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Title: Clay-Organic Associations in Marine Sediments: Carbon, Nitrogen, and Amino Acids in the fine grained fractions

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Previous work by other researchers has indicated that organic molecules can be taken up from solution and complexed to clay mineral external and internal surfaces. This can increase the concentration and stability of organic molecules in soils, marine sediments, and water column particulates. In addition, clay mineral surfaces may facilitate the vertical and horizontal transport, by wind and water, of adsorbed organic matter.

Five sediment samples, collected from diverse sedimentary environments, were divided into 6 different size fractions ranging from approximately 0.2 to 5.0 micrometers in diameter. In order to better define the composition and quantity of organic matter associated with clay mineral surfaces, organic carbon and nitrogen concentrations, clay mineral compositions, and surface areas were determined for each size fraction. Previous studies suggest that nitrogen-rich organic matter, possibly amino compounds, are most readily complexed to clay mineral surfaces. Therefore the composition and quantity of amino acids and amino sugars were also determined in each sediment size fraction.

The amount of organic carbon, nitrogen, and amino acids increased with decreasing size fraction and increasing clay content in all samples.

The relationship between organic constituents and specific surface area of the size fractions indicate that most of the organic matter present is associated with mineral surfaces.

Changes in the composition of the organic matter in the different size fractions were most evident in the red clay sample where the organic matter/clay ratio is low and detrital organic input is minimal. The C-org/N-org ratio decreased with decreasing size fraction suggesting that a relatively more N-rich organic component is concentrated in the smaller size fractions. An increase in the concentrations of β-alanine, γ-aminobutyric acid, lysine, arginine, and histidine were also correlated with a decrease in organic carbon content in the red clay sample, implying that these amino acids compose a residual organic fraction, perhaps sorbed to clay minerals, which is evident only when other organic carbon-rich compounds are absent. Regional variations in amino acid compositions and organic matter content between the different samples suggest that the relative concentrations of individual amino acids may be indicators of the degree of organic matter degradation and stabilization in the sediment.

CLAY-ORGANIC ASSOCIATIONS IN MARINE SEDIMENTS: CARBON, NITROGEN, AND AMINO ACIDS IN THE FINE GRAINED FRACTIONS

by

Karen Weliky

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Professor of Oceanography in charge of major

Redacted for privacy

Dean of Oceanography

Redacted for privacy

Dean of Graduate School

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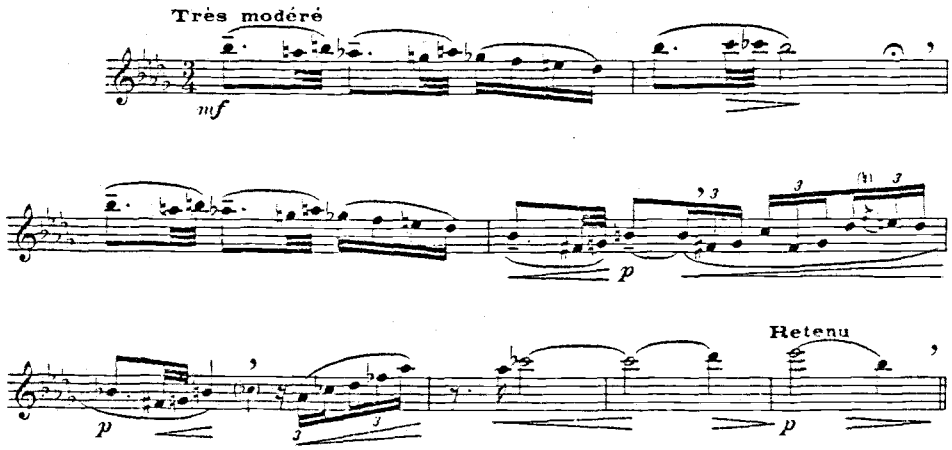
Typed by Karen Weliky for Karen Weliky

For Mom, Dad,

and Michael



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PREFACE

The main focus of this thesis was the investigation of clay mineral-organic complexes in natural sediment samples, which is discussed in chapter one. Chapters two and three describe two analytical techniques which were developed during the course of the project. Described in chapter two is a method for the direct determination of both organic carbon and carbonate carbon in sediments using phosphoric acid and a dichromate-sulfuric acid solution. Chapter three discusses a technique for quantifying clay mineral compositions and abundances in sediments using a combination of linear programming and factor analysis techniques.

Each chapter is presented as an individual manuscript to be submitted separately for publication. Chapter two will be submitted to Geochimica Cosmochimica Acta, and chapters one and three to journals yet undecided. The published form may be slightly different from that presented here.

CHAPTER I

CLAY-ORGANIC INTERACTIONS IN MARINE SEDIMENTS: CARBON, NITROGEN, AND AMINO ACIDS IN THE FINE GRAINED FRACTIONS

ABSTRACT

Previous work by other researchers has indicated that organic molecules can be taken up from solution and complexed to clay mineral external and internal surfaces. This can increase the concentration and stability of organic molecules in soils, marine sediments, and water column particulates. In addition, clay mineral surfaces may facilitate the vertical and horizontal transport, by wind and water, of adsorbed organic matter.

Five sediment samples, collected from diverse sedimentary environments, were divided into 6 different size fractions ranging from approximately 0.2 to 5.0 micrometers in diameter. In order to better define the composition and quantity of organic matter associated with clay mineral surfaces, organic carbon and nitrogen concentrations, clay mineral compositions, and surface areas were determined for each size fraction. Previous studies suggest that nitrogen-rich organic matter, possibly amino compounds, are most readily complexed to clay mineral surfaces. Therefore the composition and quantity of amino acids and amino sugars were also determined in each sediment size fraction.

The amount of organic carbon, nitrogen, and amino acids increased with decreasing size fraction and increasing clay content in all samples. The relationship between organic constituents and specific surface area of the size fractions indicate that most of the organic matter present is associated with mineral surfaces.

Changes in the composition of the organic matter in the different size fractions were most evident in the red clay sample where the

organic matter/clay ratio is low and detrital organic input is minimal. The C-org/N-org ratio decreased with decreasing size fraction suggesting that a relatively more N-rich organic component is concentrated in the smaller size fractions. An increase in the concentrations of β-alanine, γ-aminobutyric acid, lysine, arginine, and histidine were also correlated with a decrease in organic carbon content in the red clay sample, implying that these amino acids compose a residual organic fraction, perhaps sorbed to clay minerals, which is evident only when other organic carbon-rich compounds are absent. Regional variations in amino acid compositions and organic matter content between the different samples suggest that the relative concentrations of individual amino acids may be indicators of the degree of organic matter degradation and stabilization in the sediment.

INTRODUCTION

The presence of clays in terrestrial soils and marine sediments affects the stability, type, and distribution of associated organic matter. Organic compounds are taken up from dilute solutions and are sorbed onto external and interlayer clay surfaces (Weiss, 1969; Degens and Mopper, 1976; Stul et al., 1979). This can serve to concentrate the organic matter as well as protect it from microbial attack (Weiss, 1969; Theng, 1974, 1979). The amount of uptake is related to the type of clay mineral and organic molecules present as well as temperature, salinity and redox conditions (Rashid et al., 1972; Meyers and Quinn, 1973; Hedges, 1977, 1978). In addition, clay surfaces can act as catalysts in the polymerization, degradation, and synthesis of certain organic compounds including amino acids and proteins (Degens and Mopper, 1976; Cloos et al., 1981).

Clay mineral surfaces may also facilitate the vertical and horizontal transport of organic matter by wind and water. Analyses of eolian dust over the Atlantic Ocean suggest that terrestrial organic matter, adsorbed onto particulates, may be transported great distances offshore by winds (Simoneit, 1977). Adsorption of organics onto particulate matter in the water column could be a mechanism for the rapid transfer of organic matter to the sea floor.

Evaluation of the role of clays in the transformation of

organic matter (anthropogenic and natural) in soils and sediments is important to an understanding of nutrient cycling, the fate of organic compounds in different environments, and the use of organic molecular "markers" (such as specific amino acids and lipids) in the interpretation of sediment age, source, and depositional environment. In addition, clay surface sites may have played a necessary role in the origin of life, catalyzing the abiotic synthesis of organic molecules (Fripiat et al., 1974; Paecht-Horowitz, 1978; Bernal, 1951; Shimoyama et al., 1978).

MECHANISMS OF CLAY-ORGANIC REACTIONS

Because clay-organic interactions in natural systems are extremely complex, most of our knowledge about surface properties and reaction mechanisms comes from experimental sorption systems. The unique surface properties of clays are responsible for their reactivity with organic molecules.

The net charge on a clay particle in solution is the sum of the structural and edge charges. A clay particle has a negative structural charge which originates from isomorphous cation substitutions within the crystal lattice. This negative charge is neutralized by the accumulation of an equivalent amount of positive charge at the crystal internal and external surfaces, either in the form of inorganic ("exchangeable") cations or the positive end of polar water molecules. In addition, the edges of clay lattices contain exposed Al or Si cations whose charge is not compensated by

structural anions. These cations are hydroxylated in water and may react as positive or negative sites, depending on the pH of the solution. In solutions of pH greater than 3 (sea water and pore water usually ranges from pH 7 to 8), kaolinite and montmorillonite particles carry a net negative charge; that is, the positive edge charge is not large enough to neutralize the negative structural charge.

Three major reaction mechanisms explaining the formation of clay-organic complexes have been identified: (1)cation exchange reactions involving exchangeable inorganic cations and positively charged functional groups of organic molecules, (2)electron donor-acceptor reactions involving clay structural or exchangeable cations and basic or negatively charged organic molecules, and (3)relatively weak ion-dipole interactions between uncharged polar organic molecules and clay exchangeable cations or polarized water molecules on clay surfaces (Solomon, 1968; van Olphen, 1977; Theng, 1974). Transition metals such as Fe, Cu, and Zn, when present in the clay lattice, form especially stable complexes with organic molecules(Greenland, 1974; van Olphen, 1977). Experiments with amino acid and pesticide molecules of varying ionic charge indicate that complexes between clays and positively charged molecules are more stable than complexes with uncharged polar molecules. Negatively charged molecules are almost unreactive with clay surfaces and are probably repelled by the net negative charge of the mineral (Theng, 1974a,b; Fripiat et al, 1974; Sieskind, 1960). However Greenland (1974) has shown experimentally that

negatively charged humic and fulvic acid molecules can be adsorbed by montmorillonite, probably through reactions with cations, such as Al^{3+} and Si^{4+}, exposed on crystal edges.

The large surface area of clay particles partially accounts for their high adsorption capacity. In addition to a high external surface area, smectite clays (montmorillonite, nontronite, saponite) have the ability to expand their lattice structure and incorporate organic molecules into interlattice sites (Grimm, 1968; Weiss, 1969; Theng, 1979). The increase in d-spacing of expandable clays after interlayer sorption of organic molecules is evident in X-ray diffraction peaks. In fact, a shift in the position of the smectite X-ray peak after saturation of a sediment with ethylene glycol is used as an analytical tool in identifying smectites.

EVIDENCE FOR CLAY-ORGANIC COMPLEXES IN SOILS AND SEDIMENTS

There is evidence that the presence of clays in soils and sediments enhances the stability of associated metastable organic compounds. Sorensen (1972) observed that the presence of montmorillonite in soil reduced the decomposition rate of proteins. A positive correlation has also been reported between the quantity of organic matter and clay content in soils (Weiss, 1969; Fripiat et al., 1974; Schnitzer and Kahn, 1978; Theng, 1974, 1979). Chichester (1969) noted an increase in carbon and nitrogen content

and a decrease in the ratio of organic carbon to organic nitrogen, in the smaller more clay-rich fractions separated from soil samples. In pelagic marine sediments from the Central Pacific, Muller (1977) found that the C-organic/N-organic ratio and the C-organic/Al_2O_3ratio decreased with depth in the sediment until about 150 cm, after which it became constant. He attributed this to the stabilization of nitrogen-rich organic molecules by clay interlayer complexing. Grundmanis and Murray (1982) also observed similar trends in C/N ratios with depth in pelagic marine sediments from the central equatorial Pacific. These and other studies support the hypothesis that nitrogen-containing organic compounds such as amino acids, amino sugars, and proteins may be significant components of clay-organic complexes (e.g. Weiss, 1969; Stevenson and Tilo, 1971; Stevenson and Cheng, 1972; Hedges, 1977, 1978).

Attempts have been made to isolate clay-organic complexes from soil (Chichester, 1969; Satoh, 1976; Turchenek and Oades, 1979; Watson and Parsons, 1974; Spycher, 1977), although it is difficult to physically separate them from particulate organic matter and to prevent their alteration by chemical treatment. Most of the work has focused on soil systems, since the stability of nitrogen compounds affects soil fertility. Stotzky (1972) noted that the relationship between clay-organic complexes, micro-organisms, and enzyme activity in soils should be considered. Organic matter sorption by clay minerals can serve as a means of concentrating microbial food sources. However, some compounds normally metabolized by bacteria and fungi are not utilized in the presence

of clays (Stotzky, 1972; Dashman, 1977).

In both experimental and field studies, montmorillonite is found to be more effective than illite and kaolinite in complexing organic compounds (Grimm, 1968; Weiss, 1969; Fripiat et al., 1974; Theng, 1979). This is attributed to its flexible lattice, which is capable of expanding to incorporate molecules into interlayer sites. The permanence of interlayer complexes is not known. Under certain conditions molecules adsorbed into clay interlayers (determined by an increase in crystal d-spacing using X-ray diffraction) seem to be especially stable, perhaps shielded from enzymatic and microbial attack. Based upon experimental studies, Laura (1975) proposed that organic molecules are stable when complexed as a monolayer within a montmorillonite interlayer. But once multilayers of organic molecules are formed, the crystal d-spacing increases and the molecules may be susceptible to attack by soil enzymes and the proteolytic action of water. Even after maximum expansion, however, the d-spacing of montmorillonites is still about 1/1000 of the diameter of a bacterium.

Most kaolinite minerals do not have the ability to expand and therefore have fairly small adsorption capacities. However, some kaolin minerals (especially halloysite) can expand and incorporate saturated solutions of specific salts and a restricted number of organic compounds including urea, hydrazine, and amides. Once the layers are expanded, the interlayer complexes can be replaced by other molecules not normally able to intercalate with kaolin (van Olphen, 1977). Weiss (1963) suggested that this phenomenon was the

secret to the delicacy of ancient chinese porcelain. The Chinese potter buried kaolins with urine and then ground the clay to make porcelain. The intercalation of urea would cause the mineral lattices to expand, favorably altering the ceramic properties of the clay. The bond strength between crystal layers decreases upon expansion. This results in the formation of very fine and thin crystallites when the mineral is ground.

Humic substances are also intimately associated with the clay minerals in soils and sediments (Theng, 1974, 19779; Greenland, 1971). Humic materials consist of highly polymerized organic molecules, and are high in carbon relative to nitrogen. Although the nature of clay-humic bonding is not well understood, adsorption onto clay minerals seems to increase the stability of these already stable compounds (Rashid et al., 1972; Fripiat et al., 1974; Theng, 1974, 1979). Amino acids and proteins are often adsorbed onto humic substances and thereby indirectly complexed to clay surfaces. Thus the sorption of humic material by clays creates an added difficulty in the isolation of other clay-amino acid complexes.

OBJECTIVES

Laboratory experiments have established some of the sorption properties of clays; field observations indicate the presence of amino acids in sediments and a decreasing trend of C-org/N-org ratios with depth. However, very little work has been done to isolate clay-organic complexes from natural marine sediment samples. I have attempted to better define the composition and quantity of organic matter associated with clay-sized fractions of four marine sediment samples and one river sediment sample representing different chemical and depositional environments (see table 1 for sample descriptions). Four of these samples contain a relatively large amount of carbon and nitrogen attributable to marine and terrestrial detritus. However, in the pelagic red clay sediment (sample R), the ratio of organic matter to clay minerals is lower by about an order of magnitude than in the other samples. This sediment is unique in that it is from a region of low primary productivity and not influenced by terrestrial river input. Therefore, the organo-clay associations can be examined without interference from large amounts of detrital organic matter.

Five sediment samples were collected from diverse sedimentary environments (table 1), frozen on board ship, and thawed immediately before use in the laboratory. Each sample was separated by centrifugation into 6 size fractions shown in table 2 (R was separated into 8 fractions since it contained a large amount

TABLE I-1

Sample Locations, Sedimentation Rates, and Ages

Sample I.D.	Location	Description	Sed. Rate (cm/1000yrs)	Age (yrs)	Method of Age Determination
CR	46° 12.5' N 123° 3.0' W	Columbia River surface sediment	----	recent	----
OM	45° 56.6' N 125° 14.6' W	Oregon Margin, 0-3cm core W8009A-7	20-60	40	ash horizon stratigraphy (Kulm and Scheidigger, 1979)
A	62° 16.5' S 57° 38.7' W	Antarctic, 121-136cm Meteor Core #270	100	1,285	carbon-14 (E. Suess, unpublished)
NC	39° 26.8' N 127° 42.4' W	N. Calif. Margin 15-18cm W8103 44BC	2	8,000	(G.R. Heath,unpublished)
R	30° 22.0' N 157° 45.0' W	Red Clay, 0-5cm Rama 1 15BC	.23	11,000	magnetic reversals (M. Lyle, unpublished)

of fine-grained particles). Determinations of carbon, nitrogen, major inorganic elements, amino acids, amino sugars, mineralogy, and surface area were made for each sediment size fraction. Relationships between the quantity and composition of organic matter, and the mineralogy, age, and depositional environment of the sediments in each size fraction were investigated. Amino acids and amino sugars were studied in particular, in order to determine whether these nitrogen-containing compounds constitute a significant proportion of the relatively nitrogen-rich organic matter associated with clay minerals.

METHODS

SIZE FRACTIONATION

In order not to alter the clay minerals or the organic compounds present in the sediment, size fractionation was done with a minimum of chemical treatment. The work of Edwards and Bremner (1967), Parisher and Lowe (1970), and Watson and Parsons (1974) demonstrate that dispersion of soil particles can be achieved by ultrasonic vibration of the sample in distilled water, without the use of chemical dispersants or oxidizing agents. Since my samples were from the marine environment, soluble salts were first removed by repeated suspension in distilled water and high speed centrifugation, in order to minimize flocculation of clay and organic particles. Approximately 100 to 250 grams of wet sediment were dispersed in 2 liters of distilled, deionized water, and shaken vigorously by hand. I found that dispersion of the particles was enhanced if the suspension was allowed to stand overnight. The sediment suspensions were kept refrigerated throughout the separation process, to minimize decomposition of the organic matter.

The-sediment water suspension was then put in an ultrasonic bath for approximately 15 minutes, just before centrifugation. The samples were separated into size fractions using the centrifuge speeds and times shown in table 2. The appropriate centrifuge

TABLE I-2

Sediment Size Fractions: Centrifuge Speeds and Times

Sample I.D. No.		Size Fraction (microns)	Speed (rpm)	Time (minutes)
R	1	bulk sediment	---	---
	2	>5	500	2.5
	3	2 - 5	1000	4
	4	1 - 2 DK	1000	15
	5	1 - 2 LT	1000	15
	6	.5 - 1	3000	6.5
	7	.2 -.5	6000	10
	8	.1 -.2	12000	10
	9	<.1	17000	15
OM,NC,A	1	bulk sediment	---	---
	2	>5	500	2.5
	3	2 - 5	1000	4
	4	1 - 2	1000	15
	5	.5 - 1	3000	6.5
	6	.2 -.5	6000	10
	7	<.2	17000	15
CR	1	bulk sediment	---	---
	2	>63	wet sieve	---
	3	5 - 63	500	2.5
	4	2 - 5	1000	4
	5	1 - 2	1000	15
	6	.5 - 1	3000	6.5
	7	<.5	17000	15

speed and time was calculated using a modification of the Stokes settling equation as follows:

$$t = \frac{(63.0 \times 10^8)(\log R/S)(n)}{(N^2)(D^2)(Sp - Sf)}$$

t = centrifuge time (minutes)

N = centrifuge speed (rpm)

D = diameter (micrometers) of particle to be settled

n = fluid viscosity (poise) = .01002 for H_2O

R = radius (cm) from the center of the centrifuge head to the bottom of the centrifuge tube

S = radius (cm) from the center of the centrifuge head to the top of the sediment suspension in the centrifuge tube

Sp = density (g/cm^3) of the particle to be settled = an average of 2.3 for clay particles

Sf = density (g/cm^3) of the fluid = 1.0 for water

The grain sizes contained in each fraction are defined by the Stokes equation and should viewed as approximate values.

The samples were centrifuged using a Sorvall model RC2-B ultracentrifuge with a swinging bucket head containing four 50 ml cups. Successive size fractions were separated in the following manner. After each centrifugation, the supernatant was sucked off by vacuum and saved in a polypropylene bottle to be centrifuged at a higher speed for separation of the next smaller size fraction.

The procedure was continued until the supernatant was clear and there was no material left in suspension. This resulted in 8 size fractions of sample R and 6 size fractions of each of the other samples.

CARBON

Organic carbon and carbonate carbon were determined using the H_3PO_4/dichromate LECO technique described in chapter 2. Basically, C-CO_3 is measured as the CO_2 liberated during treatment of the sediment with phosphoric acid, and C-org is measured as the CO_2 evolved during subsequent oxidation of the remaining sediment and phosphoric acid mixture with dichromate. The CO_2 is detected by a thermal conductivity detector.

NITROGEN

Total nitrogen was determined using the micro-Kjeldahl digestion method described by Bremner (1960). Fixed ammonium-nitrogen was determined by the method of Silva and Bremner (1966). In this procedure, the organically bound nitrogen is first removed with potassium hypobromite. The residue is then treated with hydrofluoric acid to destroy the silicate lattice structure of clay minerals. The solution is made basic with KOH and the nitrogen is distilled as NH_3 and detected as in the micro-Kjeldahl technique. Organic nitrogen is calculated as the difference

between the measured total nitrogen and fixed nitrogen.

MAJOR INORGANIC ELEMENT CHEMISTRY

Major elemental compositions were measured by atomic absorption spectrophotometry. The sediment was initially digested in a hydrofluoric-nitric acid solution using the procedure described by Krissek et al. (1980). Silica was determined by colorimetry using the yellow silicomolybdate complex described by Strickland (1952). To distinguish the Mn and Fe present as amorphous and poorly crystalline oxyhydroxides, from Mn and Fe in alumino-silicate lattices, the fractions of samples R and NC (the only samples that contained high concentrations of Mn and Fe) were leached with an oxalic acid-ammonium oxalate solution (Schwertmann, 1964). This leach is effective in dissolving Fe and Mn oxyhydroxides without alteration of the clay minerals (Dudas and Harward, 1971). Manganese and Fe concentrations in the leachate were then determined by atomic absorption spectrophotometry. One hundred per cent of the total Mn and generally less than 2% of the total Fe was in the leachable fraction. The major element chemistry was used in conjunction with X-ray diffraction data to determine the mineral compositions of samples R and NC by the method described in chapter 3.

AMINO ACIDS AND AMINO SUGARS

Amino acids and two amino sugars, glucosamine and galactosamine, were determined following the methods outlined by Muller and Liebezeit (in preparation). Fifty milligrams of sediment were weighed into a 15 ml heavy-walled glass ampoule with 1 ml of ultrapure HCl added. Fifty microliters of Norleucine (1 nmole/microliter) were added as an internal standard in order to calibrate the amino acid recovery. The ampoule was flushed with nitrogen gas for 5 minutes and sealed under nitrogen pressure. The samples were then hydrolyzed by heating in an oven at 110°C for 22 hours. The abundances of individual amino acids were quantitatively determined on a Biotronics automated Amino Acid Analyzer equipped with a fluorometric detection system. The reaction of amino acids with the reagents o-phthalaldehyde and fluorescamine forms fluorescent products which are detectable with much greater sensitivity (in the picomole range) than was possible with previously used techniques such as the colorimetric ninhydrin method (Gardener, 1978; Dawson and Pritchard, 1978).

MINERALOGY

The abundances and compositions of smectite, illite, chlorite, feldspar, and quartz in the fractions of samples R and NC were estimated from major element chemistry and X-ray diffraction data using factor analysis and linear programming methods (described in chapter 3). Calcium carbonate was calculated as the $\%CaCO_3$ equivalent to the $\%C\text{-}CO_3$ determined by the H_3PO_4/dichromate

LECO technique (described in chapter 2), assuming all the $C\text{-}CO_3$ is present in the form of $CaCO_3$. The per cent of amorphous and poorly crystalline MnO_2 and Fe_2O_3 minerals present was calculated from leachable Mn and Fe values determined by atomic absorption.

SPECIFIC SURFACE AREA

Specific surface area measurements were performed for each sediment size fraction in order to assess the amount of mineral surface area available for adsorption of organic molecules. Since clay minerals and Fe-Mn-oxyhydroxides have high surface areas relative to quartz and feldspar, an increase in the proportion of these minerals should coincide with an increase in surface area.

External surface area was determined by nitrogen sorption using a Quantachrome Monosorb surface area analyzer. The sediment was weighed into a sample tube and heated at 125° C for 15 minutes to remove surface water and adsorbed gasses. Nitrogen gas is then allowed to flow through the sample tube. The amount of nitrogen adsorbed by the sample is measured and equated to external surface area in m^2, assuming that the N_2 molecules are adsorbed in a monolayer. The areal coverage of one N_2 molecule is assumed to be $16.2 \times 10^{-20} m^2$. The clay interlattice spaces collapse upon heating at 125°C, preventing the penetration of N_2 molecules. Therefore this measurement is of external surface area only. The absolute external surface area of the sample (in m^2), is then divided by the sample weight after analysis to give specific surface area in m^2/g.

RESULTS AND INTERPRETATION

SIZE FRACTIONATION

The size fractions separated from each sample and their weight percent of the total sediment recovered during fractionation are listed in table 4. Between 92% and 96% of the original bulk sediment was recovered in all cases. The mineralogy of each fraction was qualitatively examined using X-ray diffraction, as a partial check of the effectiveness of the size separation in isolating pure mineral fractions. The mineralogical trends of the size fractions followed the expected patterns (Gibbs, 1977): quartz and feldspar were found primarily in the largest size fractions, smectite increased with decreasing size fraction, and illite was present in all the fractions. The >5 micrometer fraction of all the samples, however, contained a large spectrum of minerals, and was not a cleanly separated fraction. It will be omitted in the discussions of individual size fraction compositions, though it will be included in budget calculations.

In all samples the size fractions varied in color, becoming increasingly dark with decreasing grain size. The 1-2 micrometer fraction of the Red Clay sediment was unusual in that it was sharply divided, after centrifugation, into two layers: a very dark black-brown layer on top with a light tan layer below. The two layers were analyzed separately and are referred to as 1-2DK and 1-2LT respectively. The Red Clay was the only sediment with

enough fine-grained material to enable the collection of a size class <.1 micrometer. The sediment in the area where the Red Clay sample was collected is thought to consist primarily of windblown quartz and clay minerals (Leinen and Heath, 1981) and it is therefore likely to contain particles of small grain size. In contrast, the Columbia River sample consisted of the most coarsely-grained sediment. The smallest size fraction obtained was the less than .5 micrometer fraction, and 93% of the sediment was greater than 5 micrometers in size.

The sediment size fractions were separated without the use of chemical treatments (other than rinsing with deionized water) in order to minimize alteration of the clay minerals and organic compounds that might be associated with them. One problem with this method of size separation is that it does not ensure the separation of pure clay-organic complexes from particulate organic material. This organic material, although not bound to mineral surfaces, may also settle out with the clay minerals. However, removal of particulate organic matter using dilute HCl (eg. Bada and Man, 1980) or $H_2O_2$is undesirable, as these treatments may also partially destroy the clay mineral structures or oxidize organic matter that is adsorbed to clay mineral surfaces (van Langeveld et al., 1978; Burford et al., 1962). Rashid et al.(1972) concluded from experiments that repeated rinsing with distilled water removed most of the particulate humic material not associated with the clay minerals. Therefore I decided to avoid using harsh chemical treatment and, for this preliminary look at clay-organic

associations, to remove the particulate organic matter by rinsing with distilled water.

NITROGEN AND CARBON

Nitrogen and carbon concentrations were determined in each sediment size fraction, enabling a comparison of the quantity and type of organic material associated with different grain sizes and mineral comositions. The results of these analyses are given in table 3 along with the calculated C-org/N-org and C-org/N-total ratios. Organic nitrogen was distinguished analytically from fixed inorganic ammonium-nitrogen. This distinction is very important when examining the nature of the organic matter present (Stevenson and Tilo, 1971) especially in the R and NC fractions where fixed-nitrogen composes 50% or more of the total nitrogen in the sample. This is exemplified by the differences between C-org/N-org and C-org/N-total ratios of these samples. Exchangeable inorganic ammonium-nitrogen was not measured because, in most marine sediments, it accounts for only a small fraction (less than 5%) of the total nitrogen and it therefore would not represent a significant fraction of the total nitrogen (Muller, 1977; Powell, 1980).

Organic Nitrogen and Carbon

Generally, organic carbon and organic nitrogen concentrations increase with decreasing size fraction in all the samples. The

TABLE I-3

CARBON AND NITROGEN

SAMPLE	% CORG	PPM NORG	C-ORG / N-ORG	PPM N-FIXED	%C-CO3	C-ORG / N-TOTAL
R BULK	0.19	325	5.9	327	.07	2.9
R >5	0.05	113	4.4	198	.05	1.6
R 2-5	0.09	48	18.7	319	.03	2.4
R 1-2 DK	1.30	667	19.5	0	.17	19.5
R 1-2 LT	0.08	123	6.5	439	.04	1.4
R .5-1	0.08	191	4.2	469	.02	1.2
R.2-.5	0.27	401	6.8	412	.04	3.3
R.1-.2	0.22	626	3.5	342	.03	2.3
R <.1	0.33	626	5.2	217	.03	3.9
NC BULK	0.70	700	10.0	428	.05	6.2
NC >5	0.43	514	8.4	25	.05	8.0
NC 2-5	0.44	302	14.6	446	.02	5.9
NC 1-2	0.52	431	12.1	515	.02	5.5
NC .5-1	0.69	542	12.7	577	.03	6.2
NC.2-.5	*1.09	1337	8.1	573	.05	5.7
NC <.2	*1.54	1658	9.3	609	.06	6.8
OM BULK	2.36	2452	9.6	264	.15	8.7
OM >5	0.68	670	10.1	156	.24	8.2
OM 2-5	1.85	1800	10.3	322	.08	8.7
OM 1-2	3.29	3627	9.1	381	.06	8.2
OM .5-1	3.47	4017	8.6	387	.06	7.9
OM.2-.5	*5.00	6010	8.3	353	.03	7.8
OM <.2	4.28	5285	8.1	325	.03	7.6
A BULK	0.92	1126	8.2	113	.05	7.4
A >5	0.23	320	7.2	80	.03	5.7
A 2-5	0.46	612	7.5	117	.03	6.3
A 1-2	0.56	787	7.1	137	.03	6.1
A.5-1	1.01	1403	7.2	170	.00	6.4
A.2-.5	1.04	1515	6.9	193	.04	6.1
A <.2	3.07	4217	7.3	283	.05	6.8
C BULK	0.61	452	13.5	13	.00	13.1
C >63	0.62	328	18.9	20	.00	17.8
C 5-63	0.28	253	11.1	10	.00	10.6
C 2-5	1.55	1292	12.0	47	.00	11.6
C 1-2	2.74	2522	10.9	57	.03	10.6
C.5-1	3.40	3079	11.0	70	.03	10.8
C <.5	4.30	4133	10.4	75	.04	10.2

* C-org values using wet oxidation method were significantly lower than those from combustion measurements. (Combustion values are given in table below):

SAMPLE	C-ORG(WET OXID)	DIFFERENCE	C-ORG/N-ORG
B .2-.5	.92	.17	6.9
B .2	1.36	.13	3.2
OM.2-.5	4.75	.25	7.9

C-org/N-org ratios of the R fractions indicate that the smaller size fractions are enriched in nitrogen relative to carbon (figure 1a). The same trends - increasing concentrations of C-org and N-org and decreasing C-org/N-org ratios with decreasing size fraction - are seen in the NC fractions (figure 1b), but the differences are not as large as in the R fractions. The absolute C-org and N-org concentrations are higher in the NC fractions. This could be due to an increase in the amount of detrital material at site NC, evidenced by an order of magnitude higher sedimentation rate (table 1).

Relatively high C-org/N-org ratios are evident in the two largest R fractions, 1-2DK (R4) and 2-5 (R3) and the three largest NC fractions, 2-5 (NC3), 1-2 (NC4), and .5-1 (NC5). This is follwed by a sharp decrease in the C-org/N-org ratios of the smaller size fractions. The decrease in C-org/N-org ratios with decreasing size fraction indicates that while carbon-rich compounds, perhaps humic substances, are associated with some of the larger fractions, relatively more nitrogen-rich organic compounds are associated with the smaller fractions. This is in contrast to the observation made by soil scientists that carbon-rich humic and fulvic acids are the major types of organic matter complexed to clay minerals (Schnitzer and Kahn, 1978; Theng, 1974, 1979; Greenland, 1975).

Fraction R 1-2DK (R4) is unusual in that organic carbon and organic nitrogen values as well as the C-org/N-org ratio are anomalously high, and no fixed ammonium was detected. Elemental

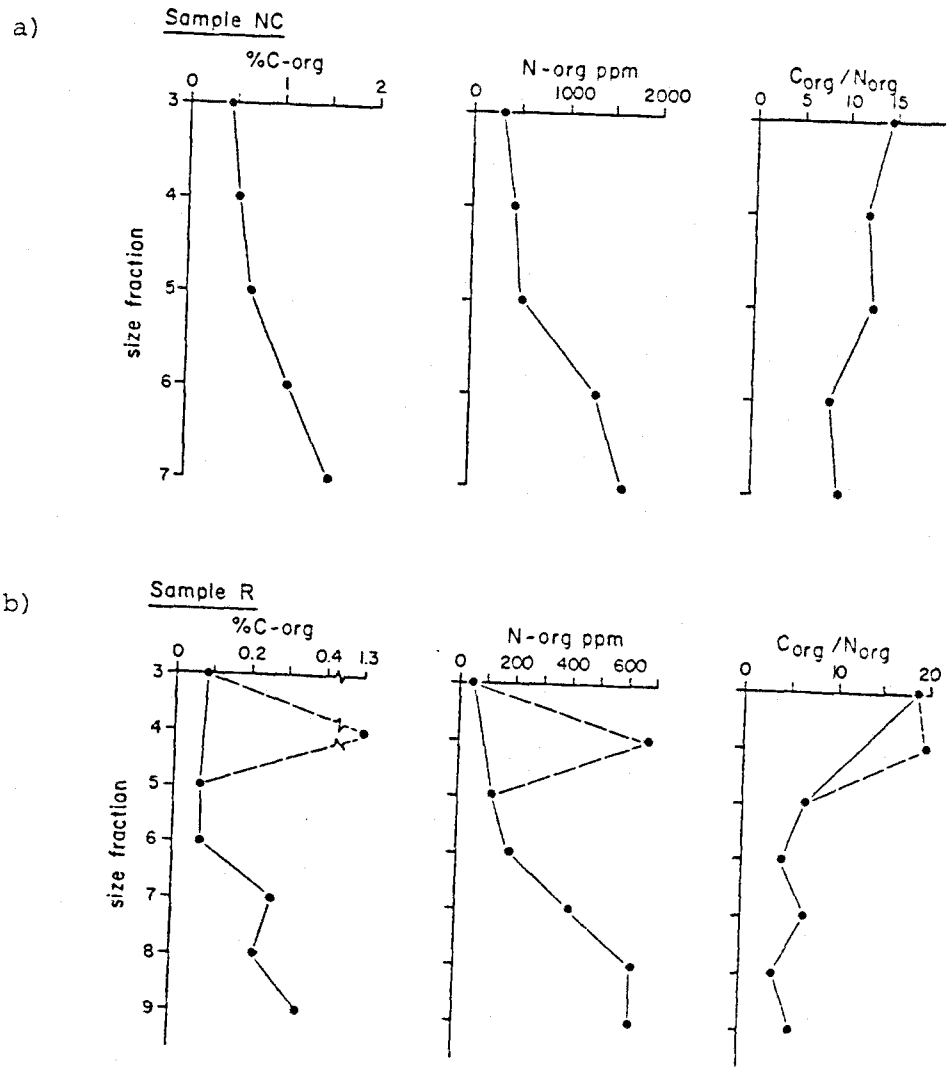


FIGURE I-1: Changes in the concentrations of organic carbon and nitrogen, and the effect on C-org/N-org ratios in the size fractions of samples R and NC. The numbers refer to the size fractions described in table I-2. Fraction R 1-2DK is shown with a dotted line.

analysis indicates concentrations of 9% leachable MnO_2 and 3.4% leachable Fe_2O_3, an order of magnitude higher than the concentrations in the other fractions (table 9). This signifies the presence of amorphous Mn-Fe-oxyhydroxide minerals which are capable of adsorbing large amounts of organic material onto their porous and active surfaces (Greenland, 1975). It is possible that a portion of the nitrogen estimated as organic nitrogen in this sample is actually exchangeable nitrogen adsorbed to oxyhydroxide surfaces, which was rinsed away during fixed nitrogen determination. Unfortunately there was insufficient sediment for an additional exchangeable nitrogen analysis.

The concentrations of C-org and N-org in samples CM, CR, and A also increase with decreasing size fraction, but only very slight changes in the C-org/N-org ratios are observed. The sites of these sediment samples have even higher sedimentation rates, are closer to regions of high primary productivity and continental influence, and therefore receive a larger amount of organic detritus.

Size Distribution and Recovery of Organic Nitrogen and Carbon

The calculated size distributions of carbon and nitrogen are shown in table 4 (see also figure 11). Although the R 1-2 DK fraction constitutes only 4% of the total weight of the sediment, 27% of the organic carbon is contained in this fraction. Both the R and NC sediments show a significant concentration of organic nitrogen in the smaller size fractions. More than 50% of the

organic nitrogen recovered in the R and NC sediment fractions is in the less than .5 micrometer size fractions. Organic carbon seems to be more evenly distributed between small and large size fractions. The other samples do not exhibit such a striking concentration of organic nitrogen in the small fractions (table 4), except for the Antarctic sediment (sample A) which has 43% of the recovered organic nitrogen in the less than .2 micrometer fraction.

The R sediment is unique in that only 76% of the total organic nitrogen, 50% of the amino acids and 37% of the amino sugars can be accounted for in the size fractions (table 4). A significant proportion of nitrogen-containing organic compounds, including amino acids and amino sugars, were lost during the size separation procedure. However, since 92% of the original sediment, approximately 100% of the total fixed nitrogen, and 95% of the total organic carbon was recovered, the loss of nitrogen compounds was probably not due to loss of sediment particles. Rather, a significant fraction of the organic matter in R may have existed as "free", uncomplexed molecules or compounds "loosely bound" to clay minerals which were rinsed away when the sediment was suspended in distilled water and centrifuged.

Fixed Inorganic Ammonium: Relationship to Clay Minerals

The presence of fixed-ammonium in soils and sediments has been explained by the replacement of K^+-ions in illite crystal lattices with NH_3^+-ions of similar ionic radius (Stevenson and Dhariwal,

TABLE I-4

SIZE DISTRIBUTION OF CORG, NORG, & AMINO ACIDS

SAMPLE	*FRACT WT %	%OF CORG IN FRACT	%OF NORG IN FRACT	%OF NFIX IN FRACT	%OF A.ACIDS IN FRACT	%OF A.SUGARS IN FRACT
R >5	12	3	4	7	1.7	.2
R 2-5	25	12	4	30	2.5	.5
R 1-2MM	4	27	8	0	4.1	4.3
R 1-2LT	20	8	8	27	6.2	3.7
R.5-1	9	4	5	13	3.4	1.3
R.2-.5	15	21	18	10	15.9	12.7
R.1-.2	11	13	21	11	12.0	9.4
R <.1	4	7	8	3	4.7	5.2
%ACCOUNTED FOR (OF TOTAL)		95%	76%	110%	50%	37%

90% OF ORIGINAL BULK SEDIMENT RECOVERED IN FRACTIONS

SAMPLE	*FRACT WT %	%OF CORG IN FRACT	%OF NORG IN FRACT	%OF NFIX IN FRACT	%OF A.ACIDS IN FRACT	%OF A.SUGARS IN FRACT
MC >5	30	19	22	2	10.5	11.2
MC 2-5	23	14	10	24	7.6	6.8
MC 1-2	13	10	8	16	4.9	4.1
MC.5-1	10	10	8	13	8.3	9.6
MC.2-.5	12	19	23	16	20.0	24.9
MC <.2	12	26	28	17	31.6	32.8
%ACCOUNTED FOR (OF TOTAL)		97%	99%	88%	83%	88%

95% OF ORIGINAL BULK SEDIMENT RECOVERED IN FRACTIONS

SAMPLE	*FRACT WT %	%OF CORG IN FRACT	%OF NORG IN FRACT	%OF NFIX IN FRACT	%OF A.ACIDS IN FRACT	%OF A.SUGARS IN FRACT
OM >5	37	11	10	22	9.2	8.2
OM 2-5	27	21	20	33	20.0	18.7
OM 1-2	13	10	10	10	19.1	18.3
OM.5-1	8	12	13	12	12.0	12.3
OM.2-.5	12	25	29	16	20.0	30.0
OM <.2	3	5	7	4	6.3	5.2
%ACCOUNTED FOR (OF TOTAL)		93%	98%	106%	96%	92%

94% OF ORIGINAL BULK SEDIMENT RECOVERED IN FRACTIONS

SAMPLE	*FRACT WT %	%OF CORG IN FRACT	%OF NORG IN FRACT	%OF NFIX IN FRACT	%OF A.ACIDS IN FRACT	%OF A.SUGARS IN FRACT
A >5	37	9	10	26	9.2	13.8
A 2-5	27	13	15	20	10.7	11.7
A 1-2	9	6	6	11	5.4	4.5
A.5-1	8	9	10	12	9.1	7.8
A.2-.5	9	9	12	15	10.5	10.3
A <.2	11	37	41	27	39.5	38.4
%ACCOUNTED FOR (OF TOTAL)		82%	95%	119%	89%	96%

96% OF ORIGINAL BULK SEDIMENT RECOVERED IN FRACTIONS

SAMPLE	*FRACT WT %	%OF CORG IN FRACT	%OF NORG IN FRACT	%OF NFIX IN FRACT	%OF A.ACIDS IN FRACT	%OF A.SUGARS IN FRACT
CR >63	28	28	20	38	20.1	17.4
CR 5-63	65	29	36	46	32.5	32.1
CR 2-5	3	8	9	9	9.0	10.7
CR 1-2	2	8	10	8	10.1	11.1
CR.5-1	1	6	7	5	7.5	8.0
CR <.5	1	7	9	5	11.2	11.4
%ACCOUNTED FOR (OF TOTAL)		85%	91%	110%	90%	91%

95% OF ORIGINAL BULK SEDIMENT RECOVERED IN FRACTIONS

*Column 2 is calculated as the weight per cent of the total sediment recovered after the size separation procedure.

1959; Mogilevkina, 1964). The ammonium (NH_3^+) ions are then "fixed" tightly within the crystal structure and removed only after destruction of the silicate lattice with hydrofluoric acid. However, a plot of fixed ammonium vs. clay mineral content (figure 2a) reveals that for the NC fractions, fixed ammonium is not dependent on the illite concentration, but is correlated with % total clay which is controlled by the smectite abundance. The illite content of these fractions varies very little. In the R fractions, however (figure 2b), fixed ammonium correlates positively with illite content (except for R4 and R8) and not at all with the smectite or the total clay content.

The fixed ammonium content (ppm), of the less than five micrometer fractions of sediments R and NC (figure 3), was then plotted against $\%K_2O$. A positive correlation is evident, and the relationship is unique for the size fractions of each of the two sediments. The difference in intercept between the R and NC samples could be due to a difference in the potassium bearing mineral phases, the phases in R being depleted in fixed ammonium relative to potassium. Possibly a potassium bearing mineral is present in R that is not associated with fixed ammonium, or the clay minerals in R do not fix ammonium as efficiently as those in the NC sediment. A positive correlation between fixed ammonium and $\%K_2O$ was also observed by Muller (1977) in bulk sediments from the Central Pacific, N.W. African margin, and Baltic Sea. He attributed this correlation to be a function of the clay mineral content of the sediment, and assumed that illite was probably most

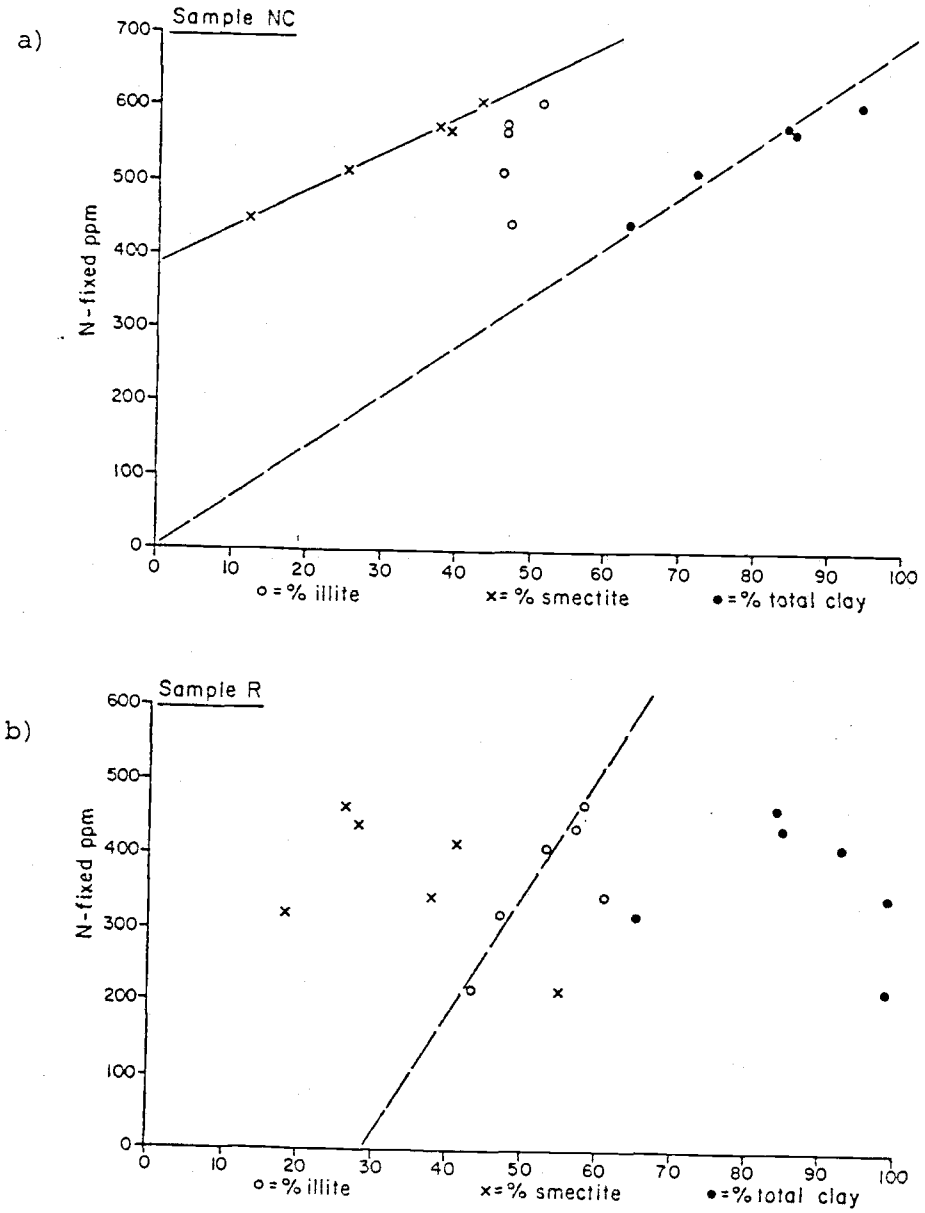


FIGURE I-2: Relationship between fixed nitrogen and clay minerals in the size fractions of samples NC and R. Correlation coefficients (r) are:

a) NC smectite vs. fixed-N r=.99

total clay vs. fixed-N r=.99

b) R illite vs. fixed-N r=.98

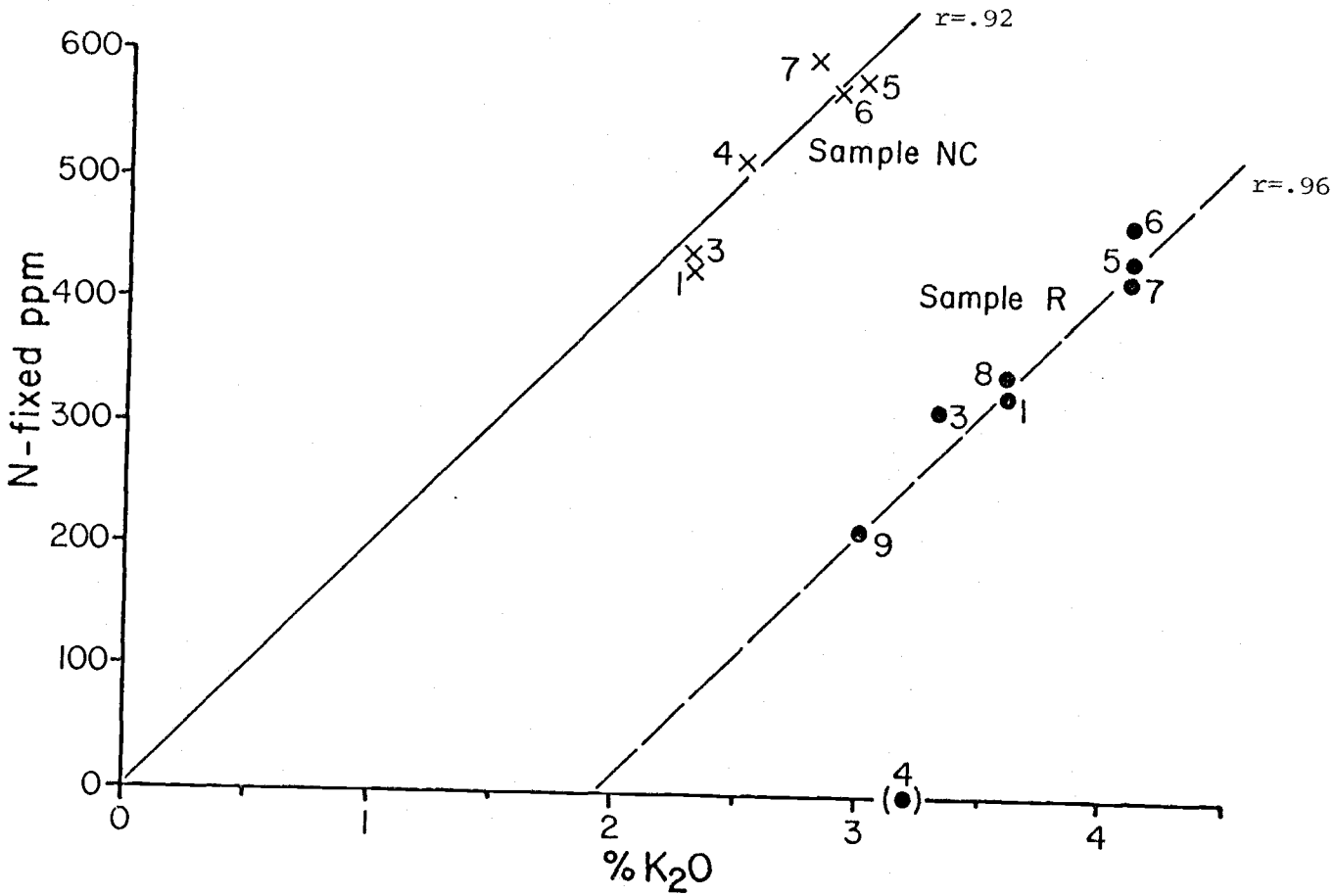


FIGURE I-3: Relationship between fixed-nitrogen and potassium in samples NC and R. X = NC ● = R
Numbers refer to the different size fractions as explained in table I-2.

influential since it is the dominant potassium-bearing clay mineral in the sediments he studied.

The fixation of ammonium in sediments NC and R seems to depend on the nature of the illite and smectite clay minerals, and not necessarily on the illite content alone. Experimental evidence indicates that clay minerals other that illite are also capable of fixing ammonium. Kudeyarov (1974) showed that montmorillonite (a type of smectite), saturated with NH_4Cl for two days, is capable of fixing up to 200 ppm ammonium-nitrogen which could not be leached with 1N NaCl but was extracted after destruction of the crystal lattice by hydrofluoric acid. Allison and Roller (1959) observed that unweathered illite, when saturated with NH_4Cl, fixed an average of only 150 ppm ammonium-nitrogen. However, partially degraded weathered illite, vermiculite, and montmorillonite fixed an average of 800 ppm ammonium-nitrogen.

The estimated compositions of illite and smectite in the R and NC sediments are very different (table 10; see also chapter 3). This could account for the differences in ammonium fixation. The smectite in sample R does not contain K_2O while the smectite in NC contains 1.9% K_2O. Since a possible mechanism of ammonium fixation is the replacement of K^+ -ions in the crystal lattice by NH_3^+-ions, the tendency of certain minerals to fix ammonium, is probably related to their potassium content.

As discussed earlier, the fixed ammonium in the NC sediment seems to be controlled by the smectite rather than the illite abundance (figure 2a). Perhaps the illite is relatively

unweathered, or even authigenic in origin, and has a low capacity for fixed ammonium compared to the K-rich smectite present. The illite of R is thought to be eolian in origin (Leinen and Heath, 1981) and is therefore likely to be weathered and able to fix large amounts of ammonium. This, along with the absence of potassium in the smectites, could explain why fixed ammonium in R is primarilly controlled by the illite concentration (figure 2b). Another possibility is that some of the nitrogen measured as fixed inorganic nitrogen, is actually organic nitrogen complexed to the smectite interlattice surfaces and released only after treatment with hydrofluoric acid (Watson and Parsons, 1974; Stevenson and Tilo, 1972). Thus, the concentration of fixed ammonium measured in sediments seems to be a function of both the source and the composition of illite and smectite clay minerals.

AMINO ACIDS, AMINO SUGARS, AND AMMONIA-NITROGEN

Figure 4 is an example of a typical amino acid chromatogram obtained from analyses of the individual size fractions. It illustrates the elution sequence of the individual amino acid, amino sugar, and free ammonnia peaks. The concentrations (nmole/g of sediment) of total amino acids and amino sugars (glucosamine + galactosamine), calculated from the sum of the individual peaks, are listed in table 5 for each sediment size fraction. Concentrations of the twenty-one individual amino acids and amino

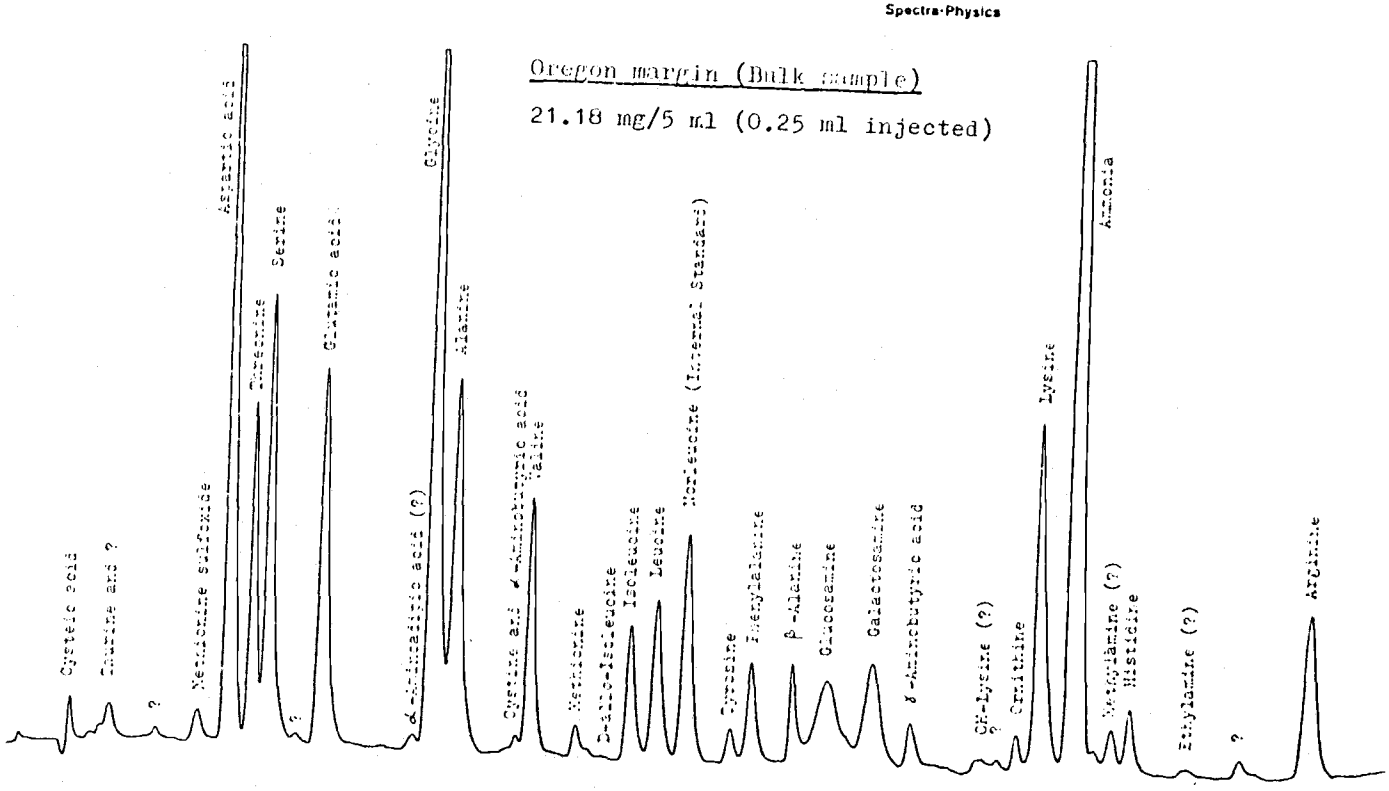


FIGURE I-4: A typical amino acid chromatogram

TABLE I-5

AMINO ACIDS, AMINO SUGARS, AND AMMONIA

SAMPLE	TOTAL A.ACIDS uMOL/GM	AMINO SUGARS uMOL/GM	NH3 PEAK uMOL/GM	%NORLEU RECOV.
R BULK	4.12	0.55	19.39	95.8%
R >5	0.58	0.01	10.36	97.1%
R 2-5	0.43	0.01	12.65	101.9%
R 1-2 DK	4.33	0.58	23.84	(39.5%)
R 1-2 LT	1.32	0.10	21.17	100.4%
R .5-1	1.59	0.08	22.44	103.7%
R.2-.5	4.46	0.45	29.25	94.7%
R.1-.2	4.60	0.46	21.67	102.2%
R <.1	4.99	0.69	14.93	99.6%
NC BULK	1.20	2.04	43.26	76.4%
NC >5	4.21	0.76	23.10	(36.1%)
NC 2-5	3.96	0.60	27.78	84.2%
NC 1-2	4.55	0.64	28.50	92.3%
NC.5-1	9.96	1.75	48.50	75.6%
NC.2-.5	20.05	4.24	68.77	76.8%
NC <.2	31.59	5.58	66.23	90.0%
OM BULK	45.71	4.54	41.98	88.4%
OM >5	11.33	1.01	11.56	90.7%
OM 2-5	33.81	3.15	30.65	93.4%
OM 1-2	67.02	6.40	67.99	89.1%
OM.5-1	68.79	6.98	86.00	89.2%
OM.2-.5	110.50	11.23	98.79	90.1%
OM <.2	96.40	7.84	76.81	92.7%
CR BULK	13.40	0.98	5.10	87.0%
CR >63	9.63	0.61	1.97	91.3%
CR 5-63	6.69	0.48	2.36	92.9%
CR 2-5	40.43	3.48	15.52	86.9%
CR 1-2	79.91	6.42	33.89	81.9%
CR.5-1	100.04	7.78	33.57	80.7%
CR <.5	150.22	10.10	51.71	80.6%
A BULK	28.24	2.23	30.39	76.5%
A >5	7.00	0.83	8.61	83.2%
A 2-5	16.46	0.97	15.75	78.9%
A 1-2	17.02	1.12	21.55	76.9%
A .5-1	32.21	2.17	31.01	80.9%
A .2-.5	32.91	2.55	33.11	80.6%
A <.2	101.46	7.80	74.45	76.2%

sugars (nmole/g and mole % of total amino acids) measured for each fraction are listed in tables 2 through 6 of the appendix. Also given in table 5 are the concentrations of free ammonia detected by the amino acid analyzer in each sediment fraction.

The source of free ammonium is not easy to determine because it not only includes inorganic ammonium (such as fixed or exchangeable ammonium), but also ammonium resulting from the partial destruction of some amino acids during hydrolysis. In most samples, the concentration of ammonium-nitrogen in the ammonia peak is equal to or greater than the total amino acid-nitrogen concentration calculated from the sum of individual amino acid peaks. Therefore, for the purpose of constructing a nitrogen budget, it is crucial to estimate the relative proportions of organic nitrogen and inorganic fixed-nitrogen contributing to the ammonia peak.

Source of Ammonia-Nitrogen

In order to assess the proportion of inorganic fixed-ammonium contained in the ammonia peak, I attempted to experimentally determine the amount of fixed-ammonium released from the sediment during hydrolysis with 6N HCl. The sediment was hydrolyzed, the remaining residue was rinsed free of the hydrolyzate, and then fixed ammonium was determined on the residue (table 6, column 2). Between 0% - 20% of the total fixed ammonium remained in the sediment after hydrolysis (column 3). Therefore, the clay silicate structure must be largely destroyed during hydrolysis, and an

TABLE I-6

EXPERIMENTAL RESULTS ON THE PROPORTION
OF INORGANIC NITROGEN INCLUDED IN THE AMMONIA PEAK

Sample	ppm Total Fixed-N	ppm Fixed-N in Hydrol. Residue	%of Fixed-N Released in Hydrol.	ppm Fixed-N in NH_3 Peak	ppm N-Total in NH_3 Peak	ppm N-Total in Hydrol. Residue
R 2-5	319	31	10%	288	177	--
R 1-2LT	439	91	21%	348	296	--
R 1-2DK	0	nd	nd	0	333	--
R .5-1	469	36	8%	433	314	--
R .2-.5	412	0	0%	412	409	34
R .1-.2	342	0	0%	342	303	--
NC 1-2	515	65	13%	450	399	85
NC.2-.5	573	36	6%	537	963	--

average of 92%±7% of the total fixed ammonium in the sediments is released and included in the ammonia peak. If this assumption is correct, the inorganic ammonium-nitrogen would then account for a maximum of half of the ammonia peak-nitrogen in the fractions of NC, OM, CR, and A. However in the R fractions (except R 1-2DK and .2-.5) and in the NC 1-2 micrometer fraction, the calculated concentration of fixed-ammonium contributing to the ammonia peak is 10% to 50% greater than the total concentration of ammonium measured in the peak (columns 4 and 5). Therefore, when calculating a nitrogen budget for these samples (table 8a-e) I assumed that 100% of the ammonia peak was attributable to inorganic ammonium. In the OM, A, CR, and most of the NC sediment fractions, where the total ammonia peak-nitrogen is much greater than the fixed ammonium-nitrogen content, I assumed 100% of the measured fixed ammonium was released during hydrolysis and included in the ammonia peak; the remaining ammonia peak-nitrogen was assumed to be organic nitrogen. Therefore the estimated organic nitrogen content of the ammonia-peak is a minimum value. Table 7 lists the calculated upper and lower limits of %organic nitrogen attributed to amino-nitrogen in each size fraction. In column 1 (the lower limit), only the sum of individual amino acid peaks are included as amino-nitrogen. In column 2 (upper limit), amino-nitrogen is estimated as the sum of the individual amino acid peaks plus the corrected value of organic nitrogen in the ammonia peak.

To estimate the proportion of organic nitrogen released, I also determined the total nitrogen concentration of the sediment

TABLE I-7

MAXIMUM AND MINIMUM ESTIMATES OF THE PER CENT ORGANIC NITROGEN PRESENT AS AMINO - NITROGEN

SAMPLE	*MINIMUM	*MAXIMUM
R BULK	22	22
R >5	10	10
R 2-5	17	17
R 1-2 DK	11	61
R 1-2 LT	19	19
R.5-1	16	16
R.2-.5	20	21
R.1-.2	13	13
R <.1	11	11
NC BULK	29	55
NC >5	14	72
NC 2-5	23	23
NC 1-2	19	19
NC.5-1	33	52
NC.2-.5	26	58
NC <.2	33	53
OM BULK	32	45
OM >5	29	30
OM 2-5	32	38
OM 1-2	32	48
OM.5-1	30	50
OM.2-.5	31	49
OM <.2	31	45
CR BULK	49	62
CR >63	49	52
CR 5-63	44	55
CR 2-5	52	65
CR 1-2	52	68
CR.5-1	54	67
CR <.5	60	76
A BULK	43	70
A >5	38	51
A 2-5	46	63
A 1-2	37	57
A.5-1	40	59
A.2-.5	38	56
A <.2	42	60

*The minimum estimate is calculated as the % of N-org accounted for in the individual amino acid peaks only. The maximum estimate is the % of N-org accounted for in the amino acid peaks plus the ammonia peak (after subtraction of fixed-ammonium).

residue after hydrolysis for fractions R 2-5 and NC 1-2 (table 6, column 6). In these two samples, 92% and 95% of the total organic nitrogen, respectively, was released during hydrolysis.

B. Recovery of Amino Acids After Hydrolysis

Before the hydrolysis of each size fraction, an internal standard, norleucine, was added to the hydrolysis tube containing the sediment sample. Table 5 lists the % norleucine recovery for each sediment fraction. This value was used as an indication of possible losses of hydrolyzate during the sample preparation for amino acid analysis. The measured individual amino acid concentrations were readjusted to 100% from the calculated norleucine recovery for each sample. This assumes that all amino acids were lost in equal proportions. In the R 1-2DK and NC >5 fractions, however, the norleucine recovery was unusually low - less than 40%. Here, the mean recoverey value of 95%, obtained for the other samples, was used to readjust the amino acid yields.

Both the R 1-2DK and NC>5 fractions also have exceptionally high MnO_2 concentrations (table 1 in appendix). A plot of $\%MnO_2$ vs. norleucine recovery for the R and NC fractions (figure 5) indicates that the presence of MnO_2 in the sediment may significantly reduce the recovery of norleucine. It is difficult to determine, at this point, whether the yields of any other amino acids are similarly affected. However, it is unlikely that the total amino acid yield is lowered significantly. If the amino acid concentrations measured for R 1-2DK and NC >5 were readjusted to

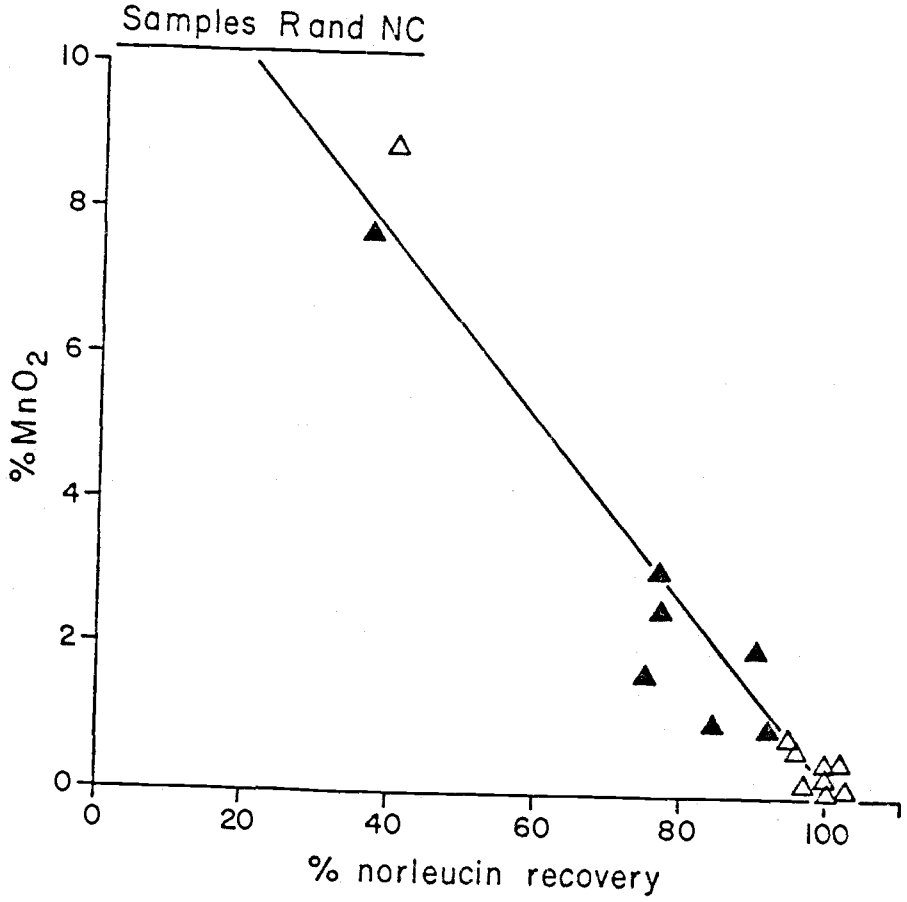


FIGURE I-5: Negative correlation between $\%MnO_2$ and %norleucine recoverey in the fractions of samples NC (closed triangles) and R (open triangles). r= -.97

100% using norleucine recovery values of 39.5% and 36.1%, the calculated total amino acid-nitrogen concentration would greatly exceed the amount of total organic nitrogen measured in the sediment. Because of the lack of information concerning the individual behavior of other amino acids in the presence of MnO_2, I assumed for the purpose of discussion that amino acid yields other than norleucine were not affected.

Organic Nitrogen and Carbon Attributed to Amino Compounds

Tables 8a-e are organic carbon and nitrogen inventories for the individual size fractions of each sediment sample. When amino acids, corrected organic ammonia nitrogen (after subtraction of fixed ammonium from the total ammonia-peak nitrogen), and amino sugars are considered, approximately 25% of the total organic nitrogen and only 8% of the total organic carbon is accounted for in the bulk sample of R. In the bulk fractions of A, CR, NC, and OM, an average of 60% of the organic nitrogen and 20% of the organic carbon is present in these amino compounds.

A general increase is evident, in the amount of organic matter accounted for by amino compounds with decreasing grain size, for the less than 5 micrometer size fractions of CR and the less than 2 micrometer fractions of NC and OM. The proportions of organic carbon and nitrogen attributable to amino compounds in A are approximately constant for all of the less than 2 micrometer fractions. In the R sediment, the % organic carbon characterized

TABLE I-8a

C_{org} and N_{org} BUDGET SAMPLE R

(all units in μmol/gm)

	R bulk	R > 5	R 2-5	R1-2 dk	R1-2 lt	R.5-1	R.2-.5	R.1-.2	R < .1
ORGANIC C (total)	158	41	75	1083	66	66	225	183	275
Amino acid C	9	2	2	18	5	6	17	18	19
Amino sugar C	3	<1	<1	3	1	1	3	3	4
C from NH_3 peak	0	0	0	119*	0	0	0	0	0
% total C_{org} accounted for in amino conpounds	8%	6%	2%	13%*	8%	10%	9%	11%	8%
ORGANIC N (total)	23	8	3	47	9	13	28	44	44
Amino acid N	5	1	1	5	2	2	6	6	5
Amino sugar N	<1	<1	1	<1	<1	<1	<1	<1	1
N_{org} from NH_3 peak	0	0	0	23*	0	0	1	0	0
% total N_{org} accounted for as amino-N	25%	10%	17%	62%*	20%	16%	22%	14%	13%
N-fixed	23	14	22	0	31	33	29	24	15
N_{total} in NH_3 peak	19	10	10	12	23	21	29	21	14

In all samples it was assumed that 100% of the fixed-N is in the NH_3 peak. Therefore the estimated N_{org}-amino is a minimum value. C_{org} from the NH_3 peak is calculated as 5 times N_{org} from the NH_3 peak.

*some of the N in the NH_3 peak of 1-2 dk may be exchangeable N (not determined). If none of the NH_3 peak is organic N, then the: $\%N_{org}$ accounted for is 12%

$\%C_{org}$ accounted for is 2%

TABLE I-8b

C_{org} and N_{org} BUDGET SAMPLE NC

(μmol/gm)

	NC bulk	NC > 5	NC 2-5	NC 1-2	NC .5-1	NC .2-.5	NC <.2
ORGANIC C (total)	583	358	367	433	575	908	1283
Amino acid C	47	16	16	18	39	78	125
Amino sugar C	12	5	4	4	10	25	33
C_{org} from NH_3 peak	63	106	0	0	36	151*	114
% total C_{org} accounted for in amino compounds	21%	36%	5%	5%	15%	28%	21%
ORGANIC N (total)	50	37	21	31	39	95	118
Amino Acid N	15	5	5	6	13	25	40
Amino sugar N	2	<1	<1	<1	2	4	6
N_{org} from NH_3 peak	13	21	0	0	7	30*	23
% total N_{org} accounted for as amino-N	59%	74%	26%	21%	56%	62%	57%
N-fixed	30	2	32	37	41	40	43
N_{total} in NH_3 peak	43	23	28	28	48	69	66

*Assuming that 94% of the N_{fixed} is included in the NH_3 peak (from experimental data, Table 7). In all other samples it was assumed that 100% of the fixed-N is in the NH_3 peak. Therefore the estimated N_{org}-amino is a minimum value. C_{org} from the ammonia peak is calculated as 5 times N_{org} from the ammonia peak.

TABLE I-8c

C_{org} and N_{org} BUDGET SAMPLE A

(μmol/gm)

	A bulk	A > 5	A 2-5	A 1-2	A .5-1	A .2-.5	A < .2
ORGANIC C (total)	766	191	383	466	841	866	2558
Amino Acid C	116	28	69	68	131	133	423
Amino Sugar C	13	5	6	7	13	15	46
C_{org} from NH_3 peak	111	14	36	56	94	96	271
% total C_{org} accounted for in amino compounds	31%	25%	29%	28%	28%	28%	29%
ORGANIC N (total)	80	22	43	56	100	108	301
Amino Acid N	34	9	20	20	39	40	125
Amino Sugar N	2	1	1	1	2	2	8
N_{org} from NH_3 peak	22	3	7	11	18	19	54
% total N_{org} accounted for as amino-N	73%	54%	65%	59%	61%	58%	62%
N-fixed	8	6	8	10	12	13	20
N_{total} in NH_3 peak	30	9	15	21	31	33	74

N_{org} from NH_3 peak assumes 100% N_{fixed} is in the NH_3 peak and is therefore a minimum value. C_{org} from the NH_3 peak is calculated as 5 times N_{org} from the NH_3 peak.

TABLE I-8d

C_{org} and N_{org} BUDGET SAMPLE OM

(μmol/gm)

	OM BULK	OM > 5	OM 2-5	OM 1-2	OM .5-1	OM .2-.5	OM <.2
ORGANIC C (total)	1966	566	1541	2741	2891	4166	3566
Amino Acid C	203	46	138	275	282	455	397
Amino Sugar C	27	6	18	38	41	67	47
C_{org} from NH_3 peak	115	2	38	20	291	367	268
% total C_{org} accounted for in amino compounds	18%	10%	13%	12%	21%	21%	20%
ORGANIC N (total)	175	47	128	258	286	429	377
Amino Acid N	55	14	41	82	85	135	115
Amino Sugar N	4	1	3	6	7	11	8
N_{org} from NH_3 peak	23	<1	8	40	58	73	53
% total N_{org} accounted for as amino-N	48%	32%	41%	50%	52%	51%	47%
N-fixed	18	11	22	27	27	25	23
N_{total} in NH_3 peak	41	11	30	67	86	98	76

N_{org} from NH_3 peak assumes 100% of the N_{fixed} is in the NH_3 peak and is therefore a minimum value. C_{org} from the NH_3 peak is calculated as 5 times N_{org} from the NH_3 peak.

TABLE I-8e

C_{org} and N_{org} BUDGET SAMPLE CR

(μmol/gm)

	CR bulk	CR > 63	CR 5-63	CR 2-5	CR 1-2	CR .5-1	CR < .5
ORGANIC C (total)	508	516	233	1291	2283	2833	3583
Amino Acid C	58	42	29	174	346	433	653
Amino Sugar C	6	4	3	20	38	46	60
C_{org} from NH_3 peak	20	3	8	60	149	142	231
% total C_{org} accounted for in amino compounds	17%	9%	17%	20%	23%	22%	26%
ORGANIC N (total)	32	23	18	92	180	219	295
Amino Acid N	15	11	8	48	93	118	178
Amino Sugar N	1	1	1	3	6	8	10
N_{org} from NH_3 peak	4	1	2	12	29	28	46
% total N_{org} accounted for as amino-N	65%	54%	56%	69%	72%	71%	80%
N-fixed	1	1	1	3	4	5	5
N_{total} in NH_3 peak	5	2	2	15	33	33	51

N_{org} from NH_3 peak assumes 100% N_{fixed} is in the NH_3 peak and is therefore a minimum value. C_{org} from the NH_3 peak is calculated as 5 times N_{org} from the NH_3 peak.

by amino compounds is constant for the smaller size fractions, and the %organic nitrogen present as amino-nitrogen seems to decrease with decreasing grain size. The trends in this sediment are difficult to evaluate, however, since a large proportion of of amino compounds were rinsed away during the size fractionation procedure, as discussed in the methods section.(table 4).

The smaller contribution (about 25%) of amino-nitrogen to the total organic nitrogen of the R fractions indicates the presence of organic compounds that may be soluble in HCl, but are not readily broken down into individual amino acids upon hydrolyis. The average age of this surface sediment sample, calculated from the sedimentation rate (.2cm/1000 yrs.), is about 11,000 years (table 1). It is much older and probably more degraded than the other sediment samples studied and is therefore more likely to contain stabilized, non-hydrolyzable organic compounds. Amino-nitrogen accounts for 50% of the organic nitrogen in the bulk sediment of sample NC, even though the age of this sediment (8,000 yrs.) is very similar to that of R. However, the sedimentation rate at location NC is an order of magnitude higher (2cm/1000 yrs.), and the sample was take at 14-18 cm depth in the sediment column. It is evident that the proportion of organic nitrogen attributable to amino-nitrogen is not merely a function of sediment age, but may also be related to sedimentation rate and depth of burial. Another explanation for the low proportion of amino-nitrogen in R is that, because of its location, the sediment contains less detrital humic material than the other samples.

Humic material could contribute significantly to the amino acid content of the sediment. Humic acid isolated from marine sediments of the N.W. African continental slope, yielded about 600 nmole/g of amino acids upon hydrolysis (Muller, 1975). Desai and Ganguly (1980) reported that humic acid isolated from marine shelf environments contained about 13 weight percent of amino acids. A large portion of these amino acids may not actually be a part of the humic acid structure, but could be adsorbed onto the surface of the humic acid molecule (Abelson and Hare, 1971). The Columbia River (CR) sample, on the other hand, probably contains a large amount of recently deposited terrestrial detrital material. The CR fractions generally seem to contain a higher per cent of organic nitrogen (55%-80%) in amino acids and amino sugars than the other samples. This could be due to a large contribution of amino acids from freshly deposited humic material.

It appears that the ratio of hydrolyzable amino-nitrogen to total organic nitrogen in the sediment may be a function of the degree of degradation and stabilization of organic matter. This, in turn, is influenced by sedimentation rate, sediment source, and depth of the sample in the sediment column. An increase in stabilization of organic matter is correlated with a decrease in the proportion of organic nitrogen present as hydrolyzable amino-nitrogen. The results of several field studies (discussed in the following section) indicate that, within a single sediment core, a decrease in the proportion of organic nitrogen characterized as amino-nitrogen occurs with increasing depth in the

sediment, and that this may be related to an increase in the diagenetic alteration of organic matter (Whelan, 1977 and references therein).

Amino-Nitrogen Reported in Other Sediments

The proportion of organic nitrogen present as amino-nitrogen in the sediments studied, is within the range of values reported for other sediments. Stevenson and Tilo (1971) accounted for 28% of the total organic nitrogen as amino-nitrogen in marine surface sediments off of Mexico, decreasing to 13% at 140 cm depth. Emery et al. (1964) reported 88% of the organic nitrogen was amino nitrogen in San Diego Trough surface sediments, and 15% in Santa Barbara Basin sediments. Kemp and Mudrochova (1972) found, in a Lake Ontario sediment, that amino acid nitrogen decreased from 37% of the total organic nitrogen at the surface to 5% at 750 cm. They attributed the high surface value to the presence of algae and plankton. The lowest values were reported by Whelan (1977), who found that only .4% of the organic nitrogen was present as amino acid-nitrogen in a red clay surface sediment from the Central Atlantic. The proportion decreased with pdepth to .0008% at 48 cm. Casagrande and Given (1974) reported that, in fresh peat samples from two locations in the Florida Everglades, an average of only 40% of the organic nitrogen was identified as amino nitrogen at the surface, decreasing to 25% at 345 cm. Some of the differences in amino nitrogen values reported for various sediments could in part be due to differences in amino acid extraction techniques and how

much of the ammonia peak-nitrogen was included in the calculation. Unfortunately, this is not always clarified in the reports.

Even in relatively fresh organic material from the water column, a large proportion of the total organic nitrogen and carbon cannot be characterized as amino acids and amino sugars. In a recent sediment trap study, Wefer et al.(1982) found that they were unable to account for more than 87% of the organic nitrogen and 52% of the organic carbon in surface plankton samples by measuring amino acid, amino sugar, and carbohydrate concentrations. They also observed that the proportion of organic nitrogen and carbon characterized by these compounds decreased with depth in the water column to 40% and 65% at 965 m, and 36% and 55% at 2540 m. The uncharacterized fraction of organic matter could include nitrogen-containing compounds such as humic acids and nucleic acids as well as carbon-rich lipid and hydrocarbon compounds.

MINERALOGY AND SURFACE AREA: RELATIONSHIP TO ORGANIC MATTER

Mineral abundances (table 9) and compositions (table 10) were computed for the size fractions of samples R and NC (chapter 3). The relationship between clay mineralogy and the type and quantity of organic matter present was examined. The mineral trends with decreasing size fraction are similar in both samples. Smectite abundance generally increases with decreasing size fraction, illite is present in all fractions, and quartz and feldspar are present

TABLE I-9

COMPUTED SAMPLE MINERALOGY (IN WT.%)

SAMPLE	%ILL (f)	%SMECT (f)	%CHLOR (f)	%QTZ (x)	%FSPAR (g)	%MNO2 (l)	%FE2O3 (l)	%CACO3 (p)
NC >5	35	7	<5	19	28	7.74	.60	.50
NC 2-5	47	12	<5	15	18	1.06	.30	.17
NC 1-2	46	25	<5	10	14	1.05	.40	.17
NC.5-1	46	38	0	6	7	1.68	.70	.17
NC.2-.5	46	39	0	<5	<5	2.59	1.10	.42
NC <.2	51	43	0	0	0	2.15	1.40	.58
NC bulk* sed.	44	22	<5	11	16	3.44	.67	.35
R >5	41	0	<5	30	25	.16	.06	.42
R 2-5	47	18	<5	20	15	.07	.06	.25
R 1-2DK	64	14	0	0	3	8.93	3.40	1.50
R 1-2LT	57	28	<5	10	5	.26	.10	.33
R.5-1	58	26	<5	5	5	.12	.10	.17
R.2-.5	53	41	0	<5	<5	.84	.70	.17
R.1-.2	61	38	0	0	0	.28	.70	.17
R <.1	43	55	0	0	0	.20	1.00	.33
R bulk** sed.	52	25	<3	12	18	.62	.41	.31

Methods of analysis:
(f) = determined by factor analysis and linear programming
(x) = calculated from X-ray diffraction peak areas
(g) = determined using graphical partitioning method
(l) = determined by atomic absorption spectroscopy of leachate
(p) = determined by phosphoric acid - LECO method

*Mineral abundances for bulk sediment calculated as
$\sum_{NC1}^{NC5}$ (%min.)(wt.% of size fract./100)

**Mineral abundances for bulk sediment calculated as
$\sum_{R1}^{R5}$ (%min.)(wt.% of size fract./100)

TABLE I-10

Clay Mineral Compositions Determined by Factor Analysis for Samples NC and R (see chapter 3)

		Smectite	Illite	Feldspar
Sample NC				
	%SiO2	44.8	55.5	63.0
	%Al2O3	25.4	13.0	24.2
	%K2O	1.9	4.7	
	%Fe2O3	7.4	11.5	
	%MgO	4.7	8.0	
	%CaO	1.3	0.0	9.1
	%Na2O	1.3	0.0	4.9
	%H2O	15.0	8.0	
Sample R				
	%SiO2	55.7	44.1	65.1
	%Al2O3	15.6	23.5	20.6
	%K2O	0.0	7.3	
	%Fe2O3	8.4	10.2	
	%MgO	3.0	6.1	
	%CaO	0.9	0.0	6.4
	%Na2O	1.5	0.8	7.9
	%H2O	15.0	8.0	

only in the coarser size fractions. Chlorite is a minor component of both sediments. The abundance of total clay minerals increases with decreasing size fraction and is almost 100% in the fractions smaller than .2 micrometer.

Fe-Mn Oxyhydroxide Minerals in R and NC Sediments

The most striking feature of the mineralogy is the variation in leachable MnO_2 and Fe_2O_3 of the sediments. One hundred per cent of the total MnO_2 and 2% to 5% of the total Fe_2O_3 in the samples was removed with an oxalic acid - ammonium oxalate leach, indicating the presence of significant amounts of amorphous Mn-Fe oxyhydroxides. The R 1-2DK fraction contains 8.9% leachable $MnO_2$and 3.4% leachable Fe_2O_3— over ten times more than is present in the other R fractions. The MnO_2concentrations of the NC fractions are all greater than 1%, the highest value, 7.7%, is in the >5 micrometer fraction. Minor X-ray diffraction peaks were detected at 2.85 and 2.98 Angstroms for the sediment of R 1-2DK, suggesting the presence of some $MnCO_3$ or $CaMnCO_3$. No pure $CaCO_3$ peaks were evident. In order to determine the maximum possible concentrations of $MnCO_3$, the CaO, MnO_2, and $MnCO_3$ contents of the NC fractions and R 1-2DK were recalculated, assuming that $\%CaCO_3$ equals zero and all the measured $C\text{-}CO_3$ is in the form of $MnCO_3$ (table 11). R 1-2DK could contain as much as 1.6% $MnCO_3$. However the maximum possible concentration of $MnCO_3$ in the NC

TABLE I-11

CALCULATED $MnCO_3$, CaO, AND MnO_2 CONCENTRATIONS, ASSUMING $\%CaCO_3 = 0$

Sample	%CaO Total	$\%CO_3$ Total	%Mn Total	%Mn in $MnCO_3$	$\%MnCO_3$	$\%MnO_2$ Remaining
NC bulk	0.98	0.05	2.0	0.23	0.48	2.75
NC > 5	1.50	0.05	4.9	0.23	0.48	7.38
NC 2-5	1.10	0.02	0.7	0.09	0.19	0.92
NC 1-2	0.98	0.02	0.7	0.09	0.19	0.90
NC .5-1	0.84	0.03	1.1	0.14	0.29	1.46
NC .2-.5	0.70	0.04	1.6	0.18	0.38	2.30
NC < .2	0.60	0.05	1.4	0.25	0.58	1.75
R 1-2dk	1.10	0.17	5.6	0.80	1.60	7.66

fractions is less than 1%, below the lower limit of detection by X-ray diffractometry. Therefore, if $MnCO_3$ is present in the NC sediment, it would not be evident in the X-ray diffraction peaks. $MnCO_3$ has been reported as an authigenic phase in anoxic marine sediments (Pedersen and Price, 1982 and referencess therein) as well as in overgrowths on foraminifera tests (Boyle, 1982; Wangersky and Joensuu, 1964), but has never been reported in oxic sediments.

Specific Surface Area: Relationship to Mineralogy

The external specific surface area (m^2/g) of the sediment increases with decreasing size fraction in all samples (table 12). A plot of surface area vs. % total clay for the fractions of R and NC (figure 6) indicates that surface area increases exponentially with increasing clay content up to about a 90% clay content is reached, after which the surface area continues to increase with decreasing size fraction even though the clay content remains the same. At 90% clay, the surface area is controlled by the size of the mineral grains rather than by their concentration. The R 1-2DK fraction deviates from the trend of the other R fractions, yielding an external surface area four times greater than expected from the clay content. This reflects the presence of Mn-Fe oxyhydroxide minerals that have highly porous surfaces which contribute significantly to the total surface area of the sediment. Surface area correlates with % smectite in the same manner as for %total

TABLE I-12

SPECIFIC EXTERNAL SURFACE AREA

Sample	Size (microns)	Specific Sfc Area (m /gm)
R1	BULK	58
R2	>5	7
R3	2-5	12
R4	1-2DK	117
R5	1-2LT	38
R6	.5-1	55
R7	.2-.5	114
R8	.1-.2	178
R9	<.1	220
NC1	BULK	43
NC2	>5	32
NC3	2-5	30
NC4	1-2	46
NC5	.5-1	61
NC6	.2-.5	78
NC7	<.2	109
O1	BULK	25
O2	>5	13
O3	2-5	28
O4	1-2	52
O5	.5-1	64
O6	.2-.5	73
O7	<.2	85
C1	BULK	6
C2	>63	4
C3	5-63	3
C4	2-5	19
C5	1-2	37
C6	.5-1	44
C7	<.5	55
A1	BULK	32
A2	>5	11
A3	2-5	19
A4	1-2	42
A5	.5-1	58
A6	.2-.5	77
A7	<.2	105

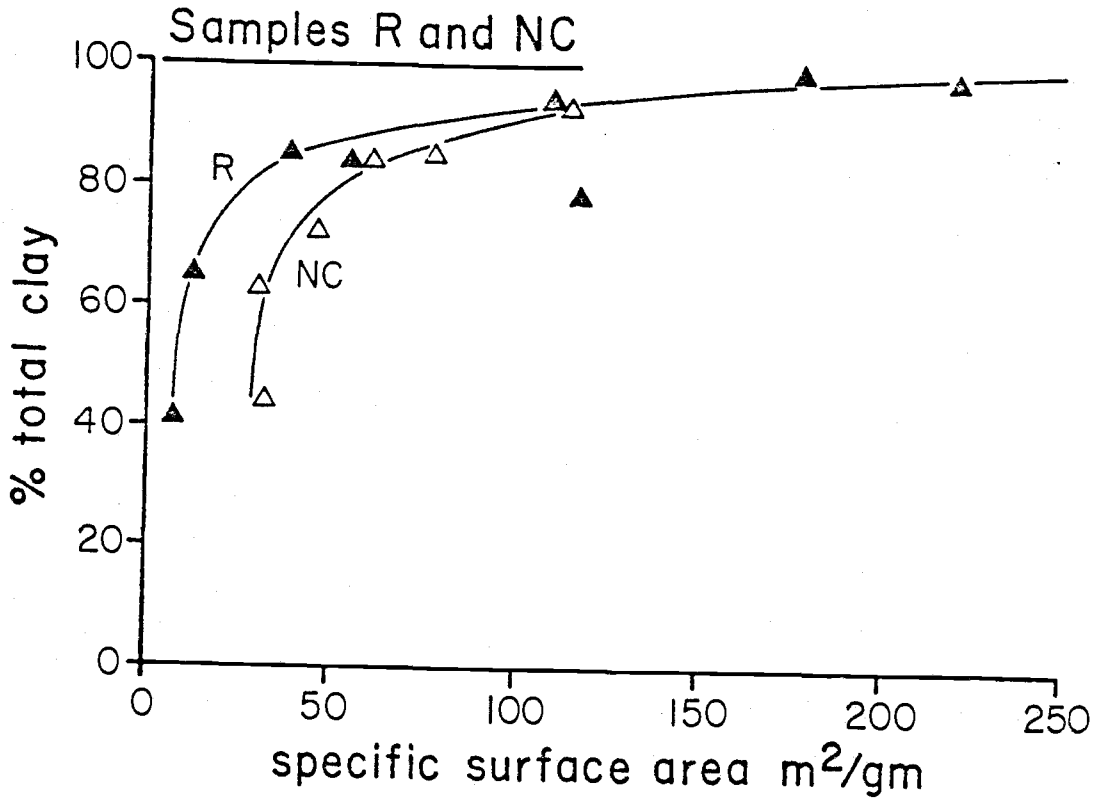


FIGURE I-6: Relationship between specific external surface area and % total clay in the size fractions of samples NC and R. Open triangles refer to NC, closed triangles to R.

clay, but there is no correlation with % illite.

Specific Surface Area: Relationship to Organic Matter Composition

Figures 7 through 9 illustrate the linear correlation between surface area and organic carbon, organic nitrogen, and amino acid concentrations in all five of the sediment samples. When these organic parameters were plotted against clay content, a trend identical to the relationship between surface area and clay content was observed, in which clay concentrations leveled off at high organic matter concentrations. It seems, therefore, that the increase in organic matter with decreasing size fraction is related to the increase in surface area of the mineral grains and not to the increase in clay mineral concentration alone.

Three distinct linear trends, with different slopes, are evident in the graph of % organic carbon vs. surface area for all the sediment fractions (figure 7a). The line with the greatest slope is defined by the Oregon Margin (OM) and Columbia River (CR) fractions. The Antarctic (A) and Northern California Margin (NC) fractions fall on a line of intermediate slope, and the R fractions constitute an independent line with the lowest slope. An expanded plot of the R fractions (figure 7b) emphasizes the linear relationship even at low organic carbon contents. An analagous plot of surface area vs %N-org is shown in figure 8a. At first glance it appears that there are also three trends in this graph, but when the scale is expanded (figure 8c), it is appears that the

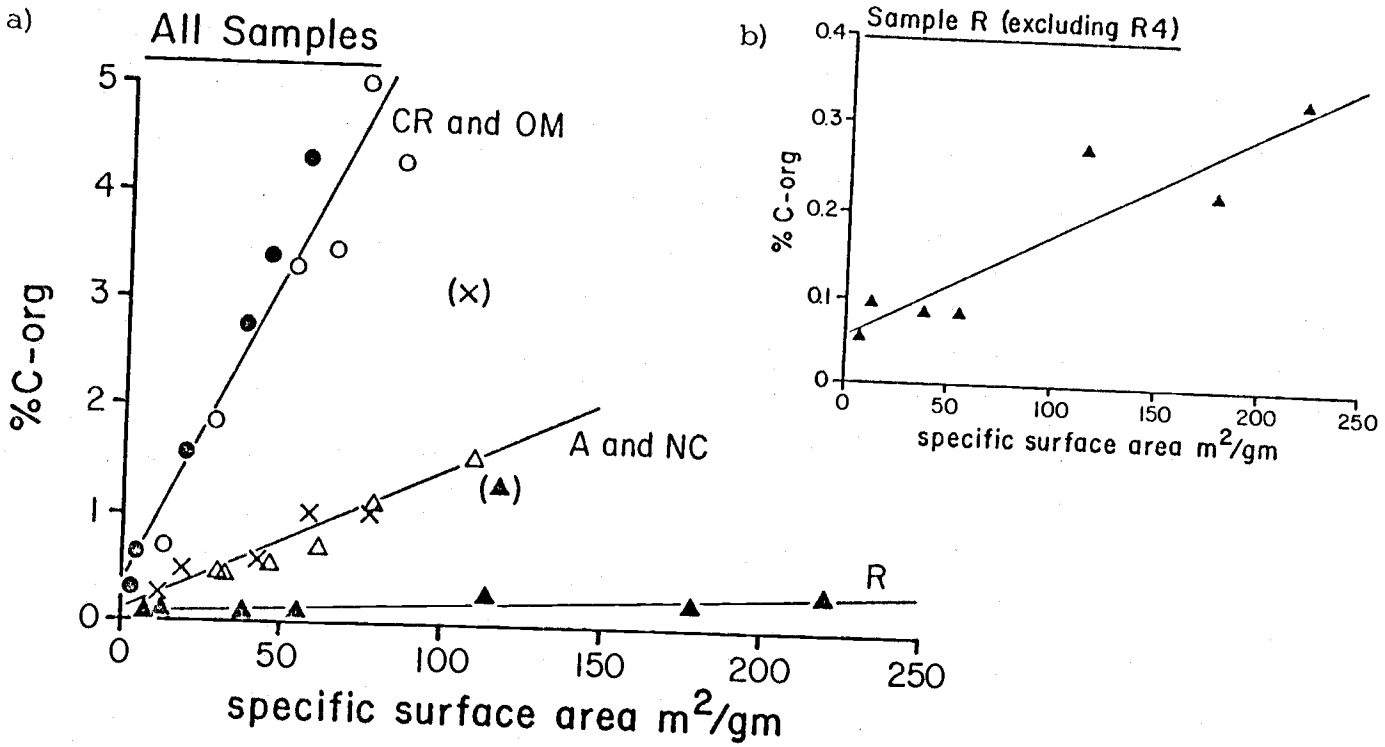


FIGURE I-7: Relationship between specific surface area and organic carbon in the fractions of samples R (▲), NC (Δ), A (X), OM (0), and CR (●). Figure b is an expansion of the relationship for R shown in figure a. Correlation coefficients are: sample R, r=.92 (excluding R 1-2DK); samples A and NC, r=.96 (excluding A <.2); samples OM and CR, r=.95

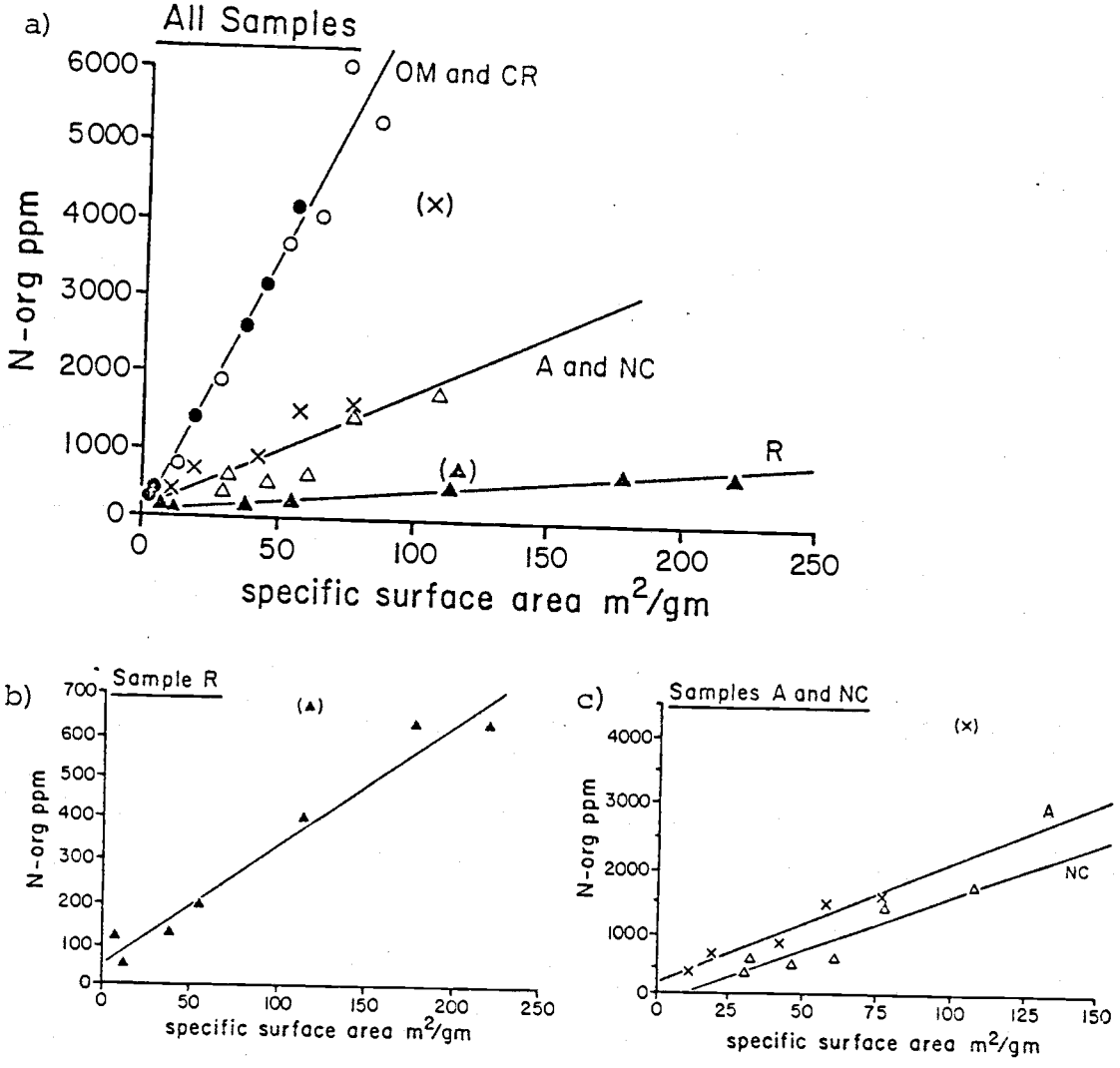


FIGURE I-8: Relationship between specific surface area and organic nitrogen in the size fractions of samples R (▲), NC (Δ), A (X), OM (0), and CR (●). Figures b and c are expansions of the individual relationships shown in b. Correlation coefficients are: sample R, r=.98; NC, r=.94; A, r=.97; OM and CR, r=.99

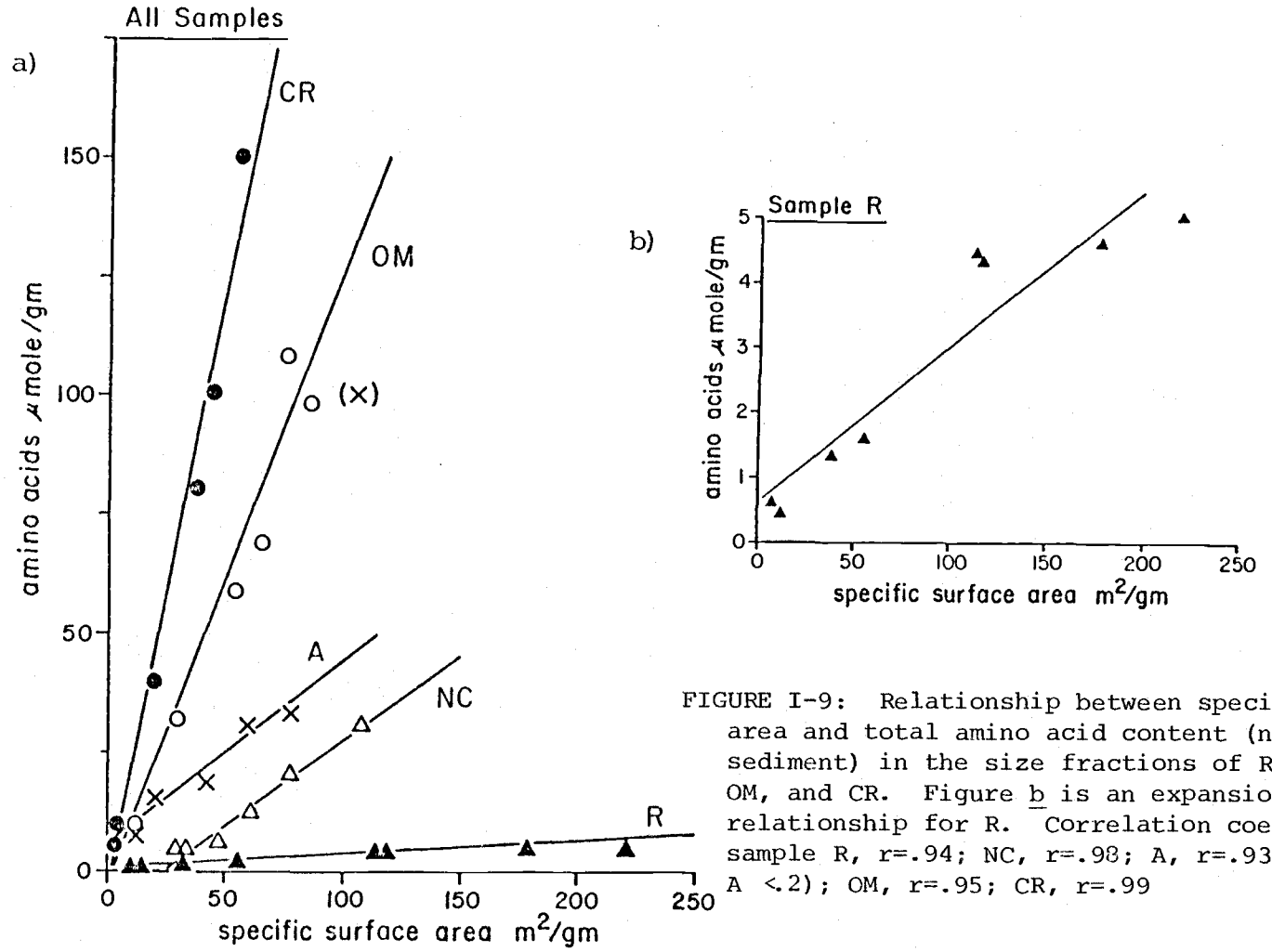


FIGURE I-9: Relationship between specific surface area and total amino acid content (nmole/g of sediment) in the size fractions of R, NC, A, OM, and CR. Figure b is an expansion of the relationship for R. Correlation coefficients are: sample R, r=.94; NC, r=.98; A, r=.93 (excluding A <.2); OM, r=.95; CR, r=.99

fractions of A and NC define two distinct lines of different intercepts.

Five linear relationships are also evident in the plot of amino acid concentration vs surface area (figure 9a and b). Apparently there are subtle differences in the nature of organic matter associated with mineral surfaces in CR and OM that are not evident from the total organic carbon and nitrogen concentrations of the sediment. Amino acid content is evidently a more sensitive indicator of organic matter variations.

The linearity of the relationships between organic matter and surface area within each sediment sample, and the near zero intercepts of the regression lines, indicate that almost all the organic matter present in the fractions may be associated with mineral surfaces and that the ability of minerals to adsorb organic matter is fairly constant within each sediment type. The differences from a zero intercept could be due to the presence of "free" particulate organic compounds not associated with clay surfaces or organic matter associated with clay internal surfaces. The differences in the slopes of the lines are probably due to differences in the sorption characteristics of the minerals and organic phases in each sediment type. The similar behavior of the Oregon Margin and Columbia River sediments is to be expected since the Columbia River is a major source of sediment to the Oregon Margin site (Karlin, 1980; Krissek, 1982).

The R 1-2DK fraction deviates from the regression lines defined by the other R fractions in figures 7 and 8 and was

excluded from the regression calculation. The organic carbon and nitrogen content of this fraction is much higher than predicted by the regression line for the measured surface area. This can be attributed to the high adsorption capacity of porous and active surfaces characteristic of the Fe-Mn oxyhydroxide minerals present in this fraction (Greenland, 1971). The high C-org/N-org ratio of this fraction suggests that the organic matter sorbed by the oxyhydroxide minerals tends to be more carbon-rich as compared to the organic matter associated with the clay mineral fractions. The less than .2 micrometer fraction of A also deviates from the regression lines defined by the other A fractions and was not included in the calculations. Either a large amount of particulate organic matter is present in this fraction that is not associated with clay external surfaces, or more likely, the surface area value was underestimated.

Quantification of Organic Matter Adsorbed on Mineral Surfaces

The amount of organic carbon or nitrogen associated with one square meter of mineral surface area can be calculated from the slopes of each line in figures 7 and 8. These values are given in table 13 as micrograms of C-org or N-org per square meter of surface area (%C-org and ppm N-org values are converted to units of µg/g of sediment, and then divided by specific surface area reported in m^2/g of sediment). The values for organic carbon range from 10 $\mu g/m^2$ in R to 600 $\mu g/m^2$ in the fractions of CR and CM. The

TABLE I-13

AMOUNT OF C-ORG AND N-ORG ASSOCIATED WITH ONE SQUARE METER OF MINERAL SURFACE (calculated from figures 7 and 8)

Sample	C-org (ugm/m^2)	N-org (ugm/m^2)
R (exluding R4)	10	2.9
NC	130	17.6
A (excluding A7)	130	18.3
CR and OM	600	69.8
R4 (1-2DK)	100	5.7
A7 (<.2)	300	40.0

organic nitrogen values range from 2.9 $\mu g/m^2$ in R to 69.8 $\mu g/m^2$ in CR and CM. These values are much lower than those reported by Suess (1973) for organic matter coatings on carbonate minerals (1.29 mg C-org/m^2 and 0.17 mg N-org/m^2).

It is possible that the observed increases in surface area are due in part to the surface area of the organic matter present. However this seems unlikely for several reasons. In most of the fractions the organic carbon and nitrogen content is less than 1%. The contribution of the organic matter surface area should be negligible compared to the surface area of the remaining 98% of the sediment, especially in the smaller size fractions which are composed almost entirely of clay minerals. If the organic matter surface area significantly influenced the surface area of the sediment, a single line would be expected in a plot of surface area vs C-org or N-org for all the sediment samples. Instead, separate linear trends are defined by the fractions in each sample (figures 7 through 9). Burford et al.(1962) reported that the presence of organic matter on clay mineral surfaces tends to decrease the surface area measured by N_2 adsorption, and that C-org contents of less than 1% in soils had little or no effect on the surface area measurement. They also pointed out that although removal of organic matter with hydrogen peroxide resulted in an increase in measured surface area, this could be due to partial destruction of clay minerals which would increase exposed clay mineral surfaces.

CONCLUSIONS:

EVIDENCE FOR CLAY-ORGANIC ASSOCIATIONS

COMPARISON OF SAMPLES

The average concentrations of organic nitrogen, organic carbon, and total amino acids in the sediment size fractions increases in the order R<NC<A=CR<OM. The average C-org/N-org ratios of the R fractions (C-org/N-org = 5) are significantly lower than those of the other sediments, indicating that R not only contains less organic material, but also contains organic matter that is more nitrogen-rich than any of the other sediments. This may reflect the presence of more humic material in the other, relatively carbon-rich, sediments (avg. C-org/N-org = 10). The reported C-org/N-org ratio of humic material, isolated from soils and marine sediments, ranges from about 12 to 17 (Desai and Ganguly, 1980; Theng, 1979).

In all five sediments, the quantity of organic matter is directly correlated to the surface area in each fraction (figures 7 through 9). Theng (1974) and Greenland (1971) state that a large part of the organic matter in soils is contained in humic and fulvic acids complexed to clay mineral surfaces. Cloos et al.(1981) observed , under laboratory conditions, that large humic acid polymers can form in situ on smectite interlayer surfaces from simple aromatic compounds in aqueous solution. Therefore it is

likely that both types of organic matter, the relatively carbon-rich compounds in NC, OM, A, and CR, and the more nitrogen-rich compounds in R are complexed in some manner to clay mineral surfaces. Since approximately 90% of the total organic carbon in the sediment samples was recovered in the individual size fractions, it appears that at most, only 10% of the organic matter in the sediments is "free" or loosely-bound and leachable in water. The remainder may be associated with clay mineral surfaces. Only in the Red Clay sediment was a significant portion of the total organic nitrogen, amino acids, and amino sugars leached with distilled water during the size separation procedure.

The individual concentrations of nineteen amino acids in each size fraction are listed in tables 2 through 6 of the appendix. The absolute concentration of each individual amino acid (nmoles/g) parallels the trend of the total amino acid concentration in all of the sediment fractions. There is a general monotonic increase in concentration with decreasing size fraction in samples NC, OM, CR, and A. In the Red Clay sediment, however, there are significant fluctuations in the concentrations of amino acids between the different size fractions, although the overall trend is also an increase in concentration with decreasing size fraction. The largest variation is in the R 1-2DK fraction which contains an anomalously high concentration of amino acids, organic carbon and organic nitrogen.

Expressing individual amino acid concentrations as mole% of the total amino acid concentration, enables a comparison to be made

of changes in the relative importance of each amino acid with decreasing size fraction. Histograms depicting the mole% abundances of individual amino acids for each sediment size fraction are shown in figures 10 a-e. The amino acid assemblages in each size fraction of sediments NC, OM, CR, and A are almost identical within each sediment sample. Also striking is the similarity in the amino acid patterns of all four sediments: glycine and aspartic acid are dominant, γ-aminobutyric acid, β-alanine, methionine, and ornithine concentrations are low, and phenylalanine and tyrosine concentrations are low or absent. In contrast, R displays a large degree of differentiation between size fractions, and the relative amino acid abundances are quite distinct from those of the other sediments: γ-aminobutyric acid and β-alanine abundances are greater than or equal to glycine, while aspartic acid, phenylalanine, tyrosine, and methionine are absent in all fractions. These differences and their significance will be discussed in detail in sections IV and V.

SORPTION MECHANISMS

The differences in relative individual amino acid concentrations between R 1-2 DK and the other size fractions of R, and between the R bulk sediment and the bulk sediments of NC, OM, CR, and A, suggest that more than one sorption mechanism may operate. The sorption of small amounts of relatively nitrogen-rich organic molecules in the less than 2 micrometer fractions of R;

FIGURE I-10 a-e: Histograms of the mole% concentrations of the individual amino acids in each size fraction of samples R, NC, A, OM, and CR. The abbreviations used are given below:

MTO	methionine sulfoxide
ASP	aspartic acid
THR	threonine
SER	serine
GLU	glutamic acid
GLY	glycine
ALA	alanine
VAL	valine
ILE	isoleucine
LEU	leucine
TYR	tyrosine
PHE	phenylalanine
BAL	β-alanine
GAB	γ-aminobutyric acid
ORN	ornithine
LYS	lysine
HIS	histidine
ARG	arginine

FIGURE I-10a

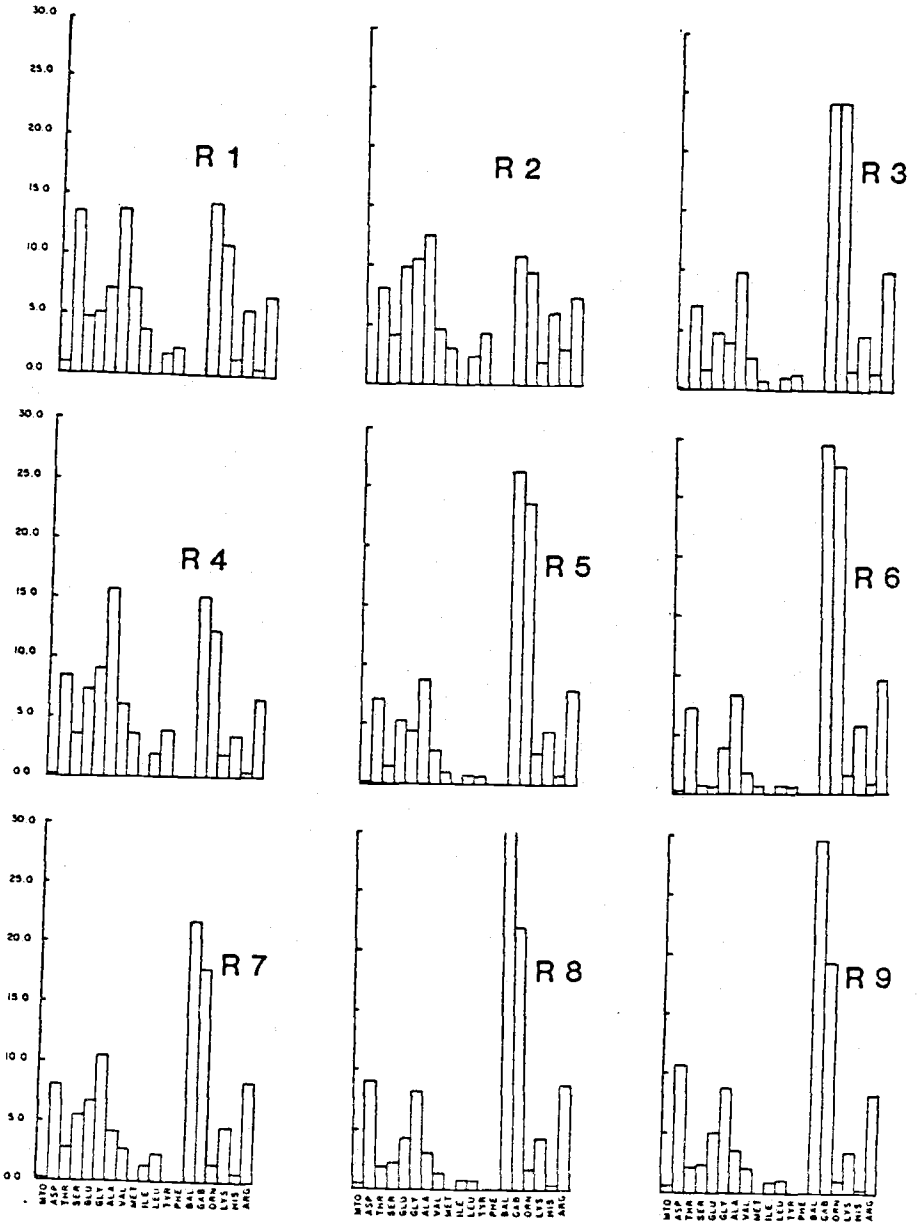


FIGURE I-10b

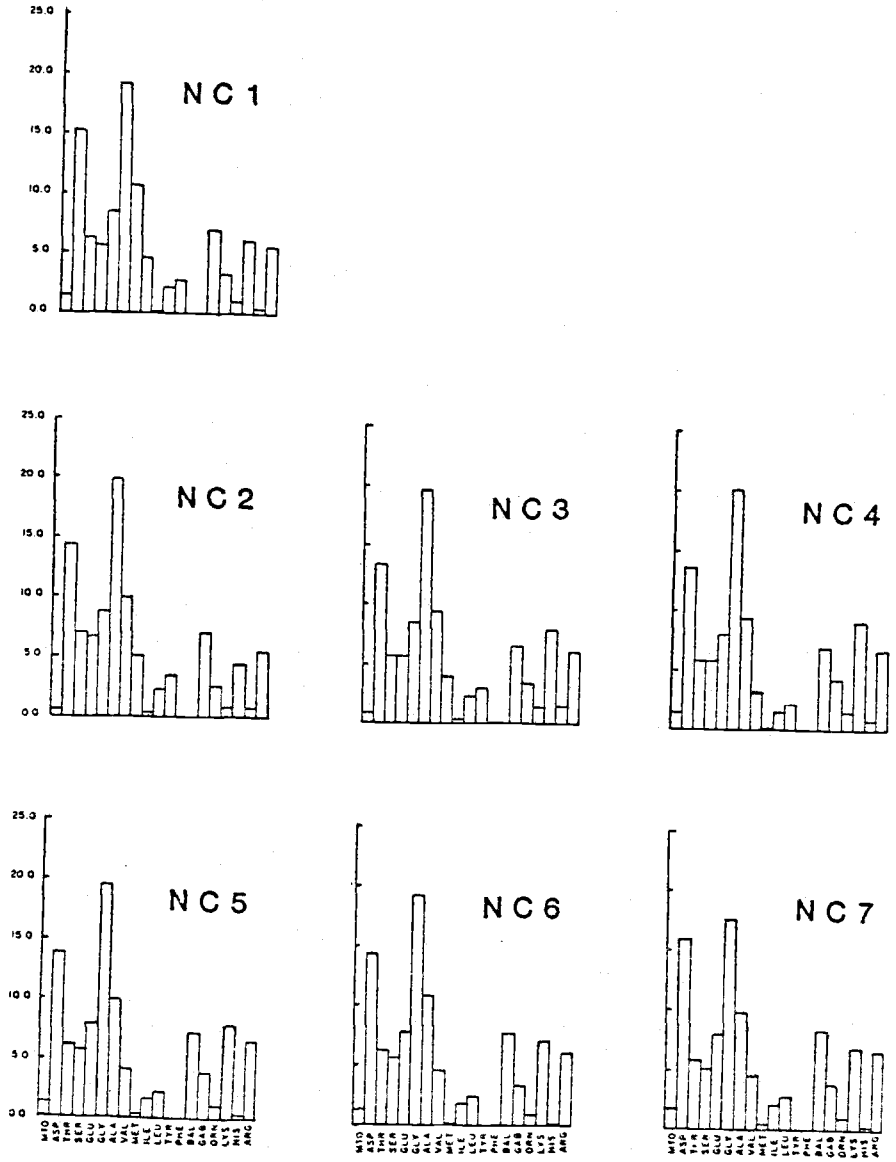


FIGURE I-10c

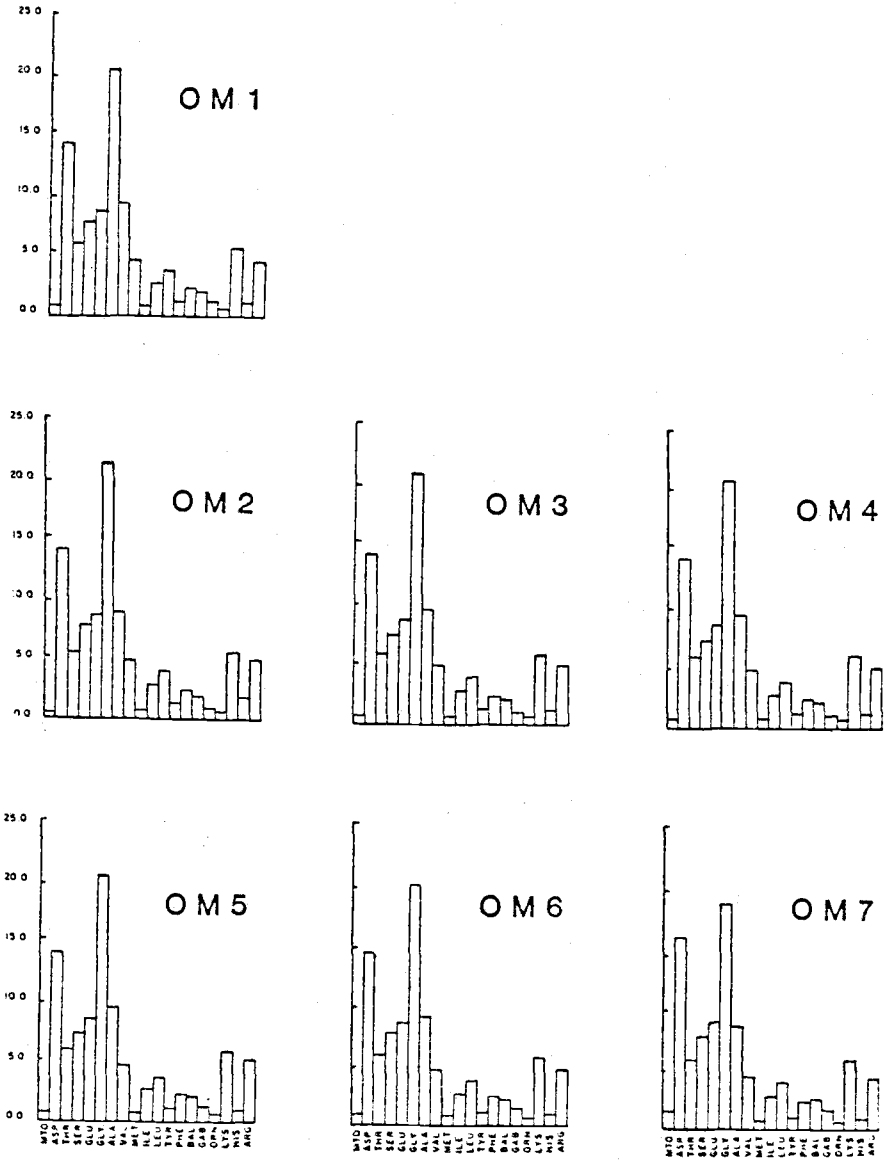


FIGURE I-10d

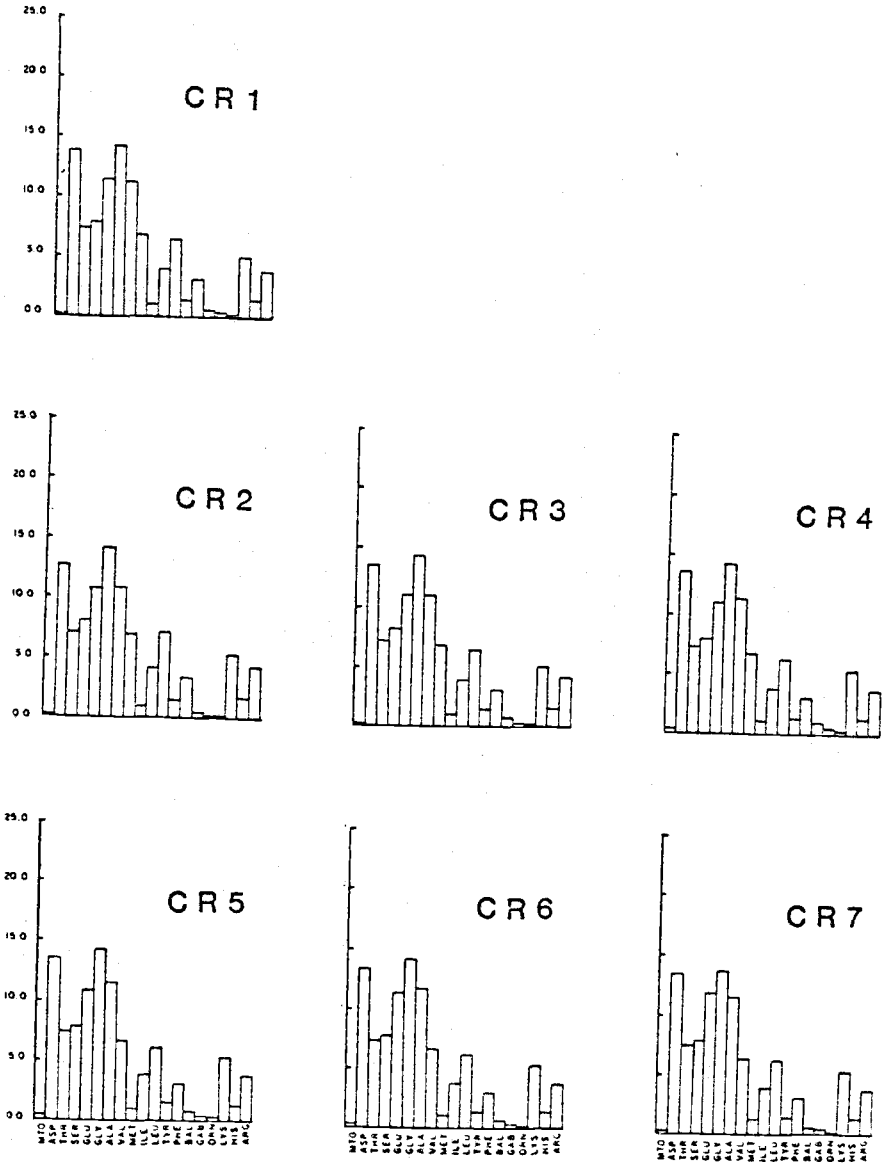
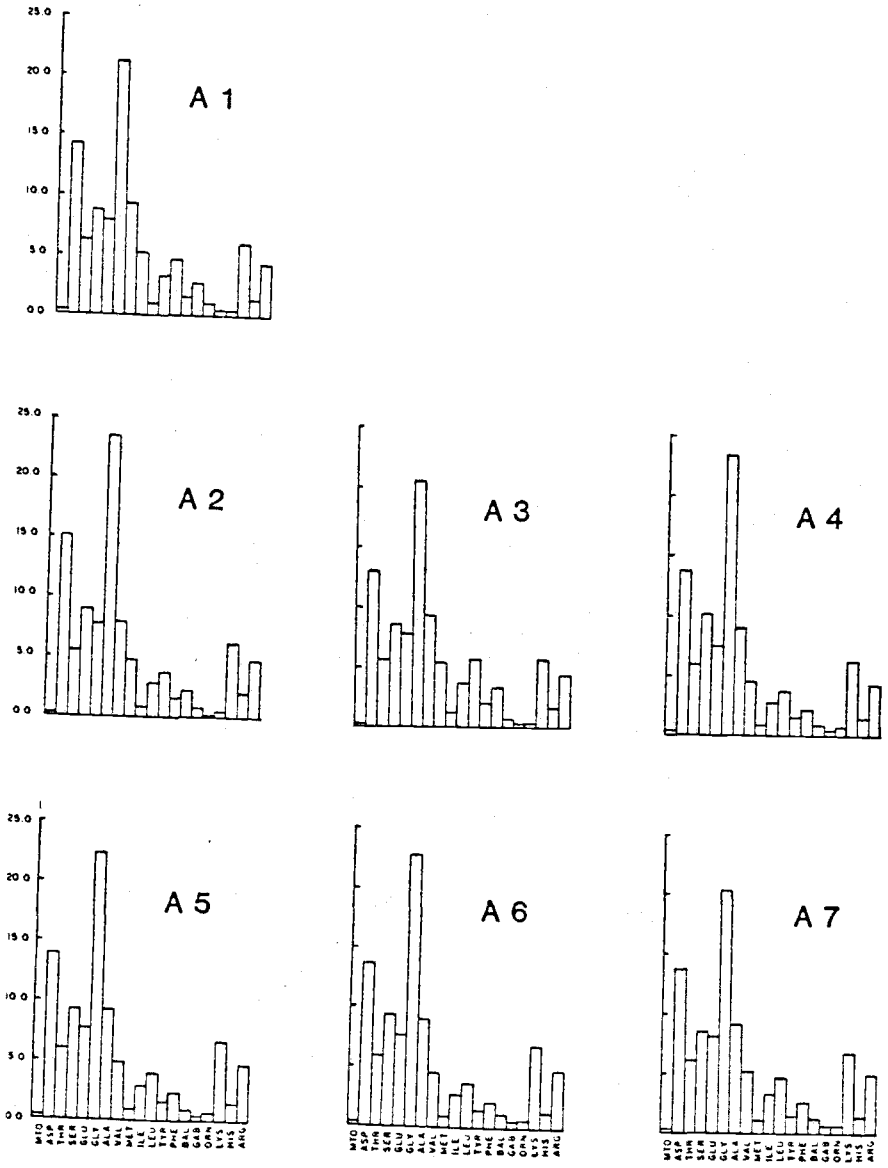


FIGURE I-10e



and the sorption of larger quantities of more carbon-rich compounds in R 1-2DK, and the fractions of NC, OM, CR, and A, may be occurring on the surfaces of clay minerals, Fe-Mn oxyhydroxides, or other organic molecules already bound to mineral surfaces.

The bulk sediments of NC, OM, CR, and A have higher organic matter contents and higher C-org/N-org ratios than the Red Clay (R) sediment. The sorption of amino acids in the more nitrogen-rich sediment fractions of R, appears to be more selective than the sorption of amino acids in the more carbon-rich sediments of the other samples. This is evidenced by the constancy of amino acid assemblages in the size fractions of NC, OM, CR, and A despite differences in mineral composition and specific surface area. On the other hand, in the R fractions, specific amino acids -- especially γ-aminobutyric acid and β-alanine -- are concentrated in the smaller size fractions.

It seems likely that the organic matter in the more carbon-rich sediments is composed largely of humic substances that are adsorbed to clay mineral surfaces. The composition of humic substances is not well defined and varies in different environments. They are considered to be polymeric condensation products of phenols, quinones, and amino acid compounds (Desai and Ganguly, 1980; Theng, 1979). In addition to amino acids present as part of the humic molecular structure, amino acids and proteins can be adsorbed onto the surfaces of humic acid molecules which are in turn, sorbed onto clay surfaces (Theng, 1979; Ableson and Hare, 1971). Therefore much of the amino acid fraction in sediments NC,

OM, CR, and A may be only indirectly associated with clay minerals. This hinders the isolation of pure amino acid-clay complexes from natural sediments. Humic and fulvic acids, thought to be complexed to clay minerals, have been isolated in soils and prepared in the laboratory (Rashid et al., 1972; Theng, 1979; Greenland, 1971). The bonding mechanism between clays and humic acids is not well understood, however it has been suggested that negatively charged humic acid molecules are bound to structural cations exposed on crystal edges, either directly, or via a water molecule "bridge" (Theng, 1974,; Greenland, 1971).

The organic matter associated with the R 1-2DK fraction is much different from the organic matter isolated in the other clay-sized (less than 2 micrometer) fractions of R. It is high in C-org relative to N-org (C-org/N-org = 19.5) and the relative individual amino acid abundances look more similar to those of the bulk sample than the smaller size fractions: the mole % of γ-aminobutyric acid and β-alanine are much lower than in the other size fractions. It seems that the mechanism influencing the distribution of organic matter may be different in the R 1-2DK fraction. This is likely due to the presence, in this fraction, of Fe-Mn oxyhydroxides which have a high affinity for adsorption of humic and fulvic acids (Greenland, 1971). The MnO_2 conentration in this fraction is 9%, compared to less than 1% in all the other fractions.

In summary, two different sorption mechanisms appear to be influencing the distribution of organic matter in the sediment size

fractions: (1)The sorption of relatively carbon-rich organic compounds by clays and Fe-Mn oxyhydroxides, in R 1-2DK and in all the size fractions of NC, OM, CR, and A. These compounds may be humic acid molecules as well as other smaller molecules (such as amino acids) adsorbed onto humic acid surfaces. (2)The sorption, by clay minerals, of relatively nitrogen-rich organic molecules, some of which have been identified as amino acids and amino sugars.

SIZE DISTRIBUTIONS OF ORGANIC MATTER AND INORGANIC MINERAL PHASES IN SAMPLE R

Figure 11 illustrates the comparative size distributions, in sample R, of organic carbon and nitrogen, total amino acids, clay minerals, fixed nitrogen, and MnO_2. This is the only sediment sample that exhibits such dramatic differences in the organic matter composition and quantity among the various size fractions. In the fractions smaller than 1-2 micrometers, the % organic carbon generally increases with decreasing size fraction, but not as rapidly as the organic nitrogen and total amino acid content. This results in a decrease in C-org/N-org with decreasing size fraction.

The 1-2DK fraction is unusual in that it contains a large proportion of C-org, N-org, amino acids, and MnO_2, even though it represents only 4% of the total sediment weight. Not only is the organic matter concentration high in this fraction, but the type of organic matter present is much higher in carbon relative to nitrogen (C-org/N-org = 19.5) than that of any other fraction,

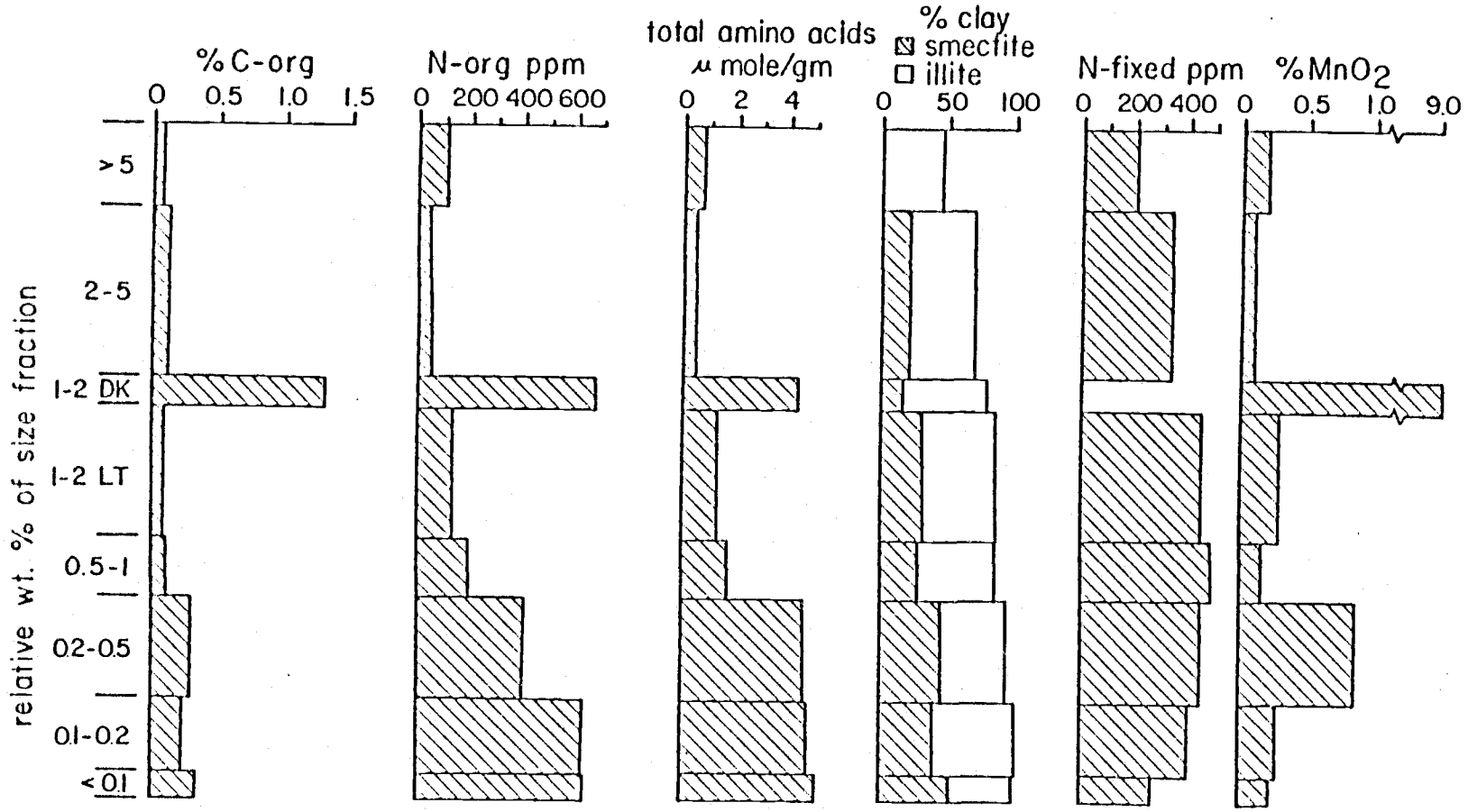


FIGURE I-11: Size distrubutions of organic carbon, organic nitrogen, amino acids, clay minerals, fixed ammonium, and MnO_2 in sample R.

except the 2-5 micrometer (table 3). This is probably due to the adsorption of humic and fulvic acids by Fe-Mn oxyhydroxide minerals. The .2-.5 micrometer fraction also has an unusually high C-org/N-org ratio (6.8) for its size (figure 1). This fraction contains an anomalously high MnO_2 concentration relative to the other fractions (.8%), though it is still ten times lower than the MnO_2 content of the dark fraction. Nevertheless, the increase in oxyhydroxide minerals may provide more adsorption sites specifically for carbon-rich organic matter. The absence of fixed nitrogen in the 1-2DK fraction is also unusual, since 78% of the sediment is composed of clay minerals, most of which is illite.

AMINO ACID-CLAY ASSOCIATIONS IN SAMPLE R

A Comparison of the Individual Amino Acid Abundances in Each Size Fraction

The inability to detect major differences in the relative abundances of individual amino acids within the size fractions of NC, OM, CR, and A may be due to the dominance of amino acids associated with humic substances or proteinaceous material in these sediments. A detailed examination of these differences in the Red Clay (R) size fractions was undertaken, since interference by particulate humic and protein material appears to be minimal in all but two size fractions of this sediment. The Red Clay sample is unique in this study, in that it provides the opportunity to study

clay-amino acid associations in a sediment of low organic matter; the organic matter concentration in the bulk sediment is only .3%. The amino acids complexed to clay minerals in the form of single amino acid molecules or short peptide chains may be a relatively significant fraction of the total organic matter in the sediment -- their concentration is not diluted by the presence of amino acids associated with larger or more carbon rich partculate organic molecules.

The differences in the type of organic matter present in each size fraction of R are evident from the differences in the abundances (in mole %) of the individual amino acids (figure 10a). At least two groups of amino acids can be identified -- based upon changes in their mole % concentrations relative to the absolute concentration of organic carbon (in weight %) in each size fraction: (1)amino acids whose relative concentrations increase parallel to increases in organic carbon content -- most of the amino acids are in this group, and (2)amino acids displaying a relative decrease in concentration where per cent organic carbon is high but which become more dominant in fractions where the concentration of organic carbon is low. In addition, some amino acids exhibit behavior intermediate between group 1 and group 2. The major group 1 amino acids are threonine, glutamic acid, valine, alanine, leucine, isoleucine, and glycine. Serine and aspartic show a similar trend but not as consistently as the others. The group 2 amino acids are γ-aminobutyric acid, β-alanine, lysine, arginine, and to a lesser extent histidine.

The behavior of group 1 and group 2 amino acids relative to % C-org in each fraction is illustrated in figures 12a and b. Figure 13 illustrates the negative correlation between a typical group 1 and group 2 amino acid. It seems likely that the group 1 amino acids, dominant when organic carbon content is high, represent amino acids associated with larger, more carbon-rich molecules such as humic acids or proteinaceous material. Group 2 amino acids may represent a residual pool of background organic matter which is most noticeable when the concentration of carbon-rich humic compounds is low. These amino acids are probably the ones most intimately associated with clay mineral external and internal surfaces -- either as single molecules or in the form of peptide chains. The possibility that group 2 amino acids represent a clay-bound amino acid fraction will be discussed in detail in the following sections.

Sources of γ-aminobutyric Acid and β-alanine

The group 2 amino acids, γ-aminobutyric acid and β-alanine, are different from the other amino acids measured in that they occur biologically in free and combined forms but are never found in proteins -- therefore they are termed non-protein amino acids. They are commonly found inside bacterial cells where they are produced during the biochemical degradation of organic molecules as part of the cells' metabolic processes (Casagrande and Given, 1980; Lehninger 1975). These and other amino acids are also components of the mureide complex, a glucosamine-amino acid polymer found in

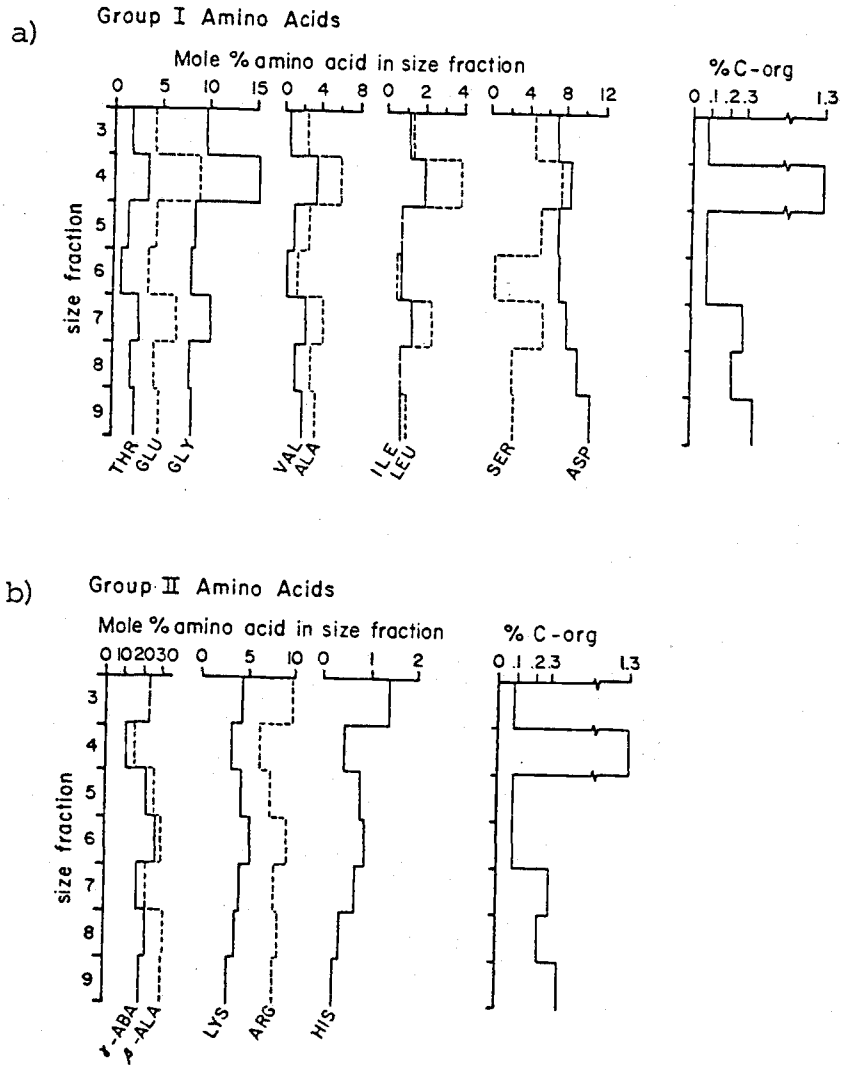


FIGURE I-12: Mole % concentrations of Group I and Group II amino acids relative to the concentration of organic carbon in each size fraction of sample R. The trends of Group I amino acids are generally parallel to the trend of organic carbon. The trends of Group II amino acids are opposite to the trend of organic carbon.

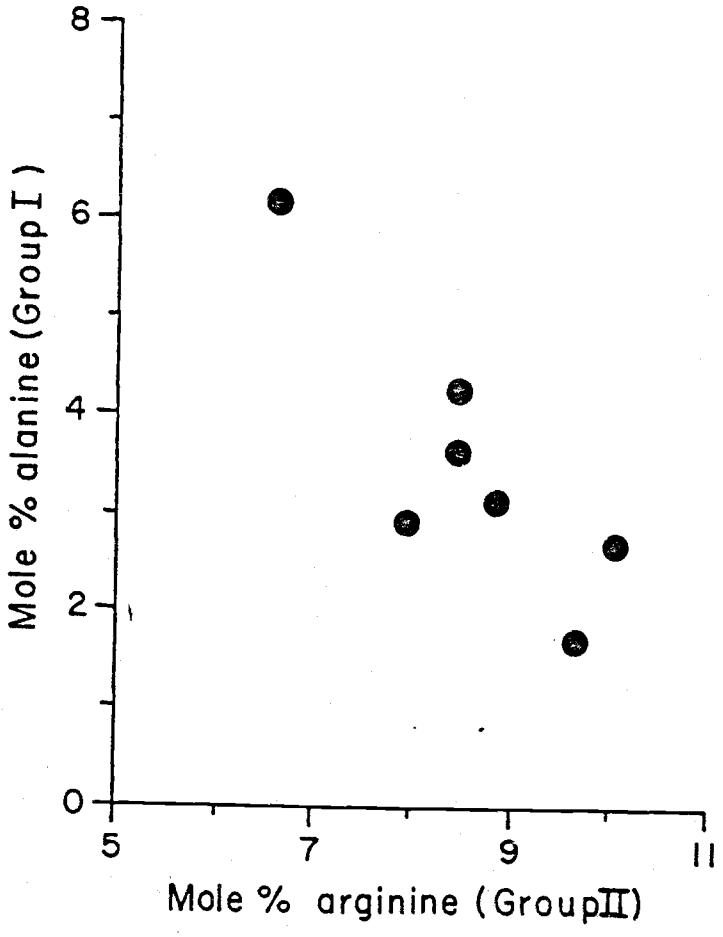


FIGURE I-13: Negative correlation between the concentrations of a typical Group I amino acid (alanine) and a Group II amino acid (arginine).
r=.84

bacterial cell walls (Martin 1966).

Significant proportions of γ-aminobutyric acid and β-alanine, relative to the total amino acid concentrations in marine sediments and suspended particulate matter, have been reported. Whelan (1977) found, in a core from the Atlantic abyssal plain, that γ-amino butyric acid and β-alanine comprised 70% of the total amino acid content of the sediments. Schroeder (1975) also observed that these non-protein amino acids were the most abundant amino acids present in carbonate sediments, 40,000 to 700,000 years old, from the Carribean Sea. He determined that they were not associated with the carbonate phase of the sediment and suggested that they might be associated with the alumino-silicate material. In a carbonate-free abyssal sediment core, at only a few centimenters depth, he found that γ-amino butyric acid and β-alanine accounted for over 90% of the total amino acids. Others have reported that even though the absolute concentrations (nmole/g) of the protein amino acids decrease with depth in the sediment, the concentrations of γ-aminobutyric acid and β-alanine increase or remain the same, and their abundance relative to the other amino acids increases with depth (Müller, 1981; Hare, 1973). This has led some investigators to conclude that γ-aminobutyric acid and β-alanine are generated with increasing diagenesis in the sediment column, from the abiotic deamination or decarboxylation of protein amino acids, and that their relative concentrations may be related to the age of the sediment (Schroeder, 1975; Bada and Man, 1980).

In a sediment trap study of the Peru margin, Lee and Cronin

(1982) observed that the absolute flux of β-alanine as well as the abundance of β-alanine relative to the other amino acids, increased with depth in the water column. They suggested that β-alanine might be somehow produced on sinking particles. The relative abundance of γ-aminobutyric acid, however, remained constant with depth. Muller and Liebezeit (1982, unpublished data) measured an increase with depth in the water column, of absolute and relative mole % concentrations of γ-aminobutyric acid and β-alanine in sediment traps deployed in the South Scotia Sea. In both sediment trap studies, the non-protein amino acids composed only a small portion (less than 1%) of the total amino acids in the samples.

It seems likely that the production of β-alanine and γ-aminobutyric acid in sediments and the water column is biochemically mediated. These two amino acids have been isolated from the intracellular material of certain marine dinoflagellates, microalgae, and bacteria (Lee and Cronin, 1982 and references therein) as well as from bacterial cell walls (Martin, 1966). Casagrande and Given (1980) observed a significant enrichment, relative to fresh plant material, of non-protein amino acids in the bacterially degraded plant material of terrestrial peat samples. They suggested that in the newly degraded peat, non-protein amino acids may indicate biochemical degradation of organic matter resulting from bacterial activity. The presence of the non-protein amino acids in some marine sediments may thus be at least partially related to the extent of bacterial degradation with relatively little input from abiotic degradation processess. Therefore,

sediment age determinations, based on amino acid degradation rates which only take into account the kinetics of abiotic proceses (Bada and Man, 1980), should be viewed as suspect until the microbial effects are studied in more detail.

Mechanisms of Group 2 Amino Acid Sorption by Clays

Regardless of the source of γ-aminobutyric acid and β-alanine, their concentration in the sediment appears to be strongly enhanced through selective sorption and stabilization by clay mineral surfaces. Three protein amino acids, lysine, arginine, and to a lesser extent histidine, follow the same pattern as γ-aminobutyric acid and β-alanine, indicating that processes other than bacterial activity are controlling their distribution and persistance in the sediment. The possibility that these five amino acids have similar chemical properties which may affect their sorption onto clay minerals is considered below.

Because of the net negative charge carried by the clay surface, organic molecules likely to react most strongly are positively charged organic cations. Uncharged polar organic molecules can be associated with clay surfaces through relatively weak ion-dipole interactions with inorganic cations or polarized water molecules, while negatively charged organic molecules tend to be repelled by the net negative charge of the clay.

Free amino acids, because of the presence of both a carboxyl group (COOH) and an amino group (NH_2), can exist in three charge

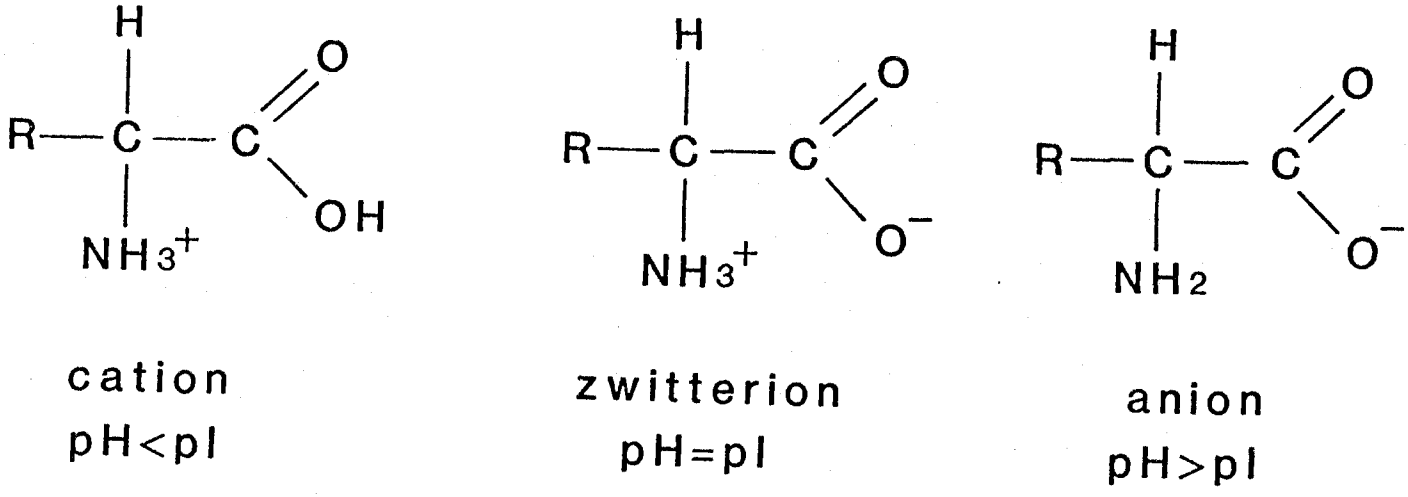


FIGURE I-14: Ionic forms of monoamino monocarboxylic acids.

forms depending on the surrounding pH: positively charged cations, neutral molecules (zwitterions), and negatively charged anions (figure 14). At pH 6-7 (the pH of the R sediment pore water is about 7.5), most of the mono-amino, mono-carboxylic acid amino acids exist in the zwitterion form. This pH, at which the molecule is uncharged, is termed the pI (isoelectric point). The pI's of the amino acids discussed are given in table 15. At a pH less than the pI, an amino acid will be positively charged. At pH greater than pI, the molecule will be negatively charged. There are two groups of exceptions to this range of pI: (1)The di-carboxylic amino acids, aspartic and glutamic, which have a pI of about 3 and will therefore be negatively charged at pH 6-7, and (2)The di-amino acids, lysine (pI=9.5), arginine (pI=10.8), and histidine (pI=7.6) which are positively charged at pH 6-7. Thus at neutral or near neutral pH's, the di-amino acids will behave like bases, that is the terminal amino group will tend to accept a proton, and the dicarboxylic acids will behave like acid compounds; the terminal carboxyl group will give up a proton.

Sieskind and Wey (1959) showed that the basicity of mono-amino acids (the ability of the amino group to accept a proton or donate an electron), in the form of either single molecules or short peptide chains, increases with increasing number of carbons between the amino and carboxyl groups, and that this affects the degree of sorption of the molecule by clay minerals. The amino group of γ-aminobutyric acid and β-alanine are on the γ- and β-carbon respectively (figure 15), while the amino groups of all the other

TABLE I-14

ABUNDANCES OF NON-PROTEIN AMINO ACIDS
(mole% of total amino acids in sample)

SAMPLE	MOLE% β-ALANINE	MOLE% γ-AMINOBUTYRIC ACID
R bulk	14.4	10.9
NC bulk	7.0	3.3
OM bulk	2.1	1.3
A bulk	1.0	0.5
CR bulk	0.6	0.3

TABLE I-15

ISOELECTRIC POINTS (pI) OF SOME AMINO ACIDS

AMINO ACID	pI
Alanine	6.11
Arginine	10.76
Aspartic	2.98
Cystine	5.02
Glutamic	3.08
Glycine	6.06
Histidine	7.64
Leucine	6.04
Lysine	9.47
Methionine	5.74
Phenylalamine	5.91
Proline	6.30
Serine	5.68
Tryptophan	5.88
Tyrosine	5.63
Valine	6.00

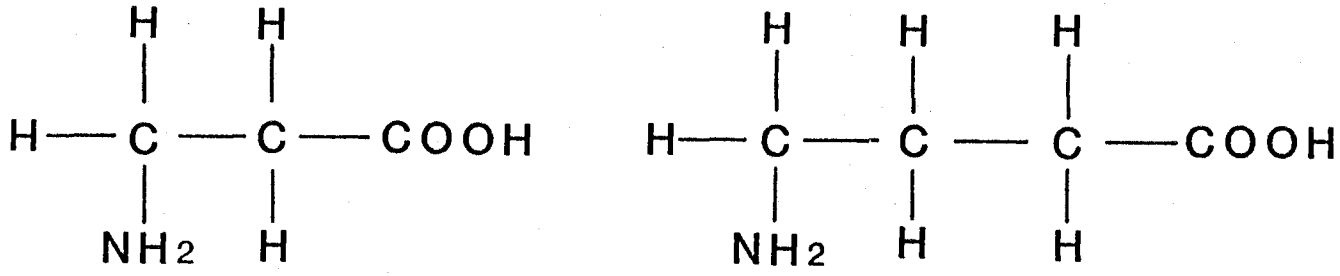


FIGURE I-15: Chemical structure of β-alanine and γ-aminobutyric acid

mono-amino acids analyzed are attached to the α-carbon. In laboratory experiments, Sieskind and Wyart (1960) and Sieskind and Wey (1959), demonstrated that the amount of amino acid taken up from solution by montmorillonite, and retained after rinsing in distilled water, increased with increasing distance between amino and carboxyl groups on the molecule in the order glycine < β-alanine < γ-aminobutyric acid. They also observed that the more basic amino acids (γ-aminobutyric acid and β-alanine) were complexed to the clay by cation exchange reactions, while glycine and alanine displaced very few exchangeable cations and may have been bound to clay surfaces through van der Waals forces or ion-dipole interactions. Friebele et al.(1980) studied the relative uptake by montmorillonite of amino acids in solution, in an attempt to determine whether the selective absorption of protein amino acids by clay surfaces could have enhanced protein synthesis necessary for the origin of life. They reacted a mixture of protein and non-protein amino acids in solution with montmorillonite and observed instead that three to four times more non-protein amino acids (γ-aminobutyric acid and β-alanine) were taken up from solution than protein amino acids.

In sediments, most of the protein amino acids probably do not exist as free, single molecules, but are incorporated into peptide chains or adsorbed onto humic subsances. These amino acids, most of which are included in the group I amino acids, appear to be adsorbed nonspecifically to mineral surfaces, their sorption perhaps influenced only by the chemistry of the two terminal

functional groups of the peptide chain. The group II amino acids, in contrast, exhibit a greater affinity for complexing with clay minerals. The protein amino acids in this group, lysine arginine, and histidine, even if complexed in a peptide chain, still have an additional free, positively charged amino group available to react with clay mineral surfaces. The non-protein amino acids in group II, γ-aminobutyric acid and β-alanine, may come into contact with the sediment largely as free molecules excreted as the metabolic by-products of microrganisms. Their basicity at the slightly basic pH of sea water would result in their preferential sorption, relative to other free α-amino acids that may be present, by clay mineral surfaces.

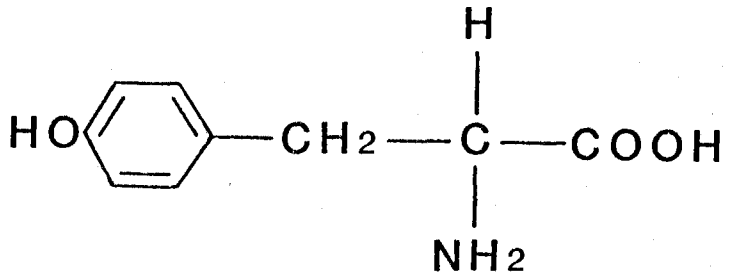
Even though the non-protein amino acids may be produced by biochemical or inorganic degradation of proteins, their presence in the sediment is not necessarily indicative of bacterial activity or sediment age. Their concentrations, especially in older sediments, may also be influenced by the availability of clay minerals and the potential for formation of stable clay-amino acid complexes.

REGIONAL VARIATIONS IN INDIVIDUAL AMINO ACID CONCENTRATIONS

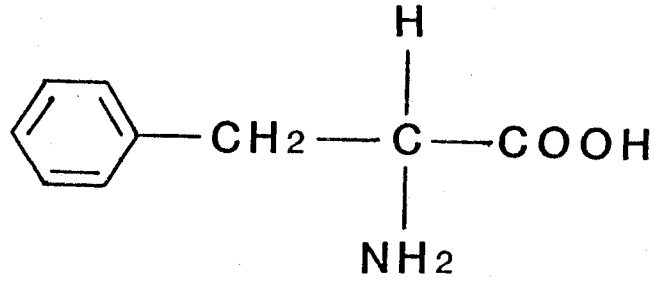
There are some differences in the amino acid assemblages of the different sediment types that may be linked to age, sedimentation rate or degree of diagenetic alteration of the

organic matter. The order of decreasing age and increasing sedimentation rate of the sediments studied is R>NC>OM>A>CR (see table I-1). The amount of variation in relative individual amino acid concentrations of each size fraction within a single sediment sample also decreases in about the same order: R>NC>OM>A=CR. It seems likely that the degree of organic matter degradation is most extensive in the Red Clay (R), the oldest sediment and the site of lowest sedimentation rate; and least extensive in the Columbia River surface sediment (CR), the youngest and most rapidly deposited sediment, containing relatively freshly deposited organic matter. Perhaps the degree of differentiation in individual amino acid contents with decreasing sediment size fraction is related to the degree of stabilization of the organic matter.

Tyrosine and phenylalanine are both absent from the two oldest sediments (which also have the slowest sedimentation rates), R and NC. The concentrations of these two amino acids relative to the other amino acids, increase in the order R=NC<OM=A<CR. They are the only amino acids analyzed that contain an aromatic functional group (figure 16). It is possible that these aromatic groups are incorporated into the structural framework of humic acid polymers which are thought to be formed by the condensation of simple aromatic compounds with carboxyl and amino acid functional groups attached. With increasing diagenesis the functional groups are lost, leaving the aromatic framework behind. Tyrosine and phenylalanine concentrations were determined in humic acids isolated from sediments of the N.W. African continental margin by



tyrosine



phenylalanine

FIGURE I-16: Chemical Structure of tyrosine and phenylalanine.

Muller (1974). They comprised a significant but not dominant proportion of the total amino acids detected: tyrosine an average of 7 mole % and phenylalanine 3 mole %. The presence of these two amino acids seems to be associated with relatively recently deposited organic matter and could be used as an indication of the presence and degree of degradation of humic compounds.

Another noticeable difference in the amino acids composition of the different sediment samples is the varying concentration of the non-protein amino acids, γ-aminobutyric acid and β-alanine relative to the protein amino acids, especially aspartic acid and glycine. The relative abundance of non-protein amino acids decreases in the order R>NC>OM>A=CR (table 14). Aspartic acid and glycine are the dominant amino acids in NC, OM, CR, and A, while γ-aminobutyric acid and β-alanine are dominant in the R sediment. There is a large increase in the mole % concentrations of the non-protein amino acids with decreasing size fraction in the R sediment. This trend is also evident, though much less dominant, in NC and OM, and not detectable in the fractions of A and CR. High relative concentrations of γ-aminobutyric acid and β-alanine in the bulk sediment and sediment fractions of R are associated with a large degree of organic matter degradation and stabilization by clays. Thus they seem to be a better indication of the degradation state of the organic matter rather than the absolute age of the sediment.

In summary, it is possible that the relative concentrations of the individual amino acids may be used roughly as qualitative

indicators of the extent of diagenetic alteration and stabilization of organic matter as follows:

a)A high degree of differentiation between the amino acid assemblages in clay sized (less than 2 micrometer) sediment fractions, may be the result of a predominance of highly stabilized clay-bound amino acids in the smaller fractions and the selective degradation of less resistant amino acids.

b)γ-aminobutyric acid and β-alanine show relative increases in concentration with increasing degradation and/or stabilization.

b)Phenylalanine and tyrosine may be indicative of the quantity and degradation state of humic acids. They may have higher mole% concentrations in relatively freshly deposited material.

c)The relative abundances of glycine and aspartic acid are highest in more recently deposited or less degraded organic matter.

SIGNIFICANCE

An understanding of the interactions between organic matter and clay minerals and amino acids is of importance to the study of:

(1)the stabilization of organic matter in soils and sediments, including the availability of organic matter complexed to clay minerals as a food source for organisms;

(2)the cycling of nitrogen and carbon in ecosystems;

(3)the transport of organic matter associated with mineral particulates by wind and water;

(4)the utilization of specific amino acid concentrations as indicators of sediment depositional environment, source, or age.

Clay minerals in sediment can affect the availability of organic matter to organisms and thus influence the rate of organic matter decomposition and the cycling of nutrients in an ecosystem. By concentrating organic molecules on mineral surfaces, clays may provide an excellent food source for microorganisms in the soil or sediment. On the other hand, some organic compounds, bound tightly to clay surfaces, may be protected from microbial and/or physical degradation. Experimental and field evidence indicates that both processes occur. Dashman (1979) and Stotzky (1972) have shown that under laboratory conditions, some clay-amino acid/peptide complexes were utilized by bacteria and fungi as their sole food source; however certain compounds, normally metabolized by these organisms in the in the absence of clay minerals, were not utilized when complexed to clay surfaces. Experiments by Arruda et al. (1982)

and Barclay et al. (1982) suggest that organic matter sorbed to suspended mineral particulates in the water column can serve as an adequate food source for some-filter feeding organisms. Dissolved organic matter may therefore re-enter the nutrient cycle via adsorption onto mineral surfaces and subsequent utilization by bacteria and filter-feeding organisms (Riley, 1970; Cauwet, 1978).

The adsorption of organic compounds from solution by mineral surfaces may affect their horizontal and vertical transport. Pierce (1974) and Theng (1974) note that clay minerals readily adsorb certain organic pesticides in solution. This process can either concentrate the pesticides in soils and sediments, or facilitate their transport to the marine environment on suspended particulates in rivers. The adsorption of organic molecules to mineral surfaces in the water column, may also be a means of rapidly transporting a utilizable food source from the ocean surface to the deep sea.

The determination of sediment age, source, or depositional environment from amino acid compositions and racemization rates, should be approached with caution -- especially when dealing with clay-rich sediments. The absolute amino acid concentrations as well as the relative proportions of individual amino acids are influenced by many factors, including clay mineralogy, pH, source of organic matter, and extent of organic matter degradation and stabilization. My data indicate that the selective sorption of certain amino acids by clay mineral surfaces -- especially the basic amino acids -- can enhance their accumulation and

preservation in the sediment. This could lead to an overestimation of the age of the sediment. Bada and Man (1980) noted an increase in the proportion of "easily extractable" amino acids in carbonate sediments relative to clay-rich sediments. They interpreted this as an indication that protein hydrolysis occurred at an accelerated rate in the carbonate sediments, and was probably catalyzed by the carbonate surfaces. However this could also be interpreted as increased stabilization of amino acids through clay-organic complexes in the clay-rich sediments. Therefore, the possibility of interaction between organic matter and clay minerals, the quantity and composition of the mineral phase, the pH of the sediment, as well as the type of organic matter present, must be considered when organic molecules are used to estimate sediment depositional history.

CHAPTER II

YET ANOTHER DISCUSSION OF ANALYSIS OF CARBON IN MARINE SEDIMENTS AND WATER COLUMN PARTICULATES

ABSTRACT

The determination of carbon concentrations in marine sediments and sea water particulates is hindered by the difficulty in analytically partitioning the total carbon between organic carbon and carbonate carbon phases. Attempts to "selectively" remove organic carbon by burning the sample at 500°C, or carbonate carbon by acidification, usually affects the carbon of the remaining phase as well.

A method is described here, enabling the direct measurement of both organic and carbonate carbon in a single sediment sample. The carbonate carbon concentration is determined from the CO_2 evolved during phosphoric acid treatment. Subsequently, a concentrated dichromate/sulfuric acid solution is added to the remaining sediment-acid mixture, and the CO_2 liberated from the oxidation of organic carbon is measured. Total carbon is calculated as the sum of organic and carbonate carbon. A LECO carbon analyzer is modified so that the amount of CO_2 evolved can be measured by the instrument's thermal conductivity detector. In addition, total carbon content is determined on another subsample using the LECO dry combustion furnace. This provides a check on the values determined by the H_3PO_4/dichromate technique.

INTRODUCTION

Carbon in marine sediments and sea water particulates is contained in two separate phases: organic matter and inorganic carbonate minerals. Numerous studies of the geochemistry of organic carbon or carbonate equilibria and distribution, in the water column and in sediments, have been plagued by the analytical problem of accurately partitioning the total carbon between these two phases (Heath et al., 1977; Boyce and Bode, 1972; Gibbs, 1977; Froelich, 1980). Partitioning can be achieved in two ways. The preferred technique is the direct measurement of carbon in each phase. But more commonly, only one carbon phase is analyzed in a sample split after the other carbon phase has been selectively removed. Then total carbon is measured on an untreated sample split and the amount of carbon in the phase previously removed is calculated by difference.

The most rapid, and consequently most popular, method of carbon analysis is based on the "selective removal" technique and invloves the measurement of CO_2 evolved during dry combustion of the sediment in oxygen at >1200°C using either a LECO induction furnace carbon analyzer or an automated CHN analyzer. The problem with this method lies not with the conversion of total carbon to CO_2, or the detection of CO_2 evolved, but with the techniques employed to partition total carbon between organic matter and carbonate minerals by the selective removal of one carbon phase. Removal of organic carbon is achieved by burning a split of the sample at

500°C for two hours (Heath et al., 1977). Alternatively, carbon associated with carbonate minerals is removed by acidification of a sample with hydrochloric or phosphoric acid (eg. Boyce and Bode, 1972). Neither of these techniques is so selective as to not affect the carbon of the remaining phase. There is evidence that thermal decomposition of some carbonate minerals commences at or even below the oxidation temperature of organic carbon (500°C), and that it is therefore not possible to differentiate accurately between carbonate and organic carbon on the basis of decomposition temperatures (Gibbs, 1977; Froelich, 1980). Carbonate removal by acidification is also unsatisfactory as it results in the solubilization and removal of a portion of the organic matter as well (Heath et al., 1977; Froelich, 1980). The dependence of the measured quantity of one carbon phase on the other, using either of these two "selective removal" techniques, can lead to multiple and compounding errors and can create misleading correlations between organic carbon and carbonate carbon in some sediment samples.

Recently, Froelich (1980) resolved the problem of organic carbon solubilization during acid treatment of the sample. He proposed a method for directly determining organic carbon by acidifying the sample to remove carbonate, and then measuring the organic carbon remaining in both the sediment residue (using a CHN analyzer) and the acid soluble fraction (using a DOC analyzer). Direct measurement of carbonate carbon, however, is not possible using this method. The weight per cent of carbonate carbon is calculated from the weight loss of the sample after acidification.

This method, although reliable for organic determinations, is not satisfactory for carbonate carbon measurements and furthermore is cumbersome and time consuming, as it requires several sample transfers and two major pieces of analytical equipment.

In a third technique, the amount of carbonate carbon and total carbon in a sample is measured directly, while the organic carbon content is calculated by difference. The amount of CO_2 released by acidification of the sample with phosphoric acid is measured either volumetrically (Kolpack and Bell, 1970) or gravimetrically by ascarite absorption (Calvert, personal communication) and equated to weight-% carbonate carbon. Total carbon is measured in an untreated subsample using a LECO Carbon Analyzer.

The only method currently in use, which enables the direct measurement of both carbon phases, involves the determination of CO_2 evolved from carbonate carbon during phosphoric acid treatment of the sample, followed by the measurement of CO_2 evolved from dichromate oxidation of organic carbon in another sample split (Schmied and Steiner, 1957; Hartmannn et al., 1976). The volume of gas produced by each reaction is measured before and after absorption of CO_2 by a KOH solution and the difference in gas volumes is converted to weight-% carbon. A relatively large amount of sample (.5-1.0 gm), especially with sediments of low carbon content, is necessary to generate a measureable amount of CO_2.

As a solution to the carbon phase partitioning problem, we propose a modification of the LECO apparatus so that CO_2 evolved from a sample during phosphoric acid treatment and subsequently by

dichromate oxidation can be measured directly using a thermal conductivity detector. This method combines the advantages of the very sensitive and accurate CO_2detection system of the LECO Carbon Analyzer, with the reliability of carbon phase partioning by acidification and subsequent dichromate oxidation. Only .05-.10 g of sample is required as both measurements are made from the same subsample.

METHODS

The apparatus used is illustrated in figure 1. The LECO carbon analyzer is modified so that it can easily be converted to run either in the combustion furnace mode (as originally designed) or the proposed H_3PO_4/dichromate mode. A 50-100 mg sample is weighed into a 50 ml round bottom boiling flask (which has been cleaned in concentrated chromic acid and rinsed with double distilled water) and attached to a condenser. A sample containing from 0.2 to 2.0 mg carbon is of the optimum size, although amounts as low as .04 mg of carbon were measured. Care must be taken to use just enough silicon grease on the condenser joint to facilitate removal of the flask without contaminating the acid with carbon from the grease.

Seven mls of 6N $H_3PO_4$are added to the flask through a teflon tube connected to a dispensing pipette and the sample is boiled in

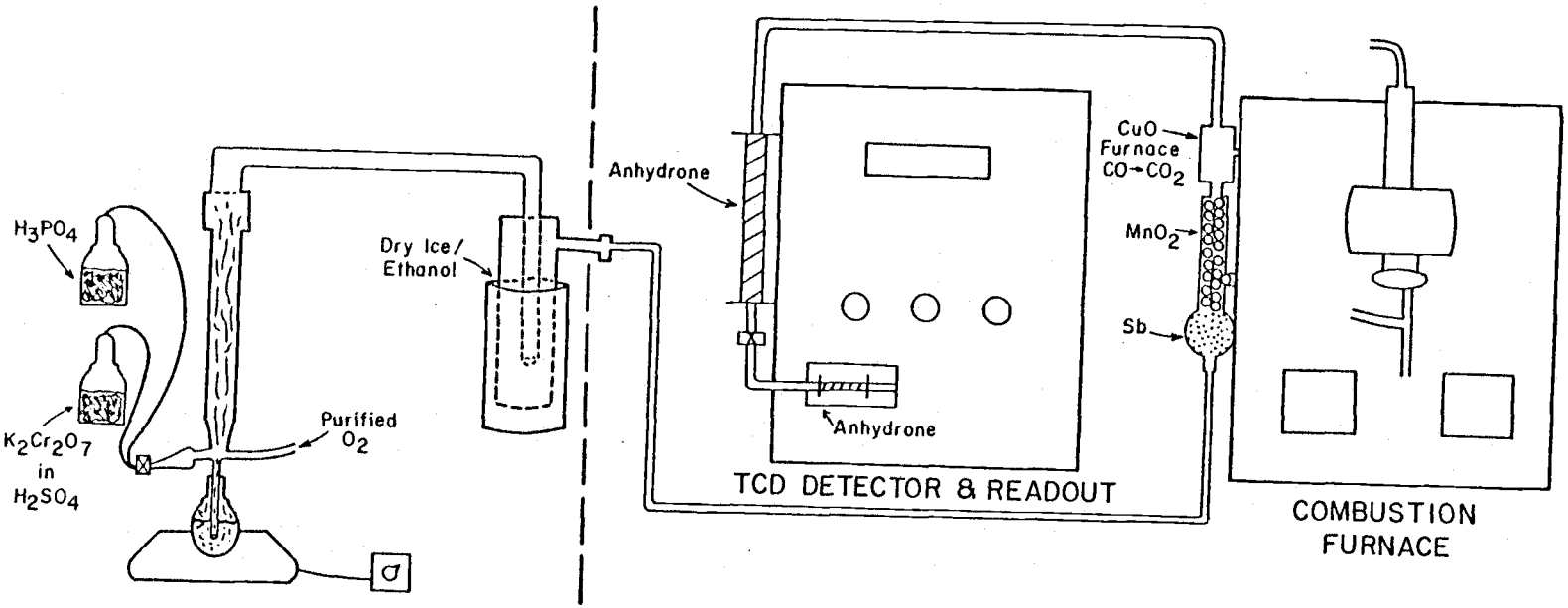


FIGURE II-1: Schematic illustration of the modified LECO apparatus used in the H_3PO_4/dichromate technique. The apparatus can be easily converted to accomodate either H_3PO_4/dichromate method or the original LECO dry combustion technique.

the acid for 5 minutes. Oxygen is continually bubbled through the solution to ensure an uninterrupted flow of gas through the system. A condenser and a series of traps prevent interference from H_2O, SO_2, and Cl_2 gasses (figure 1). The CO_2 is collected onto a molecular sieve which is part of the original LECO apparatus. After 5 minutes the gas flow is manually terminated, and the CO_2 is released by heating the molecular sieve to 320°C. The carbon dioxide, measured by a thermal conductivity detector, is assumed to originate only from the reaction of H_3PO_4 with the carbonate phases. Without removing the sample flask, an excess (20 mls--less can be used if the sample is very low in carbon) of dichromate solution (17.5 gms $K_2Cr_2O_7$ in 1 liter H_2SO_4) is added to the flask with a dispensing pipette. The sample is boiled for an additional 12 minutes and the CO_2, collected and measured as described previously, is equated to weight-% organic carbon. If the dichromate in solution becomes reduced prior to the complete oxidation of all the organic carbon in the sample (it will turn green or brown-green if exhausted), or if the per cent organic carbon measured appears to be low, additional dichromate solution can be added without removal of the flask and the procedure repeated to ensure complete oxidation. The sum of the measured carbonate carbon and organic carbon equals the total carbon in the sample and is referred to as C-sum. As a check of the completeness of organic carbon oxidation and carbonate dissolution, total carbon is also measured on an untreated subsample using the original LECO combustion furnace procedure and is here referred to as C-total.

CALIBRATION AND BLANK DETERMINATION

The LECO analyzer is initially calibrated with standard steel rings, containing known amounts of carbon, according to the original combustion furnace procedure (Laboratory Equipment Corp., 1966). At this time, since the instrument is operating in the furnace mode, the total carbon content of the samples to be analyzed may be determined by the furnace combustion method as well. The apparatus is then converted to accommodate the H_3PO_4/dichromate technique and the system is purged twice for 15 minutes with purified oxygen. The blank is estimated by running the procedure as usual with an empty flask. Both the $H_3PO_4$and dichromate blanks are consistently zero. Standards of reagent grade sucrose and $CaCO_3$are then analyzed in duplicate to check the initial calibration. If these standards are not within 2% of their theoretical values (table 1), the initial "steel ring" calibration is refined by the appropriate readjustments.

A precision of 1% was estimated for this method from replicate analyses of reagent grade $CaCO_3$, $SrCO_3$, adenine, and sucrose standards (table 1). The accuracy is 1%-2% of the carbon measured for carbon values above 1% and 0.02% carbon for carbon values less than 1%.

TABLE II-1

CARBON CALIBRATION MEASUREMENTS
(all numbers are in weight per cent carbon)

Standard	LECO furnace combustion	dichromate oxidation	H_3PO_4 digestion
Reagent grade calcite (12% C)	11.50 ± 0.20 n = 7	0.00	11.97 ± 0.11 n = 11
Reagent grade adenine (44.44% C)	44.73 ± 0.75 n = 8	44.59 ± 0.05 n = 2	0.00
Reagent grade sucrose (42.11% C)	42.24 ± 0.37 n = 4	42.41 ± 0.62 n = 13	0.00
Sucrose/SiO dilution (2.86% C)	--	2.82 ± 0.04 n = 5	0.00
Reagent grade strontianite (8.13% C)	8.10 ± 0.09	0.00	8.15 ± 0.04 n = 3
Blank	--	0.00	0.00

accuracy = 2% of the carbon measured for carbon values >1%, and ±0.02% carbon for carbon values <1%.

precision = 1%

COMPARISON OF METHODS

Sediment samples and sea water particulate matter, from a variety of environments (table 2), were analyzed using two methods of carbon phase partitioning: our proposed H_3PO_4/dichromate technique and the measurement of total carbon on the LECO combustion furnace before and after removal of organic matter by burning at 500°C. In the latter case, C-CO_3 is determined in the sediment after burning, C-total is determined on an untreated subsample, and C-org is calculated by difference.

Within a wide range of carbon values and sediment types, excellent agreement is achieved between C-total, determined by combustion, and C-sum, determined by the H_3PO_4/dichromate technique (table 3, figure 2). Both estimates agree within 2% (or 0.02% carbon if the carbon value is less than 1%). This is within the error of each technique. In only two samples, the .2-.5 um size fractions of OM and NC, C-sum was lower than C-total by more than 2%. It is possible that these small size fractions contain some refractory organic material that is not oxidized by dichromate. Thus the C-total determination by furnace combustion is necessary to check for the presence of such non-oxidizable organic carbon. Such disagreement was not evident, however, in analyses of any other sediment samples or sediment trap material. In general, it is quite clear that the measurements of total carbon by both methods are identical. Complete oxidation of organic carbon by dichromate was not a problem in this set of samples.

TABLE II-2

Description and location of samples

SAMPLE I.D.	LOCATION	DESCRIPTION
EA	25 10.3' N 16 50.7' W	Subequatorial East Atlantic core #12392-1
CP	3 59.5' N 144 49.3' W	Central Pacific core #10147-1
R	30 22.0' N 157 45.0 W	Red Clay N. of Hawaii, box core Rama 1 15BC
NC	39 26.8' N 127 42.4' W	N. Calif., box core WS103 44BC
AA	62 16.5' S 57 38.7' W	Antarctic, Bransfield Straights Meteor core #278
OM	45 56.6' N 125 14.6' W	Oregon Margin, gravity core W8009A #7
CR	46 12.5' N 123 3.0' W	Columbia River surface sediment
H	6 32.9' N 92 48.7' W	Hemipelagic sed Box Core Vulcan I 62BC
STH	6.5 N 93.0 W	Near bottom sediment trap material
STM	9 N 104 W	Near bottom sediment trap material

TABLE II-3

Comparison of carbon values determined by the H PO /dichromate method and furnace combustion. All data are reported in weight-%. C-sum and C-total values agree within the error of the two techniques; however there are large differences between C-org and C-CO3 determined by each method.

	H3PO3/dichromate			COMBUSTION			
SAMPLE	%C-ORG	%C-CO3	%C-sum	%C-TOTAL	%C-CO3	%C-ORG	%Mn in sed.
EA 20-29cm	.30	8.32	8.62	8.50	7.82	.68	-
110-120cm	1.62	7.54	9.16	9.24	7.32	1.92	-
803-813cm	.34	7.53	7.89	7.89	7.30	.59	-
CP 0-2cm	.24	8.71	8.95	8.88	7.73	1.15	-
2-4cm	.19	8.81	9.00	8.98	8.34	.64	-
4-6cm	.19	9.09	9.28	9.18	8.44	.74	-
R 0-4cm	.15	.07	.22	.26	.00	.26	.34
(.2-.5micron)	.27	.04	.31	.31	-	-	.53
NC 15-18cm	.70	.05	.75	.81	-	-	1.96
(.2-.5micron)	.92	.05	.97	1.09	-	-	1.64
AA 121-126cm	.92	.07	.99	1.02	-	-	.07
(.2-.5micron)	1.04	.04	1.08	1.09	-	-	.08
OM 0-3cm	2.36	.15	2.51	2.51	-	-	.04
(.2-.5micron)	4.75	.00	4.75	5.00	-	-	.04
CR surface	.61	.00	.61	.63	-	-	.06
H 0-2cm	.62	.06	.68	.73	.00	.73	3.46
6-8cm	.70	.20	.90	.86	.00	.86	4.44
12-14cm	.73	.85	1.59	1.62	.07	1.54	2.07
16-18cm	.70	1.36	2.07	2.13	.13	2.00	1.77
20-22cm	.58	1.39	1.98	1.97	.20	1.77	1.33
30-32cm	.46	.83	1.29	1.29	.02	1.26	1.12
STM-1	7.54	4.20	11.74	11.77	1.61	10.16	.50
STM-2	7.21	4.41	11.62	11.81	2.14	9.67	.50
STH-1	5.65	7.32	12.97	12.91	5.74	7.17	.20
STH-2	5.55	7.25	12.80	12.84	5.87	6.97	.17

* - indicates value not determined

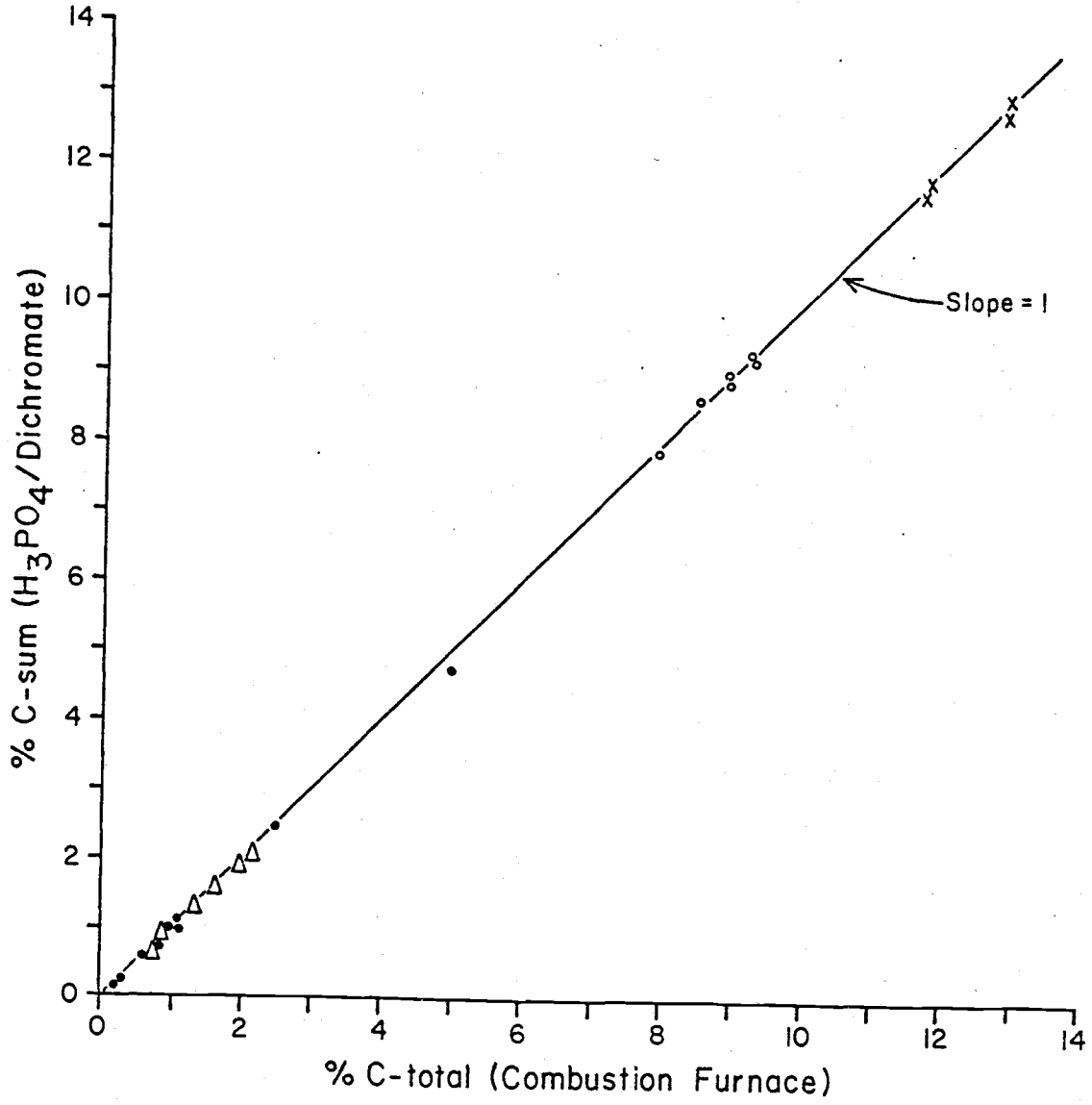


FIGURE II-2: The correlation between total carbon measurements using the H_3PO_4/dichromate technique and the LECO combustion furnace method. A variety of sediment types were analyzed: X = ST,
X = ST o = CP, EA
Δ = H ● = R, NC, A, OM, CR
(refer to table 3 for explanation of I.D. letters)

Even though the total carbon contents determined by both techniques are equivalent, there are large discrepancies between the weight-% carbon determined for the individual phases by the two methods (table 3). Per cent $C\text{-}CO_3$ in the sediment is greatly underestimated by the combustion method (figure 3), and since C-org is calculated by difference, it in turn is greatly overestimated (figure 4). The underestimation of $C\text{-}CO_3$ could be due to the thermal dissociation of some carbonate material during removal of C-org by burning at 500°C. At this temperature $(CaMg)CO_3$, $MnCO_3$, $MgCO_3$, and $FeCO_3$ which have temperatures of decomposition close to or less than 500°C (table 4), may decompose, releasing CO_2. Some $CaCO_3$ may also decompose at these temperatures, due to substitution of Fe, Mn, or Mg into the calcite lattice which lowers the decomposition temperature of the mineral.

The possibility that the H_3PO_4/dichromate technique might overestimate $C\text{-}CO_3$ was also considered. Perhaps, during the H_3PO_4 treatment of the samples, additional CO_2 might be evolved from the oxidation of labile organic matter catalyzed by metal oxides present in the sediment. This seems unlikely for several reasons. The only metal oxide present in significant amounts in the sediments studied is MnO_2. As a check on the effect of MnO_2 on the $C\text{-}CO_3$ determination by H_3PO_4, MnO_2 was added to the sucrose standard and to the metal-poor sediment, OM-bulk (table 3). Concentrations of MnO_2 from .5% to 5% were added and carbon was determined by both methods. No difference was observed in either %C-org or $\%C\text{-}CO_3$ yields when MnO_2 was present. In addition, the discrepancies

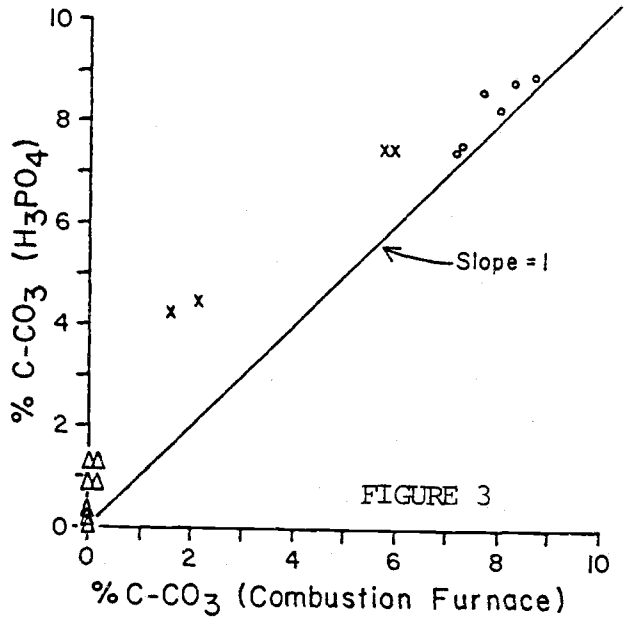


FIGURE 3

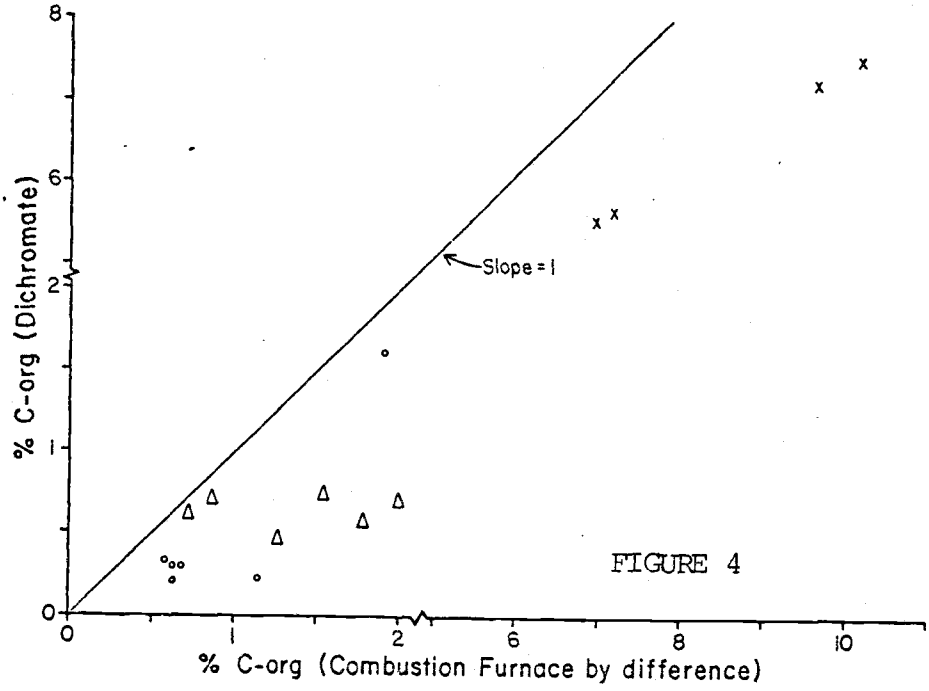


FIGURE 4

FIGURE II-3: Comparison of %Carbonate carbon measured by the H_3PO_4 /dichromate technique and the combustion furnace method where C-org is first removed by burning.

FIGURE II-4: Comparison of %Organic carbon measured by the H_3PO_4/dichromate technique and the combustion furnace method where organic carbon is calculated by difference between C-total and $C\text{-}CO_3$.

Δ = H X = ST o = CP, EA

TABLE II-4

Decomposition temperatures of various carbonate minerals

Temperatures given refer to the heat at which the mineral begins to decompose in air (from Duval 1963).

MINERAL	COMPOSITION	TEMP. (°C) OF DECOMPOSITION
Siderite	$FeCO_3$	425
Magnesite	$MgCO_3$	425
Rhodocrosite	$MnCO_3$	520
Dolomite	$CaMgCO_3$	450
Aragonite	$CaCO_3$	645
Calcite	$CaCO_3$	675
Strontianite	$SrCO_3$	865
Witherite	$BaCO_3$	1085

observed, between the values of %C-CO_3 measured by the two techniques, appear to be independent of the metal oxide content of the sediment. Large discrepancies were observed in the Vulcan I samples where Mn contents range from 1% to 4% (M. Lyle, unpublished data), as well as in the sediment trap material which contains only .2% to .5% Mn (K. Fischer, unpublished data). Finally, figure 5 illustrates that in the Vulcan I core, the %$CaCO_3$ estimated from %Ca values in the sediment (M. Lyle unpublished data) agree fairly closely with %$CaCO_3$ estimated from %C-CO_3 values determined by the H_3PO_4/dichromate technique. Therefore the metal oxides do not affect the partitioning of carbon phases in this core.

Samples of varying carbon contents were analyzed by the H_3PO_4/dichromate technique and a comparison was made between two currently used CO_2 detection systems: (1) volumetric determination, involving absorption of CO_2 gas by KOH, described in the original procedure of Schmied and Steiner (1957), and (2) measurement of CO_2 by a thermal conductivity detector present in the LECO Carbon Analyzer, and used in the procedure described here. The results from the two detection methods agree within 2% (figure 6). However, thermal conductivity detection is a much more sensitive technique and therefore has the advantage that a smaller amount of sample can be used. Incorporating the LECO apparatus into the H_3PO_4/dichromate technique also has the advantage of partially automating the procedure and provides an additional check on the carbon values obtained through a comparison of C-sum (C-CO_3 + C-org determined by H_3PO_4/dichromate) and C-total (determined by furnace

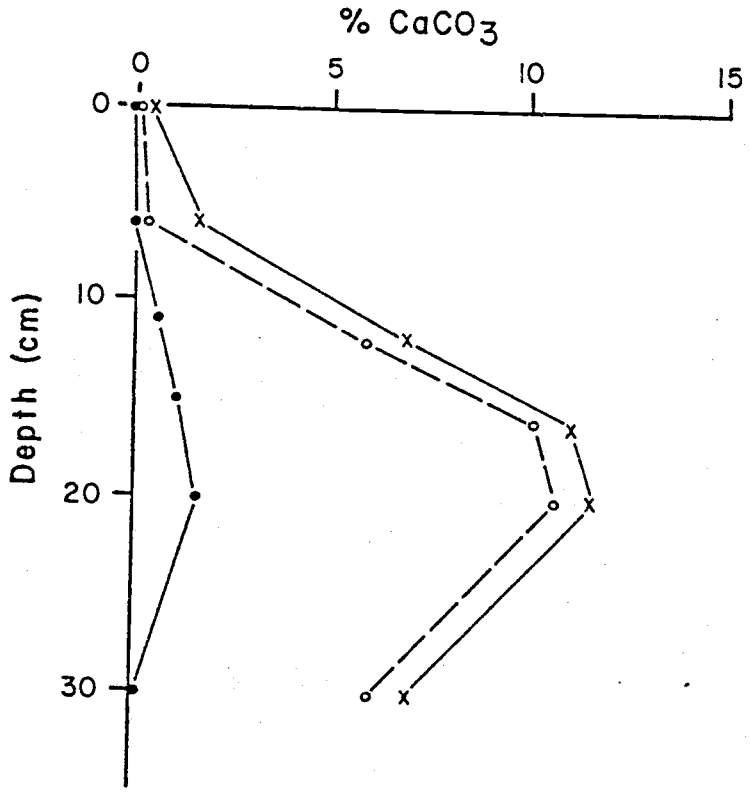


FIGURE II-5: Illustration of the differnces in depth profiles using $\%CaCO_3$ values determined by three different methods.

● = calculations from $\%C\text{-}CO_3$ measured using the LECO comustion furnace method: the subsample was first buned at 500° C to remove organic carbon.

o = calculations from Ca values (assuming a background of 1.5% Ca not in $CaCO_3$)

X = calculations from the $\%C\text{-}CO_3$ measured by the H_3PO_4/dichromate technique

Samples were taken from core VULCAN I 62 BC

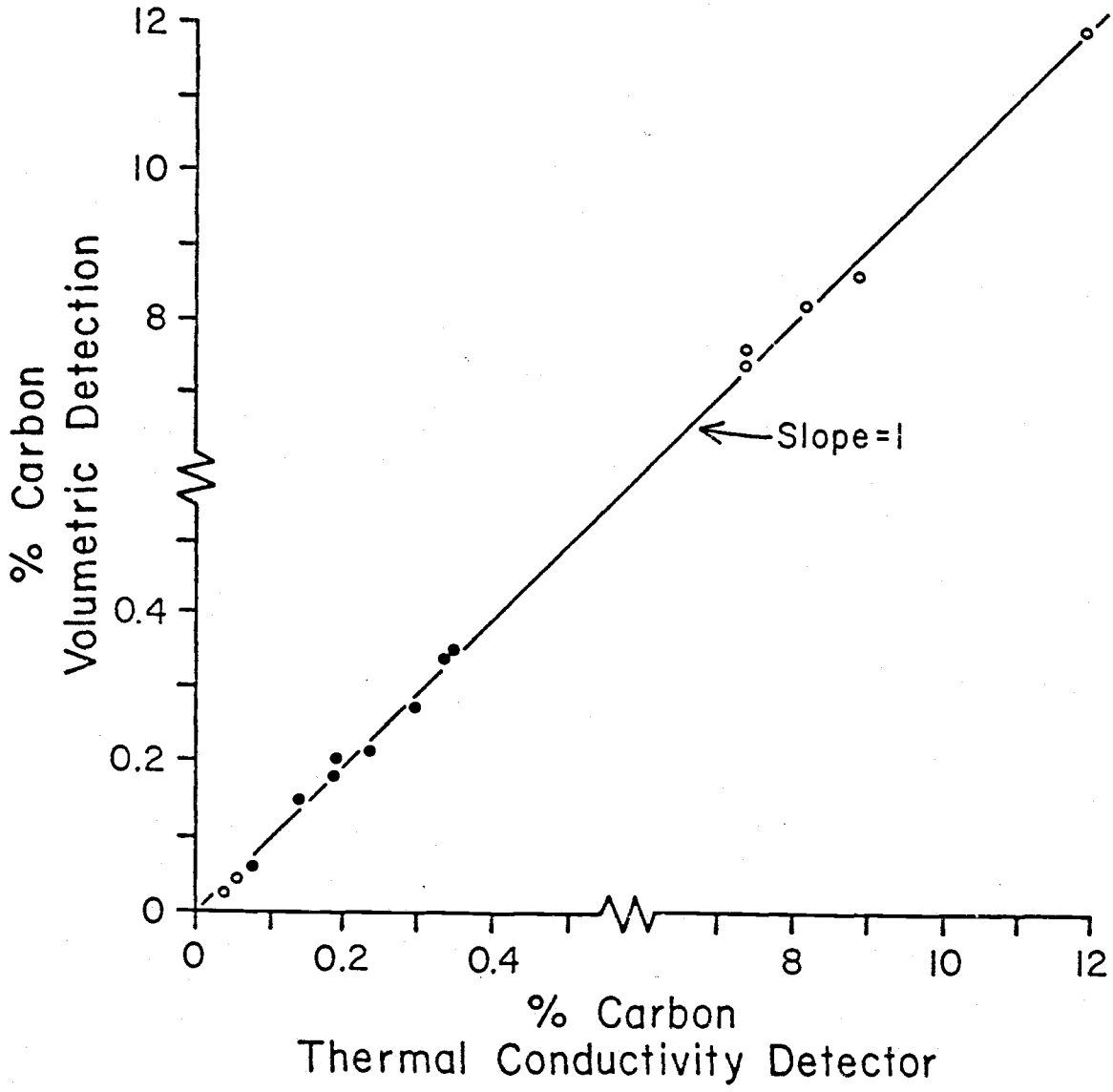


FIGURE II-6: A comparison of the %cabon values obtained using the H_3PO_4/dichromate technique with two different methods of detecting CO_2: volumetric measurement and a thermal conductivity detector.

0 = organic carbon ● = carbonate carbon

combustion of an untreated subsample).

The importance of developing a reliable method for partitioning total carbon between the inorganic and organic phases is exemplified in figure 7. The two profiles shown are of the same sediment core, Vulcan I 62 BC. The values of $C\text{-}CO_3$ and C-org in profile "a" were determined using the H_3PO_4/dichromate technique described in this paper. The values in "b" were based on C-total and $C\text{-}CO_3$ determinations using the combustion furnace method with "selective" removal of C-org by burning at 500°C. It is evident that the apparent C-org profile obtained from the combustion furnace values is merely a reflection of the $CaCO_3$ content of the sediment. Since the organic carbon values in figure 6b were calculated by difference, it appears that the high "C-org" values include carbonate carbon that was released as CO_2 during the attempt to remove organic carbon by burning. Therefore, correct carbon phase partitioning is crucial to the interpretation of C-org and $C\text{-}CO_3$ trends in sediment and water column profiles.

SUMMARY

When partitioning carbon in sediment between $C\text{-}CO_3$ and C-org, it is best to measure each phase directly rather than to attempt removing one phase and calculating the other phase by difference. "Selective removal" of organic carbon by burning at 500°C for 2

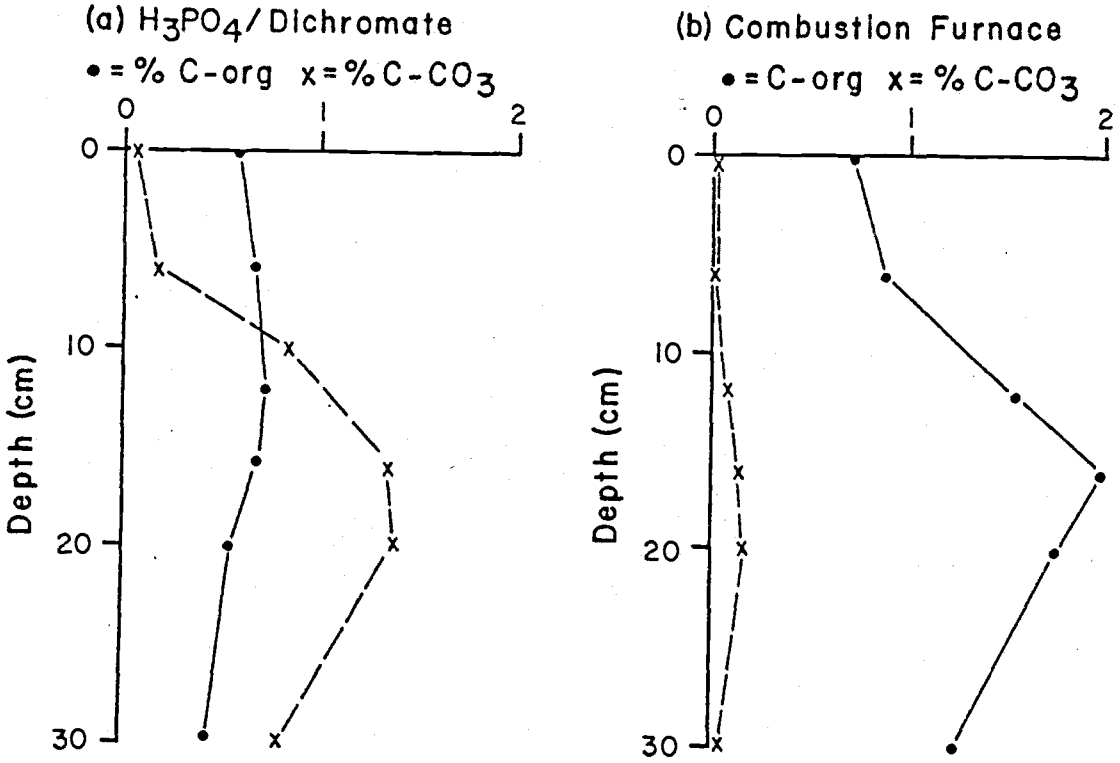


FIGURE II-7: Differences in depth profiles obtained for organic carbon and carbonate carbon using the H_3PO_4/dichromate technique and the combustion furnace method where organic carbon is first "selectively removed" by burning at 500° C. Samples were taken from core VULCAN I 62 BC.

hours underestimates carbonate carbon in the sample probably because some carbonate minerals are also inadvertently decomposed in the process. Since organic carbon is calculated as total minus carbonate carbon, organic carbon is overestimated and reflects the carbonate removed during burning. Removal of the $C\text{-}CO_3$ phase by acidification is also undesireable because some organic compounds are solubilized by this treatment and discarded with rinsing.

The technique for carbon determination, proposed in this paper, has several advantages:

1) $C\text{-}CO_3$ and C-org are determined directly on the same subsample by acidification and dichromate oxidation respectively. The amount of CO_2 released from each carbon phase is measured by the same instrument (LECO Carbon Analyzer-thermal conductivity detector). Total carbon is then calculated as the sum of the two measurements.

2) Total carbon is determined on a second subsample by furnace combustion, and the CO_2 evolved is also measured by the LECO Carbon Analyzer thermal conductivity detector. This total carbon measurement can then be compared to the calculated sum and thereby provides a good check on the completeness of organic carbon oxidation by the dichromate solution and carbonate dissolution by phosporic acid.

3) The technique can be applied to samples with a wide range of carbon contents; i.e. from <.1 to >10 weight-% carbon.

4) Only 50 to 100 mg of sample is required for analysis of average marine sediments and particualte matter.

5) The only equipment necessary is a LECO Carbon Analyzer. If this instrument is already owned, it can be easily modified to accomodate the H_3PO_4/dichromate technique.

6)Since the procedure is partially automated, the analysis can be performed more rapidly than the original Schmied and Steiner method.

CHAPTER III

A METHOD FOR COMPUTING CLAY MINERAL COMPOSITIONS AND ABUNDANCES IN MARINE SEDIMENTS FROM MAJOR ELEMENT CHEMISTRY USING FACTOR ANALYSIS AND LINEAR PROGRAMMING

ABSTRACT

A technique is presented for the determination of clay mineral phases present in a suite of samples with similar mineralogy. The compositions and abundances of clay minerals in two marine sediments were determined by separating out size different size fractions, all <5 μm in diameter, and using a combination of X-ray diffraction data and major element concentrations.

X-ray diffraction peak areas were useful in the qualitative assessment of the clay mineral phases, and quantitative determination of quartz and feldspar contents. Once the concentrations of non-clay minerals were determined, they were subtracted from the total major element oxide composition. Factor analysis of the remaining clay mineral oxides were then employed to determine the clay mineral compositions. Linear programming methods were used to estimate clay mineral abundances in the samples.

Reasonable mineral compositions and abundances were obtained for the two sets of samples. The clay mineral compositions agree well with theoretical clay mineral formulas on the basis of charge balance between tetrahedral and octahedral layer compositions. The trend of mineral abundances among the different size fractions also followed the expected patterns: quartz and feldspar were found primarily in the largest size fractions and smectite concentrations increased with decreasing grain size.

INTRODUCTION

The quantitative determination of minerals in fine grained sediments is hindered by the variability of clay mineral compositions, size, and crystallinity. Qualitative estimates of clay mineral abundances can be obtained from X-ray diffractometry. Quantitatve X-ray diffraction techniques have also been attempted, using individual peak area measurements normalized to the peak area of an internal standard such as boehmite. Absolute mineral abundances are then derived from the peak area ratios using a calibration curve generated from standard clay minerals or from pure mineral phases isolated from the sample to be analyzed (Krissek, 1982; Gibbs, 1967).

A semi-quantitative approach developed by Biscaye (1965) utilizes X-ray peak area measurements but assumes that (2 x chlorite) + (4 x illite) + (smectite) + (2 x kaolinite) = 100%. The weighting factors were estimated from the relative X-ray diffraction peak intensities of the various clay minerals in the less than 2 micron size fraction of Recent marine sediments (discussed in Johns et al., 1954). Thus the calculated mineral abundances are interdepedent and absolute amounts cannot be determined. Heath and Pisias (1979) proposed a modification of the Biscaye equation using an internal boehmite standard and linear programming methods to determine unique weighting factors for the minerals in each sample suite. The problem with any quantitative X-ray diffraction approach is that peak areas are not only related

to mineral abundance, but are also a function of mineral composition, crystalinity, and size as well as the scattering properties of the sample matrix. In addition, the peak areas of different minerals often overlap and are difficult to measure accurately and consistently.

Normative analysis of clay minerals from major element data has been attempted primarily by sedimentologists (Pearson, 1978; Meisch, 1962; Imbrie and Poldervart, 1959). This approach is difficult to carry out when both clay mineral compositions and abundances are unknown. Usually average clay mineral compositions are assumed, or if possible, a pure phase is isolated and analyzed. Unfortunately it is extremely time consuming and often virtually impossible to isolate each mineral phase. The use of average mineral compositions can potentially introduce large errors in abundance estimations: especially in marine sediments where relatively little is known about the sources and compositions of clay minerals present. Analyses of a wide range of clay minerals by Weaver and Pollard (1975) show that K_2O in smectites can range from 0% to 1.5% and in illites from 5% to 11%. Fe, Mg, Na, and Ca contents are even more variable.

I attempted to determine the composition and abundances of clay minerals in different size fractions of two marine sediment samples using a combination of X-ray diffraction and chemical data. X-ray diffraction was useful in qualitatively assessing the mineral phases present and for quantitative estimation of quartz and feldspar abundances. The percentage of Fe and Mn associated with

amorphous and poorly crystaline oxyhydroxide minerals, and the concentration of $CaCO_3$, were also measured. Once the abundance of these non-clay phases was determined, they were subtracted from the total oxide composition of the size fractions. Factor analysis of the remaining oxides was used to determine the composition of the clay minerals. Linear programing methods were then employed to estimate the clay mineral abundances within each size fraction.

METHODS

Two marine sediment samples were separated by centrifugation into the size fractions shown in table 1. Sample R is a pelagic red clay surface sample from the N.W. Pacific (RAMA 1 15BC; 30 22'N., 157 45'W.) and NC was sampled at the 14-18cm depth interval of a core from the N. California continental slope (W8103 44BC; 39 27'N., 127 42'W.). I will use the NC sample to develop the technique, making the assumption that the minerals in each of the six size fractions are of the same composition. The results obtained from analysis of the R samples will also be discussed briefly for comparison.

Random mounts for X-ray diffraction analysis were prepared from freeze-dried sediment of each size fraction. Ten per cent by weight of boehmite was added as an internal standard for each slide. Major element chemistry (table 2) was determined by atomic

TABLE III-1

SAMPLE SIZE FRACTIONS AND THEIR RELATIVE WEIGHT PER CENT OF THE TOTAL SEDIMENT RECOVERED

SAMPLE	SIZE FRACT. (MICRONS)	WT% OF TOTAL SEDIMENT
NC1	Bulk Sediment	
NC2	>5	30
NC3	2-5	23
NC4	1-2	13
NC5	.5-1	10
NC6	.2-.5	12
NC7	<.2	12
95% of the original sediment was recovered		
R1	Bulk sediment	
R2	>5	12
R3	2-5	25
R4	1-2DK	4
R5	1-2LT	20
R6	.5-1	9
R7	.2-.5	15
R8	.1-.2	11
R9	<.1	4
92% of the original sediment was recovered		

TABLE III-2

ORIGINAL OXIDE DATA IN WEIGHT PER CENT

SAMPLE	AL2O3	SIO2	NA2O	K2O	MGO	CACO3	CAO	FE2O3 LEACH.	FE2O3 CLAY	MNO2 LEACH.	TOTAL
NC1	14.4	52.2	3.5	2.3	4.3	0.42	0.7	0.7	6.0	3.1	73.3
NC2	13.4	59.0	2.6	1.8	3.1	0.50	1.2	0.6	4.1	7.7	80.6
NC3	14.2	59.2	2.1	2.3	4.0	0.17	1.0	0.3	6.0	1.1	76.2
NC4	16.2	55.6	1.5	2.5	4.6	0.17	0.9	0.4	7.0	1.0	73.7
NC5	17.2	52.0	1.1	3.0	5.1	0.17	0.7	0.7	7.4	1.7	71.9
NC6	17.4	43.3	0.9	2.9	6.0	0.42	0.5	1.1	8.9	2.6	70.8
NC7	16.6	46.2	0.5	2.8	5.8	0.58	0.2	1.4	9.0	2.1	68.6
R1	17.2	53.9	2.8	3.6	3.5	0.58	0.5	0.4	6.4	0.5	72.2
R2	13.8	65.9	2.0	2.8	2.6	1.70	0.9	0.06	4.2	0.7	80.3
R3	15.9	64.0	2.0	3.3	3.3	0.25	1.1	0.06	6.1	0.1	81.5
R4	17.0	40.2	0.9	3.2	4.3	1.50	0.3	3.4	7.6	8.9	70.3
R5	19.6	55.2	1.6	4.1	3.8	0.33	0.5	0.1	7.4	0.3	73.3
R6	20.0	52.2	1.3	4.1	3.8	0.17	0.5	0.1	7.3	0.1	69.5
R7	20.2	42.7	1.1	4.1	4.3	0.17	0.5	0.7	8.7	0.8	67.0
R8	18.7	47.3	0.9	3.6	4.6	0.17	0.3	0.7	9.6	0.3	67.5
R9	17.4	51.3	0.8	3.0	5.0	0.33	0.5	1.0	9.4	0.2	71.5

absorption spectroscopy. The procedure is divided into two parts: (1)determination of non-clay minerals and (2)partitioning of the clay mineral phases.

Determination of non-clay minerals

Qualitative determination of the crystaline mineral phases from X-ray diffractograms revealed the presence of plagioclase feldspar, quartz, chlorite, illite, and smectite.

The quartz concentration was determined (table 8, column 5) using the method of Gibbs (1967). Ratios of the quartz 4.26Å peak area to the boehmite 6.11Å peak area were compared to a calibration curve generated from known quartz/boehmite ratios. Gibbs illustrated that there is only a slight increase in peak intensity for quartz with decreasing particle size - and that this effect is almost negligible for samples with less than 10% quartz.

Per cent $CaCO_3$ was determined by the LECO-H_3PO_4 method described in chapter 2.

Plagioclase feldspar composition and abundances were determined from X-ray peak area measurements and major element chemistry. First, the assumption was made that all of the Na and Ca remaining after subtraction of Ca in $CaCO_3$, were contained in smectite and feldspars. Per cent CaO and $\%Na_2O$ were plotted against feldspar/boehmite and smectite/boehmite peak area ratios (figures 1a and 1b) in order to characterize the mineral compositions. The x-intercepts of graph 1a give the CaO/Na_2O ratio

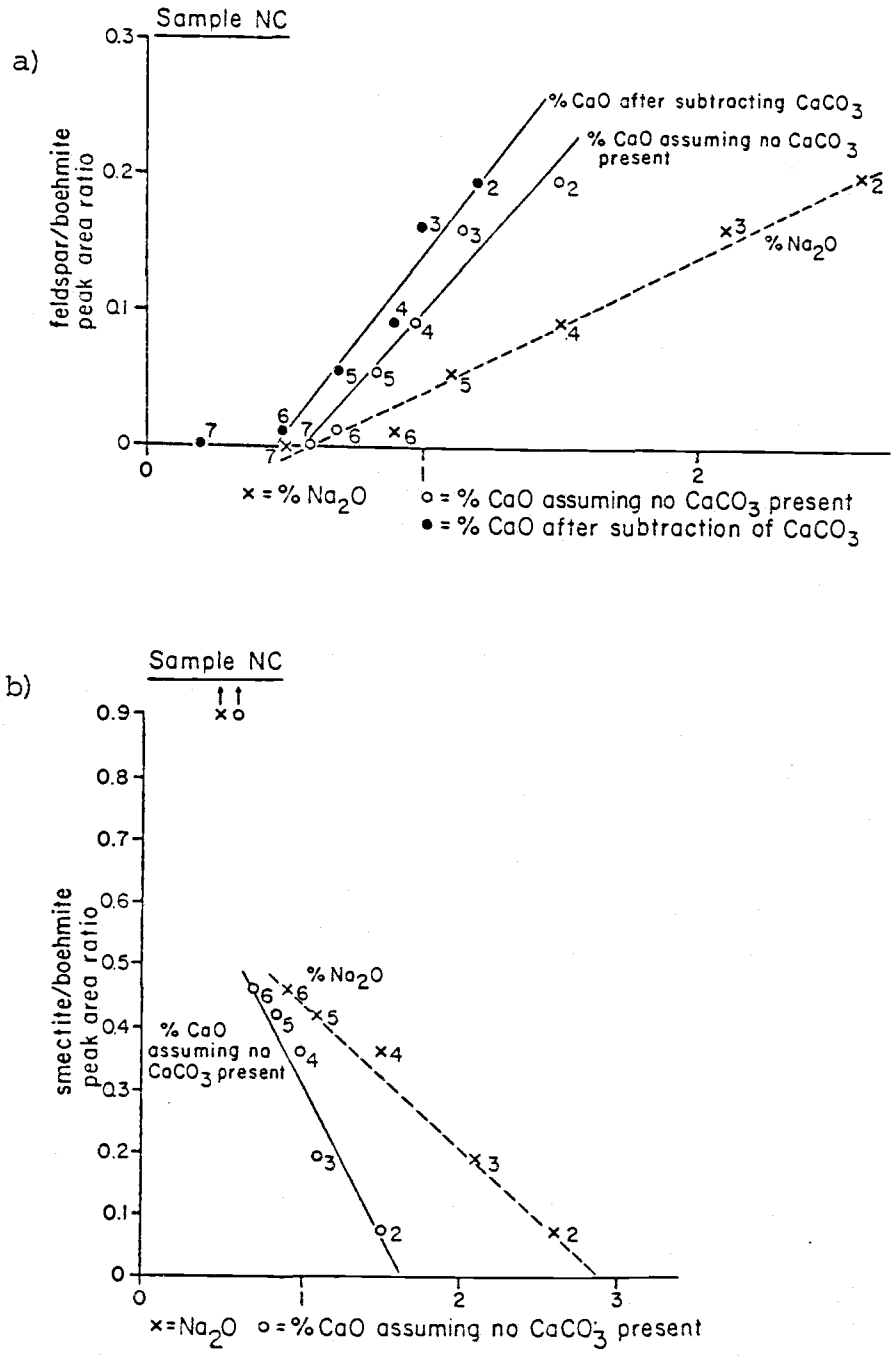


FIGURE III-1: Plots of smectite and feldspar peak areas vs %Na_2O and CaO for sample NC. The x-intercepts are used in determining feldspar composition and abundance (explained in the text).

of the smectite. The x-intercepts of 1b give the CaO/Na_2O ratio of the feldspar. When %CaO, assuming no $CaCO_3$ present, was plotted in figure 1a, the linear fit was much better than when %CaO in the $CaCO_3$ was subtracted from %total CaO: only when the CaO in $CaCO_3$ is assumed to be insignificant does fraction NC-7 fall on the line defined by the other fractions (open circles).

Since these sediments are very high in manganese (1% to 7% MnO_2) it seems plausable that a significant fraction of the $C\text{-}CO_3$ could be associated with Mn rather than Ca, in the form of $MnCO_3$ or $CaMnCO_3$ (Pedersen and Price, 1982 and references therein). In order to determine the maximum possible concentrations of $MnCO_3$ in the sediment fractions, the CaO, MnO_2, and $MnCO_3$ contents were recalculated assumung that all the measured $C\text{-}CO_3$ is in the form of $MnCO_3$ and $\%CaCO_3$ equals zero (table 3). The highest concentration of $MnCO_3$ possible in the fractions is less than 1%, the lower limit of detection by X-ray diffractometry. $MnCO_3$ could be present in the sediment even though no X-ray diffraction peaks were evident for this mineral phase. Therefore in this initial approximation of feldspar and smectite compositions, it was assumed that no $CaCO_3$ was present.

Deviations from the lines in figures 1a and b could be due to the presence of other Ca and Na bearing phases or to inaccurate peak area estimations. Smectite is especially sensitive to errors in peak area determinations, as the baseline in this region is difficult to estimate. The smallest size fraction, NC-7 (<.2u), deviates most from the line and was excluded from these

TABLE III-3

In the NC fractions there is evidence that the C-CO3 may be associated with Mn and not Ca. The MnCO3 and oxide data are recalculated assuming %CaCO3 = 0.

SAMPLE	%CaO total	%CO3 total	%Mn total	%Mn in MnCO3	%MnCO3 total	%MnO2 remaining
NC bulk	0.98	.05	2.0	.23	.48	2.75
NC > 5	1.50	.05	4.9	.23	.48	7.38
NC 2-5	1.10	.02	0.7	.09	.19	0.92
NC 1-2	0.98	.02	0.7	.09	.19	0.90
NC .5-1	0.84	.03	1.1	.14	.29	1.46
NC .2-.5	0.70	.04	1.6	.18	.38	2.30
NC < .2	0.60	.05	1.4	.25	.58	1.75

calculations. The deviation can be explained by preferred orientation of the smaller crystals. With close to 100% clay minerals in this fraction, there is a better chance that the small crystals will be oriented with the basal planes parallel to the X-ray slide surface, resulting in an anomalously large 001 reflection.

Once the CaO/Na_2O ratios for feldspar and smectite were determined graphically, %feldspar in the sample was calculated using the following equations:

(1) $Na_2Of/CaOf = 1.80$

(2) $Na_2Os/CaOs = 1.03$

(3) $CaOt = CaOs + CaOf$

(4) $Na_2Ot = Na_2Os + Na_2Of$

where CaOf and Na_2Of is the per cent of CaO and Na_2O in the sample that is due to feldspar; CaOs and Na_2Os is the per cent of CaO and Na_2O in the sample that is due to smectite; CaOt and Na_2Ot are values for %total CaO and %total Na_2O in the sample.

Solving for Na_2Of gives:

(5) $Na_2Of = (Na_2Ot - 1.03\ CaOt)2.38$

CaOf was then determined from equation (1).

The feldspar compositions and abundances were then calculated for

each sample as follows: The weight per cent of Na_2Of and CaOf, calculated using equations 1-5, were converted to mole percent values. Then the corresponding mole percent of Si and Al was determined using the fixed molar ratios of the theoretical formulas for sodic and calcic plagioclase feldspars. Once the feldspar composition was determined, the molar quantities were converted to weight percent (table 4) and summed to give the total weight per cent of feldspar in the fraction.

The same approach was used to calculate feldspar composition and abundances for the R fractions. In this case, however, the plots (figure 2a and 2b) indicated that the CaO and Na_2O contents of the fractions were controlled by more than two mineral phases. This was substantiated by the X-ray diffractograms which revealed the presence of smectite, feldspar, and illite in most of the fractions. Two of the fractions however, R3 and R5, contained only illite and feldspar as Ca and Na bearing phases. The X-intercepts of the lines defined by these two fractions were then determined, and the composition and abundances of illite and feldspar calculated as described previously. Since the $\%MnO_2$in these fractions is negligible (table 2) the effect of a $MnCO_3$phase was not considered.

Feldspar abundances were also determined using feldspar/boehmite X-ray peak area ratios and a calibration curve generated with oligoclase (Krissek, 1982). The estimated feldspar abundances using this method agreed to within 5% with those determined by the graphical partitioning technique (table 4).

TABLE III-4

FELDSPAR ABUNDANCES AND COMPOSITIONS

Abundances (in wt.%) Determined by X-Ray and Graphical Methods

	%fspar (X-Ray peaks)	%fspar (graphical)
NC 2	23	28
NC 3	19	18
NC 4	10	14
NC 5	6	7
NC 6	1	2
NC 7	0	0
R 2	20	25
R 3	20	15
R 4	2	3
R 5	6	5
R 6	4	5
R 7	2	1
R 8	0	0
R 9	0	0

Feldspar Compositions (in wt.%) Determined Graphically from Chemical Data

	NC	R
%SiO2	63.0	65.1
%Al2O3	24.2	20.6
%CaO	9.1	6.4
%Na2O	4.9	7.9

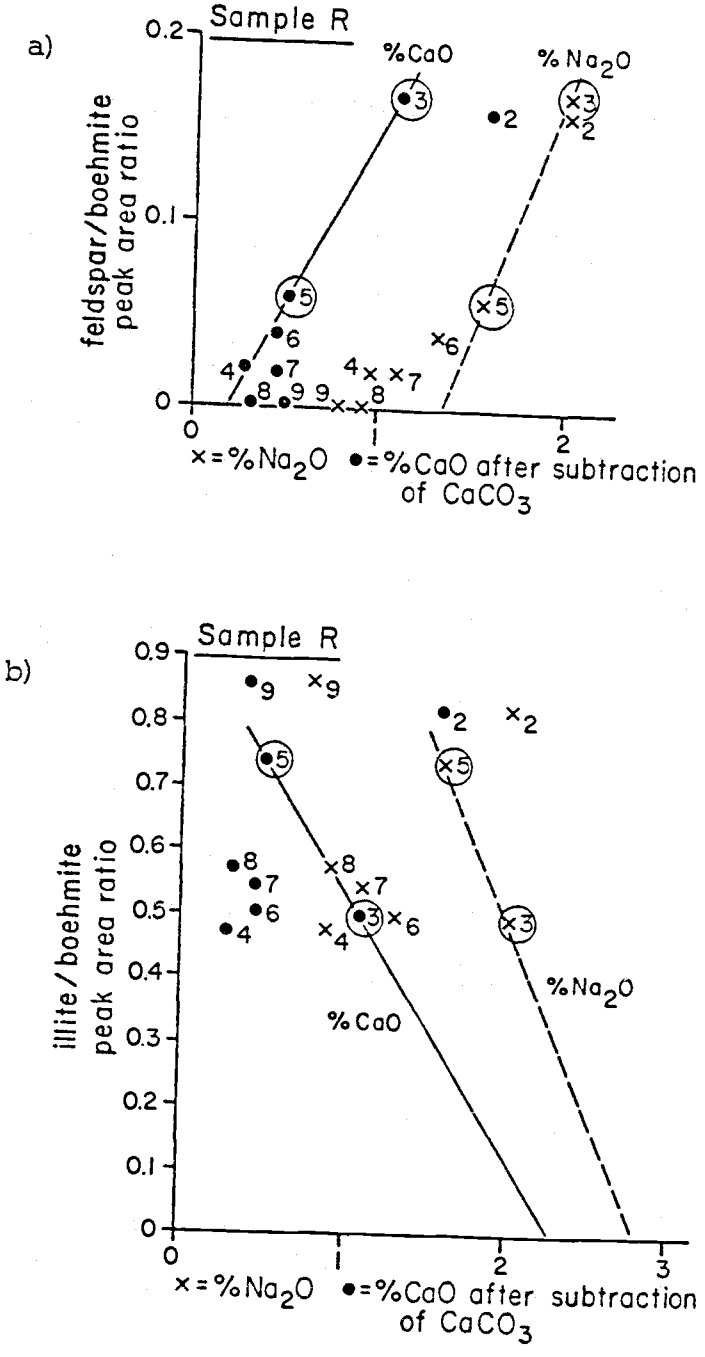


FIGURE III-2: Plots of illite and feldspar peak area vs %Na_2O and %CaO for sample R. The lines are defined by the circled points (as explained in the text).

Krissek (1982) showed that the calibration curve for feldspars varied greatly with differences in mineral compositions. Therefore, it seems that as long as the composition of the feldspar used in the calibration curve is close to that of the sample feldspar, determination of feldspar abundances from X-ray peak areas is equivalent to the graphical partitioning approach. The feldspar would have to be physically separated from the sample in order to determine the composition. A calibration curve could then be generated using the feldspar isolated from the sample.

Amorphous and poorly crystalline Fe and Mn oxyhydroxide minerals were leached with an oxalic acid-ammonium oxalate solution as described by Schwertmann (1964). This technique removes Fe and Mn oxyhydroxides without affecting smectite or goethite (Dudas and Harward, 1971). The leachate was then analyzed by atomic absorption. All of the Mn in the two sediments analyzed was present in the leachable phase, while significant proportions of Fe were present in both the leachable and leach-resistant phases (table 2, columns 9-11).

Once the non-clay mineral compositions and abundances were determined, their contributions were subtracted from the total oxides in each fraction. The residual oxides were then partitioned between the clay mineral phases.

Partitioning of the clay mineral phases

The X-ray diffraction patterns indicated the presence of

illite, smectite, and minor amounts of chlorite in both the NC and R sediments. A combination of factor analysis and linear programming methods were used to estimate the clay mineral compositions and abundances.

Q-mode factor analysis (Miesch, 1976) was performed on the residual oxides after the subtraction of non-clay minerals. In this technique, the variance in the chemical data is explained by an unspecified number of factors; the number of factors generated depends on the number of independently varying phases present. The factors were expressed in terms of oxide composition and could therefore be equated to possible mineral phases present in the sediment. Because some of the resulting factor components were given negative values, the factors were subsequently rotated toward the mean vector of the data set following the algorithm of Leinen and Pisias (1982). The three factors obtained were examined to see if they represented reasonable clay mineral compositions (table 5). Factor 1 was equated to smectite, factor 2 to illite, and factor 3 to chlorite. The compositions were then readjusted to include 15% H_2O in smectite, 8% H_2O in illite, and 15% H_2O in chlorite (table 6), so that they could be compared to actual mineral compositions reported in the literature. The resulting compositions agreed well with clay mineral analyses reported by Weaver and Pollard (1975). In addition, the octahedral, tetrahedral, and interlayer charges balanced very well when the elements of factors 1 and 2 were fit into theoretical clay mineral formulas (table 7), indicating that these independently generated factors do represent realistic clay

TABLE III-5

Clay Mineral Factors Obtained from Factor Analysis of Residual Oxide Data

	Factor 1 (Smectite)	Factor 2 (Illite)	Factor 3 (Chlorite ?)
Sample NC			
% of data variance explained	62	37	0.1
%SiO2	52 7	60.3	46.8
%Al2O3	29.9	14.1	39.4
%K2O	2.2	5.1	1.9
%Fe2O3	8.7	12.5	5.4
%MgO	5.5	8.7	5.4
%CaO	1.5	0.0	0.2
%Na2O	1.5	0.0	0.0
Sample R			
% of data variance explained	49	49	
%SiO2	65.5	47.9	
%Al2O3	18.3	25.5	
%K2O	0.0	7.9	
%Fe2O3	9.9	11.1	
%MgO	3.5	6.7	
%CaO	1.1	0.0	
%Na2O	1.8	0.9	

TABLE III-6

Clay Mineral Compositions Determined by Factor Analysis for Samples NC and R

		Smectite	Illite	Feldspar
Sample NC				
	%SiO2	44.8	55.5	63.0
	%Al2O3	25.4	13.0	24.2
	%K2O	1.9	4.7	
	%Fe2O3	7.4	11.5	
	%MgO	4.7	8.0	
	%CaO	1.3	0.0	9.1
	%Na2O	1.3	0.0	4.9
	%H2O	15.0	8.0	
Sample R				
	%SiO2	55.7	44.1	65.1
	%Al2O3	15.6	23.5	20.6
	%K2O	0.0	7.3	
	%Fe2O3	8.4	10.2	
	%MgO	3.0	6.1	
	%CaO	0.9	0.0	6.4
	%Na2O	1.5	0.8	7.9
	%H2O	15.0	8.0	

TABLE III-7

BALANCED CLAY MINERAL FORMULAS FROM THE COMPOSITIONS OF FACTORS 1 AND 2

Sample NC

Factor 1: smectite $Ca_{.10}\,Na_{.18}\,K_{.17}\,[Al_{1.34}\,Mg_{.50}\,Fe_{.40}]\,[Si_{3.20}\,Al_{.80}]\,O_{10}(OH)_2$

Factor 2: illite $K_{.45}\,[Al_{.61}\,Mg_{.99}\,Fe_{.72}]\,[Si_{3.58}\,Al_{.42}]\,O_{10}\,(OH)_2$

Sample R

Factor 1: smectite $Ca_{.07}\,Na_{.20}\,[Al_{1.25}\,Mg_{.32}\,Fe_{.45}]\,[Si_{3.95}\,Al_{.05}]\,O_{10}(OH)_2$

Factor 2: illite $K_{.65}\,Na_{.11}\,[Al_{1.07}\,Mg_{.64}\,Fe_{.54}]\,[Si_{3.12}\,Al_{.88}]\,O_{10}(OH)_2$

mineral compositions. The elements in factor 3 did not fit into a balanced formula for chlorite. This factor explains only .1% of the data variance, and therefore probably includes other small variations in the data set in addition to those attributable to chlorite. Since chlorite is a relatively unimportant mineral component in the sediment, a representative chlorite composition was entered as an end member in the linear programming analyis.

Once the clay mineral compositions were satisfactorilly determined, linear programming was employed to determine the illite, smectite, and chlorite abundances in each fraction. The residual clay oxides were partitioned between the clay mineral factors which were previously determined by factor analysis. An over-determined series of simultaneous equations were solved for each size fraction. The general form of the equation is shown below:

$$E_t = E_i(I) + E_s(S) + E_c(C)$$

where E_t equals the total weight-% concentration of a specific element oxide in the size fraction; E_i, E_s, and E_c equal the percentage of that element oxide in illite, smectite, and chlorite respectively; I, S, and C equal the percentage of illite, smectite, and chlorite in the size fraction. Such an equation is solved for each element in each size fraction. Two constraints are imposed: (1)all contributions from end members (in this case clay minerals) to each size fraction must be positive, and (2)the residual components (oxides) must be minimized. The resulting clay

and non-clay mineral abundances are shown in table 8.

The same procedure was used to analyze the R samples. In this case only two factors were obtained (table 5) representing illite and smectite. X-ray diffraction indicated minor amounts of chlorite were present only in the three coarsest fractions.

DISCUSSION AND SUMMARY

A combination of X-ray and chemical analyses can be used to determine clay mineral compositions and abundances in a suite of samples with similar mineralogy. The example I have used is unique in that six size fractions from a single sediment sample were analyzed. The assumption is reasonable that the minerals in each size fraction are of approximately the same composition. Therefore the problem of variability in the compositions of minerals present in a suite of sediment samples is minimized. The bulk sample composition, in this case, can be reconstructed from the sum of the fractions as long as the weight-% of each fraction is known (table 8).

Initially, the non-clay mineral contribution is subtracted from the total oxides. For the NC and R samples, I assumed that the non-clay fraction consisted of leachable Mn and Fe, $CaCO_3$, quartz, feldspar, and organic matter. Opal was not significant in these samples, but in some cases an opal determination may be

TABLE III-8

COMPUTED SAMPLE MINERALOGY (IN WT.%)

SAMPLE	%ILL (f)	%SMECT (f)	%CHLOR (f)	%QTZ (x)	%FSPAR (g)	%MNO2 (l)	%FE2O3 (l)	%CACO3 (p)
NC >5	35	7	<5	19	28	7.74	.60	.50
NC 2-5	47	12	<5	15	18	1.06	.30	.17
NC 1-2	46	25	<5	10	14	1.05	.40	.17
NC.5-1	46	38	0	6	7	1.68	.70	.17
NC.2-.5	46	39	0	<5	<5	2.59	1.10	.42
NC <.2	51	43	0	0	0	2.15	1.40	.58
NC bulk* sed.	44	22	<5	11	16	3.44	.67	.35
R >5	41	0	<5	30	25	.16	.06	.42
R 2-5	47	18	<5	20	15	.07	.06	.25
R 1-2DK	64	14	0	0	3	8.93	3.40	1.50
R 1-2LT	57	28	<5	10	5	.26	.10	.33
R.5-1	58	26	<5	5	5	.12	.10	.17
R.2-.5	53	41	0	<5	<5	.84	.70	.17
R.1-.2	61	38	0	0	0	.28	.70	.17
R <.1	43	55	0	0	0	.20	1.00	.33
R bulk** sed.	52	25	<3	12	18	.62	.41	.31

Methods of analysis:
(f) = determined by factor analysis and linear programming
(x) = calculated from X-ray diffraction peak areas
(g) = determined using graphical partitioning method
(l) = determined by atomic absorption spectroscopy of leachate
(p) = determined by phosphoric acid - LECO method

*Mineral abundances for bulk sediment calculated as
$\frac{\text{NC}}{\text{NC}}$ (%min.)(wt.% of size fract./100)

**Mineral abundances for bulk sediment calculated as
$\frac{\text{R}}{\text{R}}$ (%min.)(wt.% of size fract./100)

necessary in order to subtract this phase from the total SiO_2. The determination of quartz and feldspar still relies on X-ray diffraction techniques. But since these minerals are highly crystalline, a comparison of X-ray peak areas to a calibration curve is fairly reliable. The composition of the feldspar must be estimated , either graphically or by physical separation and subsequent chemical analysis.

The compositions and abundances of clay minerals are then determined from the remaining oxides. X-ray diffraction analysis is essential in initially establishing the number of clay mineral phases present. A comparison of X-ray peak areas can be used as a crude check of the relative clay abundances, but it is not a reliable means of determining absolute amounts. This is especially true for samples where mineral size and crystalinity are variable and where the smectite 001 reflection is not easily distinguishable from that of chlorite.

Clay compositions are determined using extended Q-mode factor analysis on the residual clay oxides. Since this type of analysis attempts to explain the variance in the chemical data by independent factors, the calculation of clay compositions will be most accurate in samples where each mineral varies independently from the others. The more two minerals vary together, the greater is the chance that they will be included in the same factor. In order to simplify the system, it is advantageous to subtract out as many non-clay mineral phases as possible before the factor analysis is employed. From the qualitative X-ray data, it is possible to

predict the number of factors that should be generated and what clay mineral compositions they should most closely resemble. Care must be taken to evaluate the effectiveness of the factor analysis in each case. It is essential to check whether or not hte generated factor compositions fit into balanced clay mineral formulas. Even though the factor analysis technique may not be applicable to every suite of samples, it seems valuable to first attempt this type of determination of mineral compositions from the chemical data before assuming average mineral compositions that may be unrelated to the phases present.

REFERENCES

Abelson P. H. and Hare P. E. (1971) Reactions of amino acids with natural and artificial humus and kerogens. Carnegie Inst. Wash. Yearbook No. 59, pp. 327-334.

Allison F. E. and Roller E. M. (1955) Fixation and release of ammonium ions by clay minerals. Soil Sci. 80,341-441.

Arruda J. A., Faulk R. T. and Marzolf G. R. (1982) Growth and survivorship of daphnids fed on suspended sediments with adsorbed organic matter. Abstract, Amer. Soc. of Limnol. and Oceanogr. Inc., 45th Annual Meeting.

Bada J. L. and Man E. H. (1980) Amino acid diagenesis in deep sea drilling project cores: Kinetics and mechanisms of some reactions and their applications in geochronology and in paleotemperature and heat flow determinations. Earth Sci. Rev. 16,21-55.

Barclay W. R. and Knight A. W. (1982) Adsorbed organic matter and the formation and nutritional enhancement of detritus in natural waters. Abstract, Amer. Soc. of Limnol. and Oceanogr. Inc., 45th Annual Meeting.

Bernal J. (1951) The Physical Basis of Life, London 210p.

Biscaye P. E. (1965) Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans. GSA Bull. 76,803-832.

Boyce R. E. and Bode G. W. (1972) Carbon and carbonate analyses, Leg 9. In: Hayes J. D. et el., 1972, Initial Reports of the Deep Sea Drilling Project. 9,797-816.

Boyle E. (1982) Manganese carbonate overgrowths on foraminifera tests. EOS 63,353.

Bremner J. M. (1960) Determination of nitrogen in soil by the Kjeldahl method. J. Agr. Sci. 55,11-33.

Burford J. R., Deshpande T. L., Greenland D. J. and Quirk J. P. (1964) Influence of organic materials on the determination of the specific surface areas of soils. Jour. Soil Sci. 15,192-201.

Casagrande D. J. and Given P. H. (1974) Geochemistry of amino acids in some Florida peat accumulations-I. Analytical approach and total amino acid concentrations. Gecchim.

Cosmochim. Acta 38,419-434.

Casagrande D. J. and Given P. H. (1980) Geochemistry of amino acids in some Florida peat accumulations-II. Amino acid distributions. Geochim. Cosmochim. Acta 44,1493-1507.

Cauwet G. (1978) Organic chemistry of seawater particulates: Concepts and developments. Oceanologica Acta 1,99-105.

Chichester F. W. (1969) Nitrogen in soil organo-mineral sedimentation fractions. Soil Sci. 107,356-363.

Cloos P., Badot C. and Herbillon A. (1981) Interlayer formation of humin in smectites. Nature 289,391-393.

Dashman T. (1977) Adsorption of amino acids and peptides on homoionic montmorillonite and kaolinite, and the utilization of the adsorbed amino acids and peptides by microorganisms. Ph.D. dissertation, N.Y. University, 223 p.

Dawson R. and Pritchard R. G. (1978) The determination of α-amino acids in sea water using a fluorimetric analyser. Mar. Chem. 6,27-40.

Degens E. T. and Mopper K. (1976) Organic material in marine sediments. In: Chemical Oceanography v.6, J. P. Riley and R. Chester (eds.), Academic Press, pp.59-113.

Desai M. V. and Ganguly A. K. (1980) Organo-metallic interactions of manganese and other heavy metals in the marine environment. In: Geology and Geochemistry of Manganese, v. 1, I. Varentsov and G. Grasselly (eds.). pp. 389-409.

Dudas M. J. and Harward M. E. (1971) Effect of dissolution treatment on standard soil and clays. Soil Sci. Soc. Amer. Proc. 35,134-140.

Duval C. (1963) Inorganic Thermogravimetric Analyses. Elsevier, Amsterdam, 722p.

Edwards A. P. and Bremner J. M. (1967) Dispersion of soil particles by sonic vibration. J. Soil Sci. 18,47-63.

Emery K. O., Stitt C. and Saltman P. (1964) Amino acids in basin sediments. J. Sed. Petrol. 34,433-437.

Friebele E., Shimoyama A. and Ponnamperuma C. (1980) Adsorption of protein and non-protein amino acids on a clay mineral: A possible role of selection in chemical evolution. Mol. Evol. 16,269-278.

Fripiat J. J. and Cruz-Cumplido M. I. (1974) Clays as catalysts for natural processes. Ann Rev. of Earth and Planet. Sci. 2,239-256.

Froelich, P. N. Analysis of organic carbon in marine sediments. Limnol. Oceanogr. 25,564-572.

Gardner W. (1978) Sensitive fluorometric procedure to determine individual amino acids in marine waters. Mar. Chem. 6,15-26.

Gibbs R. J. (1967) Quantitative X-Ray diffraction analysis using clay mineral standards extracted from the samples to be analyzed. Clay Miner. 7,79-90.

Gibbs R. J. (1977) Suspended sediment transport and the turbidity maximum. In: Estuaries, Geophysics and the Environment, National Acad. Sci., Wash. D.C.,pp. 104-109.

Greenland D. J. (1971) Interaction between humic and fulvic acids and clays. Soil Sci. 111,34-41.

Grim (1968) Clay Mineralogy, 2nd ed., McGraw-Hill.

Grundmanis V. and Murray W. J. (1982) Aerobic respiration in pelagic marine sediments. Geochim. Cosmochim. Acta 46,1101-1120.

Hare P. E. (1973) Amino acids, amino sugars and ammonia in sediments from the Cariaco Trench. In: Initial Reports of the Deep Sea Drilling Project, v. 20, p. 941.

Hartmann M., Muller P. J., Suess E. and van der Weijden C. H. (1976) Chemistry of late Quaternary sediments and their interstitial waters from the N. W. African continental margin. Meteor Forsch.-Ergeb. Reihe C, 24,1-67.

Heath G. R., Moore T. C. and Dauphin J. P. (1977) Organic carbon in deep-sea sediments. In: The Fate of Fossil Fuel CO2 in the Oceans (ed. N Anderson and A. Malahoff), Plenum Press, N.Y., p.605-625.

Heath G. R. and Pisias N. (1979) A method for the quantitative estimation of clay minerals in N. Pacific deep sea sediments. Clays. Clay Min. 27,175-184.

Hedges J. (1977) The association of organic molecules with clay minerals in aqueous solution. Geochim. Cosmochim. Acta 41,1119-1123.

Hedges J. (1978) The formation and clay mineral reactions of melanoidins. Geoch. Cosmoch. Acta 42,69-76.

Imbrie J. and Poldervaart A. (1959) Mineral compositions calculated from chemical analyses of sedimentary rocks. J. Sed. Petrol. 29,588-595.

Johns W. D., Grim R. E., and Bradley W. F. (1954) Quantitative estimations of clay minerals by diffraction methods. J. Sed. Petrol. 24,242-251.

Karlin R. (1980) Sediment sources and clay mineral distributions off the Oregon Coast. J. Sed. Petrol. 50,543-560.

Kemp A. L. W. and Mudrochova A. (1972) Distribution and forms of nitrogen in a Lake Ontario sediment core. Limnol. Oceanogr. 17,855-967.

Kolpack R. L. and Bell S. A. (1968) Gasometric determination of carbon in sediments by hydroxide absorption. J. Sediment. Petrol. 38,617-620.

Krissek L. A., Scheidegger K. F. and Kulm L. D. (1980) Surface sediments of the Peru-Chile continental margin and the Nazca Plate. Geol. Soc. Am. Bull. 91,321-331.

Krissek L. A. (1982) Sources, Dispersal and Contributions of Fine-grained Terrigenous Sediments on the Oregon and Washington Continental Slope. Ph.D. Dissertation, Oregon State University, 179 p.

Kudeyarov V. N., Trubin A. I. and Bashkin V. N. (1974) Forms of ammonium adsorbed by montmorillonite. Soviet Soil Sci. 12,713-718.

Kulm L. D. and Scheidegger K. F. (1979) Quaternary sedimentation on the tectonically active Oregon continental slope. In: Geology of Continental Slopes. L. J. Doyle and O. H. Pilkey (eds.), Soc. Econ. Paleont. and Mineral., Special Publication No. 27, pp. 247-263.

Laboratory Equipment Corporation (1966) Instruction manual for operation of LECO Carbon Analyzer. LECO Corp., St. Joseph, Michigan.

Laura (1975) On the protective effect of clay minerals. Soil Sci. 120,241-243.

Lee C. and Cronin C. (1982) The vertical flux of particulate organic nitrogen in the sea: Decomposition of amino acids in the Peru upwelling area and the equatorial Atlantic. J. Mar. Res. 40,227-251.

Lehninger A. L. (1975) Biochemistry, 2nd ed., Worth Publishers,

New York, 1104 p.

Leinen M. and Heath G. R. (1981) Sedimentary indicators of atmospheric activity in the Northern Hemisphere during the Cenozoic. Paleogeogr., Paleoclimat., Paleoecol. 36,1-21.

Leinen M. and Pisias N. (1982) An objective technique for determining end-member compositions and for partioning sediments according to their sources. Geochim. Cosmochim. Acta. (submitted)

Martin H. H. (1966) Biochemistry of bacterial cell walls. Ann. Rev. Biochem. 35,457-484.

Meyers P. A. and Quinn J. G. (1973) Organic matter on clay minerals and marine sediments. Chem. Geol. 13,63-68.

Miesch A. T. (1962) Computing mineral composition of sedimentary rocks form chemical analyses. J. Sed. Petrol. 32,217-225.

Miesch A. T. (1976) Q-mode factor analysis of geochemical and petrological data matrices with constant row sums. U.S. Geolog. Survey Prof. Pap. 574G.

Mogilevkina I. A. (1964) Fixation of ammonium in soil and method of determining it. Soviet Soil Sci. 2,185-196.

Muller P. J. (1975) Zur Diagenese stickstoffhaltiger Substanzen in marinen Sedimenten unter oxydierenden und reduzierenden Bedingungen. Ph.D. dissertation. University of Kiel, W. Germany, 179 p.

Muller P. (1977) C/N ratios in Pacific deep-sea sediments: Effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. Geoch. Cosmoch. Acta 41,765-776.

Muller P. and Mangini A. (1980) Organic carbon decomposition rates in sediments of the Pacific manganese nodule belt dated by Th^{230} and Pa^{231}. Earth and Planet. Sci. Lett. 51,94-114.

Paecht-Horowitz M. (1978) Clay catalyzed polymerization of amino acid adenylates and its relationship to biochemical reactions. In: Origin of Life, Proc. of 2nd ISSOL Meeting and 5th ICOL Meeting, Kyoto. H. Noda (ed.), pp. 289-295.

Parasher C. D. and Lowe L. E. (1970) Isolation of clay-size organo-mineral complexes from soils of the lower Fraser Valley. Can. J. Soil Sci. 50,403-407.

Pearson M. J. (1978) Quantitative clay mineralogical analyses from the bulk chemistry of sedimentary rocks. Clays, Clay

Miner. 26,423-433.

Pedersen T. F. and Price N. B. (1982) The geochemistry of $MnCO_3$in Panama Basin Sediments. Geochim. Cosmochim. Acta 46,59-68.

Pierce R. H., Olney C. E. and Felbeck G. T. Jr. (1974) ppDDT adsorption to suspended particulate matter in seawater. Geochim. Cosmochim. Acta 38,1061-1073.

Powell H. S. (1980) Decomposition of Organic Matter in Estuarine Sediments by Sulfate Reduction: A Field Study from Yaquina Bay and Sediment Incubation Experiments. M.S. Dissertation, Oregon State University, 173 p.

Rashid M. A., Buckley D. E. and Robertson K. R. (1972) Interactions of marine humic acid with clay minerals and a natural sediment. Geoderma 8,11-27.

Riley G. A. (1970) Particulate matter in sea water. Adv. Mar. Biol. 8,1-118.

Satoh T. (1976) Isolation and characterization of naturally occurring organo-mineral complexes in some volcanic ash soils. Soil Sci. and Plant Nutr. 17,181-185.

Schmied W. and Steiner H. (1957) Bestimmung des Gesamtkohlenstoffs im Ton und in artverwandten Materialien durch Verbrennung auf nassem Wege mit Chromschwefelsaure. Glas-Email.-Keramo-Tech. 8,215-221.

Schnitzer M. and Khan S. (1978) Soil Organic Matter, Elsevier, Amsterdam.

Schroeder R. A. (1975) Absence of β-alanine and γ-aminobutyric acid in cleaned foraminiferal shells. Earth and Planet. Sci. Let. 25,274-278.

Schwertmann U. (1964) Differenzierung der Eisenoxide des Bodens durch photochemische Extraletion mit saurer Ammoniumoxalat-Losung: Z. Pflanzenernahr. Dung. und Bodenkunde 105,194-202.

Shimoyama A., Blair N. and Ponnamperuma C. (1978) Synthesis of amino acids under primitive earth conditions in the presence of clay. Origin of Life, Proc. of 2nd ISSOL Meeting and 5th ICOL Meeting, Kyoto. H. Noda (ed.), pp. 95-99.

Sieskind O. and Wey R. (1959) Sur l'adsorption d'acides amines par la montmorillonite-H. Influence de la position relative des deux fonctions -NH et -COOH. Compt. Rend. Acad. Sci.

Paris 248,1652-1655.

Sieskind O. and Wyart J. (1960) Etude des complexes d'adsorption forme entre la montmorillonite-H et certains acides amines: Isotherms d'adsorption a pH 2 et a 20°C. Compt. Rend. Acad. Sci. Paris 250,2228-2230.

Silva J. A. and Bremner J. M. (1966) Determination and isotope-ratio analysis of different forms of nitrogen in soils: 5. Fixed ammonium. Soil Sci. Soc. Amer. Proc. 30,587-594.

Simoneit B. (1977) Organic matter in eolian dusts over the Atlantic Ocean. Mar. Chem. 5,443-464.

Solomon D. H. (1968) Clay minerals as electron acceptors and/or electron donors in organic reactions. Clays and Clay Miner. 16,31-39.

Sorensen L. (1972) Stabilization of newly formed amino acid metabolites in soil by clay minerals. Soil Sci. 114,5-11.

Spycher G. (1977) Fractionation and Some Properties of Water-dispersible Soil Organic-mineral Particles. Ph.D. Dissertation, Oregon State University, 189 p.

Stevenson F. J. and Dhariwal A. P. S. (1959) Distribution of fixed ammonium in soils. Soil Sci. Soc. Amer. Proc. 23,121-125.

Stevenson F. J. and Cheng C. N. (1972) Organic geochemistry of the Argentine Basin sediments: Carbon, nitrogen relationships and Quaternary correlations. Geochim. Cosmochim. Acta 36,653-671.

Stevenson F. J. and Tilo S. N. (1971) Nitrogenous constituents of deep sea sediments. In: Adv. in Org. Geochem. p.237-262.

Stotzky G. (1972) Activity, ecology and population dynamics of microorganisms in soil. CRC Critical Reviews in Microbiology. 2,59-137.

Strickland J. D. H. (1952) The preparation and properties of silicomolybdic acid. I. The properties of alpha silicomolybdic acid. J. Am. Chem. Soc. 74,862-867.

Stul M., Uytterhoeven J. and DeBock J. (1979) The adsorption of n-aliphatic alcohols from dilute aqueous solutions on RNH -montmorillonites. II. Interlamellar association of the adsorbate. Clays and Clay Miner. 27,377-386.

Suess E. (1973) Interaction of organic compounds with CaCO - II. Organo-carbonate association in Recent sediments. Geochim. Cosmochim. Acta. 37,2435-2447.

Theng B. K. G. (1974a) Complexes of clay minerals with amino acids and peptides. Chemie der Erde 33,125-144.

Theng B. K. G. (1974b) The Chemistry of Clay-Organic Reactions. Wiley 343p.

Theng B. (1979) Formation and Properties of Clay-Polymer Complexes, Elsevier Pub. Co., New York, 362 p.

Turchenek L. and Oades J. (1979) Fractionation of organo-mineral complexes by sedimentation and density techniques. Geoderma 21,311-343.

van Langeveld A. D., van der Gaast S. J. and Eisma D. (1978) A comparison of the effectiveness of eight methods for the removal of organic matter from clay. Clays and Clay Miner. 26,361-364.

van Olphen H. (1977) An Introduction to Clay Colloid Chemistry, 2nd ed., John Wiley and Sons, New York, 318 p.

Wangersky P. J. and Joensuu O. (1964) Strontium, magnesium and manganese in fossil foraminiferal carbonates. J. Geol. 72,477-483.

Watson J. R. and Parsons J. W. (1974) Studies of soil organo-mineral fractions: I. Isolation by ultrasonic dispersion. J. Soil Sci. 25,1-8.

Weaver C. E. and Pollard L. D. (1975) The Chemistry of Clay Minerals, Developments in Sedimentology, Elsevier, N.Y.

Wefer G., Suess E., Balzer W., Liebezeit G., Muller P., Ungerer C. A., and Zenk, W. (1982) Fluxes of biogenic components from sediment trap deployment in circumpolar waters of the Drake Passage. Nature (in press).

Weiss A. (1963) A secret of Chinese porcelain manufacture. Angew. Chem. Int. Ed. Engl. 2,697-703.

Whelan J. K. (1977) Amino acids in a surface sediment core of the Atlantic abyssal plain. Geochim. Cosmochim. Acta 41,803-810.

APPENDIX

TABLE A-1

ORIGINAL OXIDE DATA IN WEIGHT PER CENT

SAMPLE	AL2O3	SIO2	NA2O	K2O	MGO	CACO3	CAO	FE2O3 LEACH.	FE2O3 CLAY	MNO2 LEACH.	TOTAL
NC1	14.4	52.2	3.5	2.3	4.3	0.42	0.7	0.7	6.0	3.1	73.3
NC2	13.4	59.0	2.6	1.8	3.1	0.50	1.2	0.6	4.1	7.7	80.6
NC3	14.2	59.2	2.1	2.3	4.0	0.17	1.0	0.3	6.0	1.1	76.2
NC4	16.2	55.6	1.5	2.5	4.6	0.17	0.9	0.4	7.0	1.0	73.7
NC5	17.2	52.0	1.1	3.0	5.1	0.17	0.7	0.7	7.4	1.7	71.9
NC6	17.4	43.3	0.9	2.9	6.0	0.42	0.5	1.1	8.9	2.6	70.8
NC7	16.6	46.2	0.5	2.8	5.8	0.58	0.2	1.4	9.0	2.1	68.6
R1	17.2	53.9	2.8	3.6	3.5	0.58	0.5	0.4	6.4	0.5	72.2
R2	13.8	65.9	2.0	2.8	2.6	1.70	0.9	0.06	4.2	0.7	80.3
R3	15.9	64.0	2.0	3.3	3.3	0.25	1.1	0.06	6.1	0.1	81.5
R4	17.0	40.2	0.9	3.2	4.3	1.50	0.3	3.4	7.6	8.9	70.3
R5	19.6	55.2	1.6	4.1	3.8	0.33	0.5	0.1	7.4	0.3	73.3
R6	20.0	52.2	1.3	4.1	3.8	0.17	0.5	0.1	7.3	0.1	69.5
R7	20.2	42.7	1.1	4.1	4.3	0.17	0.5	0.7	8.7	0.8	67.0
R8	18.7	47.3	0.9	3.6	4.6	0.17	0.3	0.7	9.6	0.3	67.5
R9	17.4	51.3	0.8	3.0	5.0	0.33	0.5	1.0	9.4	0.2	71.5

TABLE A-2a

SAMPLE R: PELAGIC RED CLAY, SURFACE SAMPLE 0-4 CM
(NMOL/GM)

Size Fraction (microns)	Bulk	>5	2-5	1-2 (dark)	1-2 (light)	0.5-1	0.2-0.5	0.1-0.2	<0.1
METO	35.6	0.0	0.0	6.8	1.7	4.1	6.4	18.9	22.8
ASP	519.9	43.3	26.9	338.7	84.9	102.5	328.6	370.7	476.2
THR	182.4	22.2	6.4	144.3	16.6	10.1	114.3	78.6	95.3
SER	196.8	53.0	18.1	292.4	63.2	9.0	226.6	90.9	104.8
GLU	275.6	56.3	14.9	362.2	53.8	54.9	276.0	175.9	225.3
GLY	529.0	67.4	37.6	626.9	105.5	118.0	427.1	337.8	394.3
ALA	275.7	25.2	10.4	244.6	33.7	24.3	171.4	127.8	161.7
VAL	144.7	16.5	2.9	145.9	12.0	9.7	110.3	57.4	94.2
MET	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ILE	67.1	12.9	4.2	78.8	9.1	10.1	56.3	32.6	42.4
LEU	87.4	23.3	5.0	155.2	8.4	8.8	98.2	32.8	50.4
TYR	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PHE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
B-ALA	551.8	58.0	92.4	605.0	314.0	413.9	888.8	1239.0	1330.0
G-ABA	420.1	50.7	92.4	491.5	282.1	388.5	725.9	897.4	870.8
ORN	53.0	10.6	6.4	75.4	32.3	22.6	63.0	69.2	47.1
LYS	211.7	32.6	17.9	138.3	54.3	80.2	191.8	177.8	161.1
HIS	23.0	16.2	5.5	18.9	9.4	12.6	31.4	16.9	14.1
ARG	255.1	39.3	38.5	265.0	95.3	136.2	344.1	360.9	378.2
Total	3828.9	527.5	379.5	3989.9	1176.3	1405.5	4060.2	4084.6	4468.7
Others	373.0	43.0	45.0	340.0	123.0	180.0	392.0	504.0	514.0
Glucos-amine	265.9	9.1	10.5	240.4	78.0	63.9	262.1	282.0	355.3
Galactos-amine	269.5	0.0	0.0	336.1	22.1	15.7	192.8	177.6	338.1
NH3 peak	19390.0	10360.0	12650.0	23840.0	21170.0	22440.0	29250.0	21670.0	14930.0
Norleucin Recovery (%)	95.8	97.1	101.9	(39.5)	100.4	103.7	94.7	102.2	99.6

TABLE A-2b

SAMPLE R: PELAGIC RED CLAY, SURFACE SAMPLE 0-4 CM
(MOLE PER CENT OF TOTAL AMINO ACIDS)

Size Fraction (microns)	Bulk	>5	2-5	1-2 (dark)	1-2 (light)	0.5-1	0.2-0.5	0.1-0.2	<0.1
METO	0.9	0.0	0.0	0.2	0.1	0.3	0.2	0.5	0.5
ASP	13.5	8.1	7.0	8.5	7.1	7.3	8.1	9.1	10.6
THR	4.8	4.2	1.7	3.6	1.4	0.7	2.8	1.9	2.1
SER	5.1	9.9	4.7	7.3	5.3	0.6	5.6	2.2	2.3
GLU	7.2	10.5	3.9	9.1	4.5	3.9	6.8	4.3	5.0
GLY	13.8	12.6	9.8	15.7	8.8	8.4	10.5	8.3	8.8
ALA	7.2	4.7	2.7	6.1	2.8	1.7	4.2	3.1	3.6
VAL	3.8	3.1	0.8	3.7	1.0	0.7	2.7	1.4	2.1
MET	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ILE	1.8	2.4	1.1	2.0	0.8	0.7	1.4	0.8	0.9
LEU	2.3	4.3	1.3	3.9	0.7	0.6	2.4	0.8	1.1
TYR	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PHE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
B-ALA	14.4	10.8	24.2	15.2	26.3	29.4	21.8	30.3	29.7
G-ABA	10.9	9.5	24.2	12.3	23.6	27.6	17.8	22.0	19.5
ORN	1.4	2.0	1.7	1.9	2.7	1.6	1.5	1.7	1.0
LYS	5.5	6.1	4.7	3.5	4.6	5.7	4.7	4.3	3.6
HIS	0.6	3.0	1.4	0.5	0.8	0.9	0.8	0.4	0.3
ARG	6.6	7.3	10.1	6.6	8.0	9.7	8.5	8.8	8.4

TABLE A-3

SAMPLE NC: NORTHERN CALIFORNIA MARGIN 15-18 CM
(NMOL/GM)

Size Fraction (microns)	Bulk	>5	2-5	1-2	0.5-1	0.2-0.5	<0.2
METO	160.1	23.5	31.3	55.9	113.6	227.8	485.4
ASP	1650.0	540.3	481.0	567.3	1244.0	2616.0	4637.0
THR	676.7	263.3	203.5	241.5	548.1	1146.0	1682.0
SER	605.8	251.1	205.1	240.7	518.6	1039.0	1486.0
GLU	920.5	330.4	306.5	329.8	709.8	1437.0	2333.0
GLY	2077.0	746.9	707.6	839.6	1762.0	3534.0	5111.0
ALA	1161.0	375.3	337.4	391.6	894.7	1985.0	2862.0
VAL	494.2	193.7	141.1	133.8	365.7	848.5	1338.0
MET	13.7	13.9	13.0	5.7	31.2	22.9	134.6
ILE	237.5	87.4	94.6	63.6	153.8	341.0	595.6
LEU	302.0	132.8	107.6	88.6	209.5	456.3	790.3
TYR	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PHE	0.0	0.0	0.0	0.0	0.0	0.0	0.0
B-ALA	759.5	266.8	236.4	283.8	658.8	1421.0	2433.0
G-ABA	354.4	98.7	122.1	176.7	351.3	622.6	1103.0
ORN	106.9	33.2	49.4	60.4	100.3	175.4	296.3
LYS	661.4	168.9	284.3	375.0	718.7	1315.0	1992.0
HIS	43.0	29.7	53.3	34.7	38.9	31.8	57.4
ARG	616.0	207.9	217.0	274.2	601.1	1125.0	1905.0
Total	10839.7	3763.8	3591.2	4162.9	9020.1	18344.3	29241.6
Others	1158.0	444.0	365.0	387.0	941.0	1702.0	2345.0
Glucos-amine	934.5	378.1	299.0	342.2	851.6	1925.0	2606.0
Galactos-amine	1107.0	384.5	301.8	302.5	902.4	2313.0	2977.0
NH3 peak	43260.0	23100.0	27780.0	28500.0	48500.0	68770.0	66230.0
Norleucin Recovery (%)	76.4	(36.1)	84.2	92.3	75.6	76.8	90.0

SAMPLE NC: N. CALIFORNIA MARGIN, 15 - 18 CM
(MOLE PER CENT OF TOTAL AMINO ACIDS)

Size Fraction (microns)	Bulk	>5	2-5	1-2	0.5-1	0.2-0.5	<0.2
METO	1.5	0.6	0.9	1.3	1.3	1.2	1.7
ASP	15.2	14.4	13.4	13.6	13.8	14.3	15.9
THR	6.2	7.0	5.7	5.8	6.1	6.2	5.8
SER	5.6	6.7	5.7	5.8	5.8	5.7	5.1
GLU	8.5	8.8	8.5	7.9	7.9	7.8	8.0
GLY	19.2	19.8	19.7	20.2	19.5	19.3	17.5
ALA	10.7	10.0	9.4	9.4	9.9	10.8	9.8
VAL	4.6	5.2	3.9	3.2	4.1	4.6	4.6
MET	0.1	0.4	0.4	0.1	0.3	0.1	0.5
ILE	2.2	2.3	2.4	1.5	1.7	1.9	2.0
LEU	2.8	3.5	3.0	2.1	2.3	2.5	2.7
TYR	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PHE	0.0	0.0	0.0	0.0	0.0	0.0	0.0
B-ALA	7.0	7.1	6.6	6.8	7.3	7.8	8.3
G-ABA	3.3	2.6	3.4	4.2	3.9	3.4	3.8
ORN	1.0	0.9	1.4	1.5	1.1	1.0	1.0
LYS	6.1	4.5	7.9	9.0	8.0	7.2	6.8
HIS	0.4	0.8	1.5	0.8	0.4	0.2	0.2
ARG	5.7	5.5	6.0	6.6	6.7	6.1	6.5

TABLE A-4

SAMPLE OM: OREGON MARGIN 0-3 CM
(NMOL/GM)

Size Fraction (microns)	Bulk	>5	2-5	1-2	0.5-1	0.2-0.5	<0.2
METO	359.4	53.8	228.5	476.4	523.8	998.0	1393.0
ASP	6259.0	1553.0	4561.0	9019.0	9271.0	15259.0	14820.0
THR	2652.0	609.6	1904.0	3856.0	3976.0	6241.0	5411.0
SER	3436.0	860.8	2376.0	4722.0	4885.0	8216.0	7253.0
GLU	3813.0	953.6	2824.0	5546.0	5665.0	9130.0	8319.0
GLY	8949.0	2337.0	6747.0	13144.0	13428.0	21227.0	17344.0
ALA	4115.0	977.7	3097.0	6055.0	6278.0	9708.0	8010.0
VAL	2065.0	537.7	1604.0	3130.0	3119.0	5033.0	4131.0
MET	359.0	77.8	213.6	524.2	483.8	973.0	764.5
ILE	1222.0	313.8	933.7	1811.0	1837.0	2955.0	2643.0
LEU	1695.0	439.6	1293.0	2487.0	2490.0	4102.0	3656.0
TYR	543.9	149.0	396.3	814.6	773.1	1299.0	938.5
PHE	1044.0	262.4	768.8	1532.0	1563.0	2706.0	2182.0
B-ALA	927.3	203.7	688.3	1384.0	1471.0	2386.0	2347.0
G-ABA	576.3	97.1	328.0	725.7	841.1	1617.0	1538.0
ORN	298.6	69.0	227.5	491.3	484.5	751.8	591.2
LYS	5226.0	610.4	1906.0	3884.0	3951.0	6175.0	5351.0
HIS	509.0	197.0	384.3	745.1	670.5	1140.0	827.1
ARG	2043.0	547.2	1602.0	3244.0	3483.0	5124.0	3994.0
Total	46092.5	10850.2	32083.0	63591.3	65193.8	105040.8	91513.3
Others	2316.0	475.6	1728.0	3434.0	3594.0	5463.0	4884.0
Glucos-amine	2490.0	572.3	1684.0	3366.0	3703.0	6227.0	4971.0
Galactos-amine	2053.0	439.6	1463.0	3036.0	3278.0	4999.0	2870.0
NH3 peak	41985.0	11565.0	30645.0	67995.0	86004.0	98795.0	76811.0
Norleucin Recovery (%)	88.4	90.7	93.4	89.1	89.2	90.1	92.7

SAMPLE OM: OREGON MARGIN 0-3 CM
(MOLE PER CENT OF TOTAL AMINO ACIDS)

Size Fraction (microns)	Bulk	>5	2-5	1-2	0.5-1	0.2-0.5	<0.2
METO	0.8	0.5	0.7	0.7	0.8	0.9	1.5
ASP	14.4	14.3	14.2	14.2	14.2	14.5	16.2
THR	6.1	5.6	5.9	6.1	6.1	5.9	5.9
SER	7.9	7.9	7.4	7.4	7.5	7.8	7.9
GLU	8.8	8.8	8.8	8.7	8.7	8.7	9.1
GLY	20.6	21.5	21.0	20.7	20.6	20.2	19.0
ALA	9.5	9.0	9.6	9.5	9.6	9.2	8.7
VAL	4.8	5.0	5.0	4.9	4.8	4.8	4.5
MET	0.8	0.7	0.7	0.8	0.7	0.9	0.8
ILE	2.8	2.9	2.9	2.8	2.8	2.8	2.9
LEU	3.9	4.1	4.0	3.9	3.8	3.9	4.0
TYR	1.2	1.4	1.2	1.3	1.2	1.2	1.0
PHE	2.4	2.4	2.4	2.4	2.4	2.6	2.4
B-ALA	2.1	1.9	2.2	2.2	2.3	2.3	2.6
G-ABA	1.3	0.9	1.0	1.1	1.3	1.5	1.7
ORN	0.7	0.6	0.7	0.8	0.7	0.7	0.6
LYS	5.8	5.6	5.9	6.1	6.1	5.9	5.8
HIS	1.2	1.8	1.2	1.2	1.0	1.1	0.9
ARG	4.7	5.0	5.0	5.1	5.3	4.9	4.4

TABLE A-5

SAMPLE CR: COLUMBIA RIVER SURFACE SEDIMENT
(NMOL/GM)

Size Fraction (microns)	Bulk	>5	2-5	1-2	0.5-1	0.2-0.5	<0.2
METO	23.0	19.0	13.0	128.0	325.0	357.0	344.0
ASP	1825.0	1210.0	889.0	5366.0	10555.0	13048.0	19811.0
THR	972.0	676.0	471.0	2851.0	5823.0	7229.0	11021.0
SER	1041.0	766.0	535.0	3117.0	6173.0	7613.0	11586.0
GLU	1513.0	1023.0	726.0	4333.0	8501.0	11092.0	17387.0
GLY	1875.0	1347.0	941.0	5629.0	11184.0	13789.0	20095.0
ALA	1474.0	1033.0	725.0	4456.0	9019.0	11452.0	16870.0
VAL	886.0	662.0	451.0	2638.0	5244.0	6508.0	9362.0
MET	132.0	90.0	66.0	446.0	773.0	1095.0	1855.0
ILE	519.0	397.0	258.0	1483.0	2990.0	3720.0	5678.0
LEU	847.0	681.0	424.0	2462.0	4825.0	6058.0	9217.0
TYR	178.0	139.0	90.0	522.0	1155.0	1390.0	2070.0
PHE	417.0	315.0	201.0	1211.0	2424.0	2944.0	4511.0
B-ALA	76.0	47.0	46.0	373.0	611.0	694.0	856.0
G-ABA	44.0	19.0	18.0	175.0	299.0	391.0	761.0
ORN	25.0	16.0	11.0	95.0	210.0	256.0	348.0
LYS	654.0	503.0	327.0	2112.0	4132.0	5129.0	7855.0
HIS	188.0	162.0	99.0	512.0	1007.0	1306.0	1994.0
ARG	504.0	414.0	270.0	1459.0	2909.0	3642.0	5380.0
Total	13193.0	9519.0	6561.0	39368.0	78159.0	97713.0	147001.0
Others	210.0	113.0	133.0	1065.0	1755.0	2327.0	3217.0
Glucos-amine	559.0	351.0	281.0	2116.0	3659.0	4521.0	6346.0
Galactos-amine	418.0	257.0	201.0	1366.0	2764.0	3256.0	3755.0
NH3 peak	5096.0	1975.0	2362.0	15517.0	33887.0	33575.0	51710.0
Norleucin Recovery (%)	87.0	91.3	92.9	86.9	81.9	80.7	80.6

SAMPLE CR: COLUMBIA RIVER SURFACE SEDIMENT
(MOLE PER CENT OF TOTAL AMINO ACIDS)

Size Fraction (microns)	Bulk	>5	2-5	1-2	0.5-1	0.2-0.5	<0.2
METO	0.2	0.2	0.2	0.3	0.4	0.4	0.2
ASP	13.8	12.7	13.6	13.6	13.5	13.4	13.5
THR	7.4	7.1	7.2	7.2	7.4	7.4	7.5
SER	7.9	8.0	8.2	7.9	7.9	7.8	7.9
GLU	11.5	10.8	11.1	11.0	10.9	11.4	11.8
GLY	14.2	14.1	14.4	14.3	14.3	14.1	13.7
ALA	11.2	10.9	11.1	11.3	11.5	11.7	11.5
VAL	6.7	7.0	6.9	6.7	6.7	6.7	6.4
MET	1.0	0.9	1.0	1.1	1.0	1.1	1.3
ILE	3.9	4.2	3.9	3.8	3.8	3.8	3.9
LEU	6.4	7.2	6.5	6.2	6.2	6.2	6.3
TYR	1.4	1.5	1.4	1.3	1.5	1.4	1.4
PHE	3.2	3.3	3.1	3.1	3.1	3.0	3.1
B-ALA	0.6	0.5	0.7	0.9	0.8	0.7	0.6
G-ABA	0.3	0.2	0.3	0.4	0.4	0.4	0.5
ORN	0.2	0.2	0.2	0.2	0.3	0.3	0.2
LYS	5.0	5.3	5.0	5.4	5.3	5.3	5.3
HIS	1.5	1.7	1.5	1.3	1.3	1.3	1.4
ARG	3.8	4.3	4.1	3.7	3.7	3.7	3.7

TABLE A-6

SAMPLE A: ANTARCTIC, BRANSFIELD STRAITS 121-136 CM
(NMOL/GM)

Size Fraction (microns)	Bulk	>5	2-5	1-2	0.5-1	0.2-0.5	<0.2
METO	85.6	18.1	33.8	70.3	95.7	113.0	321.8
ASP	3946.0	1042.0	2106.0	2266.0	4380.0	4381.0	13590.0
THR	1721.0	382.7	915.1	981.7	1873.0	1896.0	6011.0
SER	2401.0	625.1	1388.0	1692.0	2929.0	3025.0	8481.0
GLU	2185.0	537.5	1255.0	1240.0	2434.0	2479.0	8025.0
GLY	5837.0	1613.0	3319.0	3880.0	7016.0	7278.0	20141.0
ALA	2550.0	546.8	1510.0	1504.0	2903.0	2902.0	8984.0
VAL	1429.0	332.9	864.7	750.7	1517.0	1452.0	5108.0
MET	259.4	57.7	204.3	146.1	266.4	286.0	1056.0
ILE	906.7	198.2	600.9	457.8	897.0	872.6	3295.0
LEU	1281.0	258.5	926.1	628.4	1232.0	1198.0	4614.0
TYR	420.1	110.4	320.7	257.6	486.9	459.0	1476.0
PHE	742.9	155.7	545.5	369.8	728.2	698.8	2623.0
B-ALA	279.1	56.6	108.9	140.1	280.6	366.5	1194.0
G-ABA	136.3	12.1	48.4	69.5	131.5	182.2	615.5
ORN	128.2	31.2	64.2	113.2	202.9	210.9	623.4
LYS	1663.0	426.0	921.7	1048.0	2077.0	2225.0	6678.0
HIS	366.0	140.8	267.5	234.6	447.5	403.8	1263.0
ARG	1207.0	330.9	711.9	710.1	1488.0	1556.0	4863.0
Total	27544.3	6876.2	16111.7	16559.9	31385.7	31984.8	98962.7
Others	701.0	121.0	350.0	461.0	825.0	925.0	2498.0
Glucos-amine	943.5	171.5	325.7	467.8	788.6	1194.0	3970.0
Galactos-amine	1289.0	662.1	642.4	650.9	1381.0	1354.0	3834.0
NH3 peak	30390.0	8610.0	15750.0	21550.0	31010.0	33110.0	74450.0
Norleucin Recovery (%)	76.5	83.2	78.9	76.7	80.9	80.6	76.2

SAMPLE A: ANTARCTIC, BRANSFIELD STRAITS 121-136 CM
(MOLE PER CENT OF TOTAL AMINO ACIDS)

Size Fraction (microns)	Bulk	>5	2-5	1-2	0.5-1	0.2-0.5	<0.2
METO	0.3	0.3	0.2	0.4	0.3	0.3	0.3
ASP	14.3	15.1	13.1	13.7	13.9	13.7	13.7
THR	6.2	5.6	5.7	5.9	6.0	5.9	6.1
SER	8.7	9.1	8.6	10.2	9.3	9.5	8.6
GLU	7.9	7.8	7.8	7.5	7.8	7.8	8.1
GLY	21.2	23.5	20.6	23.4	22.4	22.8	20.4
ALA	9.3	7.9	9.4	9.1	9.3	9.1	9.1
VAL	5.2	4.8	5.4	4.5	4.8	4.5	5.2
MET	0.9	0.8	1.3	0.9	0.9	0.9	1.1
ILE	3.3	2.9	3.7	2.8	2.9	2.7	3.3
LEU	4.7	3.8	5.8	3.8	3.9	3.7	4.7
TYR	1.5	1.6	2.0	1.6	1.5	1.4	1.5
PHE	2.7	2.3	3.4	2.2	2.3	2.2	2.7
B-ALA	1.0	0.8	0.7	0.9	0.9	1.1	1.2
G-ABA	0.5	0.2	0.3	0.4	0.4	0.6	0.6
ORN	0.5	0.4	0.4	0.7	0.6	0.7	0.6
LYS	6.0	6.2	5.7	6.3	6.6	6.9	6.8
HIS	1.3	2.0	1.7	1.4	1.4	1.3	1.3
ARG	4.4	4.8	4.4	4.3	4.7	4.9	4.9