	0.328
BC3803-08	7.5	7.09	30.29	3.08	1.02	1.41	1.876	0.094	0.023	0.331
BC3803-09	8.5	7.12	30.45	3.18	1.04	1.18	1.894	0.095	0.025	0.333
BC3803-10	9.5	7.55	31.45	3.35	1.07	1.48	1.922	0.097	0.031	0.343
BC3803-11	11.0	7.33	30.41	3.26	1.06	1.56	1.919	0.098	0.029	0.342
BC3803-12	13.0	7.39	30.51	3.03	1.09	1.11	1.945	0.097	0.029	0.352
BC3803-13	15.0	7.20	29.89	3.31	1.09	1.62	1.944	0.099	0.032	0.343
BC3803-14	17.0	7.36	30.67	3.14	1.13	1.15	1.968	0.103	0.029	0.356
BC3803-15	19.0	7.33	30.22	3.04	1.16	1.57	1.944	0.106	0.032	0.351
BC3803-16	21.0	7.00	30.47	2.85	1.11	1.33	1.865	0.101	0.024	0.337
BC3803-17	23.0	7.03	30.40	3.16	1.11	1.53	1.881	0.103	0.027	0.335
BC3803-18	25.0	7.10	30.30	2.92	1.15	1.24	1.896	0.106	0.030	0.344
BC3803-19	27.0	6.91	29.85	3.01	1.16	1.69	1.857	0.105	0.029	0.337
BC3803-20	29.0	7.20	30.46	3.14	1.20	1.29	1.934	0.109	0.034	0.349
BC3803-21	31.0	7.04	29.97	3.25	1.20	1.84	1.950	0.106	0.036	0.342
BC3803-22	33.0	7.09	30.18	3.04	1.22	1.55	1.915	0.109	0.030	0.343
BC3803-23	35.0	6.99	29.96	2.97	1.23	1.67	1.919	0.107	0.030	0.340
BC3803-24	37.0	7.28	30.82	3.27	1.31	1.64	1.970	0.111	0.033	0.347
BC3803-25	39.0	7.33	31.42	3.31	1.37	1.62	1.994	0.149	0.036	0.347
BC3803-26	41.0	7.03	30.31	3.22	1.30	1.29	1.962	0.107	0.033	0.345
BC3803-27	43.0	7.09	30.21	3.33	1.33	1.73	1.972	0.108	0.032	0.344
BC3803-28	45.0	6.98	30.12	3.14	1.31	1.44	1.949	0.108	0.028	0.340
BC3803-29	47.0	6.95	30.01	3.30	1.31	1.61	1.971	0.108	0.033	0.340
BC3803-30	49.0	7.04	30.31	3.29	1.33	1.31	1.977	0.110	0.031	0.342
BC3803-31	51.0	7.22	30.51	3.52	1.36	1.53	2.031	0.116	0.031	0.351
BC3803-32	53.0	7.09	29.79	3.29	1.38	1.64	1.984	0.112	0.032	0.347

APPENDIX C.7. SALT-CORRECTED MAJOR ELEMENTS										
PC38-09	148m									
Sample	Depth	Al	Si	Fe	Ca	Na	K	P	Mn	Ti
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
PC3809-01	4.0	5.88	27.14	2.60	2.10	1.37	1.299	0.240	0.023	0.322
PC3809-02	13.0	5.91	27.83	2.32	2.40	0.98	1.225	0.176	0.024	0.301
PC3809-03	23.0	7.54	26.93	2.74	1.82	1.55	1.512	0.201	0.031	0.349
PC3809-04	34.0	6.94	27.32	2.54	1.51	1.63	1.439	0.199	0.027	0.345
PC3809-05	43.0	6.99	29.26	2.59	1.95	1.58	1.557	0.250	0.036	0.391
PC3809-06	53.0	6.44	27.28	2.69	1.50	1.33	1.385	0.272	0.030	0.338
PC3809-07	62.0	5.90	25.61	2.34	2.29	1.53	1.162	0.231	0.020	0.286
PC3809-08	73.0	7.06	28.84	2.62	1.49	0.78	1.486	0.208	0.034	0.378
PC3809-09	84.0	8.08	26.10	3.12	1.12	1.28	1.699	0.165	0.031	0.412
PC3809-10	94.0	7.52	25.64	3.37	1.41	1.22	1.596	0.174	0.032	0.366
PC3809-11	104.0	6.76	26.77	2.52	1.14	1.17	1.423	0.158	0.024	0.328
PC3809-12	113.0	8.29	27.25	3.24	1.24	1.51	1.787	0.161	0.035	0.429
PC3809-13	124.0	7.33	27.04	2.60	2.04	1.29	1.566	0.239	0.032	0.405
PC3809-14	134.0	6.42	27.62	2.48	2.00	1.51	1.350	0.296	0.026	0.330
PC3809-15	144.0	5.71	28.32	2.29	1.70	1.29	1.234	0.203	0.022	0.297
PC3809-16	152.0	5.67	29.65	2.40	1.71	1.20	1.252	0.147	0.021	0.295
PC3809-17	165.0	5.50	29.57	2.25	2.42	1.28	1.188	0.241	0.024	0.297
PC3809-18	174.0	6.69	30.16	2.35	1.90	1.48	1.495	0.267	0.030	0.362
PC3809-19	185.0	5.96	31.31	2.11	2.47	1.60	1.341	0.427	0.029	0.329
PC3809-20	194.0	6.11	30.38	2.09	3.02	1.66	1.365	0.409	0.035	0.346
PC3809-21	205.0	6.78	29.56	3.12	2.77	1.80	1.530	0.155	0.049	0.383
PC3809-22	214.0	5.65	29.34	1.97	2.36	1.45	1.259	0.398	0.024	0.308
PC3809-23	224.0	5.98	33.00	1.75	2.95	1.80	1.393	0.494	0.028	0.316
PC3809-24	234.0	5.37	32.00	2.02	2.90	1.57	1.202	0.592	0.023	0.290
PC3809-25	243.0	4.35	32.27	1.93	1.69	1.34	0.983	0.347	0.023	0.225
PC3809-26	257.0	5.11	31.35	2.20	1.74	1.32	1.165	0.301	0.023	0.276
PC3809-27	267.0	5.09	31.30	1.85	3.88	1.52	1.211	1.036	0.027	0.273
PC3809-28	273.0	2.58	14.24	2.93	18.46	1.07	0.665	5.797	0.018	0.140
PC3809-29	284.0	6.02	28.57	2.87	2.04	1.43	1.309	0.314	0.035	0.338
PC3809-30	294.0	4.83	29.84	2.23	1.92	1.55	1.084	0.165	0.021	0.249
PC3809-31	304.0	6.19	29.12	2.92	1.39	1.48	1.334	0.168	0.037	0.346
PC3809-32	314.0	6.07	26.34	2.74	1.58	1.30	1.291	0.140	0.029	0.299
PC3809-33	324.0	6.30	27.87	3.17	1.63	1.37	1.349	0.222	0.033	0.346
PC3809-34	335.0	5.43	28.84	2.66	1.44	1.30	1.160	0.160	0.030	0.285
PC3809-35	344.0	4.96	29.36	2.69	1.36	1.31	1.061	0.160	0.023	0.278
PC3809-36	355.0	4.20	30.29	1.94	2.02	1.56	0.923	0.105	0.022	0.204
PC3809-37	364.0	4.11	29.56	2.05	3.23	1.17	0.893	0.102	0.020	0.198
PC3809-38	375.0	5.57	28.62	2.57	1.63	1.49	1.245	0.112	0.028	0.269
PC3809-39	384.0	5.87	28.02	2.96	2.67	1.39	1.257	0.211	0.035	0.321
PC3809-40	394.0	5.06	29.63	2.29	1.90	1.35	1.126	0.159	0.027	0.258
PC3809-41	404.0	5.62	30.26	2.55	1.19	1.41	1.270	0.122	0.031	0.287
PC3809-42	416.0	4.79	28.20	2.23	3.31	1.30	1.036	0.145	0.019	0.240
PC3809-43	424.0	5.24	30.06	2.29	1.19	1.37	1.197	0.101	0.027	0.257
PC3809-44	434.0	5.94	28.44	2.74	1.23	1.48	1.361	0.127	0.029	0.287
PC3809-45	444.0	4.90	30.13	2.45	2.48	1.37	1.084	0.140	0.027	0.246
PC3809-46	453.0	5.97	29.08	2.79	1.65	1.38	1.293	0.167	0.029	0.327
PC3809-47	465.0	5.63	28.48	2.79	2.00	1.22	1.234	0.163	0.031	0.292
PC3809-48	474.0	5.29	28.00	2.36	2.82	1.31	1.215	0.145	0.022	0.248
PC3809-49	483.0	5.78	30.05	2.78	1.45	1.45	1.320	0.176	0.029	0.313
PC3809-50	493.0	5.75	29.02	2.78	1.63	1.40	1.365	0.155	0.038	0.289
PC3809-51	504.0	6.04	29.84	2.87	1.65	1.43	1.400	0.182	0.033	0.334
PC3809-52	515.0	6.04	29.37	2.83	1.46	1.60	1.438	0.145	0.032	0.320
PC3809-53	525.0	5.65	28.27	2.56	2.24	1.49	1.319	0.118	0.030	0.271
PC3809-54	536.0	5.15	29.50	2.39	2.99	1.44	1.187	0.115	0.030	0.252
PC3809-55	544.0	6.10	28.92	3.00	2.12	1.47	1.404	0.155	0.034	0.329
PC3809-56	553.0	5.73	28.95	2.92	2.71	1.39	1.283	0.100	0.037	0.288
PC3809-57	564.0	5.30	29.92	2.70	2.62	1.37	1.155	0.104	0.034	0.278
PC3809-58	574.0	5.28	29.28	2.74	2.85	1.46	1.245	0.120	0.035	0.274
PC3809-59	585.0	5.09	29.48	2.59	3.72	1.32	1.162	0.319	0.033	0.268
PC3809-60	594.0	5.10	30.40	2.52	2.78	1.42	1.204	0.132	0.033	0.268
PC3809-61	605.0	5.72	28.62	2.96	3.20	1.33	1.326	0.188	0.038	0.304
PC3809-62	615.0	5.06	30.27	2.45	3.03	1.34	1.226	0.224	0.035	0.264
PC3809-63	625.0	5.61	29.56	2.82	2.92	1.46	1.299	0.205	0.039	0.299
PC3809-64	635.0	5.72	28.91	2.91	3.18	1.38	1.313	0.203	0.040	0.308
PC3809-65	646.0	5.03	30.67	2.40	2.58	1.33	1.129	0.139	0.031	0.259
PC3809-66	654.0	4.80	31.32	2.30	2.33	1.26	1.076	0.109	0.033	0.257
PC3809-67	664.0	4.83	31.49	2.30	2.51	1.33	1.100	0.094	0.027	0.246

APPENDIX C.7. SALT-CORRECTED MAJOR ELEMENTS										
PC38-09	148m									
Sample	Depth	Al	Si	Fe	Ca	Na	K	P	Mn	Tl
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
PC3809-68	674.0	4.21	30.53	2.22	2.12	1.08	1.010	0.084	0.027	0.230
PC3809-69	684.0	5.64	29.97	2.79	2.61	1.42	1.354	0.118	0.031	0.289
PC3809-70	694.0	6.04	29.55	2.97	2.68	1.41	1.351	0.119	0.041	0.311
PC3809-71	703.0	5.98	28.89	3.06	2.52	1.44	1.420	0.098	0.039	0.300
PC3809-72	714.0	5.45	29.33	2.75	2.88	1.48	1.283	0.138	0.032	0.285
PC3809-73	724.0	5.95	29.45	3.08	2.95	1.47	1.397	0.194	0.040	0.317
PC3809-74	734.0	6.00	28.30	3.04	3.24	1.40	1.404	0.198	0.038	0.319
PC3809-75	744.0	5.85	30.87	3.05	2.94	1.51	1.404	0.162	0.041	0.295
PC3809-76	754.0	5.38	29.89	2.75	2.78	1.34	1.273	0.104	0.036	0.278
PC3809-77	764.0	6.01	28.45	2.96	3.31	1.32	1.512	0.133	0.042	0.310
PC3809-78	774.0	6.12	28.64	3.12	3.10	1.36	1.463	0.138	0.042	0.332
PC3809-79	784.0	5.87	29.26	3.05	3.02	1.29	1.448	0.130	0.037	0.313
PC3809-80	794.0	5.89	29.39	2.87	3.05	1.32	1.474	0.150	0.036	0.314
PC3809-81	804.0	5.64	30.02	2.76	2.70	1.35	1.357	0.187	0.035	0.307
PC3809-82	813.0	5.82	29.38	3.14	3.45	1.43	1.331	0.304	0.039	0.320
PC3809-83	823.0	5.69	29.91	2.93	2.76	1.38	1.370	0.203	0.040	0.310
PC3809-84	834.0	5.90	29.38	2.87	2.70	1.35	1.399	0.165	0.037	0.320
PC3809-85	845.0	5.97	30.74	2.86	2.72	1.47	1.457	0.195	0.038	0.308
PC3809-86	854.0	6.71	29.34	3.30	2.38	1.50	1.669	0.101	0.049	0.344
PC38-10	257m									
PC3810-01	6.0	5.23	21.63	2.00	6.30	1.30	1.167	0.469	0.018	0.260
PC3810-02	14.0	5.47	25.89	1.87	5.49	1.57	1.264	1.062	0.026	0.297
PC3810-03	24.0	5.53	28.52	1.58	6.78	1.80	1.347	1.959	0.027	0.279
PC3810-04	34.0	5.53	28.61	1.48	6.49	1.69	1.311	1.027	0.021	0.278
PC3810-05	44.0	5.85	27.76	2.11	2.23	1.56	1.474	0.435	0.031	0.315
PC3810-06	54.0	5.97	28.62	2.13	1.79	1.58	1.462	0.294	0.021	0.302
PC3810-07	64.0	6.12	29.46	2.40	2.31	1.64	1.550	0.462	0.025	0.320
PC3810-08	74.0	6.32	29.83	2.27	3.07	1.72	1.601	0.705	0.030	0.327
PC3810-09	84.0	5.41	31.84	1.75	4.29	1.65	1.469	1.086	0.027	0.267
PC3810-10	94.0	5.74	30.44	1.80	5.74	1.78	1.424	1.505	0.027	0.265
PC3810-11	104.0	5.43	29.49	1.50	6.94	1.72	1.380	0.867	0.025	0.256
PC3810-11	113.0	5.58	30.38	1.47	6.23	1.73	1.352	0.579	0.027	0.253
PC3810-12	126.0	4.80	27.82	1.94	6.19	1.21	1.160	0.524	0.020	0.245
PC3810-13	134.0	4.73	27.99	2.00	4.22	1.14	1.142	0.559	0.020	0.243
PC3810-14	146.0	5.48	28.31	2.23	3.93	1.40	1.342	0.428	0.023	0.288
PC3810-15	154.0	5.07	25.91	2.11	6.53	1.16	1.213	0.433	0.025	0.262
PC3810-16	167.0	5.38	28.52	2.17	3.51	1.20	1.325	0.318	0.020	0.285
PC3810-17	174.0	5.72	29.69	2.11	2.05	1.34	1.417	0.364	0.024	0.291
PC3810-18	185.0	5.70	30.25	2.24	1.48	1.19	1.444	0.299	0.027	0.298
PC3810-19	194.0	4.84	27.72	2.06	4.27	1.05	1.203	0.273	0.021	0.239
PC3810-20	203.0	5.95	29.32	2.22	2.31	1.35	1.468	0.381	0.025	0.313
PC3810-21	216.0	4.57	27.38	1.92	4.45	1.15	1.119	0.341	0.018	0.235
PC3810-22	224.0	4.84	28.24	2.06	2.98	1.06	1.150	0.272	0.018	0.245
PC3810-23	233.0	5.54	27.65	2.26	2.63	1.23	1.372	0.300	0.026	0.288
PC3810-24	244.0	5.61	26.86	2.29	4.49	1.26	1.349	0.374	0.023	0.292
PC3810-25	254.0	5.25	28.19	1.80	5.08	1.43	1.292	0.698	0.022	0.263
PC3810-26	263.0	4.93	27.05	1.81	5.48	1.34	1.188	0.571	0.019	0.249
PC3810-27	273.0	5.55	25.93	2.30	4.67	1.22	1.361	0.322	0.026	0.288
PC3810-28	284.0	5.27	26.02	2.06	5.97	1.11	1.263	0.367	0.024	0.282
PC3810-29	295.0	4.04	22.39	1.77	9.31	0.82	0.963	0.308	0.017	0.200
PC3810-30	305.0	5.46	25.25	2.36	6.03	1.05	1.257	0.277	0.026	0.290
PC3810-31	314.0	5.72	25.65	2.16	6.05	1.18	1.331	0.325	0.022	0.306
PC3810-32	324.0	4.44	24.53	1.93	6.65	0.94	1.039	0.298	0.022	0.221
PC3810-33	335.0	5.45	25.29	2.16	5.25	1.18	1.317	0.309	0.024	0.282
PC3810-34	344.0	3.84	25.10	1.71	7.28	0.92	0.881	0.318	0.016	0.190
PC3810-35	354.0	3.56	28.68	1.45	4.31	0.97	0.837	0.240	0.008	0.176
PC3810-36	364.0	3.13	28.50	1.32	5.49	0.91	0.741	0.262	0.011	0.154
PC3810-37	374.0	3.28	29.44	1.26	4.16	0.82	0.744	0.220	0.008	0.160
PC3810-38	383.0	5.85	25.60	2.28	4.79	1.04	1.318	0.240	0.025	0.298
PC3810-39	394.0	4.75	26.22	1.74	4.27	1.01	1.088	0.297	0.017	0.244
PC3810-40	404.0	5.49	26.21	1.95	4.98	1.09	1.259	0.288	0.024	0.297
PC3810-41	417.0	4.67	23.52	1.81	7.62	0.91	1.039	0.347	0.016	0.245
PC3810-42	424.0	4.89	24.99	1.82	5.81	1.03	1.134	0.314	0.025	0.249
PC3810-43	434.0	2.31	23.05	0.95	11.66	0.66	0.536	0.380	0.008	0.117
PC3810-44	445.0	3.87	23.83	1.51	8.55	0.83	0.892	0.267	0.011	0.190

APPENDIX C.7. SALT-CORRECTED MAJOR ELEMENTS										
PC38-10	257m									
Sample	Depth	Al	Si	Fe	Ca	Na	K	P	Mn	Ti
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
PC3810-45	456.0	3.54	24.57	1.40	7.64	0.80	0.791	0.276	0.012	0.176
PC3810-46	467.0	2.44	26.27	1.00	7.88	0.72	0.573	0.215	0.003	0.120
PC3810-47	476.0	4.73	21.86	1.80	8.50	0.99	1.088	0.495	0.020	0.248
PC3810-48	484.0	4.46	21.36	1.74	9.12	0.89	1.018	0.464	0.015	0.231
PC3810-49	494.0	4.23	21.91	1.48	9.36	1.08	0.942	0.892	0.018	0.227
PC3810-50	504.0	5.23	27.19	1.60	7.88	1.68	1.266	2.404	0.020	0.265
PC3810-51	514.0	5.56	29.39	2.75	2.49	1.39	1.265	0.117	0.031	0.307
PC3810-52	524.0	6.04	30.65	2.87	2.17	1.51	1.378	0.108	0.038	0.333
PC3810-53	534.0	4.48	21.98	1.77	4.92	1.16	1.003	0.264	0.016	0.202
PC3810-54	545.0	4.51	24.92	1.74	3.79	1.27	1.071	0.204	0.017	0.208
PC3810-55	554.0	4.12	23.08	1.64	5.44	1.11	0.934	0.199	0.016	0.185
PC3810-56	564.0	3.53	24.39	1.53	7.75	1.01	0.808	0.299	0.019	0.168
PC3810-57	574.0	4.02	21.85	1.69	8.68	0.95	0.894	0.251	0.018	0.191
PC3810-58	584.0	3.96	23.65	1.68	7.48	1.09	0.954	0.192	0.021	0.188
PC3810-59	596.0	3.92	24.32	1.65	6.60	1.16	0.940	0.202	0.015	0.184
PC3810-60	604.0	3.99	23.06	1.72	8.05	1.19	0.970	0.205	0.019	0.186
PC3810-61	614.0	4.42	25.10	1.87	5.73	1.06	1.036	0.147	0.017	0.204
PC3810-62	624.0	4.77	23.99	1.97	6.69	1.02	1.178	0.204	0.022	0.231
PC3810-63	634.0	4.68	24.40	1.90	6.70	1.79	1.144	0.216	0.021	0.218
PC3810-64	645.0	4.59	25.49	2.00	5.16	1.13	1.075	0.146	0.027	0.211
PC3810-65	655.0	4.42	24.38	1.89	5.76	1.16	1.045	0.136	0.017	0.199
PC3810-66	667.0	4.86	24.94	2.05	5.50	1.19	1.196	0.176	0.021	0.220
PC3810-67	674.0	5.65	25.52	2.31	4.17	1.09	1.391	0.183	0.027	0.259
PC3810-68	683.0	5.19	25.46	2.10	4.88	1.09	1.299	0.139	0.022	0.228
PC3810-69	694.0	6.77	26.21	2.73	3.30	1.24	1.714	0.206	0.028	0.314
PC3810-70	704.0	7.50	26.93	2.64	1.83	1.22	1.970	0.193	0.035	0.364
PC3810-71	714.0	6.73	25.65	2.61	3.88	1.15	1.770	0.215	0.029	0.301
PC3810-72	724.0	5.95	25.96	2.33	4.64	0.99	1.498	0.193	0.031	0.259
PC3810-74	734.0	7.17	28.03	2.45	1.56	1.27	1.871	0.215	0.025	0.339
PC3810-75	745.0	7.92	28.11	2.87	1.57	1.47	2.058	0.202	0.037	0.382
PC3810-76	754.0	6.43	28.69	2.43	1.85	1.30	1.647	0.254	0.029	0.312
PC3810-77	764.0	7.07	29.30	2.41	2.62	1.55	1.811	0.539	0.033	0.375
PC38-02	2525m									
	(Age)									
PC3802-01	2.76	5.75	23.04	3.04	8.72	1.28	1.45	0.117	0.028	0.282
PC3802-02	6.21	5.14	20.94	2.66	11.75	1.15	1.33	0.113	0.028	0.247
PC3802-03	9.66	4.99	20.16	2.59	12.76	1.08	1.23	0.105	0.024	0.245
PC3802-04	12.77	5.46	20.04	2.71	10.78	1.12	1.42	0.096	0.025	0.256
PC3802-05	15.18	5.36	19.31	2.63	12.69	1.06	1.36	0.092	0.024	0.265
PC3802-06	17.47	5.23	19.35	2.77	12.31	1.12	1.37	0.091	0.026	0.255
PC3802-07	20.48	5.63	20.04	2.73	12.45	0.52	1.37	0.097	0.027	0.284
PC3802-08	22.65	5.50	19.67	2.79	12.06	0.93	1.40	0.095	0.023	0.275
PC3802-09	25.22	5.11	18.34	2.59	13.62	0.98	1.29	0.097	0.024	0.268
PC3802-10	28.29	4.76	17.39	2.41	14.79	1.01	1.20	0.095	0.024	0.253
PC3802-11	31.07	4.65	17.59	2.35	15.02	0.97	1.18	0.094	0.028	0.246
PC3802-12	33.86	4.30	16.85	2.34	15.84	0.94	1.13	0.089	0.022	0.231
PC3802-13	36.64	4.72	17.58	2.58	14.83	0.91	1.16	0.092	0.024	0.241
PC3802-14	39.15	5.45	19.35	2.60	12.33	1.13	1.39	0.097	0.028	0.272
PC3802-15	42.22	5.62	19.85	2.78	11.82	1.20	1.45	0.098	0.027	0.278
PC3802-16	45.00	6.12	20.89	2.98	10.87	1.02	1.59	0.103	0.030	0.308
PC3802-17	48.07	6.22	21.66	3.00	9.50	1.26	1.65	0.102	0.028	0.310
PC3802-18	50.85	5.89	23.23	3.32	8.28	1.28	1.62	0.103	0.032	0.307
PC3802-19	53.64	5.80	22.53	3.15	8.95	1.23	1.55	0.103	0.030	0.298
PC3802-20	56.42	6.16	23.32	3.15	7.79	1.30	1.64	0.103	0.029	0.320
PC3802-21	59.29	6.26	22.17	3.16	8.77	1.23	1.63	0.103	0.031	0.316
PC3802-22	62.61	6.18	22.05	3.13	9.30	1.29	1.62	0.103	0.030	0.311
PC3802-23	65.94	6.50	22.77	3.22	8.30	1.37	1.71	0.105	0.033	0.333
PC3802-24	69.26	7.24	25.99	3.58	4.32	1.60	1.98	0.111	0.034	0.372
PC3802-25	72.58	6.56	24.54	3.39	5.98	1.47	1.75	0.117	0.032	0.347
PC3802-26	76.96	5.87	22.74	3.10	8.64	1.37	1.57	0.119	0.029	0.310
PC3802-27	82.03	6.90	25.86	3.50	4.57	1.58	1.91	0.116	0.033	0.349
PC3802-28	87.11	6.94	25.42	3.48	5.09	1.49	1.94	0.113	0.029	0.342
PC3802-29	92.18	7.54	26.98	3.67	2.84	1.53	2.09	0.113	0.032	0.371
PC3802-30	97.26	7.29	26.76	3.69	3.71	1.47	2.00	0.131	0.034	0.372
PC3802-31	102.84	6.50	25.59	3.37	6.15	1.37	1.73	0.130	0.031	0.336
PC3802-32	107.92	6.62	25.01	3.45	5.99	1.39	1.80	0.124	0.033	0.336

APPENDIX C.7. SALT-CORRECTED MAJOR ELEMENTS										
PC38-02	2525m									
Sample	Age	Al	Si	Fe	Ca	Na	K	P	Mn	Ti
	(ka)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
PC3802-33	113.00	6.61	24.95	3.67	5.96	1.35	1.80	0.109	0.035	0.328
PC3802-34	118.07	6.53	25.12	3.67	6.06	1.37	1.75	0.114	0.029	0.318
PC3802-35	123.15	5.65	22.67	2.84	9.63	1.23	1.51	0.101	0.028	0.261
PC3802-36	128.22	5.48	20.16	2.79	12.08	1.10	1.40	0.089	0.029	0.252
PC3802-37	132.23	5.50	19.23	2.77	13.21	1.11	1.39	0.083	0.027	0.257
PC3802-38	135.30	5.28	18.72	2.72	13.86	1.05	1.42	0.082	0.026	0.261
PC3802-39	138.71	5.14	18.62	2.63	13.99	1.02	1.35	0.084	0.024	0.257
PC3802-40	141.79	4.95	18.13	2.51	15.06	1.07	1.32	0.087	0.026	0.249
PC3802-41	145.20	5.08	18.27	2.50	14.77	1.13	1.35	0.086	0.027	0.249
PC3802-42	148.61	5.07	18.89	2.54	14.19	1.15	1.37	0.083	0.025	0.248
PC3802-43	152.02	4.99	17.65	2.49	15.06	1.04	1.27	0.083	0.027	0.248
PC3802-44	155.44	5.18	18.66	2.55	14.16	1.14	1.40	0.087	0.025	0.263
PC3802-45	158.85	5.69	20.11	2.90	11.96	1.16	1.45	0.088	0.028	0.281
PC3802-46	162.26	6.05	20.78	3.00	10.72	1.37	1.65	0.092	0.031	0.300
PC3802-47	165.68	5.16	17.71	2.62	15.25	1.03	1.24	0.091	0.025	0.253
PC3802-48	169.43	4.88	17.24	2.53	15.74	0.78	0.93	0.090	0.026	0.252
PC3802-49	172.84	4.97	17.79	2.56	15.45	0.96	1.34	0.090	0.022	0.250
PC3802-50	176.26	5.27	18.81	2.84	14.47	1.09	1.41	0.098	0.031	0.257
PC3802-51	179.67	5.49	19.93	2.68	12.85	1.14	1.45	0.094	0.028	0.273
PC3802-52	183.08	6.06	21.81	2.99	10.40	1.38	1.75	0.096	0.030	0.276
PC3802-53	186.50	6.75	25.84	2.56	8.25	1.89	2.29	0.088	0.030	0.260
PC3802-54	189.57	7.09	24.42	3.56	6.15	1.44	1.97	0.113	0.036	0.352
PC3802-55	193.52	7.04	24.49	3.74	5.70	1.37	1.91	0.115	0.034	0.353
PC3802-56	197.42	6.71	24.39	4.18	4.48	1.28	1.86	0.115	0.033	0.349
PC3802-57	202.11	6.22	23.09	3.48	7.65	2.15	1.72	0.111	0.029	0.299
PC3802-58	206.02	6.46	22.52	3.41	8.11	1.77	1.77	0.103	0.032	0.302
PC3802-59	209.53	6.58	22.10	3.48	8.85	1.42	1.74	0.100	0.031	0.305
PC3802-60	213.44	4.92	17.05	2.69	15.96	1.01	1.20	0.096	0.024	0.246
PC3802-61	217.34	4.80	17.05	2.59	16.67	1.13	1.32	0.094	0.026	0.235
PC3802-62	221.25	5.31	18.63	2.84	14.25	1.13	1.44	0.094	0.029	0.274
PC3802-63	225.16	5.59	19.02	2.88	13.51	1.19	1.47	0.094	0.030	0.282
PC3802-64	229.06	6.26	21.31	3.15	11.48	1.25	1.65	0.102	0.031	0.302
PC3802-65	232.97	6.65	23.05	3.26	8.09	1.33	1.87	0.102	0.030	0.315
PC3802-66	237.27	6.11	22.87	3.25	8.66	1.50	1.72	0.112	0.031	0.295
PC3802-67	240.78	4.71	18.29	2.35	14.56	1.12	1.28	0.094	0.025	0.217
PC3802-68	244.50	5.34	18.73	2.59	13.71	1.12	1.48	0.085	0.027	0.252
PC3802-69	247.71	5.90	19.77	2.75	12.11	1.18	1.59	0.079	0.029	0.277
PC3802-70	250.91	5.65	19.35	2.58	12.81	1.08	1.53	0.077	0.027	0.270
PC3802-71	254.12	5.71	20.33	2.85	13.10	1.22	1.52	0.079	0.027	0.266
PC3802-72	257.32	5.48	20.11	2.63	12.28	1.14	1.53	0.081	0.027	0.268
PC3802-73	260.53	5.56	19.98	2.62	12.31	1.13	1.54	0.083	0.031	0.271
PC3802-74	263.73	5.59	20.16	2.66	11.68	1.12	1.52	0.088	0.030	0.281
PC38-11	3835m									
PC3811-01	0.80	7.12	27.18	2.44	1.88	1.21	1.69	0.313	0.029	0.376
PC3811-02	2.00	6.01	24.44	2.55	5.98	1.16	1.30	0.378	0.033	0.338
PC3811-03	2.20	6.09	26.76	2.46	5.14	1.31	1.40	0.363	0.036	0.368
PC3811-04	3.49	7.38	28.22	2.68	1.47	1.23	1.86	0.197	0.028	0.368
PC3811-05	6.17	7.27	27.36	2.45	2.33	1.21	1.82	0.169	0.030	0.359
PC3811-06	8.85	7.11	25.90	2.89	2.92	1.07	1.78	0.133	0.029	0.352
PC3811-07	11.53	7.27	26.20	2.79	3.09	1.18	1.83	0.129	0.034	0.350
PC3811-08	13.80	7.15	25.60	2.87	3.61	1.16	1.78	0.140	0.032	0.348
PC3811-09	16.44	7.14	28.48	2.68	5.23	1.97	1.79	0.271	0.038	0.318
PC3811-10	18.63	6.74	25.34	2.82	4.65	1.20	1.74	0.139	0.033	0.339
PC3811-11	20.82	6.49	24.65	2.86	5.12	1.12	1.63	0.135	0.032	0.329
PC3811-12	23.23	6.64	25.63	2.96	4.11	1.17	1.67	0.140	0.029	0.331
PC3811-13	25.11	6.83	25.51	2.90	4.22	1.19	1.78	0.134	0.031	0.339
PC3811-14	27.10	6.79	25.30	2.86	4.72	1.21	1.68	0.153	0.031	0.341
PC3811-15	29.09	7.22	26.76	2.87	4.18	1.37	1.79	0.152	0.033	0.348
PC3811-16	31.08	6.55	24.76	2.75	5.44	1.19	1.60	0.164	0.036	0.333
PC3811-17	33.07	7.38	27.02	3.00	4.67	1.40	1.82	0.152	0.034	0.341
PC3811-18	35.07	6.72	25.89	2.80	5.46	1.48	1.73	0.223	0.035	0.327
PC3811-19	37.26	6.88	25.56	2.58	3.58	1.15	1.80	0.151	0.036	0.337
PC3811-20	39.45	7.05	25.53	2.99	3.26	1.09	1.77	0.145	0.029	0.346
PC3811-21	40.84	7.15	25.99	2.95	2.47	1.16	1.87	0.139	0.029	0.342
PC3811-22	43.03	6.38	24.01	2.88	5.75	1.12	1.61	0.185	0.032	0.317

APPENDIX C.8. SALT-CORRECTED MAJOR ELEMENT/Al RATIOS									
BC38-02	2530m								
Sample	Depth	Si terr/Al	Fe/Al	Ca/Al	Na/Al	K/Al	P/Al	Mn/Al	Ti/Al
	(cm)								
BC3802-01	0.5	2.68	0.62	1.04	0.11	0.263	0.023	6.6E-03	0.0458
BC3802-02	1.5	2.69	0.62	0.98	0.07	0.265	0.021	6.4E-03	0.0454
BC3802-03	2.5	2.79	0.62	1.04	0.15	0.268	0.021	6.3E-03	0.0459
BC3802-04	3.5	2.69	0.62	1.07	0.13	0.261	0.021	4.7E-03	0.0455
BC3802-05	4.5	2.71	0.62	1.11	0.12	0.275	0.021	4.4E-03	0.0458
BC3802-06	5.5	2.75	0.61	1.13	0.17	0.279	0.022	4.6E-03	0.0454
BC3802-07	6.5	2.58	0.59	1.12	0.22	0.271	0.020	4.2E-03	0.0445
BC3802-08	7.5	2.52	0.62	1.13	0.22	0.276	0.021	4.7E-03	0.0452
BC3802-09	8.5	2.62	0.60	1.13	0.22	0.281	0.021	4.9E-03	0.0460
BC3802-10	9.5	2.52	0.59	1.18	0.20	0.275	0.020	4.6E-03	0.0464
BC3802-11	11.0	2.62	0.57	1.27	0.18	0.270	0.020	4.7E-03	0.0445
BC3802-12	13.0	2.59	0.62	1.57	0.16	0.281	0.021	4.4E-03	0.0473
BC3802-13	15.0	2.55	0.57	1.66	0.26	0.284	0.021	4.8E-03	0.0461
BC3802-13A	17.0	2.43	0.53	2.14	0.23	0.274	0.021	4.5E-03	0.0450
BC3802-14	19.0	2.49	0.54	2.56	0.24	0.280	0.023	4.7E-03	0.0464
BC3802-15	21.0	2.56	0.53	2.80	0.18	0.285	0.023	5.2E-03	0.0469
BC3802-16	23.0	2.79	0.54	2.94	0.24	0.276	0.024	4.3E-03	0.0471
BC3802-17	25.0	2.73	0.54	3.04	0.17	0.282	0.024	4.5E-03	0.0467
BC3802-18	27.0	2.73	0.53	3.15	0.23	0.273	0.023	5.1E-03	0.0465
BC3802-19	29.0	2.73	0.53	3.36	0.15	0.278	0.024	4.5E-03	0.0469
BC3802-20	31.0	2.80	0.52	3.30	0.24	0.266	0.024	4.9E-03	0.0469
BC3802-21	33.0	2.71	0.52	3.14	0.16	0.292	0.022	5.2E-03	0.0466
BC3802-21A	35.0	2.63	0.50	2.75	0.21	0.278	0.018	3.8E-03	0.0470
BC3802-22	37.0	2.70	0.51	2.91	0.15	0.272	0.020	3.4E-03	0.0466
BC3802-23	39.0	2.82	0.52	3.11	0.24	0.281	0.022	4.6E-03	0.0467
BC3802-24	41.0	2.65	0.51	2.85	0.19	0.276	0.018	4.8E-03	0.0465
BC3802-25	43.0	2.57	0.51	2.75	0.22	0.291	0.018	3.9E-03	0.0468
BC3802-26	45.0	2.57	0.52	2.76	0.17	0.292	0.018	4.8E-03	0.0482
BC3802-27	47.0	2.63	0.50	2.69	0.22	0.288	0.018	3.7E-03	0.0470
BC3802-28	49.0	2.69	0.50	2.68	0.19	0.288	0.018	4.2E-03	0.0476
BC3802-29	51.0	2.64	0.50	2.65	0.21	0.283	0.018	4.4E-03	0.0476
BC3802-30	53.0	2.65	0.49	2.60	0.20	0.277	0.019	4.8E-03	0.0471
BC38-03	4289m								
BC3803-01	0.5	1.94	0.61	0.14	0.01	0.250	0.018	1.3E-02	0.0461
BC3803-02	1.5	2.14	0.64	0.14	0.07	0.256	0.018	1.0E-02	0.0467
BC3803-03	2.5	2.06	0.64	0.14	0.05	0.257	0.018	7.2E-03	0.0468
BC3803-04	3.5	2.00	0.59	0.15	0.17	0.256	0.016	4.3E-03	0.0466
BC3803-05	4.5	1.97	0.51	0.14	0.15	0.260	0.014	3.5E-03	0.0458
BC3803-06	5.5	1.89	0.42	0.14	0.15	0.263	0.014	4.0E-03	0.0466
BC3803-07	6.5	1.96	0.42	0.14	0.20	0.267	0.014	3.7E-03	0.0471
BC3803-08	7.5	2.09	0.43	0.14	0.20	0.265	0.013	3.2E-03	0.0467
BC3803-09	8.5	2.06	0.45	0.15	0.17	0.266	0.013	3.5E-03	0.0468
BC3803-10	9.5	2.07	0.44	0.14	0.20	0.255	0.013	4.1E-03	0.0454
BC3803-11	11.0	2.14	0.44	0.14	0.21	0.262	0.013	4.0E-03	0.0467
BC3803-12	13.0	2.11	0.41	0.15	0.15	0.263	0.013	3.9E-03	0.0476
BC3803-13	15.0	2.12	0.46	0.15	0.23	0.270	0.014	4.4E-03	0.0476
BC3803-14	17.0	2.29	0.43	0.15	0.16	0.267	0.014	3.9E-03	0.0484
BC3803-15	19.0	2.25	0.41	0.16	0.21	0.265	0.014	4.4E-03	0.0479
BC3803-16	21.0	2.06	0.41	0.16	0.19	0.266	0.014	3.4E-03	0.0481
BC3803-17	23.0	1.93	0.45	0.16	0.22	0.268	0.015	3.8E-03	0.0477
BC3803-18	25.0	2.02	0.41	0.16	0.17	0.267	0.015	4.2E-03	0.0485
BC3803-19	27.0	2.04	0.44	0.17	0.24	0.269	0.015	4.2E-03	0.0488
BC3803-20	29.0	2.28	0.44	0.17	0.18	0.269	0.015	4.7E-03	0.0485
BC3803-21	31.0	2.33	0.46	0.17	0.26	0.277	0.015	5.1E-03	0.0486
BC3803-22	33.0	2.32	0.43	0.17	0.22	0.270	0.015	4.2E-03	0.0484
BC3803-23	35.0	2.25	0.42	0.18	0.24	0.275	0.015	4.3E-03	0.0486
BC3803-24	37.0	2.38	0.45	0.18	0.23	0.271	0.015	4.5E-03	0.0477
BC3803-25	39.0	2.31	0.45	0.19	0.22	0.272	0.020	4.9E-03	0.0473
BC3803-26	41.0	2.50	0.46	0.18	0.18	0.279	0.015	4.7E-03	0.0491
BC3803-27	43.0	2.46	0.47	0.19	0.24	0.278	0.015	4.5E-03	0.0485
BC3803-28	45.0	2.41	0.45	0.19	0.21	0.279	0.015	4.0E-03	0.0487
BC3803-29	47.0	2.41	0.47	0.19	0.23	0.284	0.016	4.7E-03	0.0489
BC3803-30	49.0	2.54	0.47	0.19	0.19	0.281	0.016	4.4E-03	0.0486
BC3803-31	51.0	2.52	0.49	0.19	0.21	0.281	0.016	4.3E-03	0.0486
BC3803-32	53.0	2.51	0.46	0.19	0.23	0.280	0.016	4.5E-03	0.0489

APPENDIX C.8. SALT-CORRECTED MAJOR ELEMENT/Al RATIOS									
PC38-09	148m								
Sample	Depth	Si terr/Al	Fe/Al	Ca/Al	Na/Al	K/Al	P/Al	Mn/Al	Ti/Al
	(cm)								
PC3809-01	4.0	3.28	0.44	0.36	0.233	0.221	0.041	3.9E-03	0.0548
PC3809-02	13.0	2.98	0.39	0.41	0.166	0.207	0.030	4.1E-03	0.0509
PC3809-03	23.0	2.70	0.36	0.24	0.206	0.201	0.027	4.1E-03	0.0463
PC3809-04	34.0	2.94	0.37	0.22	0.235	0.207	0.029	3.9E-03	0.0497
PC3809-05	43.0	3.71	0.37	0.28	0.226	0.223	0.036	5.2E-03	0.0559
PC3809-06	53.0	2.95	0.42	0.23	0.207	0.215	0.042	4.7E-03	0.0525
PC3809-07	62.0	2.89	0.40	0.39	0.259	0.197	0.039	3.4E-03	0.0485
PC3809-08	73.0	3.08	0.37	0.21	0.110	0.210	0.029	4.8E-03	0.0535
PC3809-09	84.0	2.61	0.39	0.14	0.158	0.210	0.020	3.8E-03	0.0510
PC3809-10	94.0	2.51	0.45	0.19	0.162	0.212	0.023	4.3E-03	0.0487
PC3809-11	104.0	2.69	0.37	0.17	0.173	0.211	0.023	3.6E-03	0.0485
PC3809-12	113.0	2.63	0.39	0.15	0.182	0.216	0.019	4.2E-03	0.0517
PC3809-13	124.0	3.17	0.35	0.28	0.176	0.214	0.033	4.4E-03	0.0553
PC3809-14	134.0	3.26	0.39	0.31	0.235	0.210	0.046	4.0E-03	0.0514
PC3809-15	144.0	3.29	0.40	0.30	0.226	0.216	0.036	3.9E-03	0.0520
PC3809-16	152.0	3.56	0.42	0.30	0.212	0.221	0.026	3.7E-03	0.0520
PC3809-17	165.0	3.68	0.41	0.44	0.233	0.216	0.044	4.4E-03	0.0540
PC3809-18	174.0	3.87	0.35	0.28	0.221	0.223	0.040	4.5E-03	0.0541
PC3809-19	185.0	4.58	0.35	0.41	0.268	0.225	0.072	4.9E-03	0.0552
PC3809-20	194.0	4.50	0.34	0.49	0.272	0.223	0.067	5.7E-03	0.0566
PC3809-21	205.0	3.78	0.46	0.41	0.265	0.226	0.023	7.2E-03	0.0565
PC3809-22	214.0	4.19	0.35	0.42	0.257	0.223	0.070	4.2E-03	0.0545
PC3809-23	224.0	5.28	0.29	0.49	0.301	0.233	0.083	4.7E-03	0.0528
PC3809-24	234.0	4.94	0.38	0.54	0.292	0.224	0.110	4.3E-03	0.0540
PC3809-25	243.0	4.65	0.44	0.39	0.308	0.226	0.080	5.3E-03	0.0517
PC3809-26	257.0	4.62	0.43	0.34	0.258	0.228	0.059	4.5E-03	0.0540
PC3809-27	267.0	5.24	0.36	0.76	0.299	0.238	0.204	5.3E-03	0.0536
PC3809-28	273.0	4.79	1.14	7.16	0.415	0.258	2.247	7.0E-03	0.0543
PC3809-29	284.0	3.69	0.48	0.34	0.238	0.217	0.052	5.8E-03	0.0561
PC3809-30	294.0	4.37	0.46	0.40	0.321	0.224	0.034	4.3E-03	0.0516
PC3809-31	304.0	3.46	0.47	0.22	0.239	0.216	0.027	6.0E-03	0.0559
PC3809-32	314.0	3.24	0.45	0.26	0.214	0.213	0.023	4.8E-03	0.0493
PC3809-33	324.0	3.41	0.50	0.26	0.217	0.214	0.035	5.2E-03	0.0549
PC3809-34	335.0	3.79	0.49	0.27	0.239	0.214	0.029	5.5E-03	0.0525
PC3809-35	344.0	3.94	0.54	0.27	0.264	0.214	0.032	4.6E-03	0.0560
PC3809-36	355.0	4.76	0.46	0.48	0.371	0.220	0.025	5.2E-03	0.0486
PC3809-37	364.0	4.38	0.50	0.79	0.285	0.217	0.025	4.9E-03	0.0482
PC3809-38	375.0	3.81	0.46	0.29	0.268	0.224	0.020	5.0E-03	0.0483
PC3809-39	384.0	3.44	0.50	0.45	0.237	0.214	0.036	6.0E-03	0.0547
PC3809-40	394.0	3.75	0.45	0.38	0.267	0.223	0.031	5.3E-03	0.0510
PC3809-41	404.0	3.66	0.45	0.21	0.251	0.226	0.022	5.5E-03	0.0511
PC3809-42	416.0	3.74	0.47	0.69	0.271	0.216	0.030	4.0E-03	0.0501
PC3809-43	424.0	3.62	0.44	0.23	0.261	0.228	0.019	5.2E-03	0.0490
PC3809-44	434.0	3.45	0.46	0.21	0.249	0.229	0.021	4.9E-03	0.0483
PC3809-45	444.0	3.86	0.50	0.51	0.280	0.221	0.029	5.5E-03	0.0502
PC3809-46	453.0	3.56	0.47	0.28	0.231	0.217	0.028	4.9E-03	0.0548
PC3809-47	465.0	3.48	0.50	0.36	0.217	0.219	0.029	5.5E-03	0.0519
PC3809-48	474.0	3.70	0.45	0.53	0.248	0.230	0.027	4.2E-03	0.0469
PC3809-49	483.0	3.74	0.48	0.25	0.251	0.228	0.030	5.0E-03	0.0542
PC3809-50	493.0	3.59	0.48	0.28	0.243	0.237	0.027	6.6E-03	0.0503
PC3809-51	504.0	4.05	0.48	0.27	0.237	0.232	0.030	5.5E-03	0.0553
PC3809-52	515.0	3.99	0.47	0.24	0.265	0.238	0.024	5.3E-03	0.0530
PC3809-53	525.0	3.86	0.45	0.40	0.264	0.233	0.021	5.3E-03	0.0480
PC3809-54	536.0	4.17	0.46	0.58	0.280	0.230	0.022	5.8E-03	0.0489
PC3809-55	544.0	3.82	0.49	0.35	0.241	0.230	0.025	5.6E-03	0.0539
PC3809-56	553.0	3.97	0.51	0.47	0.243	0.224	0.017	6.5E-03	0.0503
PC3809-57	564.0	4.06	0.51	0.49	0.258	0.218	0.020	6.4E-03	0.0525
PC3809-58	574.0	4.35	0.52	0.54	0.277	0.236	0.023	6.6E-03	0.0519
PC3809-59	585.0	4.31	0.51	0.73	0.259	0.228	0.063	6.5E-03	0.0527
PC3809-60	594.0	4.53	0.49	0.55	0.278	0.236	0.026	6.5E-03	0.0525
PC3809-61	605.0	3.95	0.52	0.56	0.233	0.232	0.033	6.6E-03	0.0531
PC3809-62	615.0	4.31	0.48	0.60	0.265	0.242	0.044	6.9E-03	0.0522
PC3809-63	625.0	4.14	0.50	0.52	0.260	0.232	0.037	7.0E-03	0.0533
PC3809-64	635.0	3.96	0.51	0.56	0.241	0.230	0.035	7.0E-03	0.0538
PC3809-65	646.0	4.34	0.48	0.51	0.264	0.224	0.028	6.2E-03	0.0515
PC3809-66	654.0	4.42	0.48	0.49	0.263	0.224	0.023	6.9E-03	0.0535
PC3809-67	664.0	4.49	0.48	0.52	0.275	0.228	0.019	5.6E-03	0.0509

APPENDIX C.8. SALT-CORRECTED MAJOR ELEMENT/Al RATIOS									
PC38-09	148m								
Sample	Depth	Si terr/Al	Fe/Al	Ca/Al	Na/Al	K/Al	P/Al	Mn/Al	Tl/Al
	(cm)								
PC3809-68	674.0	4.65	0.53	0.50	0.257	0.240	0.020	6.4E-03	0.0546
PC3809-69	684.0	4.04	0.49	0.46	0.252	0.240	0.021	5.5E-03	0.0512
PC3809-70	694.0	3.72	0.49	0.44	0.233	0.224	0.020	6.8E-03	0.0515
PC3809-71	703.0	3.69	0.51	0.42	0.241	0.237	0.016	6.5E-03	0.0502
PC3809-72	714.0	3.86	0.50	0.53	0.272	0.235	0.025	5.9E-03	0.0523
PC3809-73	724.0	3.89	0.52	0.50	0.247	0.235	0.033	6.7E-03	0.0533
PC3809-74	734.0	3.71	0.51	0.54	0.233	0.234	0.033	6.3E-03	0.0532
PC3809-75	744.0	4.05	0.52	0.50	0.258	0.240	0.028	7.0E-03	0.0504
PC3809-76	754.0	4.20	0.51	0.52	0.249	0.237	0.019	6.7E-03	0.0517
PC3809-77	764.0	3.74	0.49	0.55	0.220	0.252	0.022	7.0E-03	0.0516
PC3809-78	774.0	3.80	0.51	0.51	0.222	0.239	0.023	6.9E-03	0.0542
PC3809-79	784.0	3.98	0.52	0.51	0.220	0.247	0.022	6.3E-03	0.0533
PC3809-80	794.0	3.96	0.49	0.52	0.224	0.250	0.025	6.1E-03	0.0533
PC3809-81	804.0	4.30	0.49	0.48	0.239	0.241	0.033	6.2E-03	0.0544
PC3809-82	813.0	3.96	0.54	0.59	0.246	0.229	0.052	6.7E-03	0.0550
PC3809-83	823.0	4.25	0.51	0.49	0.243	0.241	0.036	7.0E-03	0.0545
PC3809-84	834.0	4.00	0.49	0.46	0.229	0.237	0.028	6.3E-03	0.0542
PC3809-85	845.0	4.00	0.48	0.46	0.246	0.244	0.033	6.4E-03	0.0516
PC3809-86	854.0	3.57	0.49	0.35	0.224	0.249	0.015	7.3E-03	0.0513
PC38-10	257m								
PC3810-01	6.0	3.30	0.38	1.20	0.249	0.223	0.090	3.4E-03	0.0497
PC3810-02	14.0	4.44	0.34	1.00	0.287	0.231	0.194	4.8E-03	0.0543
PC3810-03	24.0	5.06	0.29	1.23	0.325	0.244	0.354	4.9E-03	0.0505
PC3810-04	34.0	4.99	0.27	1.17	0.306	0.237	0.186	3.8E-03	0.0503
PC3810-05	44.0	4.30	0.36	0.38	0.267	0.252	0.074	5.3E-03	0.0538
PC3810-06	54.0	4.10	0.36	0.30	0.265	0.245	0.049	3.5E-03	0.0506
PC3810-07	64.0	4.14	0.39	0.38	0.268	0.253	0.075	4.1E-03	0.0523
PC3810-08	74.0	4.41	0.36	0.49	0.272	0.253	0.112	4.7E-03	0.0517
PC3810-09	84.0	5.79	0.32	0.79	0.305	0.272	0.201	5.0E-03	0.0494
PC3810-10	94.0	5.26	0.31	1.00	0.310	0.248	0.262	4.7E-03	0.0462
PC3810-10	104.0	5.35	0.28	1.28	0.317	0.254	0.160	4.6E-03	0.0471
PC3810-11	113.0	5.37	0.26	1.12	0.310	0.242	0.104	4.8E-03	0.0453
PC3810-12	126.0	4.24	0.40	1.29	0.252	0.242	0.109	4.2E-03	0.0510
PC3810-13	134.0	4.09	0.42	0.89	0.241	0.241	0.118	4.2E-03	0.0514
PC3810-14	146.0	4.11	0.41	0.72	0.255	0.245	0.078	4.2E-03	0.0526
PC3810-15	154.0	3.86	0.42	1.29	0.229	0.239	0.085	4.9E-03	0.0517
PC3810-16	167.0	3.95	0.40	0.65	0.223	0.246	0.059	3.7E-03	0.0530
PC3810-17	174.0	3.85	0.37	0.36	0.234	0.248	0.064	4.2E-03	0.0509
PC3810-18	185.0	3.90	0.39	0.26	0.209	0.253	0.052	4.7E-03	0.0523
PC3810-19	194.0	3.79	0.43	0.88	0.217	0.249	0.056	4.3E-03	0.0494
PC3810-20	203.0	3.88	0.37	0.39	0.227	0.247	0.064	4.2E-03	0.0526
PC3810-21	216.0	3.96	0.42	0.97	0.252	0.245	0.075	3.9E-03	0.0514
PC3810-22	224.0	4.00	0.43	0.62	0.219	0.238	0.056	3.7E-03	0.0506
PC3810-23	233.0	3.52	0.41	0.47	0.222	0.248	0.054	4.7E-03	0.0520
PC3810-24	244.0	3.71	0.41	0.80	0.225	0.240	0.067	4.1E-03	0.0520
PC3810-25	254.0	4.49	0.34	0.97	0.272	0.246	0.133	4.2E-03	0.0501
PC3810-26	263.0	4.34	0.37	1.11	0.272	0.241	0.116	3.9E-03	0.0505
PC3810-27	273.0	3.70	0.41	0.84	0.220	0.245	0.058	4.7E-03	0.0519
PC3810-28	284.0	3.89	0.39	1.13	0.211	0.240	0.070	4.6E-03	0.0535
PC3810-29	295.0	3.82	0.44	2.30	0.203	0.238	0.076	4.2E-03	0.0495
PC3810-30	305.0	3.54	0.43	1.10	0.192	0.230	0.051	4.8E-03	0.0531
PC3810-31	314.0	3.70	0.38	1.06	0.206	0.233	0.057	3.8E-03	0.0535
PC3810-32	324.0	3.77	0.43	1.50	0.212	0.234	0.067	5.0E-03	0.0498
PC3810-33	335.0	3.77	0.40	0.96	0.217	0.242	0.057	4.4E-03	0.0517
PC3810-34	344.0	4.32	0.45	1.90	0.240	0.229	0.083	4.2E-03	0.0495
PC3810-35	354.0	5.21	0.41	1.21	0.272	0.235	0.067	2.2E-03	0.0494
PC3810-36	364.0	4.84	0.42	1.75	0.291	0.237	0.084	3.5E-03	0.0492
PC3810-37	374.0	5.12	0.38	1.27	0.250	0.227	0.067	2.4E-03	0.0488
PC3810-38	383.0	3.21	0.39	0.82	0.178	0.225	0.041	4.3E-03	0.0509
PC3810-39	394.0	3.76	0.37	0.90	0.213	0.229	0.063	3.6E-03	0.0514
PC3810-40	404.0	3.54	0.36	0.91	0.199	0.229	0.052	4.4E-03	0.0541
PC3810-41	417.0	3.59	0.39	1.63	0.195	0.222	0.074	3.4E-03	0.0525
PC3810-42	424.0	3.40	0.37	1.19	0.211	0.232	0.064	5.1E-03	0.0509
PC3810-43	434.0	5.14	0.41	5.05	0.286	0.232	0.165	3.5E-03	0.0506
PC3810-44	445.0	3.76	0.39	2.21	0.214	0.230	0.069	2.8E-03	0.0491

APPENDIX C.8. SALT-CORRECTED MAJOR ELEMENT/Al RATIOS									
PC38-10	257m								
Sample	Depth	Si terr/Al	Fe/Al	Ca/Al	Na/Al	K/Al	P/Al	Mn/Al	Tl/Al
	(cm)								
PC3810-45	456.0	4.24	0.40	2.16	0.226	0.223	0.078	3.4E-03	0.0497
PC3810-46	467.0	5.33	0.41	3.23	0.295	0.235	0.088	1.2E-03	0.0492
PC3810-47	476.0	3.54	0.38	1.80	0.209	0.230	0.105	4.2E-03	0.0524
PC3810-48	484.0	3.58	0.39	2.04	0.200	0.228	0.104	3.4E-03	0.0518
PC3810-49	494.0	4.20	0.35	2.21	0.255	0.223	0.211	4.3E-03	0.0537
PC3810-50	504.0	5.02	0.31	1.51	0.321	0.242	0.460	3.8E-03	0.0507
PC3810-51	514.0	4.20	0.49	0.45	0.250	0.228	0.021	5.6E-03	0.0552
PC3810-52	524.0	4.17	0.48	0.36	0.250	0.228	0.018	6.3E-03	0.0551
PC3810-53	534.0	3.79	0.40	1.10	0.259	0.224	0.059	3.6E-03	0.0451
PC3810-54	545.0	3.94	0.39	0.84	0.282	0.237	0.045	3.8E-03	0.0461
PC3810-55	554.0	3.95	0.40	1.32	0.269	0.227	0.048	3.9E-03	0.0449
PC3810-56	564.0	4.16	0.43	2.20	0.286	0.229	0.085	5.4E-03	0.0476
PC3810-57	574.0	3.91	0.42	2.16	0.236	0.222	0.062	4.5E-03	0.0475
PC3810-58	584.0	4.03	0.42	1.89	0.275	0.241	0.048	5.3E-03	0.0475
PC3810-59	596.0	4.14	0.42	1.68	0.296	0.240	0.052	3.8E-03	0.0469
PC3810-60	604.0	3.82	0.43	2.02	0.298	0.243	0.051	4.8E-03	0.0466
PC3810-61	614.0	3.84	0.42	1.30	0.240	0.234	0.033	3.8E-03	0.0462
PC3810-62	624.0	3.74	0.41	1.40	0.214	0.247	0.043	4.6E-03	0.0484
PC3810-63	634.0	3.74	0.41	1.43	0.382	0.244	0.046	4.5E-03	0.0466
PC3810-64	645.0	3.77	0.44	1.12	0.246	0.234	0.032	5.9E-03	0.0460
PC3810-65	655.0	3.82	0.43	1.30	0.262	0.236	0.031	3.8E-03	0.0450
PC3810-66	667.0	3.82	0.42	1.13	0.245	0.246	0.036	4.3E-03	0.0453
PC3810-67	674.0	3.42	0.41	0.74	0.193	0.246	0.032	4.8E-03	0.0458
PC3810-68	683.0	3.55	0.40	0.94	0.210	0.250	0.027	4.2E-03	0.0439
PC3810-69	694.0	3.08	0.40	0.49	0.183	0.253	0.030	4.1E-03	0.0464
PC3810-70	704.0	3.05	0.35	0.24	0.163	0.263	0.026	4.7E-03	0.0485
PC3810-71	714.0	2.99	0.39	0.58	0.171	0.263	0.032	4.3E-03	0.0447
PC3810-72	724.0	3.27	0.39	0.78	0.166	0.252	0.032	5.2E-03	0.0435
PC3810-74	734.0	3.09	0.34	0.22	0.177	0.261	0.030	3.5E-03	0.0473
PC3810-75	745.0	3.09	0.36	0.20	0.186	0.260	0.026	4.7E-03	0.0482
PC3810-76	754.0	3.36	0.38	0.29	0.202	0.256	0.040	4.5E-03	0.0485
PC3810-77	764.0	3.71	0.34	0.37	0.219	0.256	0.076	4.7E-03	0.0530
PC38-02	2525m								
	(Age)								
PC3802-01	2.76	2.35	0.53	1.52	0.223	0.252	0.020	4.8E-03	0.0491
PC3802-02	6.21	2.43	0.52	2.29	0.223	0.258	0.022	5.5E-03	0.0481
PC3802-03	9.66	2.57	0.52	2.56	0.216	0.246	0.021	4.7E-03	0.0490
PC3802-04	12.77	2.36	0.50	1.97	0.204	0.260	0.018	4.5E-03	0.0469
PC3802-05	15.18	2.49	0.49	2.37	0.198	0.254	0.017	4.5E-03	0.0495
PC3802-06	17.47	2.48	0.53	2.35	0.214	0.262	0.017	5.0E-03	0.0488
PC3802-07	20.48	2.57	0.48	2.21	0.092	0.244	0.017	4.8E-03	0.0505
PC3802-08	22.65	2.61	0.51	2.19	0.168	0.254	0.017	4.1E-03	0.0499
PC3802-09	25.22	2.54	0.51	2.66	0.193	0.251	0.019	4.8E-03	0.0525
PC3802-10	28.29	2.38	0.51	3.11	0.211	0.251	0.020	4.9E-03	0.0532
PC3802-11	31.07	2.22	0.50	3.23	0.209	0.255	0.020	5.9E-03	0.0530
PC3802-12	33.86	2.05	0.54	3.69	0.220	0.263	0.021	5.1E-03	0.0537
PC3802-13	36.64	2.32	0.55	3.14	0.192	0.246	0.019	5.2E-03	0.0511
PC3802-14	39.15	2.48	0.48	2.26	0.206	0.255	0.018	5.2E-03	0.0499
PC3802-15	42.22	2.26	0.49	2.10	0.214	0.258	0.017	4.8E-03	0.0494
PC3802-16	45.00	2.69	0.49	1.78	0.166	0.260	0.017	4.9E-03	0.0503
PC3802-17	48.07	2.55	0.48	1.53	0.203	0.266	0.016	4.6E-03	0.0498
PC3802-18	50.85	2.49	0.56	1.41	0.218	0.275	0.018	5.4E-03	0.0521
PC3802-19	53.64	2.45	0.54	1.54	0.212	0.267	0.018	5.2E-03	0.0514
PC3802-20	56.42	2.55	0.51	1.26	0.212	0.267	0.017	4.8E-03	0.0519
PC3802-21	59.29	2.51	0.50	1.40	0.196	0.261	0.016	4.9E-03	0.0505
PC3802-22	62.61	2.61	0.51	1.50	0.208	0.262	0.017	4.9E-03	0.0503
PC3802-23	65.94	2.59	0.50	1.28	0.211	0.263	0.016	5.1E-03	0.0512
PC3802-24	69.26	2.64	0.50	0.60	0.221	0.274	0.015	4.7E-03	0.0514
PC3802-25	72.58	2.58	0.52	0.91	0.223	0.266	0.018	4.8E-03	0.0528
PC3802-26	76.96	2.53	0.53	1.47	0.233	0.267	0.020	5.0E-03	0.0528
PC3802-27	82.03	2.50	0.51	0.66	0.229	0.277	0.017	4.8E-03	0.0506
PC3802-28	87.11	2.70	0.50	0.73	0.214	0.280	0.016	4.2E-03	0.0493
PC3802-29	92.18	2.54	0.49	0.38	0.203	0.278	0.015	4.3E-03	0.0492
PC3802-30	97.26	2.58	0.51	0.51	0.202	0.275	0.018	4.7E-03	0.0511
PC3802-31	102.84	2.52	0.52	0.95	0.211	0.267	0.020	4.7E-03	0.0517
PC3802-32	107.92	2.48	0.52	0.90	0.210	0.272	0.019	5.0E-03	0.0507

APPENDIX C.8. SALT-CORRECTED MAJOR ELEMENT/Al RATIOS									
PC38-02	2525m								
Sample	Age	Si terr/Al	Fe/Al	Ca/Al	Na/Al	K/Al	P/Al	Mn/Al	Ti/Al
	(ka)								
PC3802-33	113.00	2.38	0.56	0.90	0.204	0.273	0.017	5.3E-03	0.0496
PC3802-34	118.07	2.50	0.56	0.93	0.210	0.268	0.017	4.5E-03	0.0487
PC3802-35	123.15	2.27	0.50	1.71	0.218	0.268	0.018	5.0E-03	0.0463
PC3802-36	128.22	2.17	0.51	2.21	0.200	0.255	0.016	5.3E-03	0.0460
PC3802-37	132.23	2.53	0.50	2.40	0.202	0.252	0.015	5.0E-03	0.0467
PC3802-38	135.30	2.62	0.52	2.62	0.199	0.268	0.016	4.9E-03	0.0493
PC3802-39	138.71	2.37	0.51	2.72	0.198	0.263	0.016	4.7E-03	0.0501
PC3802-40	141.79	2.40	0.51	3.04	0.216	0.267	0.018	5.2E-03	0.0503
PC3802-41	145.20	2.42	0.49	2.91	0.223	0.267	0.017	5.2E-03	0.0491
PC3802-42	148.61	2.35	0.50	2.80	0.227	0.269	0.016	4.9E-03	0.0489
PC3802-43	152.02	2.42	0.50	3.02	0.209	0.255	0.017	5.3E-03	0.0498
PC3802-44	155.44	2.53	0.49	2.74	0.220	0.271	0.017	4.8E-03	0.0508
PC3802-45	158.85	2.67	0.51	2.10	0.203	0.255	0.016	5.0E-03	0.0494
PC3802-46	162.26	2.60	0.50	1.77	0.227	0.273	0.015	5.1E-03	0.0497
PC3802-47	165.68	2.63	0.51	2.95	0.199	0.240	0.018	4.8E-03	0.0490
PC3802-48	169.43	2.59	0.52	3.23	0.160	0.190	0.018	5.3E-03	0.0517
PC3802-49	172.84	2.63	0.52	3.11	0.192	0.269	0.018	4.4E-03	0.0503
PC3802-50	176.26	2.67	0.54	2.75	0.207	0.267	0.019	5.8E-03	0.0487
PC3802-51	179.67	2.62	0.49	2.34	0.207	0.264	0.017	5.1E-03	0.0498
PC3802-52	183.08	2.83	0.49	1.71	0.227	0.289	0.016	4.9E-03	0.0456
PC3802-53	186.50	3.13	0.38	1.22	0.280	0.339	0.013	4.4E-03	0.0385
PC3802-54	189.57	2.67	0.50	0.87	0.203	0.278	0.016	5.0E-03	0.0497
PC3802-55	193.52	2.60	0.53	0.81	0.194	0.271	0.016	4.8E-03	0.0502
PC3802-56	197.42	2.35	0.62	0.67	0.191	0.278	0.017	5.0E-03	0.0521
PC3802-57	202.11	2.50	0.56	1.23	0.345	0.277	0.018	4.7E-03	0.0480
PC3802-58	206.02	2.61	0.53	1.26	0.274	0.274	0.016	4.9E-03	0.0467
PC3802-59	209.53	2.66	0.53	1.34	0.216	0.265	0.015	4.8E-03	0.0463
PC3802-60	213.44	2.63	0.55	3.24	0.204	0.244	0.019	4.9E-03	0.0499
PC3802-61	217.34	2.72	0.54	3.47	0.235	0.274	0.020	5.5E-03	0.0489
PC3802-62	221.25	2.68	0.54	2.68	0.213	0.271	0.018	5.4E-03	0.0516
PC3802-63	225.16	2.77	0.51	2.42	0.213	0.262	0.017	5.3E-03	0.0504
PC3802-64	229.06	2.69	0.50	1.83	0.200	0.263	0.016	5.0E-03	0.0483
PC3802-65	232.97	2.69	0.49	1.22	0.201	0.280	0.015	4.5E-03	0.0474
PC3802-66	237.27	2.62	0.53	1.42	0.245	0.282	0.018	5.0E-03	0.0483
PC3802-67	240.78	2.55	0.50	3.09	0.239	0.272	0.020	5.3E-03	0.0461
PC3802-68	244.50	2.72	0.48	2.56	0.209	0.277	0.016	5.1E-03	0.0471
PC3802-69	247.71	2.71	0.47	2.05	0.200	0.270	0.013	4.9E-03	0.0471
PC3802-70	250.91	2.58	0.46	2.27	0.191	0.271	0.014	4.8E-03	0.0477
PC3802-71	254.12	2.80	0.50	2.29	0.213	0.266	0.014	4.8E-03	0.0466
PC3802-72	257.32	2.63	0.48	2.24	0.208	0.279	0.015	5.0E-03	0.0488
PC3802-73	260.53	2.47	0.47	2.22	0.203	0.278	0.015	5.5E-03	0.0488
PC3802-74	263.73	2.45	0.48	2.09	0.200	0.272	0.016	5.3E-03	0.0502
PC38-11	3835m								
PC3811-01	0.80	2.69	0.34	0.26	0.169	0.237	0.044	4.1E-03	0.0528
PC3811-02	2.00	3.26	0.42	0.99	0.192	0.217	0.063	5.5E-03	0.0563
PC3811-03	2.20	3.82	0.40	0.84	0.215	0.229	0.059	5.9E-03	0.0603
PC3811-04	3.49	2.56	0.36	0.20	0.167	0.252	0.027	3.8E-03	0.0498
PC3811-05	6.17	2.48	0.34	0.32	0.167	0.251	0.023	4.2E-03	0.0494
PC3811-06	8.85	2.45	0.41	0.41	0.150	0.250	0.019	4.0E-03	0.0495
PC3811-07	11.53	2.42	0.38	0.42	0.163	0.251	0.018	4.6E-03	0.0481
PC3811-08	13.80	2.56	0.40	0.51	0.162	0.249	0.020	4.4E-03	0.0486
PC3811-09	16.44	3.47	0.38	0.73	0.275	0.251	0.038	5.3E-03	0.0445
PC3811-10	18.63	2.51	0.42	0.69	0.178	0.258	0.021	4.8E-03	0.0502
PC3811-11	20.82	2.46	0.44	0.79	0.173	0.252	0.021	4.9E-03	0.0507
PC3811-12	23.23	2.43	0.45	0.62	0.176	0.252	0.021	4.4E-03	0.0498
PC3811-13	25.11	2.39	0.42	0.62	0.174	0.261	0.020	4.5E-03	0.0496
PC3811-14	27.10	2.58	0.42	0.70	0.178	0.247	0.023	4.5E-03	0.0503
PC3811-15	29.09	2.50	0.40	0.58	0.189	0.247	0.021	4.6E-03	0.0482
PC3811-16	31.08	2.62	0.42	0.83	0.182	0.245	0.025	5.6E-03	0.0509
PC3811-17	33.07	2.50	0.41	0.63	0.190	0.247	0.021	4.7E-03	0.0462
PC3811-18	35.07	2.88	0.42	0.81	0.221	0.258	0.033	5.1E-03	0.0487
PC3811-19	37.26	2.24	0.38	0.52	0.167	0.261	0.022	5.2E-03	0.0489
PC3811-20	39.45	2.13	0.42	0.46	0.155	0.251	0.021	4.2E-03	0.0491
PC3811-21	40.84	2.06	0.41	0.35	0.163	0.262	0.019	4.1E-03	0.0478
PC3811-22	43.03	2.41	0.45	0.90	0.176	0.252	0.029	5.0E-03	0.0497

APPENDIX C.9. UNCORRECTED TRACE ELEMENTS

BC38-02 Sample	2530m Depth (cm)	Mo (ppm)	U (ppm)	Ba (ppm)	Ni (ppm)	Cr (ppm)	V (ppm)	Sc (ppm)	Cu (ppm)	Zn (ppm)	Sr (ppm)	Rb (ppm)	Zr (ppm)	Nb (ppm)	Pb (ppm)	Th (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Y (ppm)
BC3802-01	0.5	1	0	2081	26	82	101	12	50	115	396	76	107	7	12	9	25	39	23	30
BC3802-02	1.5	2	1	2080	24	80	101	11	51	117	384	76	107	6	13	8	24	40	21	29
BC3802-03	2.5	2	1	2084	25	85	99	12	52	118	394	77	107	7	12	7	21	37	22	29
BC3802-04	3.5	1	0	2034	25	84	103	12	51	118	402	76	107	7	12	8	22	39	21	29
BC3802-05	4.5	1	0	2050	25	82	103	12	53	116	409	76	109	7	12	9	22	38	22	28
BC3802-06	5.5	0	1	2044	25	85	105	8	53	116	411	76	108	6	14	7	15	39	22	28
BC3802-07	6.5	1	1	2032	27	86	111	12	57	119	413	77	107	7	13	7	21	39	22	29
BC3802-08	7.5	1	2	2012	26	87	117	11	58	176	415	77	106	7	11	7	20	39	21	29
BC3802-09	8.5	1	2	2056	27	85	126	12	60	124	414	79	111	7	13	8	21	41	13	28
BC3802-10	9.5	1	1	2073	26	86	127	12	60	123	428	79	111	7	13	8	22	37	21	29
BC3802-11	11.0	2	2	2154	28	91	117	11	61	128	471	82	115	7	12	7	20	42	23	30
BC3802-12	13.0	0	4	2018	27	84	110	10	54	123	493	75	107	7	12	7	24	38	21	28
BC3802-13	15.0	1	3	1938	25	78	120	9	61	116	499	72	102	7	10	8	24	36	21	28
BC3802-13A	17.0	1	5	1770	24	72	106	5	53	108	574	67	99	7	8	6	23	36	21	27
BC3802-14	19.0	1	6	1756	25	70	110	4	58	106	622	64	93	6	8	5	20	34	21	26
BC3802-15	21.0	2	8	1704	26	68	103	1	56	107	661	64	93	6	8	4	19	35	19	26
BC3802-16	23.0	1	9	1626	24	66	90	0	49	100	658	61	88	6	9	5	20	31	20	25
BC3802-17	25.0	1	9	1640	25	66	90	-1	50	101	674	62	90	7	8	5	19	32	19	25
BC3802-18	27.0	1	9	1531	24	64	83	0	46	98	665	61	93	6	7	5	21	37	20	26
BC3802-19	29.0	2	8	1469	26	63	82	-1	44	97	690	61	91	6	7	4	17	34	20	25
BC3802-20	31.0	2	8	1394	26	64	80	-2	43	94	669	60	91	5	8	4	16	33	19	24
BC3802-21	33.0	2	7	1406	29	66	84	0	46	100	665	63	89	6	7	4	14	32	19	25
BC3802-21A	35.0	3	8	1156	35	61	88	2	46	95	598	67	91	7	11	4	22	34	19	22
BC3802-22	37.0	2	7	1279	30	63	86	1	45	96	637	66	94	6	9	5	18	32	19	24
BC3802-23	39.0	1	6	1320	27	63	83	0	43	96	649	63	91	6	8	5	19	33	19	23
BC3802-24	41.0	3	8	1218	32	62	91	-1	48	95	631	66	94	6	8	5	17	34	19	21
BC3802-25	43.0	3	6	1290	32	63	98	0	50	97	609	68	97	6	10	6	19	31	19	21
BC3802-26	45.0	2	8	1310	31	62	101	0	50	97	602	69	98	6	10	7	20	37	20	21
BC3802-27	47.0	3	7	1316	31	61	103	1	50	96	596	69	98	6	10	6	21	35	20	22
BC3802-28	49.0	3	8	1369	32	63	105	0	51	100	600	69	99	6	12	6	17	36	20	23
BC3802-29	51.0	3	7	1365	31	62	103	0	52	99	590	69	99	6	9	5	17	32	20	24
BC3802-30	53.0	3	8	1348	31	61	100	3	50	98	581	69	100	6	11	6	10	31	20	23

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APPENDIX C.9. UNCORRECTED TRACE ELEMENTS

BC38-03	4289m																			
Sample	Depth	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(cm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
BC3803-01	0.5	2	1	1595	20	72	111	12	103	102	205	76	96	6	16	9	11	36	19	17
BC3803-02	1.5	2	1	1625	19	75	109	11	103	101	208	78	100	7	13	10	19	36	18	18
BC3803-03	2.5	0	1	1621	19	76	105	12	104	101	205	77	99	7	13	9	20	32	17	17
BC3803-04	3.5	0	2	1633	21	75	108	10	110	103	204	78	100	7	13	9	18	33	17	18
BC3803-05	4.5	1	2	1735	24	77	124	12	121	107	207	81	103	7	13	10	18	34	18	19
BC3803-06	5.5	1	3	1717	22	77	118	12	112	104	200	80	99	7	14	10	18	38	19	18
BC3803-07	6.5	1	3	1715	23	77	118	11	112	108	202	80	103	7	13	9	19	40	19	18
BC3803-08	7.5	1	4	1742	22	77	115	11	114	133	206	82	107	7	13	10	16	36	19	19
BC3803-09	8.5	1	5	1741	26	77	116	11	114	109	207	82	105	7	14	10	17	40	20	19
BC3803-10	9.5	2	6	1868	27	81	127	11	129	118	217	87	113	7	15	9	17	40	19	22
BC3803-11	11.0	1	6	1785	27	82	132	11	126	117	210	85	109	8	15	12	17	36	20	21
BC3803-12	13.0	2	7	1849	33	82	130	12	124	120	211	85	111	8	13	10	16	39	21	21
BC3803-13	15.0	2	8	1832	27	79	129	12	126	121	216	85	111	7	14	10	19	37	21	21
BC3803-14	17.0	3	8	1925	35	84	132	13	135	126	219	87	115	8	13	9	19	41	22	22
BC3803-15	19.0	3	8	1878	37	80	124	14	129	122	218	85	112	8	12	9	19	40	21	21
BC3803-16	21.0	4	6	1888	27	79	119	11	128	122	214	83	111	8	13	10	23	38	20	21
BC3803-17	23.0	2	5	1820	31	79	117	13	130	118	215	82	108	8	13	10	20	37	20	20
BC3803-18	25.0	3	8	1882	31	80	122	12	129	123	217	83	112	8	13	10	19	38	20	21
BC3803-19	27.0	4	8	1838	29	77	121	13	124	123	215	81	109	8	12	10	22	38	19	21
BC3803-20	29.0	3	9	1951	30	81	127	13	131	130	225	84	115	8	13	10	15	37	21	21
BC3803-21	31.0	2	8	1889	28	77	122	13	123	124	223	83	114	8	12	11	16	41	23	21
BC3803-22	33.0	3	8	1921	28	77	123	14	126	125	223	82	115	8	11	8	13	42	22	21
BC3803-23	35.0	3	9	1894	29	78	120	13	124	124	220	80	112	8	11	8	22	40	22	21
BC3803-24	37.0	2	9	1927	32	79	124	13	126	129	230	84	119	8	12	9	16	43	22	23
BC3803-25	39.0	3	10	1874	33	79	126	12	127	130	231	83	118	8	12	8	21	43	22	23
BC3803-26	41.0	2	9	1823	30	79	126	14	118	128	225	84	116	8	12	11	21	40	21	22
BC3803-27	43.0	2	9	1753	37	79	122	12	113	125	226	84	118	8	13	10	15	42	21	22
BC3803-28	45.0	2	9	1762	30	79	121	12	110	124	223	82	116	8	12	9	20	43	21	22
BC3803-29	47.0	3	9	1725	32	77	121	12	109	125	223	82	115	8	12	10	21	45	21	22
BC3803-30	49.0	3	8	1716	31	80	120	13	108	125	226	84	119	8	12	10	22	41	21	22
BC3803-31	51.0	2	9	1707	31	81	122	13	104	128	229	86	121	8	12	9	30	44	21	23
BC3803-32	53.0	2	11	1564	31	83	120	13	99	128	223	85	119	8	12	10	23	40	20	22

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APPENDIX C.9. UNCORRECTED TRACE ELEMENTS																				
PC38-09	148m																			
Sample	Depth	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(cm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
PC3809-01	4.0	63	9	273	61	110	99	9	27	114	184	64	121	8	13	10	18	35	16	16
PC3809-02	13.0	60	9	223	56	99	115	10	22	90	175	60	97	7	14	9	15	29	14	14
PC3809-03	23.0	55	9	274	59	114	115	12	30	102	181	71	128	9	19	11	18	42	18	18
PC3809-04	34.0	53	9	253	60	113	115	9	30	101	167	68	119	8	17	10	19	38	17	17
PC3809-05	43.0	26	8	325	42	95	101	12	22	95	230	71	190	9	16	11	17	43	20	22
PC3809-06	53.0	53	6	249	55	108	109	11	30	107	162	66	104	8	17	10	16	35	15	16
PC3809-07	62.0	91	9	224	69	116	108	8	31	95	179	54	89	7	13	8	19	29	13	14
PC3809-08	73.0	37	8	280	53	117	110	11	25	101	174	70	137	9	17	11	17	44	19	20
PC3809-09	84.0	44	7	296	58	128	128	12	31	115	157	83	127	10	20	12	21	45	21	20
PC3809-10	94.0	63	7	273	64	122	133	11	37	112	158	78	113	8	20	11	21	41	18	17
PC3809-11	104.0	77	9	271	62	111	134	10	31	112	139	68	95	7	19	10	16	37	16	15
PC3809-12	113.0	35	8	305	53	118	135	14	48	139	157	88	124	9	25	13	26	44	21	21
PC3809-13	124.0	38	9	316	49	124	111	11	20	99	204	74	160	10	18	11	22	47	22	21
PC3809-14	134.0	58	8	259	57	111	110	9	25	87	198	62	137	8	14	8	14	39	18	17
PC3809-15	144.0	63	8	241	60	110	100	9	23	86	169	57	107	7	16	9	18	33	15	15
PC3809-16	152.0	42	7	209	49	90	99	9	24	85	166	58	108	8	15	9	9	28	14	14
PC3809-17	165.0	48	9	231	49	83	97	8	22	82	203	53	127	7	13	7	12	31	15	16
PC3809-18	174.0	27	9	327	43	96	95	9	19	89	233	67	196	9	15	9	17	43	21	21
PC3809-19	185.0	31	10	308	41	77	81	10	18	82	276	57	204	7	12	8	13	34	17	20
PC3809-20	194.0	27	8	338	38	75	82	9	19	87	297	59	225	8	11	7	15	39	18	23
PC3809-21	205.0	38	5	424	35	60	110	13	34	118	246	67	147	8	17	9	15	39	18	21
PC3809-22	214.0	52	12	270	69	110	98	8	23	91	242	55	171	7	13	9	15	33	16	18
PC3809-23	224.0	13	11	383	30	56	62	9	9	59	340	54	276	8	10	7	14	46	20	23
PC3809-24	234.0	40	8	305	41	73	76	8	16	69	292	47	192	6	11	7	11	32	15	19
PC3809-25	243.0	68	9	211	59	87	95	7	21	64	170	39	94	6	10	6	2	25	11	12
PC3809-26	257.0	56	10	258	56	100	89	7	19	74	189	47	126	6	12	7	4	30	14	16
PC3809-27	267.0	31	15	323	41	82	75	7	13	83	359	48	183	7	11	6	16	33	18	24
PC3809-28	273.0	51	163	180	42	119	84	-1	9	57	1163	29	106	6	4	•	2	26	14	24
PC3809-29	284.0	65	12	232	64	128	115	12	32	99	190	58	102	7	11	8	16	34	16	19
PC3809-30	294.0	73	7	194	63	109	98	7	22	72	158	45	76	5	12	7	10	24	12	14
PC3809-31	304.0	46	7	319	57	120	109	10	33	142	161	59	98	7	12	8	12	30	15	17
PC3809-32	314.0	63	7	246	66	125	114	10	32	94	152	59	85	6	15	8	11	28	12	16

APPENDIX C.9. UNCORRECTED TRACE ELEMENTS

PC38-09	148m																			
Sample	Depth	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(cm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
PC3809-33	324.0	47	7	250	71	142	120	12	33	96	177	59	106	7	13	9	15	32	15	20
PC3809-34	335.0	66	8	206	70	128	111	10	27	78	152	48	87	6	13	8	13	27	13	16
PC3809-35	344.0	65	6	189	70	130	107	8	29	82	142	45	79	6	10	7	11	28	13	14
PC3809-36	355.0	71	5	183	59	98	113	7	19	61	142	36	59	4	9	6	9	19	9	10
PC3809-37	364.0	83	5	175	64	97	115	9	21	60	169	36	58	3	10	4	9	18	9	10
PC3809-38	375.0	90	6	236	71	125	134	8	29	78	151	51	82	6	14	7	15	24	12	14
PC3809-39	384.0	55	8	245	62	137	123	12	32	92	203	54	104	7	12	8	20	29	14	18
PC3809-40	394.0	62	7	214	67	120	117	9	27	75	167	47	82	5	11	7	17	28	13	14
PC3809-41	404.0	48	7	247	61	118	117	9	25	83	147	53	91	6	14	8	14	30	13	15
PC3809-42	416.0	79	9	192	64	117	121	9	25	72	188	44	75	5	10	7	9	24	12	13
PC3809-43	424.0	64	8	218	63	113	125	8	23	71	139	49	78	6	13	7	5	25	11	13
PC3809-44	434.0	77	9	249	80	137	148	9	35	87	156	60	91	6	14	9	15	32	14	15
PC3809-45	444.0	60	7	221	52	99	111	9	25	77	173	46	75	5	11	7	11	23	10	13
PC3809-46	453.0	48	8	258	53	122	128	10	29	85	170	57	102	7	13	8	15	29	14	17
PC3809-47	465.0	69	6	230	62	130	122	10	32	87	172	56	87	7	11	7	14	30	14	15
PC3809-48	474.0	92	9	245	63	121	129	8	27	76	188	53	78	6	14	7	14	25	12	13
PC3809-49	483.0	46	8	255	55	124	112	10	28	86	169	58	108	7	12	8	19	29	13	17
PC3809-50	493.0	61	7	1357	58	124	116	10	27	85	260	59	95	7	14	7	12	28	15	15
PC3809-51	504.0	39	9	298	51	130	108	11	28	88	185	61	122	7	13	9	11	34	16	20
PC3809-52	515.0	46	8	292	55	131	112	11	29	89	175	63	111	7	14	8	15	34	16	17
PC3809-53	525.0	73	7	240	62	125	123	9	29	81	183	56	86	6	14	7	15	31	13	14
PC3809-54	536.0	71	5	227	52	109	107	9	25	75	187	51	78	5	12	7	13	26	12	13
PC3809-55	544.0	46	6	299	48	117	118	12	29	92	192	62	110	7	15	9	15	33	15	17
PC3809-56	553.0	49	4	262	37	98	114	11	30	88	186	57	83	6	15	7	14	28	13	14
PC3809-57	564.0	48	4	257	36	95	114	9	27	80	179	51	76	5	15	7	12	23	11	13
PC3809-58	574.0	47	4	257	38	98	108	8	24	83	195	54	85	6	14	7	15	28	12	14
PC3809-59	585.0	34	5	364	32	89	109	8	19	77	263	51	93	6	14	6	13	27	13	14
PC3809-60	594.0	40	4	250	32	88	105	7	19	75	199	51	90	6	14	7	12	25	13	13
PC3809-61	605.0	37	4	269	33	103	111	11	27	92	225	59	107	8	16	9	11	34	15	17
PC3809-62	615.0	32	5	230	31	92	106	9	18	78	218	54	89	6	16	7	11	26	13	14
PC3809-63	625.0	30	5	260	31	96	111	11	24	91	220	57	102	7	16	8	14	27	14	15
PC3809-64	635.0	34	6	263	34	103	120	11	26	87	229	59	103	7	15	8	13	31	14	16

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APPENDIX C.9. UNCORRECTED TRACE ELEMENTS

PC38-09	148m																			
Sample	Depth	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(cm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
PC3809-65	646.0	44	5	216	35	85	115	8	17	70	185	48	81	5	12	6	11	26	12	12
PC3809-66	654.0	37	7	223	31	87	115	7	17	67	173	46	83	6	12	7	11	24	11	12
PC3809-67	664.0	40	8	233	31	79	117	7	17	68	174	47	76	6	12	6	7	27	12	12
PC3809-68	674.0	34	7	209	26	67	102	6	10	58	157	42	73	5	12	6	13	23	10	11
PC3809-69	684.0	40	6	282	33	90	122	8	20	81	198	59	95	6	15	8	13	32	14	15
PC3809-70	694.0	38	7	268	34	101	129	8	26	85	199	61	98	7	15	7	15	30	14	15
PC3809-71	703.0	50	6	264	36	95	135	9	27	86	189	61	95	6	18	8	17	29	14	15
PC3809-72	714.0	45	7	244	38	96	127	11	23	82	204	54	90	6	14	6	12	30	13	15
PC3809-73	724.0	31	5	286	33	97	118	11	28	87	219	62	100	7	15	7	10	31	15	16
PC3809-74	734.0	31	5	266	34	103	119	11	26	93	225	62	104	7	18	7	16	33	15	16
PC3809-75	744.0	43	7	282	35	91	123	10	26	84	211	61	98	6	17	7	15	35	14	15
PC3809-76	754.0	46	4	238	33	81	113	10	19	78	188	53	92	7	17	6	11	33	13	14
PC3809-77	764.0	38	5	276	33	91	123	10	24	90	206	66	104	8	18	8	15	35	15	17
PC3809-78	774.0	36	4	276	34	97	119	12	25	94	209	66	117	8	18	9	23	37	17	18
PC3809-79	784.0	36	6	262	35	91	116	10	25	90	204	63	108	7	17	8	15	36	17	17
PC3809-80	794.0	32	4	282	32	93	112	11	21	88	211	64	114	7	16	8	20	36	16	17
PC3809-81	804.0	31	5	307	32	94	107	11	22	81	213	58	114	7	13	7	15	34	15	16
PC3809-82	813.0	27	5	297	32	98	108	13	27	86	258	60	116	7	16	7	16	31	15	17
PC3809-83	823.0	28	4	282	33	95	102	10	22	84	219	60	120	8	13	7	18	31	15	18
PC3809-84	834.0	29	4	278	31	99	104	11	23	85	211	61	118	8	16	7	14	32	15	17
PC3809-85	845.0	36	4	284	34	97	109	10	25	80	220	63	113	7	17	7	17	32	16	17
PC3809-86	854.0	29	5	335	29	82	108	11	32	98	196	78	119	9	23	9	20	40	18	19
PC38-10	257m																			
PC3810-01	6.0	48	14	251	105	124	137	8	35	107	319	57	106	7	10	9	16	28	15	18
PC3810-02	14.0	24	19	323	74	102	87	8	24	94	418	57	194	8	10	8	30	40	20	27
PC3810-03	24.0	11	20	352	35	62	53	7	11	56	587	53	242	8	8	5	17	39	20	29
PC3810-04	34.0	17	15	328	38	67	56	5	12	59	483	54	220	7	10	6	19	42	20	28
PC3810-05	44.0	35	15	336	98	137	97	10	27	88	250	62	162	8	12	10	15	37	18	22
PC3810-06	54.0	44	14	306	88	128	120	8	28	89	221	63	153	7	13	8	18	35	16	19
PC3810-07	64.0	37	14	329	72	107	111	9	26	90	270	64	197	8	13	9	22	44	19	22

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APPENDIX C.9. UNCORRECTED TRACE ELEMENTS

PC38-10	257m																			
Sample	Depth	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(cm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
PC3810-08	74.0	29	15	383	56	100	107	9	22	90	328	68	237	7	15	10	22	45	22	25
PC3810-09	84.0	13	15	384	20	60	60	7	8	70	426	56	228	7	14	7	23	43	23	29
PC3810-10	94.0	41	27	374	30	52	52	6	9	60	498	56	261	8	10	6	17	41	20	29
PC3810-10	104.0	31	16	358	31	54	54	4	10	52	466	53	274	7	10	8	18	40	20	28
PC3810-11	113.0	17	10	342	24	45	45	5	7	50	430	53	241	7	10	6	18	39	20	27
PC3810-12	126.0	46	10	201	55	86	86	6	28	79	327	50	124	6	9	6	19	26	14	18
PC3810-13	134.0	58	12	206	70	98	98	7	32	86	266	52	110	6	10	8	13	26	13	17
PC3810-14	146.0	50	12	268	63	91	99	9	33	94	280	60	149	8	11	8	17	37	17	20
PC3810-15	154.0	43	12	251	66	97	107	8	34	92	333	56	127	7	11	7	16	30	15	19
PC3810-16	167.0	46	11	271	60	95	112	8	29	91	239	61	120	7	12	8	17	33	15	19
PC3810-17	174.0	45	12	295	66	102	115	8	34	95	213	63	125	7	13	9	20	34	15	19
PC3810-18	185.0	33	11	280	55	97	111	8	27	92	179	68	115	7	13	9	17	32	15	19
PC3810-19	194.0	57	10	250	67	93	119	7	38	90	239	56	91	6	11	8	23	28	13	16
PC3810-20	203.0	44	15	324	60	95	129	8	29	106	227	67	141	8	14	9	22	36	17	20
PC3810-21	216.0	62	11	257	68	97	124	8	33	86	245	52	91	6	12	8	13	26	13	16
PC3810-22	224.0	56	11	249	75	104	125	8	37	94	198	56	91	6	14	8	16	27	14	16
PC3810-23	233.0	55	13	282	75	113	136	10	41	100	208	63	112	7	14	9	17	32	16	19
PC3810-24	244.0	42	11	243	62	103	114	9	30	95	268	63	129	7	13	9	17	33	16	19
PC3810-25	254.0	43	14	282	53	87	102	8	23	83	336	55	169	7	13	7	9	36	17	21
PC3810-26	263.0	53	12	269	59	88	113	8	28	81	326	52	132	7	12	6	15	30	14	19
PC3810-27	273.0	42	11	269	66	109	125	9	33	106	268	63	123	8	13	8	18	33	15	20
PC3810-28	284.0	36	13	268	59	97	108	9	29	93	314	60	126	7	11	8	16	33	17	21
PC3810-29	295.0	55	10	219	68	101	115	6	33	83	395	48	69	5	10	6	16	22	12	15
PC3810-30	305.0	35	11	265	60	98	125	9	28	99	304	62	114	7	13	8	28	34	16	20
PC3810-31	314.0	34	11	276	62	104	130	10	29	103	328	64	137	8	11	9	21	37	18	20
PC3810-32	324.0	60	11	245	74	100	140	8	36	90	305	51	80	5	12	6	22	26	14	15
PC3810-33	335.0	33	12	256	72	111	136	8	28	97	287	64	112	8	11	7	21	32	16	19
PC3810-34	344.0	58	10	152	73	93	124	7	30	82	306	43	68	6	10	6	10	24	11	13
PC3810-35	354.0	61	9	209	66	79	121	6	27	74	212	39	60	5	11	5	13	20	10	11
PC3810-36	364.0	62	9	165	63	70	121	6	25	70	247	36	49	4	9	5	15	19	10	11
PC3810-37	374.0	58	11	195	63	75	126	7	22	63	197	39	50	5	9	5	9	20	10	10
PC3810-38	383.0	29	12	274	63	104	134	10	32	103	255	67	98	7	15	9	22	36	16	18

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APPENDIX C.9. UNCORRECTED TRACE ELEMENTS

Sample	Depth (cm)	Mo (ppm)	U (ppm)	Ba (ppm)	Ni (ppm)	Cr (ppm)	V (ppm)	Sc (ppm)	Cu (ppm)	Zn (ppm)	Sr (ppm)	Rb (ppm)	Zr (ppm)	Nb (ppm)	Pb (ppm)	Th (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Y (ppm)
PC3810-39	394.0	41	13	224	81	112	141	8	27	87	234	54	91	6	12	8	18	29	13	17
PC3810-40	404.0	27	12	241	64	106	114	11	24	93	274	61	122	7	13	8	27	33	16	21
PC3810-41	417.0	49	12	229	72	105	112	9	29	91	363	52	99	6	12	7	21	31	15	18
PC3810-42	424.0	44	14	200	78	107	126	8	30	95	282	54	92	7	13	8	20	29	14	17
PC3810-43	434.0	60	9	157	55	67	98	0	15	62	468	24	45	4	5	2	8	16	9	10
PC3810-44	445.0	42	11	187	66	88	119	6	22	76	363	44	64	6	11	6	14	24	12	13
PC3810-45	456.0	68	13	233	76	87	154	7	25	77	327	40	61	5	10	6	12	17	9	12
PC3810-46	467.0	66	6	170	57	62	104	2	15	57	314	25	37	3	7	3	13	15	9	9
PC3810-47	476.0	34	16	255	84	115	131	7	29	96	415	54	96	7	10	7	19	30	16	19
PC3810-48	484.0	35	14	244	87	113	124	8	30	90	433	51	93	6	11	7	15	30	15	19
PC3810-49	494.0	37	23	261	89	115	106	3	26	80	456	45	130	6	8	6	18	30	16	25
PC3810-50	504.0	14	21	313	43	65	63	7	14	61	632	49	235	8	7	4	20	38	19	32
PC3810-51	514.0	64	6	278	50	89	122	11	25	82	187	53	104	7	14	7	14	30	14	16
PC3810-52	524.0	50	6	333	44	80	129	10	26	85	184	56	114	7	15	7	16	35	15	17
PC3810-53	534.0	121	21	368	154	170	339	8	46	83	256	45	68	5	11	6	9	22	11	14
PC3810-54	545.0	104	16	309	121	139	260	9	34	74	227	47	72	5	11	7	12	22	12	14
PC3810-55	554.0	116	17	314	121	135	281	8	37	75	264	43	61	5	10	6	11	22	10	12
PC3810-56	564.0	87	10	287	66	97	201	6	20	56	379	36	64	4	9	5	10	21	11	11
PC3810-57	574.0	79	10	298	73	112	239	6	24	67	445	42	80	5	9	4	13	23	12	13
PC3810-58	584.0	75	8	321	68	105	193	8	23	67	390	41	73	5	9	4	12	21	11	13
PC3810-59	596.0	81	21	330	70	111	242	7	23	67	381	41	76	5	11	5	10	21	11	13
PC3810-60	604.0	82	16	361	68	113	233	6	25	69	417	42	72	5	10	4	12	24	11	14
PC3810-61	614.0	80	14	320	66	111	234	9	24	70	327	47	81	6	12	5	12	25	12	13
PC3810-62	624.0	73	10	315	68	109	234	7	24	79	400	53	89	6	14	6	14	28	15	16
PC3810-63	634.0	61	9	282	65	115	205	6	26	72	426	49	90	6	11	6	12	26	13	15
PC3810-64	645.0	83	10	357	60	101	199	8	25	68	296	50	76	6	13	7	11	27	13	14
PC3810-65	655.0	108	8	319	71	103	211	7	23	70	305	46	70	5	13	6	13	21	13	13
PC3810-66	667.0	99	11	280	69	107	211	9	25	78	310	52	79	6	15	6	15	25	13	15
PC3810-67	674.0	91	13	264	68	114	209	10	29	96	241	65	90	6	20	8	20	33	15	15
PC3810-68	683.0	87	11	239	66	103	201	9	26	89	255	61	80	6	20	6	13	33	15	13
PC3810-69	694.0	56	9	304	55	114	165	11	26	115	224	82	116	8	23	10	18	42	19	18
PC3810-70	704.0	46	8	332	50	128	162	11	27	117	186	93	131	9	23	11	20	45	20	21

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APPENDIX C.9. UNCORRECTED TRACE ELEMENTS

Sample	Depth (cm)	Mo (ppm)	U (ppm)	Ba (ppm)	Ni (ppm)	Cr (ppm)	V (ppm)	Sc (ppm)	Cu (ppm)	Zn (ppm)	Sr (ppm)	Rb (ppm)	Zr (ppm)	Nb (ppm)	Pb (ppm)	Th (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Y (ppm)	
PC38-10	257m																				
PC3810-71	714.0	66	8	309	51	109	154	11	28	112	240	83	107	8	21	9	19	38	17	18	
PC3810-72	724.0	74	10	274	49	91	147	9	22	97	245	72	91	6	21	8	16	33	17	15	
PC3810-74	734.0	56	11	313	46	104	146	12	24	110	176	84	123	8	25	12	18	44	20	18	
PC3810-75	745.0	36	9	355	39	98	139	12	32	130	194	95	156	8	27	12	25	47	22	20	
PC3810-76	754.0	50	9	281	48	100	127	9	29	101	185	77	155	8	19	10	18	34	17	16	
PC3810-77	764.0	29	11	371	35	94	112	12	20	100	289	80	217	9	19	11	25	48	22	24	
PC38-02	2525m																				
PC3802-01	8.0	-1	8	2044	28	84	123	16	70	123	509	79	101	7	10	7	16	33	22	23	
PC3802-02	18.0	0	6	1769	26	73	97	8	66	110	612	70	92	7	10	7	14	40	30	19	
PC3802-03	28.0	0	7	1688	22	69	90	12	56	104	647	69	92	6	9	6	19	26	23	19	
PC3802-04	38.0	2	8	1196	45	80	92	11	62	114	538	80	98	6	9	8	21	34	27	17	
PC3802-05	48.0	2	7	1243	33	72	99	14	62	104	590	77	98	7	11	8	16	41	21	17	
PC3802-06	57.5	2	6	1170	35	67	97	13	59	100	579	76	96	7	12	7	18	30	25	18	
PC3802-07	70.0	1	6	1460	35	81	110	11	69	106	557	79	103	6	12	9	18	45	32	20	
PC3802-08	79.0	2	6	1364	36	74	109	8	67	108	548	79	101	7	10	7	22	41	26	19	
PC3802-09	89.0	2	10	1344	35	68	102	13	67	105	595	75	97	7	9	6	10	40	28	19	
PC3802-10	100.0	2	6	1307	31	60	96	9	64	103	637	70	91	7	9	6	19	29	26	18	
PC3802-11	110.0	3	7	1291	30	63	89	10	61	101	641	69	90	5	9	6	16	39	27	16	
PC3802-12	120.0	4	7	1254	33	59	78	11	58	100	671	65	85	6	8	5	13	36	26	16	
PC3802-13	130.0	4	8	1326	33	57	88	12	61	99	663	70	90	7	7	9	14	36	26	17	
PC3802-14	139.0	3	6	1427	32	66	96	11	68	114	568	79	104	7	10	7	23	37	24	19	
PC3802-15	150.0	3	6	1338	34	64	98	8	64	90	553	79	101	6	10	7	14	39	29	20	
PC3802-16	160.0	3	5	1435	27	70	122	9	67	115	526	86	113	7	12	8	20	43	31	20	
PC3802-17	171.0	2	10	1469	28	74	119	15	77	126	489	88	116	8	13	7	25	42	26	22	
PC3802-18	181.0	3	10	1537	32	71	119	17	68	118	437	86	113	7	11	9	25	43	25	21	
PC3802-19	191.0	2	10	1683	35	79	118	14	73	123	478	83	111	6	11	9	21	50	33	23	
PC3802-20	201.0	2	9	1587	35	84	117	10	76	127	439	87	123	7	11	8	21	38	24	23	
PC3802-21	211.0	3	8	1451	36	76	117	15	79	124	468	88	114	7	13	10	18	42	29	23	
PC3802-22	221.0	3	9	1472	32	72	115	6	77	100	489	87	113	7	13	10	24	41	33	23	
PC3802-23	231.0	3	5	1333	30	72	129	15	77	119	439	91	117	8	13	9	24	37	27	24	

APPENDIX C.9. UNCORRECTED TRACE ELEMENTS																				
PC38-02	2525m																			
Sample	Depth	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(cm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
PC3802-24	241.0	1	7	1750	27	83	142	13	81	135	345	102	130	8	16	11	26	40	28	25
PC3802-25	251.0	3	9	1669	34	77	129	14	80	138	382	96	120	7	12	8	24	39	29	25
PC3802-26	261.0	2	9	1881	31	69	112	13	76	132	471	85	112	7	10	10	21	41	30	24
PC3802-27	271.0	3	6	1874	36	77	135	14	81	142	346	98	126	8	12	10	23	38	26	25
PC3802-28	281.0	2	8	1747	35	78	132	14	83	135	360	98	126	8	14	9	29	44	26	25
PC3802-29	291.0	1	7	1870	33	81	143	16	80	141	297	107	132	9	15	10	30	45	28	25
PC3802-30	301.0	2	8	2027	28	83	159	20	89	142	320	103	129	11	15	10	26	41	26	27
PC3802-31	312.0	2	10	1908	33	78	138	16	86	139	384	91	119	7	11	9	20	37	30	26
PC3802-32	322.0	2	10	1997	33	81	147	14	84	135	380	94	118	7	13	10	28	37	28	26
PC3802-33	332.0	1	6	1922	33	84	142	14	77	136	385	91	116	8	12	8	25	41	30	27
PC3802-34	342.0	2	8	2310	26	86	132	14	73	133	415	91	115	7	14	9	26	46	30	26
PC3802-35	352.0	1	8	1892	26	70	106	12	65	115	534	77	99	6	12	8	20	46	29	21
PC3802-36	362.0	2	7	1343	27	72	105	12	57	106	593	77	94	6	13	8	19	39	28	17
PC3802-37	372.0	1	8	1252	25	74	106	10	53	100	624	77	96	7	11	7	17	40	27	18
PC3802-38	381.0	1	7	1282	23	73	116	11	55	93	642	77	97	6	6	8	21	39	29	18
PC3802-39	391.0	1	9	1250	24	67	106	7	56	90	626	73	96	7	13	7	18	39	26	19
PC3802-40	400.0	1	8	1307	23	61	94	10	57	97	656	72	96	6	10	8	20	39	29	19
PC3802-41	410.0	2	5	1316	22	59	104	12	61	101	658	74	90	6	9	7	17	30	26	18
PC3802-42	420.0	1	6	1203	22	61	97	13	53	97	648	72	97	7	10	8	17	38	26	18
PC3802-43	430.0	0	7	1057	21	60	105	13	54	91	667	72	92	6	10	6	19	34	22	18
PC3802-44	440.0	1	11	1211	19	64	112	12	56	93	637	75	97	7	11	7	25	43	25	18
PC3802-45	450.0	1	7	1186	24	73	118	11	60	103	555	81	103	7	13	8	30	39	25	19
PC3802-46	460.0	2	7	1205	26	69	116	9	68	105	510	87	107	6	14	9	29	42	25	21
PC3802-47	470.0	1	8	1230	26	54	98	13	62	101	654	75	93	6	11	9	22	42	29	18
PC3802-48	481.0	2	9	1302	24	54	90	12	59	100	680	73	93	7	10	8	15	49	28	18
PC3802-49	491.0	2	6	1320	23	50	96	8	58	99	672	73	94	7	10	8	14	35	24	19
PC3802-50	501.0	2	8	1337	30	57	97	5	62	100	642	75	95	7	10	8	19	37	26	20
PC3802-51	511.0	1	9	1333	20	55	103	14	61	98	617	80	100	7	14	9	24	39	25	20
PC3802-52	521.0	3	6	1112	23	63	111	13	59	97	533	86	107	7	14	8	22	44	29	20
PC3802-53	531.0	0	2	1090	15	41	86	10	44	84	488	90	123	7	14	8	18	50	28	17
PC3802-54	540.0	2	6	1538	29	76	144	15	80	129	382	102	126	8	17	10	29	58	36	26
PC3802-55	550.0	3	5	1659	33	80	141	12	80	129	365	101	124	8	16	11	31	53	33	27

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APPENDIX C.9. UNCORRECTED TRACE ELEMENTS																				
PC38-02	2525m																			
Sample	Depth	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(cm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
PC3802-56	560.0	2	6	2088	50	83	139	15	90	150	329	101	120	8	12	10	38	54	35	28
PC3802-57	572.0	2	8	2040	33	77	125	16	79	133	445	89	106	7	10	10	26	45	31	26
PC3802-58	582.0	1	7	1963	32	84	123	14	80	130	470	91	112	7	14	10	18	42	30	26
PC3802-59	591.0	2	6	1844	27	79	134	16	79	125	490	93	111	8	17	10	22	47	28	25
PC3802-60	601.0	1	9	1940	23	66	105	8	67	105	765	71	89	6	11	6	20	38	27	23
PC3802-61	611.0	0	9	1704	22	61	111	7	67	101	785	68	88	6	10	7	21	40	24	21
PC3802-62	621.0	1	8	1565	22	59	125	12	65	106	648	77	98	6	17	9	13	34	24	22
PC3802-63	631.0	2	8	1389	23	60	121	16	63	85	635	81	101	7	13	8	19	46	31	22
PC3802-64	641.0	1	8	1597	23	69	129	13	67	112	564	87	108	8	11	10	19	40	30	25
PC3802-65	651.0	1	5	1775	24	79	137	17	76	127	462	95	115	7	12	10	22	43	29	25
PC3802-66	662.0	1	5	2303	28	85	128	6	82	132	511	89	111	8	12	9	19	49	30	24
PC3802-67	671.0	1	11	1922	24	65	101	12	65	103	736	70	90	6	12	8	14	39	28	19
PC3802-68	681.0	0	9	1447	22	63	125	16	59	104	674	79	100	7	13	9	20	41	28	18
PC3802-69	691.0	1	9	1299	25	65	118	15	57	104	598	85	108	7	16	8	24	38	26	18
PC3802-70	701.0	1	8	1283	23	64	107	10	59	101	618	83	106	8	14	7	17	45	31	18
PC3802-71	711.0	1	7	1459	22	70	116	15	56	102	610	83	103	7	10	8	21	42	25	19
PC3802-72	721.0	1	6	1458	24	68	103	12	62	108	589	83	104	7	10	5	22	44	25	20
PC3802-73	731.0	0	8	1421	25	64	110	15	63	102	587	84	103	8	12	9	14	50	30	21
PC3802-74	741.0	2	8	1352	29	61	110	13	69	109	551	84	105	7	10	9	22	40	30	23
PC38-11	3835m																			
PC3811-01	3.0	6	10	1212	51	116	132	16	122	163	245	94	154	9	15	9	25	49	28	25
PC3811-02	13.0	19	9	404	54	96	100	11	35	111	332	76	163	8	14	8	16	38	25	20
PC3811-03	23.0	13	7	371	46	79	96	12	28	96	318	72	214	9	14	8	21	47	28	23
PC3811-04	33.0	2	13	1908	47	111	132	15	134	173	247	97	136	9	10	10	21	38	29	28
PC3811-05	43.0	2	11	1330	53	110	123	17	97	150	242	97	131	9	10	9	28	46	28	24
PC3811-06	53.0	4	10	923	54	102	116	15	77	132	242	97	129	9	12	8	21	50	28	21
PC3811-07	63.0	5	12	790	48	95	123	15	70	128	226	97	133	9	13	9	30	51	30	10
PC3811-08	73.0	7	7	828	44	87	122	12	70	127	265	97	135	9	14	9	22	53	28	20
PC3811-09	85.0	4	5	661	31	66	96	13	34	80	366	82	158	8	14	9	23	47	29	22
PC3811-10	95.0	10	9	798	43	86	118	11	65	120	289	92	127	9	14	9	22	49	25	20

APPENDIX C.9. UNCORRECTED TRACE ELEMENTS

PC38-11	3835m																			
Sample	Depth	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(cm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
PC3811-11	105.0	10	5	734	45	89	113	15	65	118	303	90	122	8	12	10	23	49	28	20
PC3811-12	116.0	9	4	816	44	91	116	16	104	153	271	92	123	9	15	9	19	35	26	20
PC3811-13	125.0	10	5	851	43	91	123	10	71	124	277	95	124	9	14	9	22	44	30	20
PC3811-14	135.0	9	5	777	43	89	119	10	59	117	298	92	125	8	12	7	23	53	30	20
PC3811-15	145.0	9	6	859	43	88	120	15	67	122	277	95	126	8	13	8	29	41	27	20
PC3811-16	155.0	8	8	695	38	83	112	14	54	112	326	88	128	8	12	9	23	36	27	20
PC3811-17	165.0	8	8	815	40	83	118	12	62	120	292	94	122	9	14	9	25	41	26	20
PC3811-18	175.0	7	9	800	39	82	107	13	54	105	349	88	138	9	13	8	23	55	31	23
PC3811-19	186.0	11	9	1014	51	97	120	12	88	138	265	97	125	9	12	10	24	49	29	23
PC3811-20	197.0	10	6	1002	51	98	122	14	83	138	249	98	120	9	13	8	30	45	28	22
PC3811-21	204.0	6	5	1046	53	103	125	17	85	137	232	100	121	9	11	9	24	47	29	23
PC3811-22	215.0	8	10	1053	47	88	111	11	77	122	340	87	124	9	11	7	20	46	29	22
PC3811-23	225.0	9	6	1309	56	94	117	15	102	141	308	92	115	8	10	9	25	46	26	23
PC3811-24	235.0	10	10	1308	60	98	114	13	105	145	289	95	117	8	12	8	26	43	31	24
PC3811-25	245.0	11	10	1367	59	99	122	16	111	146	300	93	115	8	10	9	22	41	29	24
PC3811-26	255.0	11	9	1343	57	89	100	10	103	135	341	83	107	7	8	8	22	43	28	23
PC3811-27	265.0	10	9	1392	56	90	105	15	110	137	326	85	109	8	10	8	22	36	24	24
PC3811-28	275.0	9	9	1410	53	92	109	13	112	137	298	86	112	8	10	8	22	35	23	25
PC3811-29	285.0	8	10	1270	52	105	128	18	100	146	229	106	137	9	13	9	29	49	31	26
PC3811-30	297.0	6	9	1147	51	99	129	14	101	144	243	105	137	9	13	10	23	48	31	25
PC3811-31	305.0	8	7	1349	43	103	138	16	110	143	226	108	144	10	12	15	30	51	34	28
PC3811-32	315.0	7	10	1069	45	106	135	16	98	143	226	108	154	10	17	11	25	50	30	27
PC3811-33	325.0	16	17	489	56	89	96	5	45	99	412	69	164	8	13	7	20	45	24	23
PC3811-34	335.0	10	10	1537	52	97	121	15	113	150	231	100	126	9	10	9	23	42	27	25
PC3811-35	345.0	11	9	1452	57	101	121	13	116	153	235	99	124	9	11	9	25	42	31	25
PC3811-36	355.0	9	8	1636	54	97	115	16	113	141	236	90	116	8	10	8	20	37	26	26
PC3811-37	365.0	8	4	1486	61	107	112	15	119	152	230	93	120	9	10	8	23	43	31	28
PC3811-38	375.0	9	8	1199	71	105	122	14	121	157	235	98	121	9	11	10	26	46	30	26
PC3811-39	385.0	14	9	1278	58	107	131	14	111	167	245	106	132	10	17	11	30	50	29	29
PC3811-40	395.0	11	7	1261	51	100	139	19	115	150	249	103	131	10	13	9	29	45	28	30
PC3811-41	405.0	12	8	1309	53	101	145	16	121	149	247	104	128	9	15	11	32	55	34	30
PC3811-42	415.0	10	8	1794	47	106	147	15	136	150	223	105	135	10	13	10	28	47	28	32

APPENDIX C.10. SALT-CORRECTED TRACE ELEMENTS																				
BC38-02	2530m	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
Sample	Depth	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
	(cm)																			
BC3802-01	0.5	2	0	2289	29	90	111	13	55	126	436	84	118	8	13	10	27	43	25	33
BC3802-02	1.5	2	1	2298	27	88	112	12	56	129	424	84	118	7	14	9	27	44	23	32
BC3802-03	2.5	2	1	2247	27	92	107	13	56	127	425	83	115	8	13	8	23	40	24	31
BC3802-04	3.5	2	0	2193	27	91	111	13	55	127	433	82	115	8	13	9	24	42	23	31
BC3802-05	4.5	1	0	2219	27	89	111	13	57	126	443	82	118	8	13	10	24	41	24	30
BC3802-06	5.5	0	1	2185	27	91	112	9	57	124	439	81	115	6	15	7	16	42	24	30
BC3802-07	6.5	1	1	2153	29	91	118	13	60	126	438	82	113	7	14	7	22	41	23	31
BC3802-08	7.5	1	2	2122	27	92	123	12	61	186	438	81	112	7	12	7	21	41	22	31
BC3802-09	8.5	1	2	2168	28	90	133	13	63	131	437	83	117	7	14	8	22	43	14	30
BC3802-10	9.5	1	1	2185	27	91	134	13	63	130	451	83	117	7	14	8	23	39	22	31
BC3802-11	11.0	2	2	2272	30	96	123	12	64	135	497	86	121	7	13	7	21	44	24	32
BC3802-12	13.0	0	4	2128	28	89	116	11	57	130	520	79	113	7	13	7	25	40	22	30
BC3802-13	15.0	1	3	2040	26	82	126	9	64	122	525	76	107	7	11	8	25	38	22	29
BC3802-13A	17.0	1	5	1857	25	76	111	5	56	113	602	70	104	7	8	6	24	38	22	28
BC3802-14	19.0	1	6	1835	26	73	115	4	61	111	650	67	97	6	8	5	21	36	22	27
BC3802-15	21.0	2	8	1779	27	71	108	1	58	112	690	67	97	6	8	4	20	37	20	27
BC3802-16	23.0	1	9	1698	25	69	94	0	51	104	687	64	92	6	9	5	21	32	21	26
BC3802-17	25.0	1	9	1712	26	69	94	0	52	105	703	65	94	7	8	5	20	33	20	26
BC3802-18	27.0	1	9	1597	25	67	87	0	48	102	694	64	97	6	7	5	22	39	21	27
BC3802-19	29.0	2	9	1536	27	66	86	0	46	101	721	64	95	6	7	4	18	36	21	26
BC3802-20	31.0	2	8	1457	27	67	84	0	45	98	699	63	95	5	8	4	17	34	20	25
BC3802-21	33.0	2	7	1471	30	69	88	0	48	105	696	66	93	6	7	4	15	33	20	26
BC3802-21A	35.0	3	9	1211	37	64	92	2	48	100	626	70	95	7	12	4	23	36	20	23
BC3802-22	37.0	2	7	1339	31	66	90	1	47	101	667	69	98	6	9	5	19	34	20	25
BC3802-23	39.0	1	6	1383	28	66	87	0	45	101	680	66	95	6	8	5	20	35	20	24
BC3802-24	41.0	3	8	1275	33	65	95	0	50	99	661	69	98	6	8	5	18	36	20	22
BC3802-25	43.0	3	7	1351	34	66	103	0	52	102	638	71	102	6	10	6	20	32	20	22
BC3802-26	45.0	2	8	1373	32	65	106	0	52	102	631	72	103	6	10	7	21	39	21	22
BC3802-27	47.0	3	8	1379	32	64	108	1	52	101	624	72	103	6	10	6	22	37	21	23
BC3802-28	49.0	3	8	1433	33	66	110	0	53	105	628	72	104	6	13	6	18	38	21	24
BC3802-29	51.0	3	7	1428	32	65	108	0	54	104	617	72	104	6	9	5	18	33	21	25
BC3802-30	53.0	3	8	1412	32	64	105	3	52	103	609	72	105	6	12	6	10	32	21	24

APPENDIX C.10. SALT-CORRECTED TRACE ELEMENTS																				
BC38-03	4289m	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
Sample	Depth	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
	(cm)																			
BC3803-01	0.5	3	1	1889	24	85	131	14	122	121	243	90	114	7	19	11	13	43	23	20
BC3803-02	1.5	2	1	1842	22	85	124	12	117	114	236	88	113	8	15	11	22	41	20	20
BC3803-03	2.5	0	1	1853	22	87	120	14	119	115	234	88	113	8	15	10	23	37	19	19
BC3803-04	3.5	0	2	1802	23	83	119	11	121	114	225	86	110	8	14	10	20	36	19	20
BC3803-05	4.5	2	2	1927	27	86	138	13	134	119	230	90	114	8	14	11	20	38	20	21
BC3803-06	5.5	1	3	1898	24	85	130	13	124	115	221	88	109	8	15	11	20	42	21	20
BC3803-07	6.5	1	3	1858	25	83	128	12	121	117	219	87	112	8	14	10	21	43	21	20
BC3803-08	7.5	1	4	1891	24	84	125	12	124	144	224	89	116	8	14	11	17	39	21	21
BC3803-09	8.5	2	6	1904	28	84	127	12	125	119	226	90	115	8	15	11	19	44	22	21
BC3803-10	9.5	2	7	2023	29	88	138	12	140	128	235	94	122	8	16	10	18	43	21	24
BC3803-11	11.0	2	7	1936	29	89	143	12	137	127	228	92	118	9	16	13	18	39	22	23
BC3803-12	13.0	2	8	2003	36	89	141	13	134	130	229	92	120	9	14	11	17	42	23	23
BC3803-13	15.0	2	8	1970	29	85	139	13	135	130	232	91	119	8	15	11	20	40	23	23
BC3803-14	17.0	3	9	2071	38	90	142	14	145	136	236	94	124	9	14	10	20	44	24	24
BC3803-15	19.0	3	8	2013	40	86	133	15	138	131	234	91	120	9	13	10	20	43	23	23
BC3803-16	21.0	4	7	2017	29	84	127	12	137	130	229	89	119	9	14	11	25	41	21	22
BC3803-17	23.0	2	6	1952	33	85	125	14	139	127	231	88	116	9	14	11	21	40	21	21
BC3803-18	25.0	3	8	2014	33	86	131	13	138	132	232	89	120	9	14	11	20	41	21	22
BC3803-19	27.0	4	9	1960	31	82	129	14	132	131	229	86	116	9	13	11	23	41	20	22
BC3803-20	29.0	3	9	2079	32	86	135	14	140	139	240	90	123	9	14	11	16	39	22	22
BC3803-21	31.0	3	9	2013	30	82	130	14	131	132	238	88	121	9	13	12	17	44	25	22
BC3803-22	33.0	4	9	2039	30	82	131	15	134	133	237	87	122	8	12	8	14	45	23	22
BC3803-23	35.0	3	9	2012	31	83	127	14	132	132	234	85	119	8	12	8	23	42	23	22
BC3803-24	37.0	2	9	2039	34	84	131	14	133	136	243	89	126	8	13	10	17	45	23	24
BC3803-25	39.0	3	10	2002	35	84	135	13	136	139	247	89	126	9	13	9	22	46	23	25
BC3803-26	41.0	2	10	1943	32	84	134	15	126	136	240	90	124	9	13	12	22	43	22	23
BC3803-27	43.0	2	9	1857	39	84	129	13	120	132	239	89	125	8	14	11	16	44	22	23
BC3803-28	45.0	3	10	1867	32	84	128	13	117	131	236	87	123	8	13	10	21	46	22	23
BC3803-29	47.0	3	10	1831	34	82	128	13	116	133	237	87	122	8	13	11	22	48	22	23
BC3803-30	49.0	3	9	1822	33	85	127	14	115	133	240	89	126	8	13	11	23	44	22	23
BC3803-31	51.0	2	10	1818	33	86	130	14	111	136	244	92	129	9	13	10	32	47	22	24
BC3803-32	53.0	2	11	1663	33	88	128	14	105	136	237	90	127	9	13	11	24	43	21	23

APPENDIX C.10. SALT-CORRECTED TRACE ELEMENTS																				
PC38-09	148m																			
Sample	Depth	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(cm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
PC3809-01	4.0	68	10	295	66	119	107	10	29	123	199	69	131	9	14	11	19	38	17	17
PC3809-02	13.0	67	10	249	62	110	128	11	25	100	195	67	108	8	16	10	17	32	16	16
PC3809-03	23.0	58	10	293	63	122	123	13	32	109	194	76	137	10	20	12	19	45	19	19
PC3809-04	34.0	57	9	272	64	121	123	10	32	108	179	73	128	9	18	11	20	41	18	18
PC3809-05	43.0	27	8	339	44	99	105	13	23	99	240	74	198	9	17	11	18	45	21	23
PC3809-06	53.0	57	6	269	60	117	118	12	32	116	175	71	113	9	18	11	17	38	16	17
PC3809-07	62.0	99	10	244	75	126	118	9	34	103	195	59	97	8	14	9	21	32	14	15
PC3809-08	73.0	40	9	303	57	127	119	12	27	109	188	76	148	10	18	12	18	48	21	22
PC3809-09	84.0	47	7	316	62	137	137	13	33	123	168	89	136	11	21	13	22	48	22	21
PC3809-10	94.0	68	8	294	69	131	143	12	40	121	170	84	122	9	22	12	23	44	19	18
PC3809-11	104.0	84	10	295	67	121	146	11	34	122	151	74	103	8	21	11	17	40	17	16
PC3809-12	113.0	37	9	322	56	124	142	15	51	147	166	93	131	9	26	14	27	46	22	22
PC3809-13	124.0	40	10	332	52	130	117	12	21	104	214	78	168	11	19	12	23	49	23	22
PC3809-14	134.0	62	9	278	61	119	118	10	27	93	213	67	147	9	15	9	15	42	19	18
PC3809-15	144.0	68	8	261	65	119	108	10	25	93	183	62	116	8	17	10	20	36	16	16
PC3809-16	152.0	46	7	226	53	97	107	10	26	92	180	63	117	9	16	10	10	30	15	15
PC3809-17	165.0	52	10	250	53	90	105	9	24	89	220	57	138	8	14	8	13	34	16	17
PC3809-18	174.0	28	9	341	45	100	99	9	20	93	243	70	204	9	16	9	18	45	22	22
PC3809-19	185.0	32	11	322	43	81	85	10	19	86	289	60	213	7	13	8	14	36	18	21
PC3809-20	194.0	28	8	349	39	77	85	9	20	90	306	61	232	8	11	7	15	40	19	24
PC3809-21	205.0	39	5	441	36	62	115	14	35	123	256	70	153	8	18	9	16	41	19	22
PC3809-22	214.0	55	13	286	73	116	104	8	24	96	256	58	181	7	14	10	16	35	17	19
PC3809-23	224.0	13	11	391	31	57	63	9	9	60	347	55	282	8	10	7	14	47	20	23
PC3809-24	234.0	42	9	319	43	76	79	8	17	72	305	49	201	6	12	7	12	33	16	20
PC3809-25	243.0	74	10	230	64	95	104	8	23	70	185	43	103	7	11	7	2	27	12	13
PC3809-26	257.0	59	10	275	60	107	95	7	20	79	201	50	134	6	13	7	4	32	15	17
PC3809-27	267.0	32	15	336	43	85	78	7	14	86	374	50	190	7	11	6	17	34	19	25
PC3809-28	273.0	53	167	185	43	122	86	0	9	59	1195	30	109	6	4	0	2	27	14	25
PC3809-29	284.0	69	13	246	68	136	122	13	34	105	202	62	108	7	12	8	17	36	17	20
PC3809-30	294.0	79	7	209	68	117	105	8	24	78	170	48	82	5	13	8	11	26	13	15
PC3809-31	304.0	49	8	339	61	127	116	11	35	151	171	63	104	7	13	8	13	32	16	18
PC3809-32	314.0	67	7	263	70	133	122	11	34	100	162	63	91	6	16	9	12	30	13	17

APPENDIX C.10. SALT-CORRECTED TRACE ELEMENTS

PC38-09	148m																			
Sample	Depth	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(cm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
PC3809-33	324.0	50	8	264	75	150	127	13	35	101	187	62	112	7	14	9	16	34	16	21
PC3809-34	335.0	71	8	220	75	137	119	11	29	83	163	51	93	6	14	9	14	29	14	17
PC3809-35	344.0	70	7	203	75	140	115	9	31	88	153	48	85	6	11	8	12	30	14	15
PC3809-36	355.0	78	5	201	65	107	124	8	21	67	156	39	65	4	10	7	10	21	10	11
PC3809-37	364.0	91	5	191	70	106	126	10	23	66	185	39	63	3	11	4	10	20	10	11
PC3809-38	375.0	96	7	253	76	134	143	9	31	84	162	55	88	6	15	7	16	26	13	15
PC3809-39	384.0	58	8	258	65	144	129	13	34	97	214	57	109	7	13	8	21	31	15	19
PC3809-40	394.0	66	8	229	72	128	125	10	29	80	179	50	88	5	12	7	18	30	14	15
PC3809-41	404.0	51	8	262	65	125	124	10	26	88	156	56	96	6	15	8	15	32	14	16
PC3809-42	416.0	84	9	206	69	126	130	10	27	77	202	47	80	5	11	8	10	26	13	14
PC3809-43	424.0	68	8	234	68	121	134	9	25	76	149	53	84	6	14	8	5	27	12	14
PC3809-44	434.0	82	10	263	85	145	156	10	37	92	165	63	96	6	15	10	16	34	15	16
PC3809-45	444.0	64	8	237	56	106	119	10	27	83	186	49	80	5	12	8	12	25	11	14
PC3809-46	453.0	50	8	271	56	128	135	11	31	89	179	60	107	7	14	8	16	31	15	18
PC3809-47	465.0	73	7	245	66	138	130	11	34	93	183	60	93	7	12	7	15	32	15	16
PC3809-48	474.0	98	9	262	67	129	138	9	29	81	201	57	83	6	15	7	15	27	13	14
PC3809-49	483.0	48	9	269	58	131	118	11	29	91	178	61	114	7	13	8	20	31	14	18
PC3809-50	493.0	65	8	1438	61	131	123	11	29	90	276	63	101	7	15	7	13	30	16	16
PC3809-51	504.0	41	9	311	53	136	113	11	29	92	193	64	127	7	14	9	11	35	17	21
PC3809-52	515.0	48	8	304	57	136	117	11	30	93	182	66	116	7	15	8	16	35	17	18
PC3809-53	525.0	78	7	254	66	132	130	10	31	86	194	59	91	6	15	7	16	33	14	15
PC3809-54	536.0	76	5	242	55	116	114	10	27	80	200	54	83	5	13	7	14	28	13	14
PC3809-55	544.0	49	6	313	50	123	124	13	30	96	201	65	115	7	16	9	16	35	16	18
PC3809-56	553.0	52	4	279	39	104	121	12	32	94	198	61	88	6	16	7	15	30	14	15
PC3809-57	564.0	52	4	277	39	102	123	10	29	86	193	55	82	5	16	8	13	25	12	14
PC3809-58	574.0	50	4	275	41	105	115	9	26	89	208	58	91	6	15	7	16	30	13	15
PC3809-59	585.0	37	5	390	34	95	117	9	20	83	282	55	100	6	15	6	14	29	14	15
PC3809-60	594.0	43	5	269	34	95	113	8	20	81	214	55	97	6	15	8	13	27	14	14
PC3809-61	605.0	39	5	284	35	109	117	12	28	97	237	62	113	8	17	9	12	36	16	18
PC3809-62	615.0	35	5	247	33	99	114	10	19	84	234	58	96	6	17	8	12	28	14	15
PC3809-63	625.0	32	5	276	33	102	118	12	25	97	233	60	108	7	17	8	15	29	15	16
PC3809-64	635.0	36	7	278	36	109	127	12	27	92	242	62	109	7	16	8	14	33	15	17

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APPENDIX C.10. SALT-CORRECTED TRACE ELEMENTS																				
PC38-09	148m																			
Sample	Depth	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(cm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
PC3809-65	646.0	47	5	234	38	92	125	9	18	76	201	52	88	5	13	7	12	28	13	13
PC3809-66	654.0	40	7	241	34	94	124	8	18	72	187	50	90	6	13	8	12	26	12	13
PC3809-67	664.0	44	8	253	34	86	127	8	18	74	189	51	82	7	13	7	8	29	13	13
PC3809-68	674.0	37	8	227	28	73	111	7	11	63	171	46	79	5	13	7	14	25	11	12
PC3809-69	684.0	43	7	301	35	96	130	9	21	86	211	63	101	6	16	9	14	34	15	16
PC3809-70	694.0	40	7	285	36	107	137	9	28	90	212	65	104	7	16	7	16	32	15	16
PC3809-71	703.0	53	7	281	38	101	144	10	29	92	201	65	101	6	19	9	18	31	15	16
PC3809-72	714.0	48	7	261	41	103	136	12	25	88	218	58	96	6	15	6	13	32	14	16
PC3809-73	724.0	32	5	302	35	103	125	12	30	92	232	66	106	7	16	7	11	33	16	17
PC3809-74	734.0	33	5	281	36	109	126	12	27	98	238	65	110	7	19	7	17	35	16	17
PC3809-75	744.0	46	7	302	38	98	132	11	28	90	226	65	105	6	18	8	16	38	15	16
PC3809-76	754.0	50	4	256	35	87	121	11	20	84	202	57	99	8	18	6	12	35	14	15
PC3809-77	764.0	40	5	291	35	96	130	11	25	95	217	70	110	8	19	8	16	37	16	18
PC3809-78	774.0	38	4	289	36	102	125	13	26	99	219	69	123	8	19	9	24	39	18	19
PC3809-79	784.0	38	6	276	37	96	122	11	26	95	215	66	114	7	18	8	16	38	18	18
PC3809-80	794.0	33	5	297	34	98	118	12	22	93	222	67	120	7	17	8	21	38	17	18
PC3809-81	804.0	33	5	324	34	99	113	12	23	85	224	61	120	7	14	7	16	36	16	17
PC3809-82	813.0	29	6	311	34	103	113	14	28	90	270	63	122	7	17	7	17	32	16	18
PC3809-83	823.0	29	5	296	35	100	107	10	23	88	230	63	126	8	14	7	19	33	16	19
PC3809-84	834.0	31	5	292	33	104	109	12	24	89	221	64	124	8	17	7	15	34	16	18
PC3809-85	845.0	38	4	299	36	102	115	11	26	84	232	66	119	7	18	7	18	34	17	18
PC3809-86	854.0	31	5	351	30	86	113	12	34	103	205	82	125	9	24	9	21	42	19	20
PC38-10	257m																			
PC3810-01	6.0	52	15	272	114	135	149	9	38	116	346	62	115	8	11	10	17	30	16	20
PC3810-02	14.0	24	20	336	77	106	91	8	25	98	435	59	202	8	10	8	31	42	21	28
PC3810-03	24.0	11	20	358	36	63	54	7	11	57	597	54	246	8	8	5	17	40	20	29
PC3810-04	34.0	18	16	336	39	69	57	5	12	60	494	55	225	7	10	6	19	43	20	29
PC3810-05	44.0	37	15	354	103	144	102	11	28	93	264	65	171	8	13	11	16	39	19	23
PC3810-06	54.0	47	15	326	94	136	128	9	30	95	235	67	163	7	14	9	19	37	17	20
PC3810-07	64.0	39	15	346	76	112	117	9	27	95	284	67	207	8	14	9	23	46	20	23

APPENDIX C.10. SALT-CORRECTED TRACE ELEMENTS

PC38-10 Sample	257m Depth (cm)	Mo (ppm)	U (ppm)	Ba (ppm)	Ni (ppm)	Cr (ppm)	V (ppm)	Sc (ppm)	Cu (ppm)	Zn (ppm)	Sr (ppm)	Rb (ppm)	Zr (ppm)	Nb (ppm)	Pb (ppm)	Th (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Y (ppm)
PC3810-08	74.0	30	16	397	58	104	111	9	23	93	340	70	246	7	16	10	23	47	23	26
PC3810-09	84.0	13	15	389	20	61	61	7	8	71	431	57	231	7	14	7	23	44	23	29
PC3810-10	94.0	41	27	379	30	53	53	6	9	61	504	57	264	8	10	6	17	42	20	29
PC3810-10	104.0	32	16	364	32	55	55	4	10	53	474	54	279	7	10	8	18	41	20	28
PC3810-11	113.0	17	10	346	24	46	46	5	7	51	436	54	244	7	10	6	18	40	20	27
PC3810-12	126.0	49	11	214	58	91	91	6	30	84	348	53	132	6	10	6	20	28	15	19
PC3810-13	134.0	62	13	219	74	104	104	7	34	91	283	55	117	6	11	9	14	28	14	18
PC3810-14	146.0	53	12	281	66	95	104	9	35	98	293	63	156	8	12	8	18	39	18	21
PC3810-15	154.0	46	12	264	69	102	113	8	36	97	350	59	134	7	12	7	17	32	16	20
PC3810-16	167.0	49	12	288	64	101	119	9	31	97	254	65	128	7	13	9	18	35	16	20
PC3810-17	174.0	48	13	312	70	108	122	8	36	100	225	67	132	7	14	10	21	36	16	20
PC3810-18	185.0	35	12	295	58	102	117	8	28	97	189	72	121	7	14	9	18	34	16	20
PC3810-19	194.0	61	11	269	72	100	128	8	41	97	257	60	98	6	12	9	25	30	14	17
PC3810-20	203.0	47	15	340	63	100	135	8	30	111	238	70	148	8	15	9	23	38	18	21
PC3810-21	216.0	66	12	276	73	104	133	9	35	92	263	56	98	6	13	9	14	28	14	17
PC3810-22	224.0	60	12	267	81	112	134	9	40	101	213	60	98	6	15	9	17	29	15	17
PC3810-23	233.0	59	13	301	80	120	145	11	44	107	222	67	119	7	15	10	18	34	17	20
PC3810-24	244.0	45	11	257	65	109	120	10	32	100	283	67	136	7	14	10	18	35	17	20
PC3810-25	254.0	45	15	298	56	92	108	8	24	88	355	58	179	7	14	7	10	38	18	22
PC3810-26	263.0	57	13	287	63	94	120	9	30	86	347	55	141	7	13	6	16	32	15	20
PC3810-27	273.0	44	12	284	70	115	132	9	35	112	283	66	130	8	14	8	19	35	16	21
PC3810-28	284.0	38	13	281	62	102	113	9	30	97	329	63	132	7	12	8	17	35	18	22
PC3810-29	295.0	59	11	234	73	108	123	6	35	89	421	51	74	5	11	6	17	23	13	16
PC3810-30	305.0	37	12	279	63	103	132	9	30	104	320	65	120	7	14	8	30	36	17	21
PC3810-31	314.0	36	12	289	65	109	136	10	30	108	343	67	143	8	12	9	22	39	19	21
PC3810-32	324.0	64	12	263	79	107	150	9	39	96	327	55	86	5	13	6	24	28	15	16
PC3810-33	335.0	35	12	269	76	117	143	8	29	102	302	67	118	8	12	7	22	34	17	20
PC3810-34	344.0	62	11	164	79	100	133	8	32	88	329	46	73	6	11	6	11	26	12	14
PC3810-35	354.0	67	10	228	72	86	132	7	29	81	231	43	65	5	12	5	14	22	11	12
PC3810-36	364.0	68	10	180	69	76	132	7	27	76	270	39	53	4	10	5	16	21	11	12
PC3810-37	374.0	63	12	212	69	82	137	8	24	69	214	42	54	5	10	5	10	22	11	11
PC3810-38	383.0	30	13	289	66	110	141	11	34	109	269	71	103	7	16	9	23	38	17	19

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APPENDIX C.10. SALT-CORRECTED TRACE ELEMENTS																				
PC38-10	257m																			
Sample	Depth	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(cm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
PC3810-39	394.0	44	14	239	86	119	150	9	29	93	250	58	97	6	13	9	19	31	14	18
PC3810-40	404.0	28	13	254	67	112	120	12	25	98	288	64	128	7	14	8	28	35	17	22
PC3810-41	417.0	51	12	242	76	111	119	10	31	96	384	55	105	6	13	7	22	33	16	19
PC3810-42	424.0	47	15	212	83	114	134	8	32	101	300	57	98	7	14	8	21	31	15	18
PC3810-43	434.0	65	10	172	60	73	107	0	16	68	511	26	49	4	5	2	9	17	10	11
PC3810-44	445.0	44	12	200	70	94	127	6	23	81	388	47	68	6	12	6	15	26	13	14
PC3810-45	456.0	74	13	251	82	94	166	8	27	83	352	43	66	5	11	6	13	18	10	13
PC3810-46	467.0	73	6	188	63	69	115	2	17	63	347	28	41	3	8	3	14	17	10	10
PC3810-47	476.0	36	17	268	88	121	138	7	30	101	436	57	101	7	10	7	20	31	17	20
PC3810-48	484.0	36	15	255	91	118	130	8	31	94	453	53	97	6	12	7	16	31	16	20
PC3810-49	494.0	39	24	271	92	119	110	3	27	83	473	47	135	6	8	6	19	31	17	26
PC3810-50	504.0	15	22	318	44	66	64	7	14	62	642	50	239	8	7	4	20	39	19	33
PC3810-51	514.0	67	6	293	53	94	128	12	26	86	197	56	110	7	15	7	15	32	15	17
PC3810-52	524.0	53	6	348	46	84	135	10	27	89	193	59	119	7	16	7	17	37	16	18
PC3810-53	534.0	129	23	394	165	182	363	9	49	89	274	48	73	5	12	6	10	24	12	15
PC3810-54	545.0	111	17	329	129	148	277	10	36	79	242	50	77	5	12	7	13	23	13	15
PC3810-55	554.0	125	18	339	131	146	304	9	40	81	285	46	66	5	11	6	12	24	11	13
PC3810-56	564.0	95	10	313	72	106	219	7	22	61	413	39	70	4	10	5	11	23	12	12
PC3810-57	574.0	85	11	319	78	120	256	6	26	72	476	45	86	5	10	4	14	25	13	14
PC3810-58	584.0	80	9	346	73	113	208	9	25	72	420	44	79	5	10	4	13	23	12	14
PC3810-59	596.0	87	23	356	75	120	261	8	25	72	411	44	82	5	12	5	11	23	12	14
PC3810-60	604.0	88	17	388	73	121	250	6	27	74	448	45	77	5	11	4	13	26	12	15
PC3810-61	614.0	86	15	344	71	119	252	10	26	75	352	51	87	6	13	5	13	27	13	14
PC3810-62	624.0	78	10	334	72	116	248	7	25	84	424	56	94	6	15	6	15	30	16	17
PC3810-63	634.0	64	9	299	69	122	217	6	28	76	452	52	95	6	12	6	13	28	14	16
PC3810-64	645.0	89	11	383	64	108	214	9	27	73	318	54	82	6	14	8	12	29	14	15
PC3810-65	655.0	116	9	343	76	111	227	8	25	75	328	49	75	5	14	6	14	23	14	14
PC3810-66	667.0	106	11	299	74	114	225	10	27	83	331	55	84	6	16	6	16	27	14	16
PC3810-67	674.0	97	14	281	72	121	222	11	31	102	256	69	96	6	21	9	21	35	16	16
PC3810-68	683.0	92	11	254	70	110	214	10	28	95	271	65	85	6	21	6	14	35	16	14
PC3810-69	694.0	59	10	319	58	120	173	12	27	121	235	86	122	8	24	10	19	44	20	19
PC3810-70	704.0	48	8	347	52	134	169	11	28	122	194	97	137	9	24	11	21	47	21	22

APPENDIX C.10. SALT-CORRECTED TRACE ELEMENTS																				
PC38-10	257m																			
Sample	Depth	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(cm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
PC3810-71	714.0	69	8	325	54	115	162	12	29	118	252	87	113	8	22	9	20	40	18	19
PC3810-72	724.0	78	10	289	52	96	155	10	23	102	259	76	96	6	22	8	17	35	18	16
PC3810-74	734.0	59	11	329	48	109	153	13	25	116	185	88	129	8	26	13	19	46	21	19
PC3810-75	745.0	37	10	369	41	102	145	12	33	135	202	99	162	8	28	12	26	49	23	21
PC3810-76	754.0	52	10	296	51	105	134	9	31	106	195	81	163	8	20	11	19	36	18	17
PC3810-77	764.0	30	11	383	36	97	116	12	21	103	298	83	224	9	20	11	26	50	23	25
PC38-02	2525m																			
	(Age)																			
PC3802-01	2.76	0	9	2151	29	88	129	17	74	130	535	83	107	7	10	7	17	35	23	24
PC3802-02	6.21	0	6	1856	27	77	102	8	70	115	642	73	97	7	11	7	15	42	31	20
PC3802-03	9.66	0	8	1779	23	73	95	13	59	109	682	73	97	7	9	7	20	28	24	20
PC3802-04	12.77	2	8	1265	47	84	97	12	66	120	569	85	104	6	10	9	22	35	28	18
PC3802-05	15.18	2	8	1304	35	75	104	14	65	109	619	81	103	7	12	8	17	43	22	18
PC3802-06	17.47	3	6	1228	37	71	102	13	62	105	608	80	101	7	13	7	19	31	26	19
PC3802-07	20.48	1	6	1532	36	85	115	12	73	111	584	82	108	6	12	9	19	48	33	21
PC3802-08	22.65	3	7	1434	38	78	115	8	70	114	576	83	106	7	11	7	24	43	28	20
PC3802-09	25.22	2	10	1409	36	72	107	14	71	110	624	79	102	7	9	7	10	42	29	19
PC3802-10	28.29	2	6	1370	33	62	101	9	67	108	668	74	96	7	9	6	20	31	27	19
PC3802-11	31.07	3	7	1352	31	66	93	11	64	106	671	72	94	6	9	6	16	41	28	17
PC3802-12	33.86	4	7	1316	34	61	82	11	61	105	704	68	89	7	8	6	14	38	27	17
PC3802-13	36.64	4	8	1391	35	59	92	12	63	104	695	74	95	7	7	10	15	38	27	18
PC3802-14	39.15	3	7	1499	33	70	101	12	72	120	596	83	109	7	11	8	24	39	25	20
PC3802-15	42.22	4	6	1406	36	67	103	8	67	94	582	83	106	6	10	7	15	41	31	20
PC3802-16	45.00	3	5	1499	28	73	127	10	70	120	549	90	119	7	13	9	21	45	32	21
PC3802-17	48.07	3	10	1536	29	77	125	16	81	132	511	92	121	8	14	7	26	44	27	23
PC3802-18	50.85	3	10	1618	34	75	125	18	72	124	460	90	118	8	11	9	26	45	26	22
PC3802-19	53.64	2	11	1767	36	83	124	12	77	129	502	87	117	7	11	9	22	53	34	24
PC3802-20	56.42	2	9	1670	37	88	123	11	80	134	462	92	129	7	12	9	22	40	26	24
PC3802-21	59.29	3	9	1522	38	80	123	15	83	130	491	93	120	7	13	11	19	44	31	24
PC3802-22	62.61	3	10	1541	33	76	121	6	80	104	512	91	119	8	14	10	25	43	35	24
PC3802-23	65.94	3	5	1393	31	75	135	16	81	124	459	95	122	8	14	10	25	39	28	25

APPENDIX C.10. SALT-CORRECTED TRACE ELEMENTS																				
PC38-02	(2525m)																			
Sample	Age	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(ka)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
PC3802-24	69.26	1	7	1833	28	87	149	13	84	141	362	106	137	8	17	12	27	42	29	26
PC3802-25	72.58	3	9	1748	36	81	135	15	84	145	399	100	126	8	12	9	25	40	30	26
PC3802-26	76.96	2	9	1966	33	72	117	13	79	138	492	89	117	8	11	10	22	43	31	25
PC3802-27	82.03	3	7	1963	38	81	141	14	85	149	363	102	132	8	12	11	24	40	27	26
PC3802-28	87.11	2	8	1828	36	81	138	15	87	141	376	103	131	9	14	10	31	46	28	26
PC3802-29	92.18	1	8	1959	34	85	150	17	84	148	311	112	138	9	16	11	31	47	30	26
PC3802-30	97.26	2	9	2124	29	87	167	21	93	149	336	108	135	11	15	11	28	43	28	28
PC3802-31	102.84	2	11	2001	35	82	144	16	91	145	403	96	124	7	11	10	21	39	32	28
PC3802-32	107.92	2	10	2091	34	85	154	15	88	141	398	98	123	7	13	10	29	39	29	27
PC3802-33	113.00	1	6	2010	35	88	149	15	80	142	403	95	121	8	13	8	26	42	31	28
PC3802-34	118.07	2	8	2424	28	90	139	14	77	139	435	95	121	8	15	10	27	48	32	28
PC3802-35	123.15	1	9	1984	27	74	111	12	68	120	560	81	104	6	12	8	21	48	30	22
PC3802-36	128.22	2	7	1405	28	76	110	13	59	111	621	80	99	7	13	8	20	41	29	18
PC3802-37	132.23	1	8	1306	26	77	110	10	56	104	651	81	100	7	11	7	17	42	28	19
PC3802-38	135.30	1	7	1333	23	76	121	11	58	97	667	80	101	7	6	8	22	40	30	19
PC3802-39	138.71	1	9	1299	25	69	110	7	58	93	651	76	100	7	13	7	19	40	27	20
PC3802-40	141.79	1	8	1360	23	63	97	11	59	101	683	75	100	7	11	8	20	40	30	19
PC3802-41	145.20	2	5	1368	23	62	108	12	63	105	684	77	94	6	9	7	18	31	27	19
PC3802-42	148.61	1	6	1252	23	63	101	14	55	101	674	75	101	7	10	8	17	40	27	19
PC3802-43	152.02	0	7	1098	22	62	109	14	56	94	692	74	95	6	10	7	20	35	23	19
PC3802-44	155.44	1	12	1257	20	66	116	12	58	96	661	78	100	7	11	7	26	45	26	19
PC3802-45	158.85	1	8	1236	25	76	123	11	63	107	578	85	107	7	13	8	31	40	26	20
PC3802-46	162.26	2	7	1255	27	72	121	9	71	110	531	90	111	7	15	9	30	44	26	22
PC3802-47	165.68	1	9	1277	26	56	101	13	64	105	680	77	97	6	12	9	23	43	30	19
PC3802-48	169.43	2	10	1353	25	56	93	12	61	104	706	76	97	7	10	8	16	50	29	19
PC3802-49	172.84	2	6	1372	24	52	99	8	61	103	699	76	98	7	10	8	15	36	25	20
PC3802-50	176.26	2	8	1392	32	59	101	6	65	104	668	78	99	7	10	8	20	39	27	20
PC3802-51	179.67	1	10	1385	21	57	107	14	63	102	641	83	104	7	14	9	25	40	26	21
PC3802-52	183.08	3	6	1156	23	66	115	13	61	101	555	90	112	7	15	8	23	46	30	20
PC3802-53	186.50	0	2	1126	16	43	89	11	45	87	505	93	127	8	14	8	18	51	29	17
PC3802-54	189.57	2	6	1604	30	79	150	15	83	135	398	106	131	9	17	11	30	60	38	27
PC3802-55	193.52	3	6	1733	34	83	147	12	84	134	382	106	130	8	17	11	33	55	34	29

APPENDIX C.10. SALT-CORRECTED TRACE ELEMENTS																				
PC38-02	(2525m)																			
Sample	Age	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(ka)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
PC3802-56	197.42	3	7	2189	53	87	146	16	94	157	345	105	125	9	12	11	40	56	37	29
PC3802-57	202.11	2	9	2097	34	79	128	16	81	137	457	91	109	8	10	10	27	46	31	27
PC3802-58	206.02	1	7	2019	32	86	126	14	82	134	483	93	116	7	14	10	18	43	31	27
PC3802-59	209.53	2	7	1912	28	82	139	16	82	129	509	96	115	8	17	10	23	48	29	26
PC3802-60	213.44	1	9	2007	24	68	108	8	70	109	791	74	92	6	12	6	20	39	28	24
PC3802-61	217.34	0	9	1763	23	63	115	7	69	105	812	70	91	6	11	7	22	42	25	22
PC3802-62	221.25	1	8	1621	23	61	129	13	68	109	671	80	102	6	17	9	14	36	25	23
PC3802-63	225.16	2	8	1435	23	62	125	16	65	88	656	83	104	7	13	8	19	47	32	22
PC3802-64	229.06	1	8	1653	24	72	133	14	70	116	584	90	112	8	11	10	20	41	31	25
PC3802-65	232.97	1	5	1845	24	82	142	17	79	132	480	99	120	8	13	10	23	44	31	26
PC3802-66	237.27	1	5	2399	29	89	133	6	85	137	532	93	116	8	13	9	20	51	32	25
PC3802-67	240.78	1	12	2001	25	68	105	12	68	107	766	73	93	6	13	8	15	40	29	20
PC3802-68	244.50	0	9	1503	23	66	129	17	62	108	700	82	104	7	14	9	21	43	29	18
PC3802-69	247.71	1	9	1351	26	67	122	15	60	108	622	88	112	7	16	9	25	39	27	19
PC3802-70	250.91	1	9	1332	24	66	111	11	61	105	641	86	110	8	14	7	17	47	32	19
PC3802-71	254.12	1	8	1518	23	72	121	15	58	106	635	86	107	7	11	8	22	43	26	20
PC3802-72	257.32	1	6	1517	25	71	107	13	65	112	613	86	108	7	10	5	23	46	26	20
PC3802-73	260.53	0	8	1477	26	67	114	15	65	106	610	87	107	8	13	10	14	51	31	22
PC3802-74	263.73	2	8	1406	30	63	114	13	72	114	573	87	109	7	10	9	23	41	31	24
PC38-11	(3835m)																			
PC3811-01	0.80	6	11	1276	54	122	139	17	128	172	258	99	162	9	16	9	26	52	30	27
PC3811-02	2.00	19	9	423	56	100	105	11	37	116	348	79	171	9	15	8	16	40	26	21
PC3811-03	2.20	13	8	385	47	82	100	12	29	99	330	75	222	10	14	8	21	48	29	24
PC3811-04	3.49	3	14	2015	49	117	140	16	141	182	261	102	144	9	11	10	22	40	31	30
PC3811-05	6.17	2	11	1409	56	116	130	18	102	159	256	102	138	9	11	10	30	49	30	26
PC3811-06	8.85	4	11	975	57	108	122	16	82	140	255	103	137	10	13	9	22	53	30	22
PC3811-07	11.53	5	12	834	51	100	130	16	74	136	239	103	140	10	14	9	32	54	32	10
PC3811-08	13.80	7	8	871	46	92	128	12	73	133	279	102	142	9	14	9	23	56	30	21
PC3811-09	16.44	4	5	677	31	67	98	13	35	82	376	84	162	9	14	9	23	48	29	23
PC3811-10	18.63	10	9	838	45	91	124	11	69	126	303	97	133	9	14	9	23	52	26	21

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APPENDIX C.10. SALT-CORRECTED TRACE ELEMENTS																				
PC38-11	(3835m)																			
Sample	Depth	Mo	U	Ba	Ni	Cr	V	Sc	Cu	Zn	Sr	Rb	Zr	Nb	Pb	Th	La	Ce	Nd	Y
	(cm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
PC3811-11	20.82	10	6	771	47	93	118	16	69	124	318	95	128	8	12	10	24	52	29	21
PC3811-12	23.23	9	5	857	46	95	122	16	109	161	285	97	129	9	16	9	20	36	27	20
PC3811-13	25.11	10	5	895	45	95	130	11	74	130	291	100	130	10	15	10	23	46	32	21
PC3811-14	27.10	10	6	815	45	93	125	11	62	123	313	96	131	9	12	8	24	56	31	21
PC3811-15	29.09	10	6	904	45	93	126	16	71	128	291	99	133	9	14	8	31	43	29	21
PC3811-16	31.08	8	9	727	40	87	117	15	56	117	341	92	133	9	13	9	24	38	28	21
PC3811-17	33.07	9	8	860	42	88	124	12	66	126	308	99	129	9	15	9	26	44	27	21
PC3811-18	35.07	7	9	829	40	85	111	14	56	109	362	91	143	9	13	9	24	57	32	24
PC3811-19	37.26	11	9	1067	53	102	126	12	93	145	279	102	131	9	12	11	26	52	31	24
PC3811-20	39.45	10	6	1056	54	104	128	15	87	146	262	104	127	10	13	8	31	47	29	23
PC3811-21	40.84	6	6	1103	55	108	132	18	90	144	245	106	127	9	12	9	25	49	31	24
PC3811-22	43.03	9	11	1109	49	93	117	12	81	128	358	92	130	9	12	7	21	48	30	24
PC3811-23	45.03	9	7	1385	59	99	123	16	107	149	325	97	122	8	11	10	27	48	28	25
PC3811-24	47.02	11	10	1380	63	104	120	13	110	153	305	100	123	9	13	8	27	45	33	26
PC3811-25	49.01	11	10	1441	62	104	129	17	117	154	316	98	121	8	10	9	23	44	31	25
PC3811-26	51.00	11	10	1414	59	93	106	11	109	142	359	88	112	8	8	8	23	46	30	25
PC3811-27	52.99	11	10	1467	59	95	111	15	116	145	343	89	114	8	11	9	23	38	25	25
PC3811-28	54.99	9	10	1486	55	97	115	13	118	144	314	91	119	8	10	8	23	37	24	26
PC3811-29	56.98	8	10	1335	54	110	134	19	105	154	241	112	144	10	14	10	30	51	32	27
PC3811-30	59.62	6	9	1194	54	103	134	15	105	150	253	109	143	9	14	10	24	50	33	26
PC3811-31	62.28	8	7	1408	45	107	144	17	115	149	236	112	150	10	12	16	31	53	35	29
PC3811-32	65.60	7	10	1114	47	111	141	17	102	149	235	113	160	11	18	11	26	53	32	28
PC3811-33	68.93	16	17	501	57	91	98	5	46	102	423	71	168	8	13	7	21	46	24	24
PC3811-34	72.25	10	10	1613	54	102	127	16	119	157	243	104	133	10	11	9	24	44	28	26
PC3811-35	74.95	11	9	1525	59	106	127	14	122	160	247	104	130	9	12	9	27	44	32	26
PC3811-36	77.04	10	9	1721	57	102	121	17	119	148	248	95	122	9	10	9	21	39	27	27
PC3811-37	79.12	9	4	1561	64	112	117	16	125	159	241	97	126	9	10	9	24	45	33	29
PC3811-38	81.20	10	9	1258	74	111	128	15	127	165	247	103	127	9	11	11	27	49	31	27
PC3811-39	83.29	14	9	1337	61	112	137	15	116	175	256	110	138	10	18	11	31	52	30	30
PC3811-40	85.37	11	7	1316	53	105	146	20	120	156	260	107	137	10	13	9	30	47	29	31
PC3811-41	87.45	12	8	1368	56	106	151	16	127	155	258	108	134	10	15	12	33	57	35	31
PC3811-42	89.54	10	8	1874	49	111	154	16	142	157	233	110	141	10	13	10	29	49	29	33

APPENDIX C.11. TRACE ELEMENT RATIOS								
CD38-02	Box	(2530m)						
Sample	Depth	I/Org.C	Br/Org.C	I/Br	Ba/Al	Zr/Rb	K/Rb	Mo/U
	(cm.)	(x10-4)	(x10-4)		(x10-4)		(x10-3)	
BC3802-01	0.5	343.1	101.4	3.38	352.70	1.41	20.42	3.50
BC3802-02	1.5	312.5	83.5	3.74	349.24	1.41	20.73	2.83
BC3802-03	2.5	357.3	127.2	2.81	352.19	1.39	20.60	2.86
BC3802-04	3.5	298.9	119.5	2.50	345.35	1.41	20.21	3.50
BC3802-05	4.5	271.0	107.4	2.52	349.45	1.43	21.24	0.00
BC3802-06	5.5	260.9	127.0	2.05	350.16	1.42	21.42	0.31
BC3802-07	6.5	235.9	131.2	1.80	334.84	1.39	21.37	1.20
BC3802-08	7.5	212.0	117.5	1.80	341.71	1.38	21.13	0.74
BC3802-09	8.5	214.8	110.4	1.95	342.50	1.41	21.34	0.72
BC3802-10	9.5	208.2	95.4	2.18	347.38	1.41	20.77	1.00
BC3802-11	11.0	223.3	70.4	3.17	343.72	1.40	20.67	0.94
BC3802-12	13.0	180.9	60.4	2.99	363.14	1.43	20.83	0.00
BC3802-13	15.0	175.9	95.0	1.85	352.33	1.42	21.66	0.32
BC3802-13	17.0	127.6	66.0	1.93	337.02	1.48	21.44	0.30
BC3802-14	19.0	154.6	75.1	2.06	362.65	1.45	21.19	0.14
BC3802-15	21.0	165.6	57.1	2.90	356.51	1.45	21.25	0.27
BC3802-16	23.0	157.1	74.5	2.11	350.83	1.44	21.00	0.16
BC3802-17	25.0	153.1	49.1	3.12	353.72	1.45	21.11	0.13
BC3802-18	27.0	161.7	76.1	2.12	336.21	1.52	20.41	0.16
BC3802-19	29.0	154.8	46.8	3.31	327.51	1.49	20.45	0.25
BC3802-20	31.0	168.7	78.6	2.15	313.33	1.52	19.70	0.29
BC3802-21	33.0	156.9	50.6	3.10	304.55	1.41	21.37	0.25
BC3802-21	35.0	137.4	52.7	2.61	240.28	1.36	19.98	0.32
BC3802-22	37.0	147.1	49.0	3.00	269.96	1.42	19.49	0.30
BC3802-23	39.0	167.2	71.5	2.34	289.33	1.44	20.36	0.19
BC3802-24	41.0	167.6	55.7	3.01	252.48	1.42	20.18	0.37
BC3802-25	43.0	182.0	59.4	3.06	263.35	1.43	20.98	0.47
BC3802-26	45.0	163.8	49.0	3.34	272.42	1.42	20.38	0.27
BC3802-27	47.0	147.3	54.4	2.71	266.73	1.42	20.57	0.38
BC3802-28	49.0	154.4	52.6	2.94	276.11	1.43	20.71	0.39
BC3802-29	51.0	163.7	59.9	2.73	275.14	1.43	20.33	0.48
BC3802-30	53.0	140.3	53.5	2.62	269.47	1.45	20.06	0.32
CD38-03	(4289m)							
Sample	Depth	I/Org.C	Br/Org.C	I/Br	Ba/Al	Zr/Rb	K/Rb	Mo/U
	(cm.)	(x10-4)	(x10-4)		(x10-4)		(x10-3)	
BC3803-01	0.5	314.2	109.6	2.87	263.09	1.26	19.91	2.09
BC3803-02	1.5	330.0	109.3	3.02	264.66	1.28	20.15	3.60
BC3803-03	2.5	286.2	102.8	2.79	265.85	1.29	20.38	0.00
BC3803-04	3.5	255.2	135.1	1.89	265.00	1.28	20.24	0.24
BC3803-05	4.5	218.5	122.4	1.79	267.64	1.27	20.79	0.67
BC3803-06	5.5	161.0	95.4	1.69	269.60	1.24	20.95	0.39
BC3803-07	6.5	195.0	124.1	1.57	266.57	1.29	21.49	0.32
BC3803-08	7.5	210.4	125.5	1.68	266.71	1.30	21.08	0.24
BC3803-09	8.5	189.6	106.3	1.78	267.42	1.28	21.12	0.26
BC3803-10	9.5	181.3	92.1	1.97	267.95	1.30	20.40	0.24
BC3803-11	11.0	189.2	98.1	1.93	264.12	1.28	20.82	0.22
BC3803-12	13.0	151.2	58.1	2.60	271.04	1.31	21.13	0.26
BC3803-13	15.0	156.1	75.4	2.07	273.61	1.31	21.27	0.23
BC3803-14	17.0	145.6	55.7	2.61	281.39	1.32	21.02	0.36
BC3803-15	19.0	136.6	67.7	2.02	274.62	1.32	21.34	0.36
BC3803-16	21.0	147.8	79.4	1.86	288.14	1.34	21.04	0.58
BC3803-17	23.0	140.4	86.5	1.62	277.67	1.32	21.39	0.28
BC3803-18	25.0	120.8	64.4	1.88	283.66	1.35	21.35	0.43
BC3803-19	27.0	122.8	66.8	1.84	283.65	1.35	21.50	0.49
BC3803-20	29.0	126.9	52.4	2.42	288.75	1.37	21.61	0.30
BC3803-21	31.0	132.8	64.4	2.06	285.94	1.37	22.05	0.29
BC3803-22	33.0	126.7	59.4	2.13	287.59	1.40	22.00	0.40
BC3803-23	35.0	124.9	61.6	2.03	287.84	1.40	22.58	0.37
BC3803-24	37.0	110.8	54.5	2.03	280.08	1.42	22.17	0.23
BC3803-25	39.0	119.5	54.3	2.20	273.12	1.42	22.49	0.31
BC3803-26	41.0	121.8	50.3	2.42	276.39	1.38	21.92	0.19
BC3803-27	43.0	122.8	60.8	2.02	261.92	1.40	22.16	0.25
BC3803-28	45.0	119.7	54.3	2.21	267.48	1.41	22.43	0.27
BC3803-29	47.0	110.2	52.3	2.11	263.45	1.40	22.64	0.30
BC3803-30	49.0	118.7	46.3	2.56	258.81	1.42	22.17	0.37
BC3803-31	51.0	114.7	51.2	2.24	251.80	1.41	22.17	0.20
BC3803-32	53.0	110.1	59.2	1.86	234.56	1.40	21.95	0.22

APPENDIX C.11. TRACE ELEMENT RATIOS									
CD38-09	(148m)								
Sample	Depth	I/Org.C	Br/Org.C	I/Br	Ba/Al	Zr/Rb	K/Rb	Mo/U	Mo/Uorg
	(cm.)	(x10-4)	(x10-4)		(xE-4)		(xE-3)		
PC3809-01	4.0	14.0	68.0	0.21	50.17	1.89	18.80	6.66	12.82
PC3809-02	13.0	12.0	59.9	0.20	42.13	1.62	18.30	6.75	11.29
PC3809-03	23.0	13.4	46.3	0.29	38.86	1.80	19.89	6.07	12.45
PC3809-04	34.0	13.6	40.9	0.33	39.19	1.75	19.71	6.13	12.33
PC3809-05	43.0	13.5	49.3	0.27	48.50	2.68	21.02	3.21	9.59
PC3809-06	53.0	11.0	40.8	0.27	41.77	1.58	19.39	9.38	117.25
PC3809-07	62.0	8.6	38.6	0.22	41.36	1.65	19.77	10.39	20.15
PC3809-08	73.0	13.6	46.2	0.29	42.92	1.96	19.62	4.43	9.66
PC3809-09	84.0	13.7	38.0	0.36	39.11	1.53	19.18	6.53	18.08
PC3809-10	94.0	12.2	35.0	0.35	39.10	1.45	19.01	8.99	22.39
PC3809-11	104.0	8.8	32.5	0.27	43.64	1.40	19.24	8.57	14.49
PC3809-12	113.0	10.3	39.1	0.26	38.84	1.41	19.26	4.35	9.71
PC3809-13	124.0	11.1	39.1	0.28	45.29	2.16	20.13	4.14	9.55
PC3809-14	134.0	9.5	33.7	0.28	43.30	2.21	20.27	6.94	20.50
PC3809-15	144.0	8.8	34.4	0.26	45.71	1.88	19.98	8.21	17.04
PC3809-16	152.0	10.3	35.0	0.29	39.86	1.86	19.96	6.42	13.03
PC3809-17	165.0	9.7	28.6	0.34	45.45	2.40	20.68	5.07	9.76
PC3809-18	174.0	12.6	37.2	0.34	50.97	2.93	21.40	3.00	7.96
PC3809-19	185.0	8.7	35.6	0.24	54.03	3.58	22.50	3.04	11.64
PC3809-20	194.0	13.7	31.8	0.43	57.12	3.81	22.42	3.51	85.00
PC3809-21	205.0	9.6	33.9	0.28	65.04	2.19	21.93	7.88	58.35
PC3809-22	214.0	10.8	35.0	0.31	50.62	3.11	21.64	4.27	9.51
PC3809-23	224.0	14.4	33.0	0.44	65.38	5.11	25.27	1.22	6.26
PC3809-24	234.0	8.6	28.1	0.30	59.40	4.09	24.45	4.81	
PC3809-25	243.0	5.5	23.0	0.24	52.87	2.41	23.11	7.51	19.06
PC3809-26	257.0	4.4	24.0	0.19	53.82	2.68	23.25	5.80	13.00
PC3809-27	267.0	5.5	20.8	0.26	66.01	3.81	24.24	2.11	
PC3809-28	273.0	6.6	24.7	0.27	71.71	3.66	22.32	0.36	0.81
PC3809-29	284.0	3.1	15.4	0.20	40.86	1.76	21.25	5.39	10.32
PC3809-30	294.0	3.7	17.6	0.21	43.27	1.69	22.38	10.96	21.65
PC3809-31	304.0	3.2	15.8	0.20	54.77	1.66	21.29	6.34	13.54
PC3809-32	314.0	2.3	16.9	0.13	43.33	1.44	20.49	9.16	17.92
PC3809-33	324.0	3.7	15.7	0.24	41.90	1.80	21.67	6.41	16.85
PC3809-34	335.0	3.4	16.3	0.21	40.52	1.81	22.59	8.38	14.73
PC3809-35	344.0	2.9	16.6	0.18	40.93	1.76	21.90	10.16	20.39
PC3809-36	355.0	2.4	17.1	0.14	47.86	1.64	23.38	14.16	25.75
PC3809-37	364.0	3.1	15.6	0.20	46.47	1.61	22.67	17.29	31.94
PC3809-38	375.0	2.5	18.2	0.14	45.42	1.61	22.80	14.27	25.74
PC3809-39	384.0	1.9	16.1	0.12	43.95	1.93	22.13	6.95	15.51
PC3809-40	394.0	3.0	14.4	0.21	45.26	1.74	22.40	8.66	16.18
PC3809-41	404.0	4.5	17.5	0.26	46.62	1.72	22.63	6.80	12.06
PC3809-42	416.0	2.2	17.4	0.13	43.01	1.70	21.94	9.15	14.08
PC3809-43	424.0	2.8	17.5	0.16	44.66	1.59	22.75	8.49	12.99
PC3809-44	434.0	3.2	18.2	0.18	44.28	1.52	21.46	8.49	12.96
PC3809-45	444.0	3.3	18.5	0.18	48.37	1.63	21.96	8.28	14.41
PC3809-46	453.0	2.5	19.0	0.13	45.39	1.79	21.56	6.30	12.70
PC3809-47	465.0	3.6	18.8	0.19	43.52	1.55	20.69	11.13	26.18
PC3809-48	474.0	1.8	17.9	0.10	49.53	1.47	21.45	10.53	16.59
PC3809-49	483.0	3.1	23.3	0.13	46.54	1.86	21.61	5.68	10.94
PC3809-50	493.0	2.9	21.9	0.13	250.09	1.61	21.83	8.38	16.30
PC3809-51	504.0	2.9	21.7	0.14	51.49	2.00	21.99	4.34	8.02
PC3809-52	515.0	2.7	24.8	0.11	50.33	1.76	21.93	5.94	11.12
PC3809-53	525.0	2.3	19.5	0.12	44.96	1.54	22.22	10.93	19.54
PC3809-54	536.0	3.9	22.2	0.18	46.99	1.53	21.82	14.45	33.57
PC3809-55	544.0	1.6	21.2	0.08	51.31	1.77	21.62	8.44	26.84
PC3809-56	553.0	3.4	17.5	0.19	48.69	1.46	21.16	11.88	40.53
PC3809-57	564.0	0.9	18.2	0.05	52.26	1.49	21.01	13.00	52.94
PC3809-58	574.0	1.3	18.3	0.07	52.08	1.57	21.58	11.39	43.20
PC3809-59	585.0	3.0	20.1	0.15	76.62	1.82	21.26	7.00	
PC3809-60	594.0	2.5	18.8	0.13	52.75	1.76	21.92	9.02	30.87
PC3809-61	605.0	1.2	18.7	0.06	49.65	1.81	21.32	8.39	132.19
PC3809-62	615.0	1.6	20.3	0.08	48.81	1.65	21.12	7.02	106.31
PC3809-63	625.0	3.4	18.8	0.18	49.20	1.79	21.49	6.14	50.60
PC3809-64	635.0	2.1	18.4	0.11	48.60	1.75	21.08	5.44	17.79
PC3809-65	646.0	2.8	22.3	0.13	46.52	1.69	21.70	8.70	23.42
PC3809-66	654.0	2.0	23.3	0.09	50.21	1.80	21.63	5.64	9.60
PC3809-67	664.0	1.9	21.4	0.09	52.38	1.62	21.58	5.39	8.11
PC3809-68	674.0	3.7	23.2	0.16	53.92	1.74	22.14	4.81	7.07
PC3809-69	684.0	4.3	22.6	0.19	53.37	1.61	21.53	6.57	13.46

APPENDIX C.11. TRACE ELEMENT RATIOS									
CD38-09	(148m)								
Sample	Depth	I/Org.C	Br/Org.C	I/Br	Ba/Al	Zr/Rb	K/Rb	Mo/U	Mo/Uorg
	(cm.)	(x10-4)	(x10-4)		(xE-4)		(xE-3)		
PC3809-70	694.0	3.9	19.3	0.20	47.19	1.61	20.83	5.56	10.69
PC3809-71	703.0	2.4	18.2	0.13	46.99	1.56	21.84	7.87	14.85
PC3809-72	714.0	4.5	19.3	0.23	47.89	1.67	22.25	6.47	12.16
PC3809-73	724.0	2.0	18.2	0.11	50.76	1.61	21.31	6.12	42.22
PC3809-74	734.0	2.0	18.0	0.11	46.83	1.68	21.44	6.64	83.62
PC3809-75	744.0	3.0	18.9	0.16	51.62	1.61	21.48	6.62	15.65
PC3809-76	754.0	1.9	20.8	0.09	47.58	1.74	22.35	12.49	53.37
PC3809-77	764.0	3.5	19.5	0.18	48.42	1.58	21.72	8.26	34.84
PC3809-78	774.0	4.9	17.8	0.28	47.22	1.77	21.14	9.53	206.25
PC3809-79	784.0	4.0	17.0	0.24	47.02	1.71	21.78	6.62	17.60
PC3809-80	794.0	3.0	18.2	0.16	50.42	1.78	21.89	7.33	53.01
PC3809-81	804.0	4.9	17.7	0.27	57.45	1.97	22.20	6.35	38.75
PC3809-82	813.0	4.2	18.0	0.24	53.44	1.93	21.18	5.07	
PC3809-83	823.0	4.1	18.2	0.23	52.02	2.00	21.76	6.36	617.74
PC3809-84	834.0	1.7	15.9	0.11	49.49	1.93	21.86	6.84	74.51
PC3809-85	845.0	5.3	20.1	0.26	50.08	1.79	21.97	8.62	
PC3809-86	854.0	3.7	17.2	0.21	52.31	1.53	20.44	5.88	18.01
CD38-10	(257m)								
PC3810-01	6.0	14.6	50.0	0.29	52.01	1.86	18.86	3.40	6.84
PC3810-02	14.0	16.8	53.4	0.32	61.43	3.40	21.31	1.23	7.14
PC3810-03	24.0	10.6	44.7	0.24	64.74	4.57	24.99	0.56	
PC3810-04	34.0	14.6	41.6	0.35	60.76	4.07	23.73	1.13	
PC3810-05	44.0	6.3	33.8	0.19	60.51	2.61	22.54	2.43	4.83
PC3810-06	54.0	4.6	35.4	0.13	54.61	2.43	21.80	3.20	5.20
PC3810-07	64.0	9.9	37.9	0.26	56.54	3.08	23.06	2.57	5.68
PC3810-08	74.0	6.0	35.4	0.17	62.82	3.49	22.71	1.94	8.17
PC3810-09	84.0	14.7	30.0	0.49	71.90	4.07	25.91	0.86	
PC3810-10	94.0	6.2	32.9	0.19	66.03	4.66	25.11	1.52	10.01
PC3810-10	104.0	6.6	30.7	0.21	67.03	5.17	25.62	2.00	17.83
PC3810-11	113.0	12.7	27.8	0.46	62.01	4.55	25.19	1.65	50.94
PC3810-12	126.0	6.5	26.2	0.25	44.58	2.48	21.82	4.45	21.89
PC3810-13	134.0	3.8	22.4	0.17	46.30	2.12	20.66	4.92	17.86
PC3810-14	146.0	4.4	22.9	0.19	51.28	2.48	21.35	4.27	11.03
PC3810-15	154.0	5.3	21.2	0.25	52.07	2.27	20.58	3.67	9.20
PC3810-16	167.0	4.6	23.6	0.20	53.53	1.97	20.42	4.07	8.07
PC3810-17	174.0	3.8	22.8	0.17	54.55	1.98	21.28	3.66	7.52
PC3810-18	185.0	4.0	26.3	0.15	51.75	1.69	20.16	2.95	5.80
PC3810-19	194.0	4.7	30.4	0.15	55.58	1.63	19.98	5.65	10.63
PC3810-20	203.0	4.4	24.1	0.18	57.14	2.10	20.88	3.06	5.72
PC3810-21	216.0	4.5	26.8	0.17	60.39	1.75	20.05	5.50	10.85
PC3810-22	224.0	4.3	25.2	0.17	55.17	1.63	19.12	5.07	8.80
PC3810-23	233.0	4.1	22.4	0.19	54.33	1.78	20.42	4.40	7.63
PC3810-24	244.0	5.3	22.2	0.24	45.81	2.05	20.28	3.92	9.69
PC3810-25	254.0	8.6	33.7	0.26	56.76	3.07	22.22	3.09	13.46
PC3810-26	263.0	7.1	29.2	0.24	58.22	2.54	21.45	4.30	14.84
PC3810-27	273.0	4.6	19.1	0.24	51.17	1.95	20.49	3.73	7.55
PC3810-28	284.0	5.5	20.4	0.27	53.32	2.10	20.08	2.90	5.86
PC3810-29	295.0	4.7	19.7	0.24	57.92	1.44	18.80	5.44	10.64
PC3810-30	305.0	4.6	20.5	0.22	51.10	1.84	19.24	3.20	5.97
PC3810-31	314.0	4.5	21.1	0.21	50.52	2.14	19.89	2.98	6.19
PC3810-32	324.0	3.9	18.7	0.21	59.23	1.57	19.00	5.25	9.17
PC3810-33	335.0	5.2	24.1	0.22	49.36	1.75	19.57	2.81	5.25
PC3810-34	344.0	4.0	22.6	0.18	42.71	1.58	19.03	5.72	11.18
PC3810-35	354.0	4.1	19.7	0.21	64.04	1.54	19.67	6.67	11.33
PC3810-36	364.0	3.9	24.4	0.16	57.51	1.36	18.86	6.60	11.40
PC3810-37	374.0	5.5	48.6	0.11	64.63	1.28	17.54	5.34	7.86
PC3810-38	383.0	4.0	24.1	0.17	49.40	1.46	18.66	2.34	3.82
PC3810-39	394.0	3.1	30.3	0.10	50.32	1.69	18.89	3.09	4.92
PC3810-40	404.0	4.3	25.5	0.17	46.27	2.00	19.62	2.15	3.76
PC3810-41	417.0	4.7	17.7	0.26	51.82	1.90	18.88	4.19	8.24
PC3810-42	424.0	4.5	17.1	0.26	43.35	1.70	19.77	3.22	5.21
PC3810-43	434.0	3.9	17.6	0.22	74.46	1.88	20.44	6.36	14.53
PC3810-44	445.0	4.5	16.3	0.27	51.68	1.45	18.98	3.71	6.07
PC3810-45	456.0	4.4	18.2	0.24	70.90	1.53	18.35	5.47	8.33
PC3810-46	467.0	3.6	18.8	0.19	77.05	1.48	20.71	11.80	26.28
PC3810-47	476.0	4.0	18.6	0.21	56.66	1.78	19.19	2.12	4.06
PC3810-48	484.0	4.2	18.0	0.23	57.17	1.82	19.07	2.46	5.04

APPENDIX C.11. TRACE ELEMENT RATIOS									
CD38-10	(257m)								
Sample	Depth	I/Org.C	Br/Org.C	I/Br	Ba/Al	Zr/Rb	K/Rb	Mo/U	Mo/Uorg
	(cm.)	(x10-4)	(x10-4)		(xE-4)		(xE-3)		
PC3810-49	494.0	4.7	17.8	0.26	64.07	2.89	20.17	1.63	3.81
PC3810-50	504.0	7.4	23.2	0.32	60.80	4.80	25.42	0.67	
PC3810-51	514.0	3.3	18.0	0.18	52.70	1.96	22.67	11.34	25.18
PC3810-52	524.0	2.5	18.4	0.14	57.62	2.04	23.52	8.26	17.31
PC3810-53	534.0	3.2	20.7	0.15	87.95	1.51	20.84	5.64	6.97
PC3810-54	545.0	2.2	28.3	0.08	72.95	1.53	21.37	6.45	8.21
PC3810-55	554.0	2.8	33.2	0.08	82.28	1.42	20.11	6.86	8.44
PC3810-56	564.0	2.6	21.4	0.12	88.67	1.78	20.60	9.09	17.24
PC3810-57	574.0	2.6	21.0	0.12	79.35	1.90	19.91	7.62	12.58
PC3810-58	584.0	2.7	22.4	0.12	87.37	1.78	21.62	8.89	14.59
PC3810-59	596.0	3.0	22.2	0.14	90.82	1.85	21.27	3.83	4.56
PC3810-60	604.0	2.1	20.6	0.10	97.24	1.71	21.50	5.27	6.77
PC3810-61	614.0	3.2	22.4	0.14	77.83	1.72	20.50	5.70	7.13
PC3810-62	624.0	3.4	20.0	0.17	70.02	1.68	20.95	7.55	12.39
PC3810-63	634.0	3.1	19.9	0.16	63.89	1.84	22.01	6.82	12.19
PC3810-64	645.0	2.9	23.5	0.12	83.44	1.52	20.03	8.38	11.89
PC3810-65	655.0	2.3	24.3	0.09	77.60	1.52	21.11	13.12	19.41
PC3810-66	667.0	2.7	19.5	0.14	61.52	1.52	21.56	9.27	13.61
PC3810-67	674.0	2.8	18.0	0.16	49.73	1.38	20.13	6.83	9.54
PC3810-68	683.0	2.0	18.5	0.11	48.94	1.31	20.00	8.16	11.46
PC3810-69	694.0	3.9	19.0	0.21	47.12	1.41	19.92	6.04	12.03
PC3810-70	704.0	3.9	16.8	0.23	46.27	1.41	20.30	6.03	15.59
PC3810-71	714.0	3.1	17.7	0.18	48.29	1.29	20.27	8.53	21.95
PC3810-72	724.0	3.3	18.5	0.18	48.57	1.26	19.69	7.73	13.57
PC3810-74	734.0	3.6	21.9	0.17	45.89	1.46	21.20	5.33	10.03
PC3810-75	745.0	2.1	24.9	0.09	46.59	1.64	20.82	3.89	8.74
PC3810-76	754.0	2.7	35.9	0.08	46.03	2.01	20.29	5.45	12.64
PC3810-77	764.0	1.4	27.0	0.05	54.17	2.71	21.95	2.71	22.81
CD38-02	(2525m)								
PC3802-01	8.0	148.7	88.4	1.68	374.44	1.29	17.49	0.00	0.00
PC3802-02	18.0	150.1	90.1	1.67	361.24	1.33	18.19	0.03	0.06
PC3802-03	28.0	156.9	87.0	1.80	356.27	1.33	16.95	0.00	0.00
PC3802-04	38.0	133.2	79.7	1.67	231.61	1.22	16.73	0.24	0.34
PC3802-05	48.0	170.0	72.6	2.34	243.09	1.27	16.80	0.26	0.38
PC3802-06	57.5	152.0	69.0	2.20	234.67	1.27	17.24	0.39	0.63
PC3802-07	70.0	151.9	47.2	3.22	271.99	1.31	16.64	0.10	0.18
PC3802-08	79.0	159.3	65.9	2.42	260.57	1.28	16.85	0.38	0.62
PC3802-09	89.0	131.1	62.8	2.09	275.58	1.29	16.35	0.20	0.27
PC3802-10	100.0	121.2	62.6	1.94	287.76	1.30	16.24	0.35	0.56
PC3802-11	110.0	164.4	84.6	1.94	291.04	1.30	16.40	0.47	0.70
PC3802-12	120.0	127.3	76.6	1.66	306.08	1.30	16.58	0.52	0.72
PC3802-13	130.0	121.7	63.8	1.91	294.36	1.29	15.74	0.47	0.65
PC3802-14	139.0	150.9	75.0	2.01	274.78	1.31	16.71	0.48	0.80
PC3802-15	150.0	111.8	57.0	1.96	250.19	1.28	17.56	0.62	1.12
PC3802-16	160.0	116.6	46.8	2.49	245.01	1.32	17.72	0.56	1.38
PC3802-17	171.0	103.9	60.1	1.73	247.09	1.32	18.02	0.25	0.35
PC3802-18	181.0	127.1	66.7	1.90	274.65	1.31	17.95	0.34	0.48
PC3802-19	191.0	113.6	61.8	1.84	304.52	1.33	17.72	0.15	0.20
PC3802-20	201.0	114.3	62.1	1.84	270.97	1.41	17.92	0.26	0.37
PC3802-21	211.0	109.7	54.7	2.00	243.26	1.29	17.59	0.38	0.57
PC3802-22	221.0	116.8	55.5	2.10	249.14	1.30	17.71	0.30	0.44
PC3802-23	231.0	118.4	57.4	2.06	214.24	1.28	18.01	0.53	1.30
PC3802-24	241.0	105.4	53.7	1.96	253.27	1.28	18.63	0.20	0.39
PC3802-25	251.0	92.5	56.9	1.62	266.33	1.26	17.45	0.31	0.47
PC3802-26	261.0	117.0	65.2	1.80	334.91	1.32	17.60	0.19	0.28
PC3802-27	271.0	82.0	54.7	1.50	284.32	1.29	18.70	0.42	0.81
PC3802-28	281.0	101.9	63.8	1.60	263.42	1.28	18.91	0.24	0.40
PC3802-29	291.0	83.9	54.3	1.54	259.93	1.23	18.68	0.18	0.34
PC3802-30	301.0	89.5	61.7	1.45	291.55	1.25	18.52	0.22	0.40
PC3802-31	312.0	99.5	53.4	1.86	307.82	1.30	18.10	0.17	0.24
PC3802-32	322.0	109.4	56.6	1.93	315.92	1.26	18.34	0.19	0.28
PC3802-33	332.0	113.5	58.8	1.93	304.26	1.27	18.95	0.23	0.49
PC3802-34	342.0	99.0	72.2	1.37	371.40	1.27	18.37	0.23	0.38
PC3802-35	352.0	92.0	70.3	1.31	351.48	1.29	18.72	0.06	0.09
PC3802-36	362.0	109.5	66.3	1.65	256.44	1.22	17.35	0.25	0.40
PC3802-37	372.0	102.3	67.3	1.52	237.40	1.24	17.18	0.12	0.17
PC3802-38	381.0	120.3	56.5	2.13	252.19	1.26	17.72	0.12	0.19

APPENDIX C.11. TRACE ELEMENT RATIOS									
Sample	Depth (cm.)	I/Org.C (x10-4)	Br/Org.C (x10-4)	I/Br	Ba/Al (xE-4)	Zr/Rb	K/Rb (xE-3)	Mo/U	Mo/Uorg
CD38-02	(2525m)								
PC3802-39	391.0	116.8	56.3	2.07	252.78	1.32	17.79	0.16	0.22
PC3802-40	400.0	110.6	56.7	1.95	274.70	1.34	17.69	0.14	0.21
PC3802-41	410.0	113.1	54.8	2.06	269.55	1.23	17.68	0.31	0.58
PC3802-42	420.0	127.9	57.5	2.23	246.99	1.34	18.12	0.10	0.16
PC3802-43	430.0	123.4	53.8	2.30	220.21	1.29	17.12	0.04	0.06
PC3802-44	440.0	99.6	54.2	1.84	242.91	1.29	18.02	0.11	0.13
PC3802-45	450.0	118.8	64.6	1.84	217.30	1.27	17.09	0.07	0.11
PC3802-46	460.0	113.6	67.2	1.69	207.47	1.23	18.33	0.29	0.51
PC3802-47	470.0	102.5	50.8	2.02	247.37	1.25	15.99	0.09	0.12
PC3802-48	481.0	90.7	47.6	1.91	277.33	1.27	12.14	0.20	0.26
PC3802-49	491.0	67.3	39.0	1.73	276.05	1.29	17.64	0.41	0.67
PC3802-50	501.0	76.4	39.6	1.93	264.09	1.27	18.01	0.23	0.34
PC3802-51	511.0	67.4	45.7	1.47	252.27	1.25	17.45	0.14	0.20
PC3802-52	521.0	93.1	78.7	1.18	190.72	1.24	19.54	0.49	1.01
PC3802-53	531.0	91.0	57.4	1.58	166.98	1.36	24.59	0.22	0.00
PC3802-54	540.0	91.0	60.5	1.50	226.24	1.24	18.63	0.36	0.83
PC3802-55	550.0	74.7	60.3	1.24	246.10	1.22	18.00	0.60	1.63
PC3802-56	560.0	79.2	50.7	1.56	326.16	1.19	17.69	0.38	0.73
PC3802-57	572.0	98.5	94.2	1.05	337.12	1.19	18.89	0.27	0.43
PC3802-58	582.0	77.6	74.1	1.05	312.42	1.24	19.04	0.11	0.20
PC3802-59	591.0	89.9	69.7	1.29	290.68	1.19	18.07	0.25	0.50
PC3802-60	601.0	74.3	61.2	1.21	408.00	1.25	16.25	0.10	0.14
PC3802-61	611.0	90.9	82.1	1.11	367.34	1.30	18.77	0.05	0.06
PC3802-62	621.0	103.8	62.8	1.65	305.40	1.28	18.03	0.06	0.10
PC3802-63	631.0	81.3	48.8	1.67	256.72	1.25	17.57	0.27	0.41
PC3802-64	641.0	84.0	53.8	1.56	264.08	1.24	18.31	0.09	0.15
PC3802-65	651.0	85.4	59.8	1.43	277.32	1.21	18.83	0.10	0.26
PC3802-66	662.0	90.8	90.4	1.00	392.56	1.25	18.56	0.15	0.47
PC3802-67	671.0	78.6	100.9	0.78	425.09	1.28	17.61	0.08	0.10
PC3802-68	681.0	80.6	56.3	1.43	281.18	1.26	17.99	0.01	0.02
PC3802-69	691.0	88.0	42.6	2.07	229.12	1.27	18.01	0.11	0.16
PC3802-70	701.0	80.4	39.7	2.03	235.82	1.28	17.83	0.13	0.19
PC3802-71	711.0	101.6	62.1	1.64	265.81	1.23	17.60	0.14	0.21
PC3802-72	721.0	88.0	47.1	1.87	276.80	1.25	17.78	0.19	0.33
PC3802-73	731.0	87.6	46.2	1.90	265.79	1.23	17.68	0.05	0.07
PC3802-74	741.0	96.4	43.1	2.24	251.30	1.26	17.46	0.19	0.27
CD38-11	(3835m)								
PC3811-01	3.0	121.0	77.6	1.56	179.12	1.64	17.13	0.56	1.10
PC3811-02	13.0	51.8	64.3	0.81	70.40	2.16	16.47	2.08	5.40
PC3811-03	23.0	43.8	62.1	0.71	63.14	2.98	18.73	1.74	7.71
PC3811-04	33.0	134.7	70.8	1.90	272.99	1.41	18.22	0.18	0.27
PC3811-05	43.0	117.6	69.8	1.68	193.75	1.35	17.86	0.21	0.31
PC3811-06	53.0	102.0	64.6	1.58	137.20	1.33	17.33	0.38	0.55
PC3811-07	63.0	97.5	59.7	1.63	114.74	1.36	17.78	0.42	0.58
PC3811-08	73.0	101.4	58.9	1.72	121.87	1.38	17.38	0.93	1.62
PC3811-09	85.0	93.3	53.0	1.76	94.83	1.93	21.38	0.78	
PC3811-10	95.0	90.9	59.6	1.53	124.22	1.37	17.92	1.14	1.74
PC3811-11	105.0	78.9	58.6	1.35	118.96	1.35	17.28	1.83	3.89
PC3811-12	116.0	78.6	59.4	1.32	129.06	1.34	17.31	2.05	6.39
PC3811-13	125.0	89.5	58.7	1.52	131.05	1.30	17.75	1.85	4.37
PC3811-14	135.0	81.5	59.6	1.37	120.02	1.36	17.45	1.72	4.28
PC3811-15	145.0	87.8	61.0	1.44	125.17	1.34	17.95	1.63	3.86
PC3811-16	155.0	79.8	58.4	1.36	111.00	1.44	17.33	0.93	1.54
PC3811-17	165.0	81.6	58.7	1.39	116.52	1.30	18.35	1.11	2.01
PC3811-18	175.0	86.4	56.2	1.54	123.50	1.56	18.96	0.79	1.60
PC3811-19	186.0	94.9	62.1	1.53	155.02	1.28	17.57	1.22	1.87
PC3811-20	197.0	88.1	62.5	1.41	149.78	1.22	17.07	1.58	3.27
PC3811-21	204.0	85.4	61.1	1.40	154.31	1.20	17.71	1.13	2.69
PC3811-22	215.0	77.0	53.8	1.43	174.00	1.42	17.52	0.82	1.20
PC3811-23	225.0	86.9	53.3	1.63	211.10	1.25	16.87	1.44	2.67
PC3811-24	235.0	84.8	51.9	1.64	206.42	1.23	16.50	1.04	1.49
PC3811-25	245.0	86.9	52.5	1.66	214.61	1.24	17.05	1.11	1.61
PC3811-26	255.0	86.6	53.3	1.62	241.10	1.28	16.44	1.18	1.65
PC3811-27	265.0	89.3	54.9	1.63	247.15	1.28	16.52	1.11	1.53
PC3811-28	275.0	83.2	52.6	1.58	237.52	1.30	16.77	0.93	1.36
PC3811-29	285.0	79.5	51.0	1.56	177.17	1.29	18.04	0.80	1.20
PC3811-30	297.0	82.5	53.1	1.56	161.56	1.31	17.53	0.66	1.07

APPENDIX C.12. BIOGENIC COMPONENTS									
BC38-02	2530m	Corq	CaCO3	Bio.SiO2	PC38-09	148m	Corq	CaCO3	Bio.SiO2
Sample	Depth	(wt.%)	(wt.%)	(wt.%)	Sample	Depth	(wt.%)	(wt.%)	(wt.%)
	(cm)					(cm)			
BC3802-01	0.5	1.02	12.34	8.48	PC3809-01	4.0	6.70	2.16	16.85
BC3802-02	1.5	1.20	11.58	8.45	PC3809-02	13.0	6.65	3.34	21.87
BC3802-03	2.5	1.06	12.11	7.68	PC3809-03	23.0	6.03	1.23	14.02
BC3802-04	3.5	1.14	12.54	8.15	PC3809-04	34.0	6.14	0.64	14.89
BC3802-05	4.5	1.13	13.23	8.09	PC3809-05	43.0	3.66	1.29	7.07
BC3802-06	5.5	1.08	13.31	7.73	PC3809-06	53.0	5.93	0.25	17.81
BC3802-07	6.5	1.13	13.46	7.97	PC3809-07	62.0	8.26	2.75	18.39
BC3802-08	7.5	1.12	13.23	8.90	PC3809-08	73.0	5.44	0.47	15.17
BC3802-09	8.5	1.02	13.57	7.78	PC3809-09	84.0	5.76	0.00	10.77
BC3802-10	9.5	1.00	14.20	8.32	PC3809-10	94.0	6.60	0.42	14.48
BC3802-11	11.0	0.88	16.40	7.82	PC3809-11	104.0	6.93	0.08	18.47
BC3802-12	13.0	0.89	18.99	7.83	PC3809-12	113.0	4.87	0.00	11.67
BC3802-13	15.0	0.87	19.97	7.74	PC3809-13	124.0	5.09	1.54	8.18
BC3802-13A	17.0	1.09	25.67	7.44	PC3809-14	134.0	6.06	1.35	14.35
BC3802-14	19.0	0.93	28.88	7.57	PC3809-15	144.0	6.33	1.45	20.44
BC3802-15	21.0	0.86	31.38	7.07	PC3809-16	152.0	5.05	1.82	20.27
BC3802-16	23.0	0.89	32.14	5.81	PC3809-17	165.0	4.96	3.00	20.04
BC3802-17	25.0	0.96	33.43	5.91	PC3809-18	174.0	3.35	1.12	9.13
BC3802-18	27.0	0.94	34.02	5.49	PC3809-19	185.0	3.21	1.65	8.61
BC3802-19	29.0	1.09	36.15	5.47	PC3809-20	194.0	2.96	3.10	6.14
BC3802-20	31.0	1.09	35.10	4.98	PC3809-21	205.0	2.16	4.00	8.36
BC3802-21	33.0	1.28	34.50	5.15	PC3809-22	214.0	5.59	1.75	12.11
BC3802-21A	35.0	1.83	30.66	5.06	PC3809-23	224.0	1.59	2.32	3.10
BC3802-22	37.0	1.51	32.64	5.04	PC3809-24	234.0	2.43	1.73	11.78
BC3802-23	39.0	1.19	33.78	4.58	PC3809-25	243.0	4.69	0.76	25.82
BC3802-24	41.0	1.43	32.47	4.91	PC3809-26	257.0	4.17	0.97	16.56
BC3802-25	43.0	1.45	31.64	5.23	PC3809-27	267.0	2.34	1.21	9.91
BC3802-26	45.0	1.57	31.28	5.21	PC3809-28	273.0	1.62	5.62	4.02
BC3802-27	47.0	1.70	31.10	4.82	PC3809-29	284.0	5.16	1.41	13.58
BC3802-28	49.0	1.69	31.18	4.63	PC3809-30	294.0	5.37	2.48	18.74
BC3802-29	51.0	1.54	30.75	4.86	PC3809-31	304.0	4.63	0.72	16.56
BC3802-30	53.0	1.76	30.37	4.71	PC3809-32	314.0	5.75	1.46	14.31
					PC3809-33	324.0	5.71	0.95	13.66
BC38-03	4289m				PC3809-34	335.0	6.08	1.17	17.70
					PC3809-35	344.0	6.43	1.11	21.08
BC3803-01	0.5	1.72	0.04	17.86	PC3809-36	355.0	5.85	3.34	22.09
BC3803-02	1.5	1.89	0.04	16.05	PC3809-37	364.0	5.67	6.40	24.81
BC3803-03	2.5	2.10	0.04	16.60	PC3809-38	375.0	6.19	1.94	15.87
BC3803-04	3.5	1.97	0.09	16.59	PC3809-39	384.0	5.07	3.73	16.74
BC3803-05	4.5	1.98	0.01	16.99	PC3809-40	394.0	5.74	2.42	22.87
BC3803-06	5.5	2.48	0.03	17.18	PC3809-41	404.0	4.68	0.70	20.73
BC3803-07	6.5	2.03	0.07	16.50	PC3809-42	416.0	5.89	6.12	22.02
BC3803-08	7.5	1.76	0.05	15.48	PC3809-43	424.0	5.54	0.98	23.72
BC3803-09	8.5	1.85	0.08	15.76	PC3809-44	434.0	6.55	0.74	16.99
BC3803-10	9.5	1.74	0.00	15.79	PC3809-45	444.0	4.66	4.00	24.07
BC3803-11	11.0	1.52	0.06	14.76	PC3809-46	453.0	4.71	1.44	16.83
BC3803-12	13.0	1.66	0.12	14.89	PC3809-47	465.0	5.52	2.47	19.07
BC3803-13	15.0	1.46	0.18	14.65	PC3809-48	474.0	5.89	4.75	18.07
BC3803-14	17.0	1.62	0.22	13.84	PC3809-49	483.0	4.56	0.93	18.07
BC3803-15	19.0	1.81	0.31	13.70	PC3809-50	493.0	5.07	1.55	17.96
BC3803-16	21.0	1.82	0.31	16.08	PC3809-51	504.0	4.18	1.30	11.53
BC3803-17	23.0	1.99	0.30	16.83	PC3809-52	515.0	4.78	1.10	11.24
BC3803-18	25.0	1.93	0.37	15.97	PC3809-53	525.0	6.00	3.39	13.81
BC3803-19	27.0	1.89	0.45	15.74	PC3809-54	536.0	5.22	5.40	17.24
BC3803-20	29.0	1.80	0.47	14.06	PC3809-55	544.0	4.08	2.64	11.98
BC3803-21	31.0	1.67	0.52	13.58	PC3809-56	553.0	3.62	4.58	13.28
BC3803-22	33.0	1.71	0.54	13.74	PC3809-57	564.0	3.41	4.44	18.01
BC3803-23	35.0	1.75	0.62	14.22	PC3809-58	574.0	3.45	4.91	13.57
BC3803-24	37.0	1.79	0.70	13.46	PC3809-59	585.0	2.88	5.75	16.18
BC3803-25	39.0	1.54	0.84	14.47	PC3809-60	594.0	3.18	4.70	15.64
BC3803-26	41.0	1.46	0.77	12.72	PC3809-61	605.0	3.31	5.19	12.94
BC3803-27	43.0	1.55	0.81	12.80	PC3809-62	615.0	3.43	4.71	18.09
BC3803-28	45.0	1.49	0.81	13.29	PC3809-63	625.0	3.04	4.39	13.61
BC3803-29	47.0	1.63	0.82	13.28	PC3809-64	635.0	3.44	5.04	13.44
BC3803-30	49.0	1.48	0.82	12.43	PC3809-65	646.0	3.47	4.18	18.91
BC3803-31	51.0	1.52	0.86	12.34	PC3809-66	654.0	2.91	3.81	21.65
BC3803-32	53.0	1.65	0.94	11.97	PC3809-67	664.0	3.14	4.36	20.96

APPENDIX C.12. BIOGENIC COMPONENTS										
PC38-09	148m		Corq	CaCO3	Bio.SiO2	PC38-10	257m	Corq	CaCO3	Bio.SiO2
Sample	Depth		(wt.%)	(wt.%)	(wt.%)	Sample	Depth	(wt.%)	(wt.%)	(wt.%)
	(cm)						(cm)			
PC3809-68	674.0		2.47	3.61	23.48	PC3810-45	456.0	6.30	15.89	20.51
PC3809-69	684.0		3.33	4.22	15.36	PC3810-46	467.0	5.95	17.38	28.42
PC3809-70	694.0		3.42	4.28	15.20	PC3810-47	476.0	6.55	16.03	10.94
PC3809-71	703.0		3.39	4.04	14.59	PC3810-48	484.0	6.80	17.92	11.57
PC3809-72	714.0		3.97	4.84	17.77	PC3810-49	494.0	6.47	15.66	8.85
PC3809-73	724.0		3.11	4.45	13.49	PC3810-50	504.0	2.01	0.97	1.99
PC3809-74	734.0		3.42	5.15	12.90	PC3810-51	514.0	3.94	3.14	12.98
PC3809-75	744.0		3.32	4.68	15.32	PC3810-52	524.0	3.16	2.17	11.68
PC3809-76	754.0		3.28	4.81	15.64	PC3810-53	534.0	11.92	8.97	10.70
PC3809-77	764.0		2.83	5.74	12.74	PC3810-54	545.0	9.85	6.47	15.28
PC3809-78	774.0		2.96	5.16	11.52	PC3810-55	554.0	10.65	10.83	14.56
PC3809-79	784.0		2.71	5.07	12.59	PC3810-56	564.0	6.27	16.01	20.77
PC3809-80	794.0		2.86	5.01	12.99	PC3810-57	574.0	6.85	18.47	13.13
PC3809-81	804.0		3.09	3.96	12.36	PC3810-58	584.0	6.96	15.91	16.47
PC3809-82	813.0		2.64	4.96	13.56	PC3810-59	596.0	7.37	13.67	17.34
PC3809-83	823.0		2.99	3.98	12.22	PC3810-60	604.0	7.38	17.25	16.77
PC3809-84	834.0		3.08	4.04	12.33	PC3810-61	614.0	7.10	11.65	17.42
PC3809-85	845.0		3.05	3.86	14.75	PC3810-62	624.0	6.28	13.47	13.21
PC3809-86	854.0		2.32	3.42	11.60	PC3810-63	634.0	6.34	13.46	14.76
						PC3810-64	645.0	6.47	10.13	17.54
PC38-10	257m					PC3810-65	655.0	7.46	11.81	16.04
						PC3810-66	667.0	6.58	10.66	13.61
PC3810-01	6.0		9.21	10.58	9.38	PC3810-67	674.0	6.39	6.94	13.32
PC3810-02	14.0		5.04	4.23	3.47	PC3810-68	683.0	6.29	9.21	15.09
PC3810-03	24.0		1.75	1.14	1.14	PC3810-69	694.0	4.63	4.05	11.44
PC3810-04	34.0		2.04	6.83	2.23	PC3810-70	704.0	4.48	0.15	8.73
PC3810-05	44.0		6.84	0.29	5.56	PC3810-71	714.0	4.85	5.47	11.85
PC3810-06	54.0		6.90	0.11	8.84	PC3810-72	724.0	5.03	7.87	13.95
PC3810-07	64.0		4.08	0.08	8.86	PC3810-74	734.0	3.98	0.00	12.61
PC3810-08	74.0		3.04	0.19	4.26	PC3810-75	745.0	2.97	0.00	7.74
PC3810-09	84.0		0.88	0.94	1.11	PC3810-76	754.0	4.10	0.23	15.25
PC3810-10	94.0		0.87	1.54	0.48	PC3810-77	764.0	2.46	0.00	6.62
PC3810-10	104.0		1.05	9.06	0.99					
PC3810-11	113.0		0.79	9.19	0.84	PC38-02	2525m			
PC3810-12	126.0		3.90	9.92	16.01	(Age)				
PC3810-13	134.0		5.39	4.84	18.54	PC3802-01	2.76	1.49	16.84	9.54
PC3810-14	146.0		4.26	4.65	12.42	PC3802-02	6.21	1.33	24.93	8.44
PC3810-15	154.0		4.80	11.32	13.56	PC3802-03	9.66	1.31	27.60	7.30
PC3810-16	167.0		4.70	4.42	15.60	PC3802-04	12.77	2.67	22.24	7.12
PC3810-17	174.0		5.32	0.33	16.45	PC3802-05	15.18	1.86	27.11	5.96
PC3810-18	185.0		4.59	0.00	17.23	PC3802-06	17.47	1.95	26.27	6.36
PC3810-19	194.0		5.47	6.89	20.10	PC3802-07	20.48	1.92	26.27	5.54
PC3810-20	203.0		4.21	0.72	13.41	PC3802-08	22.65	1.86	25.41	5.30
PC3810-21	216.0		5.75	7.00	19.94	PC3802-09	25.22	2.04	29.64	5.35
PC3810-22	224.0		6.30	3.70	19.04	PC3802-10	28.29	2.08	32.87	6.05
PC3810-23	233.0		6.23	2.33	17.41	PC3802-11	31.07	1.60	33.53	7.26
PC3810-24	244.0		5.09	6.40	13.00	PC3802-12	33.86	1.89	35.90	8.03
PC3810-25	254.0		3.95	5.76	9.92	PC3802-13	36.64	1.94	32.99	6.60
PC3810-26	263.0		4.56	7.79	12.12	PC3802-14	39.15	1.79	26.13	5.84
PC3810-27	273.0		5.38	7.24	11.56	PC3802-15	42.22	2.32	24.69	7.13
PC3810-28	284.0		4.52	10.27	11.79	PC3802-16	45.00	1.59	21.91	4.41
PC3810-29	295.0		5.89	19.61	14.90	PC3802-17	48.07	1.81	18.38	5.78
PC3810-30	305.0		5.11	10.98	12.68	PC3802-18	50.85	1.62	15.62	8.56
PC3810-31	314.0		4.64	10.57	9.59	PC3802-19	53.64	1.82	17.38	8.29
PC3810-32	324.0		6.57	12.88	16.70	PC3802-20	56.42	2.04	14.17	7.59
PC3810-33	335.0		5.90	8.84	10.22	PC3802-21	59.29	2.14	16.52	6.48
PC3810-34	344.0		6.42	14.58	18.27	PC3802-22	62.61	1.78	17.93	5.92
PC3810-35	354.0		6.22	7.80	21.73	PC3802-23	65.94	1.49	15.14	5.93
PC3810-36	364.0		5.78	10.77	28.61	PC3802-24	69.26	1.63	4.56	6.90
PC3810-37	374.0		6.05	7.68	27.10	PC3802-25	72.58	1.96	9.29	7.61
PC3810-38	383.0		4.95	7.96	14.65	PC3802-26	76.96	1.55	16.55	7.89
PC3810-39	394.0		7.06	6.82	17.96	PC3802-27	82.03	2.17	5.46	8.61
PC3810-40	404.0		5.22	8.27	14.48	PC3802-28	87.11	1.69	6.75	6.66
PC3810-41	417.0		5.94	14.85	14.50	PC3802-29	92.18	1.71	0.60	7.82
PC3810-42	424.0		6.39	10.47	17.92	PC3802-30	97.26	1.29	2.99	7.97
PC3810-43	434.0		4.93	25.71	23.97	PC3802-31	102.84	1.59	9.77	9.22
PC3810-44	445.0		5.75	18.06	19.90	PC3802-32	107.92	1.46	9.26	8.63

APPENDIX C.12. BIOGENIC COMPONENTS										
2525m					3835m					
PC38-02	Age	Corq	CaCO3	Bio.SiO2	PC38-11	Age	Corq	CaCO3	Bio.SiO2	
Sample	(ka)	(wt.%)	(wt.%)	(wt.%)	Sample	(ka)	(wt.%)	(wt.%)	(wt.%)	
PC3802-33	113.00	1.36	9.20	9.26	PC3811-23	45.03	4.22	10.42	10.28	
PC3802-34	118.07	1.04	9.53	8.80	PC3811-24	47.02	4.55	9.16	10.52	
PC3802-35	123.15	1.29	19.21	9.83	PC3811-25	49.01	4.34	9.97	10.66	
PC3802-36	128.22	1.40	25.48	8.24	PC3811-26	51.00	3.90	14.50	13.04	
PC3802-37	132.23	1.25	28.29	5.34	PC3811-27	52.99	3.94	12.47	13.74	
PC3802-38	135.30	1.04	30.10	4.90	PC3811-28	54.99	3.60	9.89	13.25	
PC3802-39	138.71	1.15	30.53	6.43	PC3811-29	56.98	3.76	2.11	8.62	
PC3802-40	141.79	1.20	33.37	6.23	PC3811-30	59.62	3.24	3.89	8.43	
PC3802-41	145.20	1.16	32.55	6.01	PC3811-31	62.28	2.87	1.10	8.47	
PC3802-42	148.61	1.03	31.11	6.96	PC3811-32	65.60	3.04	1.21	6.99	
PC3802-43	152.02	1.11	33.36	5.56	PC3811-33	68.93	3.16	20.92	3.47	
PC3802-44	155.44	1.09	30.93	5.56	PC3811-34	72.25	3.58	2.12	12.67	
PC3802-45	158.85	1.17	25.00	4.91	PC3811-35	74.95	3.79	2.78	13.92	
PC3802-46	162.26	1.28	21.59	5.05	PC3811-36	77.04	3.51	2.52	16.76	
PC3802-47	165.68	1.45	33.68	4.15	PC3811-37	79.12	4.09	2.23	13.78	
PC3802-48	169.43	1.41	35.14	4.58	PC3811-38	81.20	4.25	3.24	12.02	
PC3802-49	172.84	1.61	34.35	4.72	PC3811-39	83.29	3.94	3.25	9.07	
PC3802-50	176.26	1.69	31.64	4.72	PC3811-40	85.37	3.41	4.01	8.84	
PC3802-51	179.67	1.41	27.40	5.54	PC3811-41	87.45	3.66	4.05	8.75	
PC3802-52	183.08	1.33	20.77	4.66	PC3811-42	89.54	2.96	0.17	10.29	
PC3802-53	186.50	0.82	14.81	4.72	PC3811-43	91.62	3.05	1.82	12.07	
PC3802-54	189.57	1.40	9.27	5.47	PC3811-44	93.70	3.06	6.63	13.85	
PC3802-55	193.52	1.50	8.18	6.16	PC3811-45	95.79	3.16	4.28	15.01	
PC3802-56	197.42	1.79	5.41	8.62	PC3811-46	97.87	3.22	0.31	10.00	
PC3802-57	202.11	1.26	13.77	7.52	PC3811-47	99.95	3.14	0.06	9.44	
PC3802-58	206.02	1.41	14.71	5.62	PC3811-48	102.04	3.17	2.97	11.99	
PC3802-59	209.53	1.15	16.44	4.62	PC3811-49	104.12	2.67	0.23	12.03	
PC3802-60	213.44	1.11	35.65	4.14	PC3811-50	106.20	2.28	0.22	14.66	
PC3802-61	217.34	0.96	37.54	4.01	PC3811-51	108.29	2.66	0.08	14.56	
PC3802-62	221.25	1.06	31.04	4.44	PC3811-52	110.37	2.51	0.18	14.03	
PC3802-63	225.16	1.15	28.95	3.52	PC3811-53	112.45	2.29	0.00	16.43	
PC3802-64	229.06	1.16	23.30	4.50	PC3811-54	114.54	2.37	0.42	14.39	
PC3802-65	232.97	1.14	14.49	5.17	PC3811-55	116.62	2.33	0.90	17.83	
PC3802-66	237.27	1.18	16.37	6.87	PC3811-56	118.70	2.08	0.35	18.09	
PC3802-67	240.78	1.26	32.34	6.29	PC3811-57	120.79	2.31	0.89	17.09	
PC3802-68	244.50	1.16	29.66	4.18						
PC3802-69	247.71	1.27	25.19	3.78						
PC3802-70	250.91	1.28	27.16	4.79						
PC3802-71	254.12	0.82	27.81	4.33						
PC3802-72	257.32	1.23	25.97	5.72						
PC3802-73	260.53	1.24	25.98	6.27						
PC3802-74	263.73	1.55	24.38	6.44						
PC38-11	3835m									
PC3811-01	0.80	3.87	2.19	7.99						
PC3811-02	2.00	4.27	12.82	4.85						
PC3811-03	2.20	3.30	10.70	3.46						
PC3811-04	3.49	2.97	1.06	9.34						
PC3811-05	6.17	3.28	3.26	9.32						
PC3811-06	8.85	3.59	4.78	8.48						
PC3811-07	11.53	3.63	5.14	8.57						
PC3811-08	13.80	3.30	6.50	7.30						
PC3811-09	16.44	1.62	10.55	3.69						
PC3811-10	18.63	3.33	9.24	8.43						
PC3811-11	20.82	3.39	10.50	8.68						
PC3811-12	23.23	3.56	7.93	9.52						
PC3811-13	25.11	3.44	8.13	9.20						
PC3811-14	27.10	3.26	9.40	7.76						
PC3811-15	29.09	3.40	7.88	8.67						
PC3811-16	31.08	2.97	11.29	7.60						
PC3811-17	33.07	3.15	9.05	8.55						
PC3811-18	35.07	2.55	11.27	6.54						
PC3811-19	37.26	3.77	6.51	10.12						
PC3811-20	39.45	4.04	5.66	10.50						
PC3811-21	40.84	4.03	3.65	11.25						
PC3811-22	43.03	3.70	12.12	8.67						

APPENDIX C.13. PARTITIONED P, U, Y and Sr CONCENTRATIONS																	
CD38-09	(148m)																
Sample	Depth	P	Pterr	Porg	Pphos	Phos	U	Uterr	Uphos	Uorg	Y	Yphos	Yterr	Sr	Srphos	Srterr	Srca1
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
					(non -ve)			(non -ve)									
PC3809-01	4.0	0.240	0.051	0.036	0.153	1.85	10	3	2	5	17	2	15	199	28	126	44
PC3809-02	13.0	0.176	0.052	0.035	0.089	1.07	10	3	1	6	16	1	15	195	17	127	52
PC3809-03	23.0	0.201	0.066	0.032	0.103	1.24	10	3	1	5	19	1	18	194	19	162	13
PC3809-04	34.0	0.199	0.061	0.033	0.106	1.28	9	3	1	5	18	1	17	179	20	149	11
PC3809-05	43.0	0.250	0.061	0.019	0.169	2.04	8	3	2	3	23	2	21	240	32	150	59
PC3809-06	53.0	0.272	0.056	0.031	0.184	2.22	6	3	3	0	17	2	15	175	34	138	3
PC3809-07	62.0	0.231	0.052	0.044	0.136	1.64	10	3	2	5	15	2	14	195	25	126	43
PC3809-08	73.0	0.208	0.062	0.029	0.117	1.42	9	3	2	4	22	1	20	188	22	151	15
PC3809-09	84.0	0.165	0.071	0.031	0.064	0.77	7	4	1	3	21	1	21	168	12	173	0
PC3809-10	94.0	0.174	0.066	0.035	0.073	0.88	8	3	1	3	18	1	17	170	14	161	0
PC3809-11	104.0	0.158	0.059	0.037	0.062	0.75	10	3	1	6	16	1	16	151	12	145	0
PC3809-12	113.0	0.161	0.073	0.026	0.063	0.76	9	4	1	4	22	1	21	166	12	178	0
PC3809-13	124.0	0.239	0.064	0.027	0.148	1.78	10	3	2	4	22	2	20	214	28	157	30
PC3809-14	134.0	0.296	0.056	0.032	0.208	2.51	9	3	3	3	18	3	16	213	39	138	36
PC3809-15	144.0	0.203	0.050	0.034	0.119	1.44	8	3	2	4	16	1	15	183	22	122	39
PC3809-16	152.0	0.147	0.050	0.027	0.071	0.85	7	3	1	4	15	1	14	180	13	122	45
PC3809-17	165.0	0.241	0.048	0.026	0.167	2.01	10	3	2	5	17	2	15	220	31	118	71
PC3809-18	174.0	0.267	0.059	0.018	0.191	2.30	9	3	3	3	22	2	20	243	35	143	64
PC3809-19	185.0	0.427	0.052	0.017	0.358	4.32	11	3	5	3	21	4	17	289	67	128	94
PC3809-20	194.0	0.409	0.053	0.016	0.340	4.10	8	3	5	0	24	4	20	306	63	131	112
PC3809-21	205.0	0.155	0.059	0.011	0.084	1.02	5	3	1	1	22	1	21	256	16	145	95
PC3809-22	214.0	0.398	0.049	0.030	0.319	3.85	13	3	4	6	19	4	15	256	59	121	76
PC3809-23	224.0	0.494	0.052	0.008	0.433	5.23	11	3	6	2	23	5	18	347	81	128	138
PC3809-24	234.0	0.592	0.047	0.013	0.532	6.42	9	2	8	0	20	6	13	305	99	115	91
PC3809-25	243.0	0.347	0.038	0.025	0.284	3.43	10	2	4	4	13	3	10	185	53	93	39
PC3809-26	257.0	0.301	0.045	0.022	0.234	2.82	10	2	3	5	17	3	14	201	44	110	48
PC3809-27	267.0	1.036	0.045	0.012	0.979	11.81	15	2	14	0	25	12	13	374	182	109	82
PC3809-28	273.0	5.797	0.023	0.009	5.766	69.55	148	1	81	65	25	70	-45	1195	1072	55	67
PC3809-29	284.0	0.314	0.053	0.027	0.234	2.82	13	3	3	7	20	3	17	202	44	129	29
PC3809-30	294.0	0.165	0.042	0.028	0.094	1.14	7	2	1	4	15	1	14	170	18	104	49
PC3809-31	304.0	0.168	0.054	0.025	0.089	1.08	8	3	1	4	18	1	17	171	17	133	22
PC3809-32	314.0	0.140	0.053	0.030	0.056	0.68	7	3	1	4	17	1	16	162	10	130	22

APPENDIX C.13. PARTITIONED P, U, Y and Sr CONCENTRATIONS																		
CD38-09	(148m)																	
Sample	Depth	P	Pterr	Porg	Pphos	Phos	U	Uterr	Uphos	Uorg	Y	Yphos	Yterr	Sr	Srphos	Srterr	Srca1	
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	
				(non -ve)				(non -ve)										
PC3809-33	324.0	0.222	0.055	0.030	0.137	1.65	8	3	2	3	21	2	19	187	25	135	26	
PC3809-34	335.0	0.160	0.048	0.032	0.080	0.97	8	3	1	5	17	1	16	163	15	116	31	
PC3809-35	344.0	0.160	0.043	0.034	0.083	1.00	7	2	1	3	15	1	14	153	15	106	31	
PC3809-36	355.0	0.105	0.037	0.031	0.037	0.45	5	2	1	3	11	0	11	156	7	90	59	
PC3809-37	364.0	0.102	0.036	0.030	0.036	0.43	5	2	1	3	11	0	11	185	7	88	90	
PC3809-38	375.0	0.112	0.049	0.033	0.030	0.37	7	3	0	4	15	0	15	162	6	119	37	
PC3809-39	384.0	0.211	0.051	0.027	0.133	1.60	8	3	2	4	19	2	17	214	25	126	63	
PC3809-40	394.0	0.159	0.044	0.030	0.084	1.02	8	2	1	4	15	1	14	179	16	108	54	
PC3809-41	404.0	0.122	0.049	0.025	0.048	0.58	8	3	1	4	16	1	15	156	9	120	26	
PC3809-42	416.0	0.145	0.042	0.031	0.072	0.87	9	2	1	6	14	1	13	202	13	103	86	
PC3809-43	424.0	0.101	0.046	0.029	0.026	0.31	8	2	0	5	14	0	14	149	5	112	32	
PC3809-44	434.0	0.127	0.052	0.035	0.040	0.49	10	3	1	6	16	0	15	165	7	127	30	
PC3809-45	444.0	0.140	0.043	0.025	0.072	0.87	8	2	1	4	14	1	13	186	13	105	67	
PC3809-46	453.0	0.167	0.052	0.025	0.090	1.08	8	3	1	4	18	1	17	179	17	128	34	
PC3809-47	465.0	0.163	0.049	0.029	0.084	1.02	7	3	1	3	16	1	15	183	16	121	47	
PC3809-48	474.0	0.145	0.046	0.031	0.067	0.81	9	2	1	6	14	1	13	201	13	113	75	
PC3809-49	483.0	0.176	0.051	0.024	0.101	1.22	9	3	1	4	18	1	17	178	19	124	35	
PC3809-50	493.0	0.155	0.050	0.027	0.078	0.94	8	3	1	4	16	1	15	276	14	123	138	
PC3809-51	504.0	0.182	0.053	0.022	0.107	1.29	9	3	2	5	21	1	20	193	20	129	44	
PC3809-52	515.0	0.145	0.053	0.025	0.067	0.81	8	3	1	4	18	1	17	182	12	129	40	
PC3809-53	525.0	0.118	0.049	0.032	0.037	0.44	7	3	1	4	15	0	14	194	7	121	66	
PC3809-54	536.0	0.115	0.045	0.028	0.042	0.51	5	2	1	2	14	1	13	200	8	110	81	
PC3809-55	544.0	0.155	0.053	0.022	0.080	0.97	6	3	1	2	18	1	17	201	15	131	55	
PC3809-56	553.0	0.100	0.050	0.019	0.031	0.37	4	3	0	1	15	0	15	198	6	123	69	
PC3809-57	564.0	0.104	0.046	0.018	0.040	0.48	4	2	1	1	14	0	14	193	7	114	72	
PC3809-58	574.0	0.120	0.046	0.018	0.056	0.67	4	2	1	1	15	1	14	208	10	113	85	
PC3809-59	585.0	0.319	0.045	0.015	0.259	3.13	5	2	4	0	15	3	12	282	48	109	125	
PC3809-60	594.0	0.132	0.045	0.017	0.071	0.85	5	2	1	1	14	1	13	214	13	109	92	
PC3809-61	605.0	0.188	0.050	0.018	0.120	1.45	5	3	2	0	18	1	16	237	22	123	92	
PC3809-62	615.0	0.224	0.044	0.018	0.162	1.95	5	2	2	0	15	2	13	234	30	108	96	
PC3809-63	625.0	0.205	0.049	0.016	0.140	1.69	5	3	2	1	16	2	14	233	26	120	87	
PC3809-64	635.0	0.203	0.050	0.018	0.135	1.63	7	3	2	2	17	2	15	242	25	123	94	

APPENDIX C.13. PARTITIONED P, U, Y and Sr CONCENTRATIONS

Sample	Depth (cm)	P (wt.%)	Pterr (wt.%)	Porg (wt.%)	Pphos (wt.%)	Phos (wt.%)	U (ppm)	Uterr (ppm)	Uphos (ppm)	Uorg (ppm)	Y (ppm)	Yphos (ppm)	Yterr (ppm)	Sr (ppm)	Srphos (ppm)	Srterr (ppm)	Srca1 (ppm)
CD38-09	(148m)																
					(non -ve)				(non -ve)								
PC3809-65	646.0	0.139	0.044	0.018	0.077	0.92	5	2	1	2	13	1	12	201	14	108	79
PC3809-66	654.0	0.109	0.042	0.015	0.052	0.62	7	2	1	4	13	1	12	187	10	103	75
PC3809-67	664.0	0.094	0.042	0.017	0.035	0.42	8	2	0	5	13	0	13	189	7	104	79
PC3809-68	674.0	0.084	0.037	0.013	0.034	0.41	8	2	0	5	12	0	12	171	6	90	74
PC3809-69	684.0	0.118	0.049	0.018	0.051	0.62	7	3	1	3	16	1	15	211	9	121	81
PC3809-70	694.0	0.119	0.053	0.018	0.048	0.58	7	3	1	4	16	1	15	212	9	129	73
PC3809-71	703.0	0.098	0.052	0.018	0.028	0.33	7	3	0	4	16	0	16	201	5	128	68
PC3809-72	714.0	0.138	0.048	0.021	0.069	0.84	7	3	1	4	16	1	15	218	13	117	88
PC3809-73	724.0	0.194	0.052	0.016	0.125	1.51	5	3	2	1	17	2	15	232	23	128	81
PC3809-74	734.0	0.198	0.053	0.018	0.127	1.54	5	3	2	0	17	2	15	238	24	129	85
PC3809-75	744.0	0.162	0.051	0.018	0.093	1.12	7	3	1	3	16	1	15	226	17	125	83
PC3809-76	754.0	0.104	0.047	0.017	0.040	0.48	4	2	1	1	15	0	15	202	7	115	79
PC3809-77	764.0	0.133	0.053	0.015	0.065	0.79	5	3	1	1	18	1	17	217	12	129	76
PC3809-78	774.0	0.138	0.054	0.016	0.069	0.83	4	3	1	0	19	1	18	219	13	131	75
PC3809-79	784.0	0.130	0.051	0.014	0.064	0.78	6	3	1	2	18	1	17	215	12	126	78
PC3809-80	794.0	0.150	0.052	0.015	0.083	1.00	5	3	1	1	18	1	17	222	15	126	80
PC3809-81	804.0	0.187	0.049	0.016	0.121	1.46	5	3	2	1	17	1	15	224	23	121	81
PC3809-82	813.0	0.304	0.051	0.014	0.239	2.88	6	3	3	0	18	3	15	270	44	125	101
PC3809-83	823.0	0.203	0.050	0.016	0.137	1.66	5	3	2	0	19	2	17	230	26	122	82
PC3809-84	834.0	0.165	0.052	0.016	0.097	1.17	5	3	1	0	18	1	17	221	18	126	77
PC3809-85	845.0	0.195	0.052	0.016	0.127	1.53	4	3	2	0	18	2	16	232	24	128	80
PC3809-86	854.0	0.101	0.059	0.012	0.030	0.36	5	3	0	2	20	0	20	205	6	144	56
PC38-10	(257m)																
PC3810-01	6.0	0.469	0.046	0.049	0.374	4.52	15.3	2.4	5.3	7.6	20	4.5	15.0	346	70	112	164
PC3810-02	14.0	1.062	0.048	0.027	0.987	11.91	19.9	2.5	13.9	3.4	28	11.9	16.2	435	184	117	134
PC3810-03	24.0	1.959	0.048	0.009	1.901	22.94	19.9	2.6	26.8	0.0	29	23.0	6.5	597	354	119	125
PC3810-04	34.0	1.027	0.048	0.011	0.968	11.67	15.7	2.6	13.6	0.0	29	11.7	16.9	494	180	119	196
PC3810-05	44.0	0.435	0.051	0.036	0.348	4.19	15.3	2.7	4.9	7.7	23	4.2	19.0	264	65	125	74
PC3810-06	54.0	0.294	0.052	0.037	0.205	2.48	14.7	2.8	2.9	9.0	20	2.5	17.7	235	38	128	69
PC3810-07	64.0	0.462	0.054	0.022	0.387	4.67	15.1	2.8	5.5	6.8	23	4.7	18.4	284	72	131	80

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APPENDIX C.13. PARTITIONED P, U, Y and Sr CONCENTRATIONS																	
CD38-10	(257m)																
Sample	Depth	P	Pterr	Porg	Pphos	Phos	U	Uterr	Uphos	Uorg	Y	Yphos	Yterr	Sr	Srphos	Srterr	Srca1
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
					(non -ve)				(non -ve)								
PC3810-08	74.0	0.705	0.055	0.016	0.634	7.64	15.5	2.9	8.9	3.7	26	7.7	18.2	340	118	135	87
PC3810-09	84.0	1.086	0.047	0.005	1.034	12.47	15.4	2.5	14.6	0.0	29	12.5	16.8	431	192	116	123
PC3810-10	94.0	1.505	0.050	0.005	1.450	17.49	27.2	2.7	20.4	4.1	29	17.5	11.8	504	270	123	112
PC3810-10	104.0	0.867	0.048	0.006	0.814	9.82	15.8	2.5	11.5	1.8	28	9.8	18.6	474	151	116	206
PC3810-11	113.0	0.579	0.049	0.004	0.526	6.34	10.3	2.6	7.4	0.3	27	6.4	21.0	436	98	120	218
PC3810-12	126.0	0.524	0.042	0.021	0.461	5.56	10.9	2.2	6.5	2.2	19	5.6	13.6	348	86	103	159
PC3810-13	134.0	0.559	0.041	0.029	0.489	5.90	12.5	2.2	6.9	3.5	18	5.9	12.2	283	91	101	90
PC3810-14	146.0	0.428	0.048	0.023	0.357	4.31	12.4	2.5	5.0	4.8	21	4.3	16.6	293	66	117	109
PC3810-15	154.0	0.433	0.044	0.025	0.363	4.38	12.4	2.3	5.1	5.0	20	4.4	15.6	350	68	109	174
PC3810-16	167.0	0.318	0.047	0.025	0.246	2.97	12.0	2.5	3.5	6.1	20	3.0	17.2	254	46	115	93
PC3810-17	174.0	0.364	0.050	0.028	0.286	3.45	13.0	2.6	4.0	6.3	20	3.5	16.6	225	53	123	49
PC3810-18	185.0	0.299	0.050	0.024	0.225	2.71	11.8	2.6	3.2	6.0	20	2.7	17.3	189	42	122	25
PC3810-19	194.0	0.273	0.042	0.029	0.202	2.43	10.9	2.2	2.8	5.8	17	2.4	14.8	257	38	104	116
PC3810-20	203.0	0.381	0.052	0.022	0.307	3.70	15.2	2.8	4.3	8.1	21	3.7	17.3	238	57	128	54
PC3810-21	216.0	0.341	0.040	0.030	0.271	3.26	12.0	2.1	3.8	6.1	17	3.3	13.9	263	50	98	115
PC3810-22	224.0	0.272	0.042	0.033	0.196	2.37	11.8	2.2	2.8	6.8	17	2.4	14.8	213	37	104	72
PC3810-23	233.0	0.300	0.048	0.033	0.219	2.64	13.3	2.6	3.1	7.7	20	2.6	17.6	222	41	119	62
PC3810-24	244.0	0.374	0.049	0.027	0.298	3.59	11.4	2.6	4.2	4.6	20	3.6	16.5	283	55	120	107
PC3810-25	254.0	0.698	0.046	0.021	0.631	7.61	14.7	2.4	8.9	3.4	22	7.6	14.6	355	117	113	125
PC3810-26	263.0	0.571	0.043	0.024	0.504	6.08	13.2	2.3	7.1	3.8	20	6.1	14.1	347	94	106	148
PC3810-27	273.0	0.322	0.049	0.029	0.245	2.95	11.9	2.6	3.5	5.9	21	3.0	18.1	283	46	119	118
PC3810-28	284.0	0.367	0.046	0.024	0.297	3.58	13.1	2.4	4.2	6.5	22	3.6	18.4	329	55	113	161
PC3810-29	295.0	0.308	0.035	0.031	0.241	2.91	10.8	1.9	3.4	5.5	16	2.9	13.1	421	45	87	290
PC3810-30	305.0	0.277	0.048	0.027	0.202	2.44	11.6	2.5	2.9	6.2	21	2.4	18.6	320	38	117	166
PC3810-31	314.0	0.325	0.050	0.025	0.250	3.02	11.9	2.6	3.5	5.7	21	3.0	17.9	343	47	123	174
PC3810-32	324.0	0.298	0.039	0.035	0.224	2.71	12.2	2.1	3.2	7.0	16	2.7	13.4	327	42	95	190
PC3810-33	335.0	0.309	0.048	0.031	0.230	2.77	12.4	2.5	3.2	6.6	20	2.8	17.2	302	43	117	142
PC3810-34	344.0	0.318	0.034	0.034	0.250	3.02	10.9	1.8	3.5	5.6	14	3.0	11.0	329	47	82	201
PC3810-35	354.0	0.240	0.031	0.033	0.176	2.12	10.0	1.6	2.5	5.9	12	2.1	9.9	231	33	76	122
PC3810-36	364.0	0.262	0.027	0.031	0.204	2.46	10.3	1.4	2.9	5.9	12	2.5	9.5	270	38	67	165
PC3810-37	374.0	0.220	0.029	0.032	0.159	1.92	11.7	1.5	2.2	8.0	11	1.9	8.9	214	30	70	114
PC3810-38	383.0	0.240	0.051	0.026	0.163	1.96	12.9	2.7	2.3	7.9	19	2.0	17.0	269	30	125	113

APPENDIX C.13. PARTITIONED P, U, Y and Sr CONCENTRATIONS																	
CD38-10	(257m)																
Sample	Depth	P	Pterr	Porg	Pphos	Phos	U	Uterr	Uphos	Uorg	Y	Yphos	Yterr	Sr	Srphos	Srterr	Srcal
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
					(non -ve)					(non -ve)							
PC3810-39	394.0	0.297	0.042	0.037	0.218	2.63	14.2	2.2	3.1	8.9	18	2.6	15.5	250	41	102	107
PC3810-40	404.0	0.288	0.048	0.028	0.212	2.56	12.9	2.5	3.0	7.4	22	2.6	19.5	288	39	118	131
PC3810-41	417.0	0.347	0.041	0.031	0.275	3.31	12.3	2.2	3.9	6.2	19	3.3	15.7	384	51	100	233
PC3810-42	424.0	0.314	0.043	0.034	0.237	2.86	14.7	2.3	3.3	9.1	18	2.9	15.2	300	44	105	151
PC3810-43	434.0	0.380	0.020	0.026	0.334	4.02	10.3	1.1	4.7	4.5	11	4.0	6.9	511	62	50	400
PC3810-44	445.0	0.267	0.034	0.030	0.203	2.44	12.0	1.8	2.9	7.3	14	2.5	11.4	388	38	83	267
PC3810-45	456.0	0.276	0.031	0.033	0.212	2.55	13.5	1.6	3.0	8.8	13	2.6	10.4	352	39	76	237
PC3810-46	467.0	0.215	0.021	0.032	0.162	1.96	6.2	1.1	2.3	2.8	10	2.0	8.0	347	30	52	265
PC3810-47	476.0	0.495	0.041	0.035	0.419	5.05	16.9	2.2	5.9	8.8	20	5.1	14.9	436	78	101	256
PC3810-48	484.0	0.464	0.039	0.036	0.389	4.69	14.8	2.1	5.5	7.2	20	4.7	15.2	453	72	96	285
PC3810-49	494.0	0.892	0.037	0.034	0.821	9.90	23.7	2.0	11.6	10.1	26	9.9	16.0	473	153	91	230
PC3810-50	504.0	2.404	0.046	0.011	2.348	28.32	21.8	2.4	33.1	0.0	33	28.4	4.1	642	437	112	94
PC3810-51	514.0	0.117	0.049	0.021	0.047	0.57	5.9	2.6	0.7	2.7	17	0.6	16.3	197	9	119	69
PC3810-52	524.0	0.108	0.053	0.017	0.038	0.46	6.4	2.8	0.5	3.0	18	0.5	17.3	193	7	129	56
PC3810-53	534.0	0.264	0.039	0.063	0.162	1.95	22.9	2.1	2.3	18.5	15	2.0	13.0	274	30	96	148
PC3810-54	545.0	0.204	0.039	0.052	0.112	1.36	17.2	2.1	1.6	13.5	15	1.4	13.6	242	21	97	125
PC3810-55	554.0	0.199	0.036	0.056	0.107	1.28	18.3	1.9	1.5	14.8	13	1.3	11.7	285	20	88	177
PC3810-56	564.0	0.299	0.031	0.033	0.235	2.83	10.5	1.6	3.3	5.5	12	2.8	9.1	413	44	76	294
PC3810-57	574.0	0.251	0.035	0.036	0.180	2.17	11.1	1.9	2.5	6.7	14	2.2	11.7	476	33	86	356
PC3810-58	584.0	0.192	0.035	0.037	0.120	1.45	9.0	1.8	1.7	5.5	14	1.5	12.5	420	22	85	313
PC3810-59	596.0	0.202	0.034	0.039	0.129	1.55	22.7	1.8	1.8	19.1	14	1.6	12.5	411	24	84	303
PC3810-60	604.0	0.205	0.035	0.039	0.131	1.58	16.7	1.8	1.8	13.0	15	1.6	13.5	448	24	86	338
PC3810-61	614.0	0.147	0.039	0.038	0.071	0.85	15.2	2.0	1.0	12.1	14	0.9	13.1	352	13	95	244
PC3810-62	624.0	0.204	0.042	0.033	0.129	1.56	10.3	2.2	1.8	6.3	17	1.6	15.4	424	24	102	298
PC3810-63	634.0	0.216	0.041	0.034	0.141	1.71	9.4	2.2	2.0	5.3	16	1.7	14.2	452	26	100	325
PC3810-64	645.0	0.146	0.040	0.034	0.072	0.86	10.6	2.1	1.0	7.5	15	0.9	14.2	318	13	98	206
PC3810-65	655.0	0.136	0.039	0.040	0.058	0.70	8.8	2.0	0.8	6.0	14	0.7	13.3	328	11	95	223
PC3810-66	667.0	0.176	0.043	0.035	0.099	1.19	11.4	2.2	1.4	7.8	16	1.2	14.8	331	18	104	208
PC3810-67	674.0	0.183	0.049	0.034	0.100	1.20	14.1	2.6	1.4	10.1	16	1.2	14.7	256	19	121	117
PC3810-68	683.0	0.139	0.045	0.033	0.060	0.73	11.3	2.4	0.8	8.0	14	0.7	13.1	271	11	111	149
PC3810-69	694.0	0.206	0.059	0.025	0.122	1.47	9.8	3.1	1.7	4.9	19	1.5	17.4	235	23	145	67
PC3810-70	704.0	0.193	0.066	0.024	0.104	1.25	8.0	3.5	1.5	3.1	22	1.3	20.7	194	19	161	14

APPENDIX C.13. PARTITIONED P, U, Y and Sr CONCENTRATIONS																	
Sample	Depth (cm)	P (wt.%)	Pterr (wt.%)	Porg (wt.%)	Pphos (wt.%)	Phos (wt.%)	U (ppm)	Uterr (ppm)	Uphos (ppm)	Uorg (ppm)	Y (ppm)	Yphos (ppm)	Yterr (ppm)	Sr (ppm)	Srphos (ppm)	Srterr (ppm)	Srcal (ppm)
					(non -ve)				(non -ve)								
CD38-10	(257m)																
PC3810-71	714.0	0.215	0.059	0.026	0.130	1.57	8.1	3.1	1.8	3.1	19	1.6	17.4	252	24	144	84
PC3810-72	724.0	0.193	0.052	0.027	0.114	1.38	10.1	2.8	1.6	5.8	16	1.4	14.5	259	21	128	110
PC3810-74	734.0	0.215	0.063	0.021	0.131	1.58	11.0	3.3	1.8	5.9	19	1.6	17.3	185	24	154	7
PC3810-75	745.0	0.202	0.069	0.016	0.117	1.41	9.6	3.7	1.6	4.3	21	1.4	19.4	202	22	170	10
PC3810-76	754.0	0.254	0.056	0.022	0.176	2.12	9.6	3.0	2.5	4.1	17	2.1	14.7	195	33	138	24
PC3810-77	764.0	0.539	0.062	0.013	0.464	5.60	11.1	3.3	6.5	1.3	25	5.6	19.1	298	86	152	60
PC38-02	(2525m)																
	(Age)																
PC3802-01	2.76	0.117	0.050	0.008	0.059	0.71	9	2.7	0.8	5.1	24	1	24	535	11	123	401
PC3802-02	6.21	0.113	0.045	0.007	0.061	0.73	6	2.4	0.9	3.1	20	1	19	642	11	110	521
PC3802-03	9.66	0.105	0.044	0.007	0.054	0.65	8	2.3	0.8	4.7	20	1	19	682	10	107	565
PC3802-04	12.77	0.096	0.048	0.014	0.034	0.41	8	2.5	0.5	5.5	18	0	18	569	6	117	446
PC3802-05	15.18	0.092	0.047	0.010	0.035	0.42	8	2.5	0.5	4.8	18	0	18	619	6	115	497
PC3802-06	17.47	0.091	0.046	0.010	0.035	0.42	6	2.4	0.5	3.5	19	0	18	608	6	112	489
PC3802-07	20.48	0.097	0.049	0.010	0.038	0.45	6	2.6	0.5	3.0	21	0	21	584	7	121	456
PC3802-08	22.65	0.095	0.048	0.010	0.037	0.45	7	2.5	0.5	3.6	20	0	20	576	7	118	451
PC3802-09	25.22	0.097	0.045	0.011	0.041	0.49	10	2.4	0.6	7.3	19	0	19	624	8	110	507
PC3802-10	28.29	0.095	0.042	0.011	0.043	0.51	6	2.2	0.6	3.2	19	1	19	668	8	102	558
PC3802-11	31.07	0.094	0.041	0.008	0.045	0.54	7	2.1	0.6	4.3	17	1	17	671	8	100	564
PC3802-12	33.86	0.089	0.038	0.010	0.042	0.50	7	2.0	0.6	4.9	17	1	16	704	8	92	604
PC3802-13	36.64	0.092	0.041	0.010	0.040	0.48	8	2.2	0.6	5.1	18	0	17	695	7	101	586
PC3802-14	39.15	0.097	0.048	0.009	0.040	0.48	7	2.5	0.6	3.4	20	0	20	596	7	117	472
PC3802-15	42.22	0.098	0.049	0.012	0.037	0.44	6	2.6	0.5	2.7	20	0	20	582	7	120	454
PC3802-16	45.00	0.103	0.054	0.008	0.041	0.50	5	2.8	0.6	1.6	21	0	21	549	8	131	410
PC3802-17	48.07	0.102	0.054	0.010	0.038	0.46	10	2.9	0.5	6.6	23	0	22	511	7	133	371
PC3802-18	50.85	0.103	0.052	0.009	0.043	0.52	10	2.7	0.6	6.8	22	1	21	460	8	126	326
PC3802-19	53.64	0.103	0.051	0.010	0.042	0.51	11	2.7	0.6	7.3	24	1	24	502	8	124	370
PC3802-20	56.42	0.103	0.054	0.011	0.039	0.47	9	2.9	0.5	6.0	24	0	24	462	7	132	323
PC3802-21	59.29	0.103	0.055	0.011	0.037	0.45	9	2.9	0.5	5.4	24	0	24	491	7	134	350
PC3802-22	62.61	0.103	0.054	0.009	0.039	0.47	10	2.9	0.6	6.2	24	0	23	512	7	133	372
PC3802-23	65.94	0.105	0.057	0.008	0.041	0.49	5	3.0	0.6	1.8	25	0	24	459	8	139	312

APPENDIX C.13. PARTITIONED P, U, Y and Sr CONCENTRATIONS																	
CD38-02	(2525m)																
Sample	Age	P	Pterr	Porg	Pphos	Phos	U	Uterr	Uphos	Uorg	Y	Yphos	Yterr	Sr	Srphos	Srterr	Srca1
	(ka)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
					(non -ve)					(non -ve)							
PC3802-24	69.26	0.111	0.063	0.009	0.039	0.47	7	3.3	0.6	3.0	26	0	25	362	7	155	199
PC3802-25	72.58	0.117	0.057	0.010	0.050	0.60	9	3.0	0.7	5.5	26	1	25	399	9	141	250
PC3802-26	76.96	0.119	0.051	0.008	0.060	0.72	9	2.7	0.8	5.4	25	1	24	492	11	126	356
PC3802-27	82.03	0.116	0.060	0.011	0.044	0.53	7	3.2	0.6	2.9	26	1	26	363	8	148	206
PC3802-28	87.11	0.113	0.061	0.009	0.043	0.52	8	3.2	0.6	4.4	26	1	25	376	8	149	219
PC3802-29	92.18	0.113	0.066	0.009	0.038	0.45	8	3.5	0.5	3.5	26	0	26	311	7	162	143
PC3802-30	97.26	0.131	0.064	0.007	0.060	0.73	9	3.4	0.9	4.4	28	1	27	336	11	156	168
PC3802-31	102.84	0.130	0.057	0.008	0.064	0.78	11	3.0	0.9	6.9	28	1	27	403	12	139	252
PC3802-32	107.92	0.124	0.058	0.008	0.058	0.70	10	3.1	0.8	6.3	27	1	26	398	11	142	246
PC3802-33	113.00	0.109	0.058	0.007	0.044	0.53	6	3.1	0.6	2.6	28	1	28	403	8	142	253
PC3802-34	118.07	0.114	0.057	0.006	0.051	0.62	8	3.0	0.7	4.6	28	1	27	435	10	140	286
PC3802-35	123.15	0.101	0.049	0.007	0.045	0.54	9	2.6	0.6	5.4	22	1	22	560	8	121	431
PC3802-36	128.22	0.089	0.048	0.007	0.034	0.41	7	2.5	0.5	3.8	18	0	17	621	6	117	497
PC3802-37	132.23	0.083	0.048	0.007	0.028	0.34	8	2.5	0.4	5.1	19	0	18	651	5	118	528
PC3802-38	135.30	0.082	0.046	0.006	0.030	0.37	7	2.4	0.4	4.2	19	0	19	667	6	113	548
PC3802-39	138.71	0.084	0.045	0.006	0.032	0.39	9	2.4	0.5	6.4	20	0	19	651	6	110	535
PC3802-40	141.79	0.087	0.043	0.006	0.037	0.45	8	2.3	0.5	5.1	19	0	19	683	7	106	570
PC3802-41	145.20	0.086	0.044	0.006	0.035	0.42	5	2.3	0.5	2.6	19	0	19	684	7	109	569
PC3802-42	148.61	0.083	0.044	0.005	0.033	0.40	6	2.3	0.5	3.6	19	0	19	674	6	109	560
PC3802-43	152.02	0.083	0.044	0.006	0.033	0.40	7	2.3	0.5	4.5	19	0	18	692	6	107	579
PC3802-44	155.44	0.087	0.045	0.006	0.036	0.43	12	2.4	0.5	8.9	19	0	18	661	7	111	544
PC3802-45	158.85	0.088	0.050	0.006	0.032	0.39	8	2.6	0.5	4.6	20	0	19	578	6	122	451
PC3802-46	162.26	0.092	0.053	0.007	0.032	0.39	7	2.8	0.5	3.5	22	0	21	531	6	130	395
PC3802-47	165.68	0.091	0.045	0.008	0.038	0.46	9	2.4	0.5	5.6	19	0	18	680	7	111	562
PC3802-48	169.43	0.090	0.043	0.007	0.040	0.48	10	2.3	0.6	6.7	19	0	18	706	7	105	594
PC3802-49	172.84	0.090	0.043	0.009	0.038	0.46	6	2.3	0.5	3.3	20	0	20	699	7	107	585
PC3802-50	176.26	0.098	0.046	0.009	0.043	0.51	8	2.4	0.6	5.4	20	1	20	668	8	113	547
PC3802-51	179.67	0.094	0.048	0.007	0.038	0.46	10	2.5	0.5	6.5	21	0	20	641	7	118	516
PC3802-52	183.08	0.096	0.053	0.007	0.036	0.44	6	2.8	0.5	2.4	20	0	20	555	7	130	418
PC3802-53	186.50	0.088	0.059	0.004	0.025	0.30	2	3.1	0.3	0.0	17	0	17	505	5	145	356
PC3802-54	189.57	0.113	0.062	0.007	0.044	0.53	6	3.3	0.6	2.3	27	1	26	398	8	152	238
PC3802-55	193.52	0.115	0.062	0.008	0.046	0.55	6	3.3	0.6	1.6	29	1	28	382	9	151	222

APPENDIX C.13. PARTITIONED P, U, Y and Sr CONCENTRATIONS

Sample	Age (ka)	P (wt.%)	Pterr (wt.%)	Porg (wt.%)	Pphos (wt.%)	Phos (wt.%)	U (ppm)	Uterr (ppm)	Uphos (ppm)	Uorg (ppm)	Y (ppm)	Yphos (ppm)	Yterr (ppm)	Sr (ppm)	Srphos (ppm)	Srterr (ppm)	Srca1 (ppm)
CD38-02	(2525m)																
					(non -ve)				(non -ve)								
PC3802-56	197.42	0.115	0.059	0.010	0.047	0.57	7	3.1	0.7	2.9	29	1	28	345	9	144	192
PC3802-57	202.11	0.111	0.054	0.007	0.050	0.60	9	2.9	0.7	5.0	27	1	26	457	9	133	314
PC3802-58	206.02	0.103	0.057	0.007	0.039	0.47	7	3.0	0.6	3.2	27	0	26	483	7	138	337
PC3802-59	209.53	0.100	0.058	0.006	0.036	0.44	7	3.0	0.5	3.0	26	0	26	509	7	141	361
PC3802-60	213.44	0.096	0.043	0.006	0.047	0.57	9	2.3	0.7	6.2	24	1	23	791	9	105	677
PC3802-61	217.34	0.094	0.042	0.005	0.047	0.57	9	2.2	0.7	6.2	22	1	21	812	9	103	701
PC3802-62	221.25	0.094	0.046	0.006	0.042	0.51	8	2.5	0.6	5.0	23	1	22	671	8	114	550
PC3802-63	225.16	0.094	0.049	0.006	0.039	0.47	8	2.6	0.5	5.2	22	0	22	656	7	120	529
PC3802-64	229.06	0.102	0.055	0.006	0.041	0.49	8	2.9	0.6	4.6	25	0	25	584	8	134	442
PC3802-65	232.97	0.102	0.058	0.006	0.038	0.46	5	3.1	0.5	1.7	26	0	26	480	7	143	330
PC3802-66	237.27	0.112	0.053	0.006	0.053	0.64	5	2.8	0.7	1.2	25	1	24	532	10	131	391
PC3802-67	240.78	0.094	0.041	0.007	0.046	0.55	12	2.2	0.6	8.7	20	1	19	766	9	101	657
PC3802-68	244.50	0.085	0.047	0.006	0.032	0.38	9	2.5	0.4	6.1	18	0	18	700	6	115	579
PC3802-69	247.71	0.079	0.052	0.007	0.020	0.24	9	2.7	0.3	6.2	19	0	19	622	4	126	492
PC3802-70	250.91	0.077	0.049	0.007	0.021	0.25	9	2.6	0.3	5.7	19	0	19	641	4	121	516
PC3802-71	254.12	0.079	0.050	0.004	0.025	0.30	8	2.6	0.3	4.7	20	0	20	635	5	122	508
PC3802-72	257.32	0.081	0.048	0.007	0.026	0.32	6	2.5	0.4	3.1	20	0	20	613	5	117	491
PC3802-73	260.53	0.083	0.049	0.007	0.028	0.34	8	2.6	0.4	5.3	22	0	21	610	5	119	486
PC3802-74	263.73	0.088	0.049	0.008	0.030	0.37	8	2.6	0.4	5.4	24	0	23	573	6	120	447
PC38-11	(3835m)																
PC3811-01	0.80	0.31	0.062	0.021	0.231	2.78	11	3.3	3.3	4.4	27	3	24	258	43	153	62
PC3811-02	2.00	0.38	0.053	0.023	0.303	3.65	9	2.8	4.3	2.3	21	4	17	348	56	129	162
PC3811-03	2.20	0.36	0.053	0.017	0.292	3.52	8	2.8	4.1	0.6	24	4	20	330	54	131	145
PC3811-04	3.49	0.20	0.065	0.016	0.117	1.41	14	3.4	1.7	8.7	30	1	28	261	22	158	81
PC3811-05	6.17	0.17	0.064	0.017	0.088	1.06	11	3.4	1.2	6.8	26	1	25	256	16	156	84
PC3811-06	8.85	0.13	0.062	0.019	0.052	0.63	11	3.3	0.7	6.5	22	1	22	255	10	152	93
PC3811-07	11.53	0.13	0.064	0.019	0.046	0.56	12	3.4	0.7	8.1	10	1	10	239	9	156	74
PC3811-08	13.80	0.14	0.063	0.018	0.060	0.72	8	3.3	0.8	3.6	21	1	20	279	11	153	115
PC3811-09	16.44	0.27	0.062	0.009	0.200	2.41	5	3.3	2.8	0.0	23	2	20	376	37	153	185
PC3811-10	18.63	0.14	0.059	0.018	0.063	0.76	9	3.1	0.9	5.0	21	1	20	303	12	145	147

APPENDIX C.13. PARTITIONED P, U, Y and Sr CONCENTRATIONS																	
CD38-11	(3835m)																
Sample	Depth	P	Pterr	Porg	Pphos	Phos	U	Uterr	Uphos	Uorg	Y	Yphos	Yterr	Sr	Srphos	Srterr	Srca1
	(cm)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
				(non -ve)				(non -ve)									
PC3811-11	20.82	0.13	0.057	0.018	0.060	0.72	6	3.0	0.8	1.8	21	1	20	318	11	139	168
PC3811-12	23.23	0.14	0.058	0.019	0.063	0.76	5	3.1	0.9	0.6	20	1	20	285	12	142	131
PC3811-13	25.11	0.13	0.060	0.018	0.056	0.67	5	3.2	0.8	1.5	21	1	20	291	10	146	134
PC3811-14	27.10	0.15	0.059	0.017	0.076	0.92	6	3.1	1.1	1.3	21	1	20	313	14	146	153
PC3811-15	29.09	0.15	0.063	0.018	0.070	0.85	6	3.3	1.0	1.6	21	1	20	291	13	155	123
PC3811-16	31.08	0.16	0.057	0.016	0.091	1.10	9	3.0	1.3	4.5	21	1	20	341	17	140	184
PC3811-17	33.07	0.15	0.065	0.017	0.070	0.85	8	3.4	1.0	3.5	21	1	20	308	13	158	137
PC3811-18	35.07	0.22	0.059	0.014	0.151	1.82	9	3.1	2.1	3.6	24	2	22	362	28	144	189
PC3811-19	37.26	0.15	0.060	0.020	0.070	0.85	9	3.2	1.0	5.0	24	1	23	279	13	147	118
PC3811-20	39.45	0.15	0.062	0.021	0.062	0.75	6	3.3	0.9	2.2	23	1	23	262	12	151	99
PC3811-21	40.84	0.14	0.063	0.021	0.055	0.66	6	3.3	0.8	1.6	24	1	23	245	10	153	81
PC3811-22	43.03	0.18	0.056	0.020	0.110	1.32	11	2.9	1.5	6.4	24	1	22	358	20	137	201
PC3811-23	45.03	0.15	0.057	0.022	0.072	0.87	7	3.0	1.0	2.5	25	1	24	325	13	141	172
PC3811-24	47.02	0.15	0.059	0.024	0.069	0.83	10	3.1	1.0	6.2	26	1	25	305	13	143	149
PC3811-25	49.01	0.16	0.059	0.023	0.073	0.88	10	3.1	1.0	6.0	25	1	24	316	14	144	158
PC3811-26	51.00	0.15	0.051	0.021	0.076	0.92	10	2.7	1.1	5.8	25	1	24	359	14	126	219
PC3811-27	52.99	0.15	0.052	0.021	0.077	0.93	10	2.7	1.1	6.1	25	1	24	343	14	127	202
PC3811-28	54.99	0.15	0.055	0.019	0.080	0.96	10	2.9	1.1	5.7	26	1	25	314	15	134	165
PC3811-29	56.98	0.15	0.066	0.020	0.068	0.82	10	3.5	1.0	5.9	27	1	27	241	13	162	67
PC3811-30	59.62	0.16	0.065	0.017	0.078	0.94	9	3.4	1.1	5.0	26	1	25	253	15	158	80
PC3811-31	62.28	0.16	0.067	0.015	0.073	0.88	7	3.6	1.0	2.7	29	1	28	236	14	165	58
PC3811-32	65.60	0.20	0.070	0.016	0.114	1.38	10	3.7	1.6	4.6	28	1	26	235	21	171	43
PC3811-33	68.93	0.44	0.047	0.017	0.375	4.53	17	2.5	5.3	9.3	24	5	19	423	70	116	238
PC3811-34	72.25	0.15	0.059	0.019	0.074	0.90	10	3.1	1.0	6.0	26	1	25	243	14	144	85
PC3811-35	74.95	0.15	0.059	0.020	0.073	0.88	9	3.1	1.0	5.3	26	1	25	247	14	144	90
PC3811-36	77.04	0.15	0.056	0.019	0.079	0.96	9	3.0	1.1	4.4	27	1	26	248	15	137	96
PC3811-37	79.12	0.16	0.058	0.022	0.077	0.93	4	3.1	1.1	0.0	29	1	28	241	14	143	85
PC3811-38	81.20	0.14	0.060	0.023	0.056	0.68	9	3.2	0.8	4.5	27	1	26	247	11	147	90
PC3811-39	83.29	0.15	0.065	0.021	0.067	0.81	9	3.4	0.9	5.0	30	1	29	256	13	159	85
PC3811-40	85.37	0.16	0.066	0.018	0.073	0.89	7	3.5	1.0	2.7	31	1	30	260	14	162	84
PC3811-41	87.45	0.15	0.064	0.019	0.070	0.84	8	3.4	1.0	3.5	31	1	30	258	13	156	90
PC3811-42	89.54	0.16	0.070	0.016	0.075	0.91	8	3.7	1.1	3.6	33	1	32	233	14	171	48

APPENDIX C.14. NEW PRODUCTION DATA (after DYMOND et al., 1992)

APPENDIX C.14. NEW PRODUCTION DATA (after DYMOND et al., 1992)												
CD38-02	(2525m)											
Age	Babio	F Babio	Pnew	Age	Babio	F Babio	Pnew	Age	Babio	F Babio	Pnew	
(ka)	(ppm)	(ug/cm2/kyr)	(qC/m2/yr)	(ka)	(ppm)	(ug/cm2/kyr)	(qC/m2/yr)	(ka)	(ppm)	(ug/cm2/kyr)	(qC/m2/yr)	
2.76	1720	6.26	22.08	76.96	1526	4.44	13.17	179.67	973	4.24	12.26	
6.21	1471	5.56	18.49	82.03	1445	4.10	11.66	183.08	702	3.00	7.32	
9.66	1405	5.04	15.92	87.11	1307	3.77	10.29	186.50	621	2.95	7.11	
12.77	856	3.89	10.80	92.18	1394	3.95	11.03	189.57	1072	4.43	13.11	
15.18	902	4.57	13.75	97.26	1578	4.44	13.15	193.52	1205	4.37	12.84	
17.47	835	4.22	12.20	102.84	1514	4.22	12.20	197.42	1685	5.83	19.84	
20.48	1110	5.59	18.61	107.92	1595	4.53	13.59	202.11	1630	7.68	30.02	
22.65	1021	5.05	15.97	113.00	1515	4.36	12.81	206.02	1534	7.15	26.97	
25.22	1026	4.63	14.04	118.07	1935	5.36	17.49	209.53	1419	5.70	19.19	
28.29	1013	4.60	13.90	123.15	1561	4.37	12.85	213.44	1638	6.86	25.33	
31.07	1004	4.62	13.97	128.22	994	2.85	6.75	217.34	1403	5.85	19.95	
33.86	994	4.46	13.24	132.23	893	3.66	9.87	221.25	1223	5.05	15.97	
36.64	1036	4.68	14.27	135.30	936	4.04	11.42	225.16	1016	4.35	12.78	
39.15	1090	4.83	14.94	138.71	914	3.95	11.06	229.06	1184	4.89	15.24	
42.22	985	4.32	12.64	141.79	989	4.23	12.25	232.97	1346	5.23	16.86	
45.00	1040	4.92	15.38	145.20	987	4.25	12.35	237.27	1941	7.31	27.87	
48.07	1070	5.02	15.82	148.61	872	3.72	10.07	240.78	1648	6.25	22.03	
50.85	1176	5.08	16.12	152.02	724	3.18	7.98	244.50	1102	5.09	16.19	
53.64	1332	5.93	20.34	155.44	869	3.85	10.64	247.71	909	4.11	11.74	
56.42	1208	5.21	16.76	158.85	809	3.38	8.74	250.91	909	4.22	12.18	
59.29	1053	4.12	11.76	162.26	801	3.37	8.69	254.12	1090	4.91	15.33	
62.61	1077	4.33	12.67	165.68	890	3.90	10.81	257.32	1106	4.98	15.65	
65.94	905	3.71	10.06	169.43	987	4.31	12.58	260.53	1060	4.86	15.08	
69.26	1290	5.15	16.44	172.84	999	4.30	12.57	263.73	986	4.45	13.21	
72.58	1256	5.02	15.84	176.26	996	4.21	12.17					

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APPENDIX C.15. URANIUM/THORIUM RADIOGENIC ISOTOPE RESULTS

Two duplicate samples from base of phosphorite nodule at 273cm in CD38-09

	Sample H				Sample I			
	U-238	U-234	Th-232	Th-230	U-238	U-234	Th-232	Th-230
Isotope corrected counts	8373.145	9264.984	81.4551	7840.986	9178.314	10294.25	23.3521	934.7183
Spike counts (U-232/Th-228)	17444.58	17444.58	25037.17	25037.17	22791.39	22791.39	3352.682	3352.682
Spike activity (dpm/0.1ml)	62.92	62.92	68.87	68.87	62.92	62.92	68.87	68.87
Spike volume (ml)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Error on spike added	0.88088	0.88088	0.96418	0.96418	0.88088	0.88088	0.96418	0.96418
Sample weight (g)	0.36851	0.36851	0.36851	0.36851	0.30708	0.30708	0.30708	0.30708
Activity of isotope (dpm/g)	81.953	90.683	0.606	58.528	82.514	92.547	1.562	62.527
Error	±0.583	±0.635	±0.025	±0.411	±0.473	±0.522	±0.100	±0.759
Element concentration (ppm)	109.9	(Uranium)	2.5	(Thorium)	110.61	(Uranium)	6.34	(Thorium)
Chemical yield (%)	26.8		35.1		35.0		5.6	
	Sample H	Sample I						
U-234/U-238	1.10652	1.12159						
(Error)	(±0.011)	(±0.009)						
Th-230/U-234	0.64541	0.67562						
(Error)	(±0.006)	(±0.009)						
Age (kyr)	109.895	118.595						
(Error)	(±1.5)	(±2.6)						
Average age of phosphorite (kyr)	114.2							
(Error)	(±6.4)							

APPENDIX C.17. PRINCIPAL COMPONENT ANALYSIS RESULTS								
CD38-09	148m							
Eigenvalue	12.567	6.467	3.869	1.970	1.272	0.928	0.658	0.467
Proportion	0.419	0.216	0.129	0.066	0.042	0.031	0.022	0.016
Cumulative	0.419	0.634	0.763	0.829	0.872	0.902	0.924	0.940
Variable	PCF 1	PCF 2	PCF 3	PCF 4	PCF 5	PCF 6	PCF 7	PCF 8
Corg	-0.068	0.320	0.230	0.127	-0.026	0.018	0.164	-0.066
Bio.Silica	0.107	0.308	-0.073	0.128	0.174	0.132	-0.207	0.162
CaCO3	0.139	-0.071	-0.228	-0.256	0.287	0.099	0.592	0.058
Phos.	0.127	-0.185	0.329	-0.270	0.036	-0.007	-0.084	0.016
Terr.	-0.204	-0.047	-0.268	0.218	-0.195	-0.097	0.043	-0.112
Al	-0.278	-0.012	-0.003	-0.029	-0.023	-0.006	-0.016	-0.045
K	-0.260	-0.082	-0.099	-0.108	-0.051	0.029	-0.047	-0.160
Ti	-0.269	-0.076	-0.016	0.002	-0.081	-0.072	0.006	0.138
I	-0.162	0.065	0.293	0.230	0.347	0.139	0.075	0.060
Br	-0.134	0.137	0.278	0.211	0.347	0.202	0.174	0.129
Mo	0.063	0.317	0.187	0.028	-0.061	0.059	0.212	-0.179
U	0.118	-0.140	0.360	-0.296	0.051	0.005	-0.109	-0.003
Ni	-0.028	0.281	0.286	0.130	-0.263	-0.088	0.084	-0.064
Cr	-0.059	0.245	0.225	-0.204	-0.340	-0.117	0.081	-0.138
V	-0.065	0.272	-0.102	-0.374	0.052	0.045	-0.062	-0.295
Cu	-0.170	0.217	0.015	-0.272	-0.204	-0.066	0.069	0.307
Sr	0.120	-0.242	0.278	-0.254	0.020	0.088	0.052	0.019
Ba	-0.054	-0.068	-0.029	0.011	-0.401	0.881	-0.023	-0.037
Zn	-0.232	0.057	0.071	-0.163	0.013	0.029	-0.002	0.527
Rb	-0.270	-0.023	-0.027	-0.141	0.108	0.084	-0.051	-0.053
Zr	-0.111	-0.284	0.103	0.328	-0.093	-0.072	0.109	-0.068
Zr/Rb	-0.215	0.196	0.010	-0.116	0.103	-0.101	-0.357	-0.087
Nb	-0.232	-0.137	0.102	-0.009	0.108	0.075	-0.080	0.060
Pb	-0.216	0.023	-0.145	-0.217	0.266	0.137	-0.180	-0.150
Th	-0.259	0.083	0.022	0.084	0.095	-0.027	-0.083	0.043
La	-0.218	0.002	-0.019	-0.105	0.092	-0.042	0.427	-0.373
Ce	-0.236	-0.157	0.097	0.035	0.076	-0.029	-0.019	-0.178
Nd	-0.226	-0.189	0.131	0.033	-0.002	0.020	0.017	-0.114
Y	-0.140	-0.268	0.205	-0.028	-0.210	-0.164	0.066	0.061
Sc	-0.215	0.039	-0.179	-0.101	-0.142	-0.051	0.275	0.374
CD38-10	257m							
Eigenvalue	13.434	7.480	3.128	2.013	0.888	0.677	0.434	0.408
Proportion	0.448	0.249	0.104	0.067	0.030	0.023	0.014	0.014
Cumulative	0.448	0.697	0.801	0.869	0.898	0.921	0.935	0.949
Variable	PCF 1	PCF 2	PCF 3	PCF 4	PCF 5	PCF 6	PCF 7	PCF 8
Corg	0.198	0.192	-0.235	0.021	-0.067	0.013	-0.023	-0.009
Bio.Silica	0.209	0.108	0.243	-0.131	0.159	0.164	-0.037	0.213
CaCO3	0.215	-0.077	0.032	-0.059	-0.502	-0.294	0.040	-0.176
Phos.	-0.120	-0.273	-0.161	-0.029	0.012	0.211	0.253	0.298
Terr.	-0.248	0.077	-0.044	0.131	0.222	-0.029	-0.125	-0.174
Al	-0.250	0.133	-0.003	0.069	-0.033	-0.044	0.066	-0.027
K	-0.249	0.125	0.028	0.103	-0.008	-0.048	0.098	0.022
Ti	-0.251	0.118	-0.013	-0.050	-0.019	0.037	-0.032	-0.178
I	0.040	0.050	-0.352	-0.388	0.179	-0.522	0.127	0.128
Br	0.114	0.141	-0.360	-0.128	0.369	-0.278	-0.069	0.173
Mo	0.186	0.145	-0.031	0.366	0.076	-0.015	0.026	0.176
U	-0.025	-0.126	-0.431	0.061	-0.112	0.425	0.148	0.414
Ni	0.157	0.167	-0.347	-0.057	-0.028	0.178	-0.048	-0.163
Cr	0.066	0.277	-0.282	0.072	-0.219	0.043	0.012	-0.221
V	0.147	0.189	-0.135	0.395	-0.160	-0.074	-0.057	0.094
Cu	0.073	0.281	-0.124	-0.183	-0.067	0.372	-0.014	-0.241
Sr	0.028	-0.301	-0.154	0.057	-0.425	-0.197	0.162	0.005
Ba	-0.136	0.004	-0.217	0.481	0.038	-0.147	-0.302	-0.081
Zn	-0.104	0.293	0.028	-0.238	-0.231	0.028	0.157	0.082
Rb	-0.214	0.207	0.057	0.005	-0.105	-0.053	0.144	0.102
Zr	-0.229	-0.164	-0.124	0.032	0.108	0.016	-0.058	-0.097
Zr/Rb	-0.149	-0.278	-0.153	0.043	0.127	0.039	-0.058	-0.121
Nb	-0.242	0.069	-0.061	-0.101	-0.032	0.020	0.287	-0.184
Pb	-0.137	0.242	0.175	0.187	-0.086	-0.156	0.199	0.398
Th	-0.186	0.231	-0.001	-0.119	0.061	0.020	0.003	-0.033
La	-0.182	0.038	-0.006	-0.276	-0.308	0.020	-0.746	0.350
Ce	-0.265	0.023	-0.027	0.017	-0.063	-0.067	0.028	0.026
Nd	-0.262	-0.024	-0.053	0.008	-0.099	-0.140	-0.004	0.060
Y	-0.224	-0.153	-0.177	-0.074	-0.082	0.093	-0.036	-0.080
Sc	-0.130	0.270	0.001	0.071	0.003	0.053	0.050	0.081

APPENDIX C.17. PRINCIPAL COMPONENT ANALYSIS RESULTS								
CD38-02	2525m							
Eigenvalue	14.675	4.516	2.412	1.408	1.215	0.976	0.732	0.697
Proportion	0.489	0.151	0.08	0.047	0.041	0.033	0.024	0.023
Cumulative	0.489	0.64	0.72	0.767	0.808	0.84	0.865	0.888
Variable	PCF 1	PCF 2	PCF 3	PCF 4	PCF 5	PCF 6	PCF 7	PCF 8
Corg	-0.038	0.431	-0.145	-0.031	0.073	-0.065	-0.059	0.07
Bio.Silica	-0.109	0.224	0.316	0.097	-0.195	-0.027	0.374	-0.156
CaCO3	0.253	-0.033	0.002	-0.113	0.091	-0.022	-0.092	-0.022
Phos.	-0.059	-0.166	0.494	-0.033	-0.18	0.037	-0.085	-0.224
Terr.	-0.254	-0.02	-0.06	0.107	-0.065	0.031	0.036	0.052
Al	-0.248	-0.063	-0.12	0.103	-0.049	0.034	0.003	0.063
K	-0.227	-0.106	-0.148	0.149	-0.148	0.046	0.064	0.031
Ti	-0.251	0.019	-0.064	0.075	0.031	-0.078	-0.118	-0.068
I	0.028	0.432	-0.07	0.084	-0.021	0.057	0.049	0.189
Br	-0.011	0.414	0.072	-0.013	-0.013	0.166	0.032	0.179
Mo	-0.048	0.285	-0.247	-0.115	0.058	-0.138	-0.204	-0.612
U	0.014	0.05	0.285	-0.056	0.498	-0.651	-0.064	0.124
Ni	-0.116	0.379	-0.021	-0.207	0.071	0.066	0	0.011
Cr	-0.195	0.13	0.193	-0.041	0.013	0.167	-0.028	0.367
V	-0.233	-0.102	0.082	0.024	0.152	0.02	-0.148	0.033
Cu	-0.227	0.11	0.142	-0.12	0.042	-0.039	-0.234	-0.037
Sr	0.25	-0.069	0.063	-0.106	0.064	-0.003	-0.089	0.048
Ba	-0.17	-0.011	0.421	-0.131	-0.123	0.072	-0.065	0.037
Zn	-0.232	0.102	0.183	0.006	0.022	0.054	-0.022	-0.026
Rb	-0.251	-0.038	-0.14	0.049	0.03	0.024	0.01	0.006
Zr	-0.243	-0.008	-0.138	0.166	-0.096	-0.144	0	0.037
Zr/Rb	0.073	0.119	0.048	0.384	-0.458	-0.584	-0.032	0.09
Nb	-0.206	-0.05	-0.083	0.163	-0.045	-0.046	0.04	-0.277
Pb	-0.156	-0.184	-0.176	0.042	0.092	-0.065	-0.177	0.397
Th	-0.202	-0.049	-0.082	-0.103	0.117	-0.126	0.035	0.105
La	-0.181	-0.052	-0.079	-0.015	0.155	0.042	-0.284	-0.124
Ce	-0.129	-0.134	-0.175	-0.44	-0.166	-0.225	0.298	0.084
Nd	-0.127	-0.025	-0.085	-0.591	-0.224	-0.171	0.232	0.007
Y	-0.234	-0.038	0.165	-0.101	-0.009	-0.009	-0.193	-0.099
Sc	-0.131	-0.048	0.058	0.21	0.49	0.021	0.622	-0.145
CD38-11	3835m							
Eigenvalue	12.217	5.051	4.289	2.218	1.127	0.985	0.865	0.590
Proportion	0.407	0.168	0.143	0.074	0.038	0.033	0.029	0.020
Cumulative	0.407	0.576	0.719	0.793	0.830	0.863	0.892	0.911
Variable	PCF 1	PCF 2	PCF 3	PCF 4	PCF 5	PCF 6	PCF 7	PCF 8
Corg	0.085	0.205	-0.374	0.049	-0.025	0.139	0.178	-0.083
Bio.Silica	-0.137	0.283	0.233	-0.020	0.112	0.131	0.126	0.038
CaCO3	0.265	0.035	-0.043	-0.122	-0.213	-0.047	-0.070	-0.065
Phos.	0.140	-0.205	0.143	0.412	0.024	-0.077	0.036	-0.055
Terr.	-0.207	-0.259	-0.113	0.065	0.134	-0.062	-0.060	0.060
Al	-0.236	-0.159	-0.092	-0.098	0.009	-0.084	-0.202	-0.126
K	-0.257	-0.128	-0.029	-0.134	-0.054	-0.049	-0.128	-0.051
Ti	-0.213	-0.238	-0.112	0.110	0.106	0.044	-0.007	-0.080
I	-0.037	0.206	-0.354	-0.065	0.142	-0.310	-0.052	0.064
Br	0.064	0.160	-0.356	0.058	0.395	0.027	0.191	0.061
Mo	0.156	0.023	-0.204	0.135	-0.330	0.546	-0.020	-0.122
U	0.078	0.055	-0.160	0.332	-0.247	-0.547	-0.340	-0.031
Ni	0.019	0.255	-0.287	0.249	-0.188	0.072	0.178	-0.011
Cr	-0.194	0.129	-0.203	0.288	0.053	-0.067	0.057	0.044
V	-0.266	-0.001	0.036	0.056	-0.106	0.029	-0.063	-0.090
Cu	-0.221	0.208	0.099	0.190	-0.099	0.054	-0.074	0.005
Sr	0.263	-0.008	0.038	-0.029	-0.224	-0.110	-0.122	-0.033
Ba	-0.187	0.196	0.229	0.169	-0.054	-0.031	-0.051	-0.001
Zn	-0.212	0.224	-0.101	0.193	0.018	0.017	-0.111	0.020
Rb	-0.251	-0.007	-0.181	-0.153	-0.059	0.024	-0.074	-0.009
Zr	0.070	-0.346	-0.039	0.348	0.111	0.009	0.100	0.041
Zr/Rb	0.178	-0.239	0.062	0.339	0.083	0.030	0.129	0.004
Nb	-0.178	-0.226	-0.168	0.041	0.126	0.158	-0.050	-0.013
Pb	0.014	-0.289	-0.267	-0.059	0.021	0.224	-0.223	-0.151
Th	-0.158	-0.108	-0.099	-0.014	-0.321	0.158	-0.160	0.771
La	-0.183	-0.054	-0.100	-0.108	-0.342	-0.031	0.083	-0.501
Ce	-0.084	-0.215	-0.108	-0.106	-0.316	-0.303	0.557	0.069
Nd	-0.205	-0.079	0.064	-0.030	-0.133	-0.060	0.477	0.093
Y	-0.188	0.063	0.212	0.301	-0.195	0.145	-0.002	-0.095
Sc	-0.232	0.046	0.111	0.051	0.188	-0.012	0.047	-0.168

APPENDIX C.18. MULTI-COMPONENT ANALYSIS RESULTS											
CD38-09 (148m)						CD38-10 (257m)					
Depth	TERR	BIOG	AUTH	RESID	HYDRO	Depth	TERR	BIOG	AUTH	RESID	HYDRO
(cm)	(%)	(%)	(%)	(%)	(%)	(cm)	(%)	(%)	(%)	(%)	(%)
4.0	71.75	26.35	1.89	0.00	0.00	6.0	64.89	30.40	4.71	0.00	0.00
13.0	68.12	30.84	1.04	0.00	0.00	14.0	72.54	14.19	13.27	0.00	0.00
23.0	79.94	18.95	1.11	0.00	0.00	24.0	70.94	4.34	24.72	0.00	0.00
34.0	78.26	20.53	1.21	0.00	0.00	34.0	74.30	12.53	13.18	0.00	0.00
43.0	85.54	12.35	2.10	0.00	0.00	44.0	80.49	14.66	4.85	0.00	0.00
53.0	74.52	23.32	2.16	0.00	0.00	54.0	79.51	17.73	2.77	0.00	0.00
62.0	69.36	29.03	1.62	0.00	0.00	64.0	80.46	14.38	5.15	0.00	0.00
73.0	78.88	19.79	1.33	0.00	0.00	74.0	83.26	8.29	8.46	0.00	0.00
84.0	84.76	14.57	0.68	0.00	0.00	84.0	80.70	3.67	15.63	0.00	0.00
94.0	80.00	19.21	0.79	0.00	0.00	94.0	77.03	3.25	19.72	0.00	0.00
104.0	75.42	23.88	0.70	0.00	0.00	104.0	75.55	12.98	11.47	0.00	0.00
113.0	85.09	14.26	0.65	0.00	0.00	113.0	79.46	12.95	7.59	0.00	0.00
124.0	84.02	14.26	1.72	0.00	0.00	126.0	61.75	32.24	6.01	0.00	0.00
134.0	75.90	21.61	2.49	0.00	0.00	134.0	61.89	31.63	6.48	0.00	0.00
144.0	69.62	28.90	1.48	0.00	0.00	146.0	71.78	23.47	4.74	0.00	0.00
152.0	70.68	28.42	0.89	0.00	0.00	154.0	63.93	31.43	4.64	0.00	0.00
165.0	68.57	29.32	2.10	0.00	0.00	167.0	69.82	26.95	3.24	0.00	0.00
174.0	83.36	14.23	2.41	0.00	0.00	174.0	72.72	23.60	3.68	0.00	0.00
185.0	79.96	15.18	4.86	0.00	0.00	185.0	73.45	23.62	2.94	0.00	0.00
194.0	81.70	13.70	4.60	0.00	0.00	194.0	62.28	35.09	2.63	0.00	0.00
205.0	83.86	15.08	1.06	0.00	0.00	203.0	76.27	19.75	3.98	0.00	0.00
214.0	74.27	21.48	4.25	0.00	0.00	216.0	60.21	36.18	3.61	0.00	0.00
224.0	85.33	8.41	6.26	0.00	0.00	224.0	64.72	32.62	2.66	0.00	0.00
234.0	74.09	18.47	7.44	0.00	0.00	233.0	69.75	27.46	2.79	0.00	0.00
243.0	59.88	36.16	3.96	0.00	0.00	244.0	70.40	25.81	3.79	0.00	0.00
257.0	71.27	25.42	3.31	0.00	0.00	254.0	69.64	21.87	8.48	0.00	0.00
267.0	70.57	15.67	13.76	0.00	0.00	263.0	65.77	27.42	6.81	0.00	0.00
273.0	26.89	9.86	60.90	0.00	2.35	273.0	70.89	25.94	3.17	0.00	0.00
284.0	75.73	21.29	2.98	0.00	0.00	284.0	67.53	28.61	3.86	0.00	0.00
294.0	67.47	31.20	1.33	0.00	0.00	295.0	52.61	44.20	3.19	0.00	0.00
304.0	76.23	22.66	1.11	0.00	0.00	305.0	67.56	29.90	2.53	0.00	0.00
314.0	76.50	22.78	0.72	0.00	0.00	314.0	71.00	25.86	3.15	0.00	0.00
324.0	77.34	20.96	1.70	0.00	0.00	324.0	57.63	39.42	2.95	0.00	0.00
335.0	71.38	27.55	1.07	0.00	0.00	335.0	70.05	26.95	3.00	0.00	0.00
344.0	66.59	32.28	1.12	0.00	0.00	344.0	51.95	44.62	3.43	0.00	0.00
355.0	61.18	38.27	0.55	0.00	0.00	354.0	52.81	44.55	2.64	0.00	0.00
364.0	56.73	42.77	0.50	0.00	0.00	364.0	43.90	53.20	2.90	0.00	0.00
375.0	73.13	26.46	0.41	0.00	0.00	374.0	47.74	49.92	2.35	0.00	0.00
384.0	72.03	26.32	1.65	0.00	0.00	383.0	70.23	27.79	1.98	0.00	0.00
394.0	65.28	33.62	1.10	0.00	0.00	394.0	62.13	34.98	2.89	0.00	0.00
404.0	71.49	27.90	0.62	0.00	0.00	404.0	68.16	29.17	2.67	0.00	0.00
416.0	62.04	37.02	0.94	0.00	0.00	417.0	59.02	37.46	3.52	0.00	0.00
424.0	67.12	32.54	0.33	0.00	0.00	424.0	60.73	36.28	2.99	0.00	0.00
434.0	74.06	25.43	0.51	0.00	0.00	434.0	31.93	63.40	4.67	0.00	0.00
444.0	63.45	35.60	0.95	0.00	0.00	445.0	49.95	47.40	2.65	0.00	0.00
453.0	74.71	24.15	1.14	0.00	0.00	456.0	48.22	48.86	2.92	0.00	0.00
465.0	70.48	28.45	1.07	0.00	0.00	467.0	35.10	62.53	2.36	0.00	0.00
474.0	68.08	31.04	0.88	0.00	0.00	476.0	59.35	53.33	5.33	0.00	0.00
483.0	73.52	25.17	1.31	0.00	0.00	484.0	56.44	38.57	4.99	0.00	0.00
493.0	72.85	26.15	1.00	0.00	0.00	494.0	55.19	33.96	10.85	0.00	0.00
504.0	79.72	18.85	1.43	0.00	0.00	504.0	65.16	5.20	29.64	0.00	0.00
515.0	80.05	19.06	0.90	0.00	0.00	514.0	76.23	23.11	0.66	0.00	0.00
525.0	73.99	25.52	0.49	0.00	0.00	524.0	80.45	19.03	0.52	0.00	0.00
536.0	68.37	31.07	0.57	0.00	0.00	534.0	61.39	36.36	2.24	0.00	0.00
544.0	78.69	20.26	1.05	0.00	0.00	545.0	61.97	36.47	1.56	0.00	0.00
553.0	75.74	23.85	0.41	0.00	0.00	554.0	56.79	41.72	1.49	0.00	0.00
564.0	70.55	28.92	0.53	0.00	0.00	564.0	47.80	48.97	3.22	0.00	0.00
574.0	73.55	25.67	0.78	0.00	0.00	574.0	54.09	43.46	2.45	0.00	0.00
585.0	68.44	28.03	3.53	0.00	0.00	584.0	53.61	44.74	1.65	0.00	0.00
594.0	71.36	27.64	1.00	0.00	0.00	596.0	53.89	44.32	1.79	0.00	0.00
605.0	74.84	23.56	1.60	0.00	0.00	604.0	52.50	45.75	1.75	0.00	0.00
615.0	68.13	29.67	2.20	0.00	0.00	614.0	58.70	40.35	0.95	0.00	0.00
625.0	74.61	23.51	1.88	0.00	0.00	624.0	62.19	36.10	1.70	0.00	0.00
635.0	74.31	23.92	1.77	0.00	0.00	634.0	60.57	37.57	1.86	0.00	0.00
646.0	68.54	30.40	1.06	0.00	0.00	645.0	60.95	38.09	0.96	0.00	0.00
654.0	66.34	32.93	0.72	0.00	0.00	655.0	59.37	39.84	0.79	0.00	0.00
664.0	66.56	32.95	0.49	0.00	0.00	667.0	64.36	34.32	1.32	0.00	0.00
674.0	62.58	36.91	0.51	0.00	0.00	674.0	70.72	28.02	1.26	0.00	0.00
684.0	74.05	25.27	0.68	0.00	0.00	683.0	66.36	32.86	0.78	0.00	0.00
694.0	75.39	24.01	0.61	0.00	0.00	694.0	78.86	19.69	1.44	0.00	0.00
703.0	76.11	23.54	0.36	0.00	0.00	704.0	85.94	12.86	1.20	0.00	0.00
714.0	70.30	28.79	0.91	0.00	0.00	714.0	77.14	21.34	1.51	0.00	0.00
724.0	75.84	22.54	1.62	0.00	0.00	724.0	71.51	27.10	1.39	0.00	0.00
734.0	75.64	22.73	1.63	0.00	0.00	734.0	82.45	16.02	1.53	0.00	0.00
744.0	74.02	24.79	1.20	0.00	0.00	745.0	88.61	10.07	1.33	0.00	0.00
754.0	72.57	26.89	0.54	0.00	0.00	754.0	77.91	19.93	2.16	0.00	0.00
764.0	76.40	22.76	0.84	0.00	0.00	764.0	85.15	9.19	5.66	0.00	0.00
774.0	78.07	21.04	0.89	0.00	0.00						
784.0	76.77	22.38	0.85	0.00	0.00						
794.0	76.23	22.68	1.09	0.00	0.00						
804.0	76.28	22.05	1.66	0.00	0.00						
813.0	74.23	22.68	3.09	0.00	0.00						
823.0	76.46	21.67	1.87	0.00	0.00						
834.0	77.31	21.41	1.29	0.00	0.00						
845.0	75.40	22.98	1.62	0.00	0.00						
854.0	81.86	17.77	0.37	0.00	0.00						

APPENDIX C.18. MULTI-COMPONENT ANALYSIS RESULTS											
CD38-02 (2525m)						CD38-11 (3035m)					
Age	TERR	BIOG	AUTH	RESID	HYDRO	Age	TERR	BIOG	AUTH	RESID	HYDRO
(ka)	(%)	(%)	(%)	(%)	(%)	(ka)	(%)	(%)	(%)	(%)	(%)
2.76	70.38	28.69	0.73	0.21	0.00	1.2	83.44	13.83	2.74	0.00	0.00
6.21	63.23	35.87	0.76	0.15	0.00	2.0	73.65	22.59	3.76	0.00	0.00
9.66	61.64	37.55	0.68	0.13	0.00	2.5	77.56	18.67	3.76	0.00	0.00
12.77	66.73	32.85	0.42	0.00	0.00	5.2	85.60	13.02	1.38	0.00	0.00
15.18	64.37	35.20	0.42	0.00	0.00	9.2	83.64	15.33	1.03	0.00	0.00
17.47	64.02	35.55	0.43	0.00	0.00	12.3	82.87	16.51	0.62	0.00	0.00
20.48	66.24	33.31	0.45	0.00	0.00	13.1	82.87	16.59	0.53	0.00	0.00
22.65	66.49	33.06	0.45	0.00	0.00	14.0	82.68	16.62	0.70	0.00	0.00
25.22	61.86	37.63	0.50	0.00	0.00	15.0	82.30	15.36	2.34	0.00	0.00
28.29	57.73	41.75	0.52	0.00	0.00	15.8	78.69	20.57	0.74	0.00	0.00
31.07	56.30	43.15	0.55	0.00	0.00	16.6	76.82	22.46	0.72	0.00	0.00
33.86	52.48	46.98	0.52	0.02	0.00	17.5	78.41	20.83	0.76	0.00	0.00
36.64	57.24	42.26	0.49	0.01	0.00	18.3	79.14	20.21	0.65	0.00	0.00
39.15	65.48	34.04	0.48	0.00	0.00	19.1	79.12	19.98	0.90	0.00	0.00
42.22	65.92	33.64	0.44	0.00	0.00	20.0	80.52	18.69	0.80	0.00	0.00
45.00	71.95	27.56	0.49	0.00	0.00	20.8	77.24	21.67	1.09	0.00	0.00
48.07	73.68	25.86	0.46	0.00	0.00	21.6	80.26	18.96	0.77	0.00	0.00
50.85	72.70	26.76	0.54	0.00	0.00	22.4	78.28	19.94	1.78	0.00	0.00
53.64	71.12	28.30	0.53	0.05	0.00	23.4	79.41	19.77	0.82	0.00	0.00
56.42	75.15	24.38	0.48	0.00	0.00	25.3	80.02	19.26	0.72	0.00	0.00
59.29	74.44	25.12	0.45	0.00	0.00	29.3	81.29	18.08	0.63	0.00	0.00
62.61	73.83	25.70	0.48	0.00	0.00	35.7	74.62	24.08	1.30	0.00	0.00
65.94	77.05	22.46	0.49	0.00	0.00	41.6	75.17	24.00	0.83	0.00	0.00
69.26	86.40	13.13	0.47	0.00	0.00	47.4	76.05	23.15	0.79	0.00	0.00
72.58	80.06	19.32	0.61	0.00	0.00	53.2	75.55	23.61	0.84	0.00	0.00
76.96	72.27	26.86	0.74	0.12	0.00	59.0	68.33	30.77	0.90	0.00	0.00
82.03	83.03	16.41	0.54	0.02	0.00	60.7	69.46	29.63	0.91	0.00	0.00
87.11	84.10	15.37	0.53	0.00	0.00	62.5	72.89	26.16	0.94	0.00	0.00
92.18	89.45	10.09	0.45	0.00	0.00	64.2	85.42	13.80	0.78	0.00	0.00
97.26	86.95	12.28	0.73	0.05	0.00	66.3	84.21	14.89	0.90	0.00	0.00
102.84	78.31	20.83	0.78	0.07	0.00	67.7	87.29	11.87	0.84	0.00	0.00
107.92	79.64	19.55	0.71	0.10	0.00	69.5	88.27	10.45	1.28	0.00	0.00
113.00	79.39	20.00	0.54	0.07	0.00	71.3	66.67	28.62	4.70	0.00	0.00
118.07	79.35	19.78	0.63	0.23	0.00	73.0	80.61	18.49	0.90	0.00	0.00
123.15	68.42	30.88	0.55	0.15	0.00	75.0	78.86	20.27	0.87	0.00	0.00
128.22	64.73	34.86	0.40	0.00	0.00	77.0	76.22	22.82	0.96	0.00	0.00
132.23	65.03	34.63	0.34	0.00	0.00	79.1	79.03	20.05	0.93	0.00	0.00
135.30	63.35	36.29	0.37	0.00	0.00	81.2	80.13	19.20	0.67	0.00	0.00
138.71	61.38	38.23	0.39	0.00	0.00	83.3	83.77	15.46	0.77	0.00	0.00
141.79	58.83	40.72	0.45	0.00	0.00	85.4	84.02	15.16	0.82	0.00	0.00
145.20	60.08	39.50	0.42	0.00	0.00	87.5	83.34	15.85	0.81	0.00	0.00
148.61	60.43	39.16	0.40	0.00	0.00	89.5	86.91	12.25	0.83	0.00	0.00
152.02	59.48	40.11	0.40	0.00	0.00	91.6	81.86	17.10	0.96	0.08	0.00
155.44	61.84	37.72	0.44	0.00	0.00	93.7	76.10	22.28	1.40	0.22	0.00
158.85	68.27	31.34	0.39	0.00	0.00	95.8	76.66	21.90	1.28	0.16	0.00
162.26	71.78	27.83	0.39	0.00	0.00	97.9	86.01	12.88	1.11	0.00	0.00
165.68	60.73	38.81	0.46	0.00	0.00	100.0	87.28	11.83	0.89	0.00	0.00
169.43	58.26	41.26	0.48	0.00	0.00	102.0	82.49	16.49	1.02	0.00	0.00
172.84	58.99	40.55	0.46	0.00	0.00	104.1	85.16	13.99	0.85	0.00	0.00
176.26	61.93	37.56	0.51	0.00	0.00	106.2	82.71	16.21	1.09	0.00	0.00
179.67	65.24	34.29	0.46	0.00	0.00	108.3	82.89	16.20	0.91	0.00	0.00
183.08	72.64	26.92	0.44	0.00	0.00	110.4	82.90	16.04	1.06	0.00	0.00
186.50	79.55	20.15	0.29	0.00	0.00	112.5	81.55	17.58	0.85	0.02	0.00
189.57	83.51	15.97	0.52	0.00	0.00	114.5	81.21	17.49	1.22	0.09	0.00
193.52	83.64	15.81	0.55	0.00	0.00	116.6	78.91	19.89	1.14	0.06	0.00
197.42	82.86	16.42	0.59	0.13	0.00	118.7	79.12	19.49	1.25	0.14	0.00
202.11	76.08	23.17	0.62	0.14	0.00	120.8	78.47	20.03	1.38	0.12	0.00
206.02	77.54	21.91	0.48	0.08	0.00						
209.53	77.54	21.99	0.44	0.03	0.00						
213.44	58.42	40.80	0.56	0.21	0.00						
217.34	56.94	42.36	0.57	0.13	0.00						
221.25	63.01	36.44	0.51	0.03	0.00						
225.16	66.13	33.41	0.47	0.00	0.00						
229.06	71.68	27.85	0.47	0.00	0.00						
232.97	78.84	20.70	0.45	0.00	0.00						
237.27	74.20	24.90	0.65	0.26	0.00						
240.78	57.95	41.24	0.57	0.24	0.00						
244.50	64.26	35.35	0.39	0.00	0.00						
247.71	69.72	30.04	0.24	0.00	0.00						
250.91	66.77	32.98	0.25	0.00	0.00						
254.12	67.15	32.56	0.29	0.00	0.00						
257.32	66.25	33.43	0.32	0.00	0.00						
260.53	66.16	33.50	0.34	0.00	0.00						
263.73	67.05	32.58	0.37	0.00	0.00						

APPENDIX C.19. MASS ACCUMULATION RATE FLUXES						
CD38-02	All MARs in (mg/cm2/kyr)					Palaeoprod. (g/m2/yr)
	2525m Age	Al MAR	Siterr MAR	CorqMAR	BioSilMAR	
2.76	96.23	311.35	25.03	159.83	282.07	44.1
6.21	90.30	298.86	23.42	148.28	438.15	43.3
9.66	82.12	275.47	21.49	120.11	453.87	37.1
12.77	120.88	369.85	59.01	157.53	491.95	60.1
15.18	135.49	417.49	46.89	150.55	684.64	54.6
17.47	131.69	412.13	49.11	160.16	661.20	57.0
20.48	141.25	437.56	48.15	138.82	658.66	55.7
22.65	134.84	421.28	45.58	129.95	622.64	51.5
25.22	112.22	347.67	44.88	117.35	650.45	63.4
28.29	105.22	321.85	45.86	133.80	726.29	65.2
31.07	104.26	318.71	35.96	162.82	752.49	51.9
33.86	93.53	285.06	41.09	174.61	781.06	57.5
36.64	103.70	318.22	42.58	144.86	724.04	60.1
39.15	116.87	356.11	38.26	125.13	559.83	52.7
42.22	119.01	349.83	49.19	150.91	522.89	67.0
45.00	142.19	437.69	36.91	102.39	509.06	55.2
48.07	142.81	435.64	41.56	132.75	422.29	61.5
50.85	122.28	399.28	33.65	177.75	324.39	44.9
53.64	125.03	402.07	39.14	178.57	374.49	54.3
56.42	127.80	410.05	42.34	157.41	293.80	56.5
59.29	114.83	351.28	39.26	118.89	303.11	69.5
62.61	117.32	365.87	33.76	112.30	340.09	61.8
65.94	126.48	389.09	29.07	115.34	294.56	54.6
69.26	136.03	428.14	30.72	129.65	85.69	55.7
72.58	123.77	395.76	36.92	143.57	175.14	67.2
76.96	71.13	230.88	18.74	95.57	200.43	64.7
82.03	80.89	255.95	25.40	100.87	64.00	84.8
87.11	83.09	267.24	20.29	79.70	80.79	69.3
92.18	88.18	273.02	19.98	91.50	6.98	66.6
97.26	84.53	267.35	14.96	92.50	34.65	49.4
102.84	74.61	244.30	18.29	105.78	112.13	59.8
107.92	77.88	246.91	17.13	101.51	108.94	57.4
113.00	78.95	246.54	16.25	110.60	109.94	55.3
118.07	74.36	239.36	11.83	100.30	108.58	38.4
123.15	65.09	208.50	14.87	113.34	221.54	48.9
128.22	101.39	301.83	25.95	152.55	471.52	49.3
132.23	107.14	326.07	24.38	103.91	550.93	48.8
135.30	109.48	340.58	21.54	101.45	623.57	45.9
138.71	106.92	324.88	24.00	133.70	635.07	51.3
141.79	101.66	312.49	24.56	127.96	685.28	51.9
145.20	105.03	320.02	24.10	124.38	673.51	51.3
148.61	103.51	319.46	21.04	142.12	635.34	44.2
152.02	105.74	319.11	23.56	117.95	707.34	51.4
155.44	110.99	344.42	23.37	119.27	663.31	51.6
158.85	113.32	354.96	23.25	97.84	498.12	47.6
162.26	121.43	369.80	25.72	101.43	433.41	53.1
165.68	108.93	332.76	30.68	87.61	710.43	66.6
169.43	102.53	317.27	29.69	96.33	738.40	64.2
172.84	102.82	322.36	33.34	97.69	710.38	70.9
176.26	106.56	335.90	34.11	95.45	639.88	70.9
179.67	115.01	363.21	29.61	116.15	573.94	63.8
183.08	124.51	403.17	27.34	95.59	426.43	57.7
186.50	157.49	551.69	19.06	110.24	345.64	45.8
189.57	126.37	389.73	24.91	97.55	165.24	57.0
193.52	121.86	374.17	26.04	106.62	141.52	57.8
197.42	109.58	332.58	29.28	140.79	88.38	61.3
202.11	148.82	468.47	30.25	179.84	329.46	93.3
206.02	152.67	469.99	33.28	132.78	347.43	101.3
209.53	129.45	392.48	22.66	90.94	323.52	57.3
213.44	101.84	313.12	22.92	85.65	738.20	61.0
217.34	98.88	312.74	19.83	82.52	773.44	52.5
221.25	107.93	336.88	21.48	90.23	631.35	56.2
225.16	119.02	369.95	24.42	75.02	616.40	66.9
229.06	127.54	391.52	23.63	91.58	474.75	61.9
232.97	125.63	389.62	21.59	97.62	273.55	52.4
237.27	110.93	356.97	21.37	124.63	297.15	49.8
240.78	86.23	281.29	23.08	115.13	592.26	54.3
244.50	120.65	378.70	26.26	94.44	669.55	52.8
247.71	129.71	396.14	27.91	83.14	554.23	54.6
250.91	128.17	388.12	28.97	108.71	616.09	58.5
254.12	124.98	400.65	17.98	94.68	608.71	35.0
257.32	119.83	381.43	26.84	125.13	567.93	52.2
260.53	124.13	381.09	27.63	140.05	580.54	54.9
263.73	122.55	375.88	33.95	140.95	534.07	66.2

APPENDIX D

Reprint of McNeill, G.W. and Shimmield, G.B. (1991) Diagenetic controls on uranium, molybdenum and vanadium enrichment in organic-rich marine shelf sediments. *Proceedings of the 8th International Conference on Heavy Metals in the Environment*, (Ed. J.G.Farmer), pp.436–439.CEP Consultants, Edinburgh.

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DIAGENETIC CONTROLS ON URANIUM, MOLYBDENUM AND VANADIUM ENRICHMENT IN ORGANIC-RICH MARINE SHELF SEDIMENTS

G.W.McNeill* and G.B.Shimmield*

ABSTRACT

Organic-rich marine sediments are known to preferentially incorporate heavy metals *via* a variety of redox/organo-complex reactions. The elevated concentrations of redox-sensitive metals, such as U and Mo, are used increasingly as indicators of palaeoenvironmental O₂ conditions at the benthic boundary layer. This study presents a detailed investigation of U, Mo and V enrichment in reducing sediments in the absence of anthropogenic influence. This allows us to define the natural behaviour of these important redox-sensitive metals for investigation of both palaeoceanographic and pollution applications.

Sediment cores from the Peruvian upwelling margin record the variation in U, Mo and V with organic carbon and display a variety of redox and diagenetic controls on these metals. A model for U partitioning based on phosphorite diagenesis and organic matter complexation is presented. In contrast, Mo and V appear to be predominantly controlled by water column scavenging by the high organic matter flux followed by post-depositional redox processes.

INTRODUCTION

Study of heavy metal deposition in the coastal marine environment is very important for the understanding of the complex pathways in which metals are incorporated into the sediment. Before any polluted environment can be examined, the natural, steady-state baseline for heavy metal enrichment associated with organic matter and/or diagenetic processes needs to be quantified.

The various mechanisms for uranium enrichment in organic-rich, anoxic marine sediments have been reviewed by Anderson *et al* (1989, ref 1) and for molybdenum and vanadium by Francois (1988, ref 2). Bertine and Turekian (1973, ref 3) used the Mo/U ratio as a palaeoenvironmental indicator of bottom-water oxygen conditions.

One site in which such marine sediments have a high organic matter content and accumulate these redox-sensitive metals to elevated concentrations, is under the upwelling zone in the coastal basins off Peru. This study measures the concentrations of organic carbon (C_{org}), U, Mo and V in sediments taken from this area and examines the organo-metallic relationships of Mo and V and the partitioning of U into phases according to organic and mineral diagenetic associations in a natural, unpolluted environment.

METHODS

The samples analysed in this study were taken from piston cores collected during the R.R.S. *Charles Darwin* Leg 38 cruise (April-May 1989) off Peru, from the locations and water depths shown in Table 1. C_{org} was determined by an initial acid digestion of carbonate material, followed by combustion of the sample and measurement of the CO₂ evolved using a LECO 572-100 carbon analyser (% std. deviation = 4.66%, n=48). Trace elements (U, Mo and V) were analysed by X-ray fluorescence of pressed pellet samples, using a Philips PW1480 X-ray spectrophotometer (XRF estimated reproducibility, U and Mo = ±1ppm, V = ±5ppm). All concentrations were corrected for their salt content, which was calculated by measuring the % weight loss upon drying each sample and assuming constant salinity of 35‰.

RESULTS

The offshore basins on the continental shelf off Peru form sites for the accumulation of

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organic-rich marine sediments. Coastal upwelling of cold, nutrient-rich water, caused by offshore Ekman transport of surface nutrient-depleted water, supports intense biological productivity.

Organic material falling down through the water column is decomposed by marine organisms and only a small proportion survives down to the benthic boundary layer for incorporation into the sediment. However, off Peru, there is a large organic matter flux resulting in an oxygen minimum zone (OMZ) at 100-400m water depth (ref 4, 5).

The reducing sediments from cores CD38-09 and CD38-10 are extremely rich in organic matter with mean values of 4.4 & 5.4 wt.% C_{org} respectively, with a maximum of 11.9 wt.% in CD38-10 (Table 2).

Station	CD38-09	CD38-10		CD38-09	CD38-10
Latitude	10°58'S	11°04'S	C_{org} (wt.%)	1.6-8.3(4.38)	0.8-11.9(5.37)
Longitude	77°57'W	78°04'W	U (ppm)	4.0-167.4(9.3)	5.9-27.2(13.1)
Water depth	148m	257m	Mo (ppm)	13-99(52.1)	11-129(56.9)
Core length	895cm	822cm	V (ppm)	63-156(118.6)	46-363(147.1)

Table 1. Core stations

	CD38-09	CD38-10
U_{org} (ppm)	0-89.7(5.0)	0.7-20.9(7.9)
$U_{org}/C_{org}(x10^{-4})$	0-55.4(1.50)	0.7-6.2(1.47)
Mo/ U_{org}	0-34.1(19.3)	3.1-24.1(8.5)

Table 3. Concentration and ratios of U_{org}

	CD38-09	CD38-10
$U/C_{org}(x10^{-4})$	0.9-103.3(3.01)	1.0-31.3(3.47)
Mo/ $C_{org}(x10^{-4})$	7.4-32.6(12.2)	4.9-47.6(11.4)
V/ $C_{org}(x10^{-4})$	14.3-53.2(29.8)	14.9-69.3(29.4)
Mo/U	0.3-17.3(7.37)	0.6-13.1(4.81)

Table 2. Range and (mean) values for salt-corrected element concentrations and ratios

Heavy metals which are known to have an affinity with organic matter (ref 2, 3, 6, 7) are also enriched in these sediments. The range and mean concentrations of U, Mo and V are shown in Table 2, along with their ratios to C_{org} and the Mo/U ratios. Depth profiles of C_{org} , Mo, U and V for CD38-10 are displayed in Fig. 1. The profile of C_{org} does not show a simple exponential decrease with depth, but has peaks and troughs which implies a time-varying input, due to changes in either primary productivity or dilution by other components. The Mo and V depth profiles are very similar to that of C_{org} (especially over the 150-550cm depth range) and illustrate a large dynamic range in concentration associated with natural fluctuations. Regression analyses on the data from CD38-10 (Fig. 2a,b) indicate an organo-metallic relationship between C_{org} and V ($r^2 = 0.61$) and Mo ($r^2 = 0.53$).

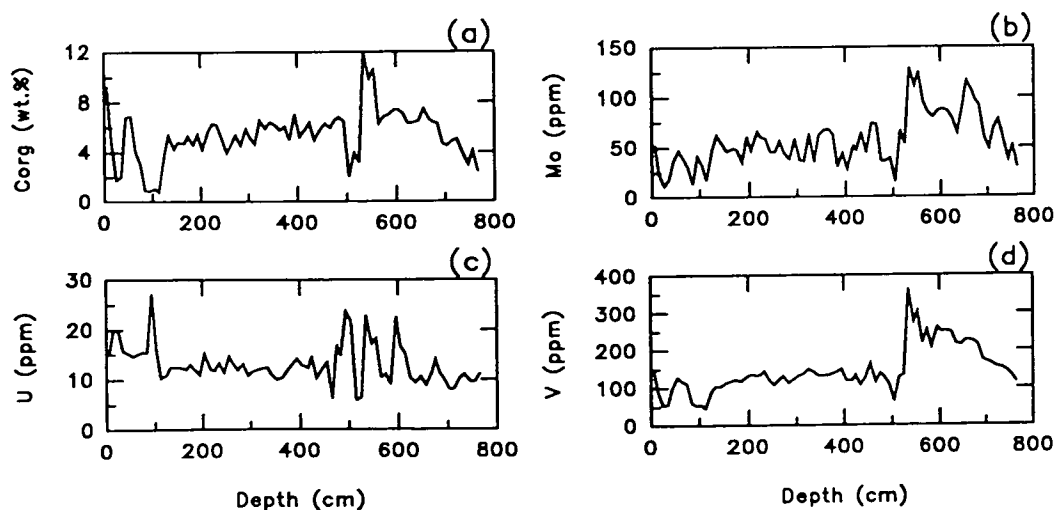


Figure 1. CD38-10(257m) : a) C_{org} b) Mo c) U d) V versus depth

The depth profile of U does not display such a good correspondence to C_{org} (the plot of U

against C_{org} in Fig. 2c gives $r^2 = 0.005$). Therefore, we have to consider other possible sources for the uranium enrichment in these sediments. As well as organic matter content, the mineralogy of the sediment is important because U can be incorporated into both detrital and diagenetic minerals.

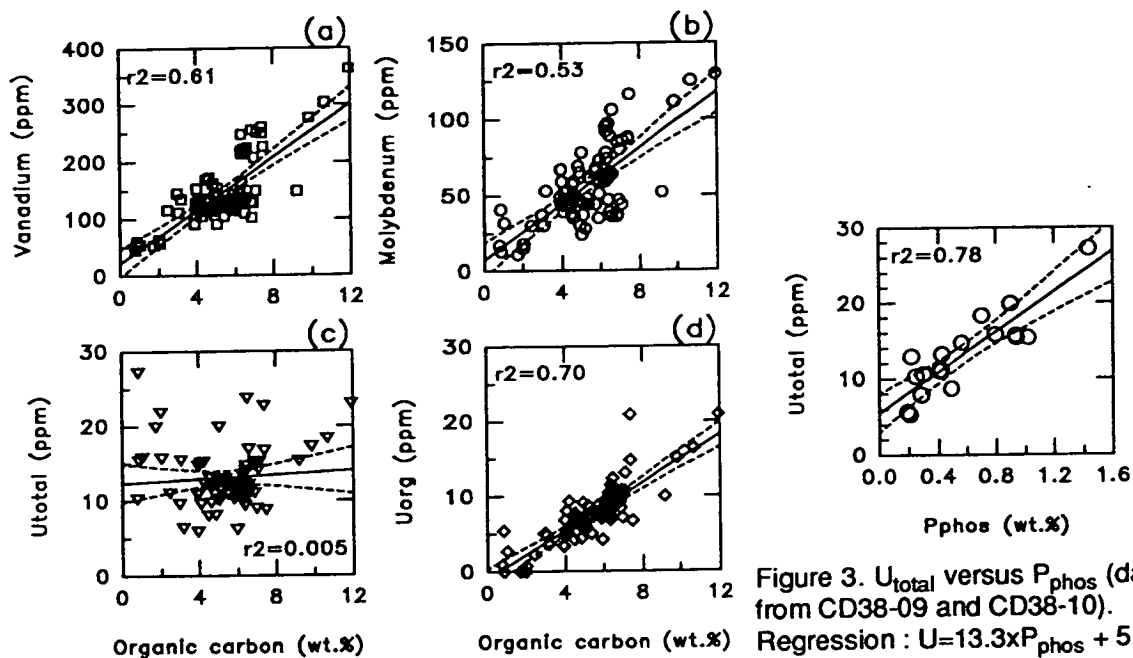


Figure 3. U_{total} versus P_{phos} (data from CD38-09 and CD38-10).
Regression : $U = 13.3 \times P_{phos} + 5.5$

Figure 2. CD38-10(257m) : a) V b) Mo c) U_{total} d) U_{org} versus C_{org}

The diagenetic formation of phosphorite is known to preferentially take up U from bottom waters (ref 8, 9) and this process has occurred to various degrees in this coastal environment throughout the Late Quaternary (ref 4, 10). In order to estimate the contribution of these various sources to the total uranium content, the following partitioning equations are used. Zones where phosphorite formation has been significant have anomalously high P/Al ratios. The total phosphorus in the sediment can be partitioned into detrital, organic and phosphorite phases. Hence,

$$P_{phos} = P_{total} - (P_{det} + P_{org}) \quad (1)$$

where, $P_{det} = Al \times 0.00875$ (ave. shale, ref 11) and $P_{org} = C_{org} / 41.0$ (ref 12). A regression analysis between the U_{total} and P_{phos} contents of sediments in these phosphorite zones for cores CD38-09 and CD38-10, as shown in Fig. 3, gives a regression line of :

$$U_{total} \text{ (ppm)} = 13.33 P_{phos} + 5.5 \quad (r^2 = 0.78) \quad (2)$$

This accounts for uranium enrichment in these zones and allows for the quantitative partitioning of U into its detrital, organic and phosphorite phases for all the other organic-rich sediments. Hence,

$$U_{org} = U_{total} - (U_{det} + U_{phos}) \quad (3)$$

where, $U_{det} = Al \times 0.4625$ (ave. shale, ref 11) and $U_{phos} = 13.33 \times P_{phos}$ (eqn. 2). The fraction of uranium associated with organic matter can now be calculated and the concentrations are shown in Table 3 and Fig. 4a. Regression analysis between C_{org} and U_{org} for CD38-10 gives an organo-metallic relationship with $r^2 = 0.70$ (Fig. 2d).

DISCUSSION/CONCLUSIONS

The concentration of C_{org} and associated heavy metals, Mo and V, in the coastal basins off Peru (Table 2 and Figs. 1 and 2) illustrate the high level and range of these elements possible in a natural marine environment. The enrichment of these two metals is predominantly controlled by water column scavenging by the high organic matter flux (ref 2, 13), resulting in close organo-metallic relationships. There may also be some post-depositional redox processes operating on the Mo and V concentrations, as organic matter undergoes bacterial decomposition upon burial (ref 6).

Mineral diagenesis may also affect the concentration of heavy metals in the marine environment. The formation of phosphorite can considerably enrich the U concentration of the sediment. By partitioning the total U content into U_{det} , U_{phos} (eqn. 2) and U_{org} (eqn. 3), the relative influences of phosphorite or organic matter can be seen (Fig. 4a).

The organo-metallic relationships in the Peru sediments can be quantified (given by the mean values of V/C_{org} and Mo/C_{org} in Table 2 and U_{org}/C_{org} in Table 3) and may be used in any future studies in a polluted coastal marine environment as the natural, baseline flux for comparison with any anthropogenic input (ref 13).

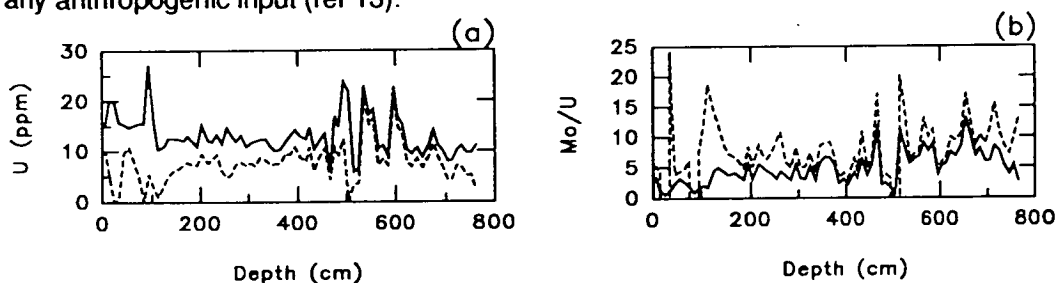


Figure 4. CD38-10(257m) : a) U b) U/Mo versus depth. Full line = U_{total} , dotted line = U_{org}

The Mo/U ratios are of interest because these two heavy metals have previously been used as palaeoenvironmental indicators of oxygen conditions at the benthic boundary layer, producing a Mo/U ratio of close to unity for anoxic sediments (ref 3) and higher values (3-4) for oxic, deep-sea sediments. Figure 4b displays the high Mo/U measured for the sediments in this study (4.8 and 7.4, Table 2) and even higher Mo/ U_{org} calculated (19.3 and 8.5, Table 3) in zones where phosphorite formation is minimal. From this study, we suggest that the natural processes contributing to U and Mo enrichment in anoxic marine sediments result in variable Mo/U ratios. Consequently the statement of Bertine and Turekian (1973, ref 3) that anoxic sediments have a ratio of unity is invalid.

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