A

THESIS

entitled

THE GEOCHEMISTRY OF PHOSPHORITE CONCRETIONS FROM THE CONTINENTAL SHELF OFF MOROCCO

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JOHN MALCOLM McARTHUR

Applied Geochemistry Research Group
Imperial College

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ABSTRACT

Phosphorite Rock outcrops on the Moroccan continental margin as pelletal, conglomeratic and massive phosphorite. The geochemistry of each type has been examined by x-ray fluorescence and mass spectrometry, optical emission spectrography, and atomic absorption spectrophotometry, in order to assess the principal trace element controls and the influence of the environment of deposition on the element assemblage. Comparisons of element assemblages in offshore Moroccan, onshore Moroccan, and many world phosphorites are used to assess the influence of sub-aerial weathering on the element assemblage. The occurrence of uranium and rare-earth elements in phosphorites, and the substitutional chemistry of carbonate-apatite are treated in detail. The petrography and mineralogy of the phosphorites is presented and related to their mode and environment of deposition, and to their geochemistry.

R-mode cluster analysis and correlation coefficients have proven useful in identifying the main trace-element controls in offshore Moroccan phosphorites as iron oxide, iron sulphide and organic carbon, with carbonate-apatite playing a secondary role. Sea water is the source of most of the elements, including uranium and the rare earths. Detrital contributions are small.

Sub-aerial weathering of phosphorites enriches many trace elements, but reduces the concentration of the major substituting species within the carbonate-apatite lattice. The trace substituent uranium, and rare earths fractionation patterns appear unaffected.

Sulphur is shown to be an important lattice substituent in carbonate-apatite of marine origin. The extent of substitution of the major substituents in carbonate-apatite is shown to be virtually independent of depositional environment.

The offshore Moroccan phosphorites were formed by phosphatisation of calcareous sediments, reworking and further phosphatisation of which gave rise to pelletal phosphorite. Uplift and erosion of phosphatised carbonate sediments resulted in the conglomeratic phosphorites.

Low-magnesian calcite, dolomite, and glauconite of the disordered type are the principal accessory minerals, with minor amounts of illitic clay being present in most samples.

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

GENERAL INTRODUCTION

Phosphorite rock has been found in many parts of the world's oceans since its initial discovery on the Agulhas Bank off South Africa, by the Challenger Expedition of 1873-6 (Murray and Reynard, 1891). The existence of phosphorite on the Moroccan continental margin was first noted by Murray and Chumley in 1883, but it was not until 1968 that its occurrence in this area was shown to be widespread (Tooms and Summerhayes, 1968). This discovery was made during a systematic survey of the geology, structure, and sedimentology of the Moroccan continental margin, undertaken in 1967 by the Applied Geochemistry Research Group of Imperial College.

This thesis presents a detailed study of the geochemistry and mineralogy of the phosphorite rocks collected during the survey, and is a development of the basic geological and geochemical reconnaissance of the Moroccan continental margin rocks (both phosphatic and non-phosphatic) presented by Summerhayes (1970). This present work, and that of Summerhayes (1970) and Bee (Ph. D. thesis, in preparation) indicate that some of the phosphatic rocks are true phosphorites, containing more than 18% P_20_5 (Bushinsky, 1964), whilst others are phosphatic limestones. Most of the nodules are of Upper-Cretaceous or Eocene age, with some being of Miocene age.

The general characteristics of the phosphatic rocks occurring on the continental margin off Morocco, have been investigated only by Summerhayes (1970) in a large scale reconnaissance study of their geochemistry and petrography, using semiquantitative data. However, the geochemistry of the offshore phosphorites is still largely unknown, and as McConnell (1973) points out "our knowledge of the geochemistry of phosphorites is still quite meagre". This is because of a paucity of detailed mineralogical, petrographic, and chemical data on phosphorites, whether they be from the seafloor, or marine deposits now on land.

The reasons for this study were therefore (1) to provide comprehensive data on the geochemistry and mineralogy of these newly explored deposits; (2) to establish the influence on their geochemistry of environmental change subsequent to their formation; (3) to fully elucidate the factors controlling the mineralogy and geochemistry of the deposits; and (4) to investigate the substitutional chemistry of carbonate-apatite occurring in the deposits, as no such study has been made on seafloor phosphorites. The investigation of these areas was undertaken because at the conception of this study no such comprehensive study of a phosphorite deposit had been attempted, and up to the time of completion the writer is not aware of any attempts having been made to systematically investigate seafloor phosphorites. Only by such systematic investigation can their origin and mode of formation be explained. This thesis also presents the first application of multi-element statistical analysis of quantitative, reliable data in elucidating trace element controls in seafloor phosphorites. As shown in the text, this approach has proved useful and would probably merit application to other seafloor deposits in order to better understand their geochemistry.

The mineralogy of the deposits has been determined by a combination of chemical analysis for Mg, $C0_2$, $Si0_2$, and P_20_5, and semi-quantitative x-ray diffraction for quartz, dolomite and calcite. Petrographic examination has also assisted in determining the presence of these phases. Qualitative x-ray diffraction spectrometry has been used, together with chemical data, to define the clay mineralogy, as the clay mineral content was too small to merit extensive quantitative work.

The geochemistry has been investigated by a variety of analytical methods. Phosphorus was determined by classical analysis and Na and K by flame photometry. However, most of the analytical results were obtained by x-ray fluorescence spectrometry. Optical emission spectrography has been used in the analysis of acid soluble fractions of phosphorites, after evaporation of the fractions to dryness. Rare earth investigations were conducted by mass spectrography.

The geochemical controls in the samples were investigated by comparing the data obtained on differing sample types, and by comparison of element data with crustal and sea water element abundances in order to establish the influence of detrital material and sea water on the geochemistry. Also, as previously stated, multi-element statistical methods involving computation of correlation coefficients and the use of cluster analysis, has proved very useful in this context. The analysis of acid soluble fractions, and acid insoluble residues has been used in an attempt to confirm the results obtained by the previous methods, and to obtain information on adsorbed and absorbed ions on and in the various mineral phases. This approach has proved useful but requires refining before it can be usefully applied elsewhere. Finally, a theoretical assessment has been made of the control of the trace element assemblage by iron phases and organic carbon, and is shown to be in good agreement with the experimental results.

In the following pages the writer first describes the collection of the samples and the locations from which they were obtained and then presents, in chapter 2, a detailed investigation of the factors controlling the geochemistry of the group of elements selected for study. The following two chapters deal with the geochemistry of selected elements (R.E.E. and U) in greater depth. The R.E.E. were chosen for study because of the recent uncertainty concerning the La/Ce ratio in phosphorites which makes additional data on this topic useful, and also to assist in resolving the uncertainty concerning the source of R.E.E. in seafloor minerals (cf. Ehrlich, 1968; and Piper, 1972). In addition, the R.E.E. were investigated in order to assess the effects of weathering on R.E.E. fractionation patterns, and the influence of the environment of formation of the phosphorite on the levels of R.E.E. substitution in the carbonate-apatite lattice. Uranium was investigated in an attempt to assess its mode of incorporation in the carbonate-apatite lattice, and to establish the relationship between U and P_20_5, and the effect of weathering on the U concentration in carbonate-apatite, in view of the developing use of radiation detectors for subsea and aerial phosphorite prospecting.

Chapter 5 deals in detail with the substitutional chemistry of Sr, Na, CO_3^{2-} and SO_4^{2-} in the Moroccan and world samples.

In chapter 6, the mode of formation of the Moroccan phosphorites, and phosphorites in general is considered with respect to the various proposed mechanisms of formation.

Finally, chapter 7 presents a summary of the main conclusions presented in earlier sections, together with suggestions for future work.

As the main function of this thesis is to present a geochemical study of the Moroccan phosphorites, the subsidiary studies of their mineralogy and petrography are presented as appendices 2 and 3 and are followed by details of the analytical methods used in this study (appendices 4 - 9).

CHAPTER 1

SAMPLE LOCATION AND COLLECTION

Sample Location.

On the basis of geographical location, the samples may be classified into three main groups:

Group 1 Thirty-two rock samples from the Moroccan continental margin, referred to here as offshore samples, were obtained from twenty-six separate locations (fig. 1.1, table 1.1). A northern sample group, comprising massive phosphatised limestone and pelletal phosphorite, centres on a point 33.2°N, 9°W, located approximately 150 km WSW of Casablanca, and is approximately 40 km square. A southern group, comprising glauconitic conglomerates and massive iron rich phosphatic limestones, centres on a point 31.3° N, 10.3° W, located approximately 150 km NNW of Agadir, and is also approximately 40 km square. The two groups, which represent two distinct geological regions, are approximately 250 km apart.

Group 2 comprises nine phosphate rock samples, here referred to as onshore samples, which were obtained from three separate deposits of phosphate within Morocco, two deposits being near Khouribga, the other approximately 100 km away near Benguerir (fig. 1.1).

Group 3 comprises twenty-three samples obtained from nine land phosphate deposits of marine origin, and six seafloor deposits. These are termed world samples (table 1.2).

Sample Collection.

The offshore samples were collected during two cruises to the coast of Morocco on the RRS John Murray during 1968 and 1969.

The samples were obtained by dredging with a standard rock dredge fitted with a 5 cm mesh cable bag. Most of the samples were collected from depths between 100 m and 400 m, with one sample (883) being dredged from 890 m. Dredge stations were operated where seismic reflection profiles and precision depth recordings indicated outcropping on the seabed. Each dredge station was limited to 0.4 km in length in order to obtain a reasonably accurate sample location. Samples numbered 134-157 inclusive were collected during the first cruise, the remainder during the second (for sample numbering scheme see appendix 1).

The offshore Moroccan samples analysed here were selected as visually representative of each dredge haul containing phosphorite. Where more than one type of phosphorite was found in a single dredge haul, representative specimens of each type were selected. Large specimens were chosen in preference to small in order to minimise the effects of exposure to seawater on the geochemistry, and provide a more homogeneous sample for analysis. Where samples of boulder size were obtained, representative pieces were chosen after the boulders had been reduced to hand size fragments.

In preparing all samples for analysis the outer surfaces and encrustations were removed to a depth of up to approximately 2 cm with a diamond coated phosphor-bronze rock cutting wheel, and the remainder was then crushed to coarse sand size with a tungsten carbide anvil. The resulting material was ground to minus 80 mesh in an agate Tema mill. The residual coarse fraction from this process was reduced to minus 80 mesh by hand grinding in a porcelain pestle and mortar.

Onshore samples, which were obtained as screened and water washed sands, were subjected only to the last two stages of this preparation.

The sample preparation used here has been in general use within the Applied Geochemistry Research Group at Imperial College for a number of years, and appears to introduce no observable contamination for the elements examined in this thesis, at the levels examined.

Fig. 1.1

Moroccan sample locations

■ Onshore

× Offshore

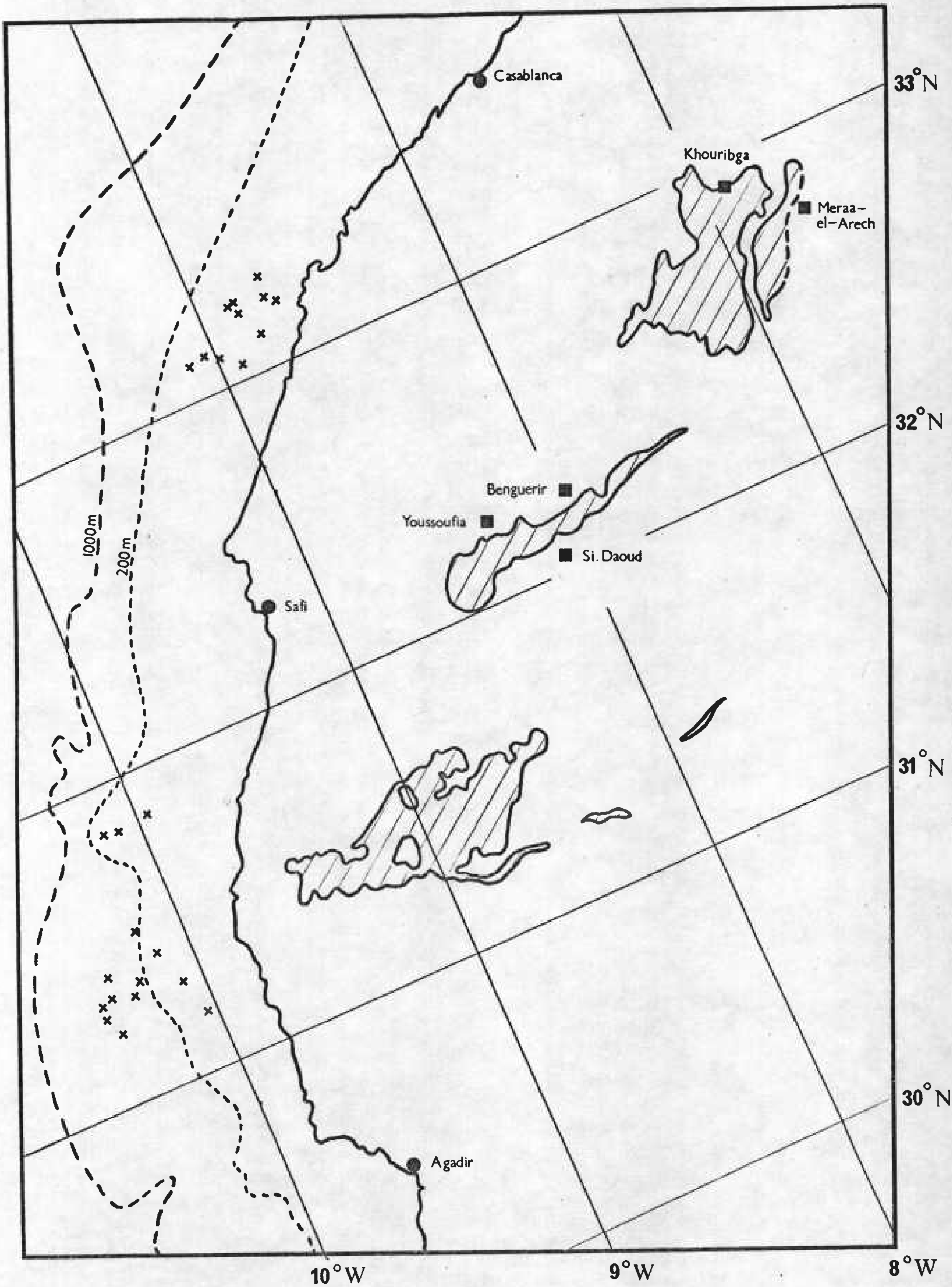

Casablanca
33°N
Khouribga
Meraa-el-Arech
32°N
Benguerir
Youssoufia
Si. Daoud
1000m
200m
Safi
31°N
30°N
Agadir
10°W
9°W
8°W

TABLE 1. 1

Locations and depths of offshore

Moroccan samples

Sample Number	Latitude °N	Longitude °W	Depth (Corrected Metres)
Northern Province			
135	33° 13.5′	8° 53.0′	113
136	33° 12.6′	8° 51.6′	113
139	33° 10.3′	8° 43.7′	76
959	33° 05.8′	9° 09.8′	126
966	33° 02.6′	8° 56.8′	92
982	33° 06.4′	9° 00.1′	109
988	33° 07.2′	8° 48.7′	90
1004	33° 07.1′	9° 04.4′	119
1016	33° 12.1′	8° 44.3′	87
1022	33° 14.1′	8° 52.0′	110
1038	33° 16.8′	8° 43.5′	102
Southern Conglomerates			
152	31° 21.7′	10° 05.4′	130
154	31° 20.4′	10° 16.4′	340
155	31° 19.5′	10° 18.9′	433
833	31° 11.3′	10° 04′	124
847	31° 15.4′	10° 24.6′	305
865	31° 26.1′	10° 09.7′	139
877	31° 31.0′	10° 12.3′	151
883	31° 25.3′	10° 22.0′	888
896	31° 51.0′	10° 07.5′	136
898	31° 51.7′	10° 10.2′	143
Southern Non Conglomerates			
148	31° 17.3′	10° 25.3′	288
156	31° 20.5′	10° 23.4′	480
157	31° 19.9′	10° 24.7′	302
847	31° 15.4′	10° 24.6′	305
893	31° 52.2′	9° 59.7′	139

TABLE 1.2

Locations and descriptions of
world samples

ONSHORE PHOSPHATES

LOCATION	NO. OF SAMPLES	SAMPLE DESIGNATION
AUSTRALIA	8	PC/1(1) - PC/7
SAUDI ARABIA	2	PC/8 - PC/9
JORDAN	1	-
SENEGAL	1	-
INDIA	1	PC/10
U.S.A.	3	U.S.G.S. 22, 41, 47
NEW ZEALAND	1	CLARENDON

PC/1(1), shelly sand phosphorite, Monastery Creek, Burke River Outlier, Duchess, Queensland.
PC/1(2), shelly sand phosphorite, Monastery Creek, Burke River Outlier, Duchess, Queensland.
PC/2, phosphatised limestone, Roufous Creek, Lady Annie Deposit, Queensland
PC/3, shelly conglomerate, Roufous Creek, Lady Annie Deposit, Queensland.
PC/4, fine grained silty phosphorite, D-tree Deposit, Galah Creek, Queensland.
PC/5, sandy phosphorite, D-tree Deposit, Galah Creek, Queensland.
PC/6, pelletal phosphorite, Burke River Outlier, Duchess, Queensland.
PC/7, pelletal phosphorite, Burke River Outlier, Duchess, Queensland.
PC/8, friable conglomerate, West Thaniyate Deposit, N. Saudi Arabia.
PC/9, friable conglomerate, West Thaniyate Deposit, N. Saudi Arabia.
PC/10, black siliceous phosphorite, Partibba Deposit, Mussoorie, U.P., India.
JORDAN, phosphatic limestone, Amman, Jordan
CLARENDON, flocculent phosphorite, Clarendon Formation, New Zealand.
SENEGAL, no information available
U.S.G.S. 22, phosphorite from Mead Peak phosphatic shale member, Phosphoria Formation, Montana, U.S.A. (Gulbrandsen, 1966).
U.S.G.S. 41, pelletal phosphorite, Mead Peak phosphatic shale member, Phosphoria Formation, Idaho, U.S.A. (Gulbrandsen, 1966).
U.S.G.S. 47, microphanitic phosphorite, Mead Peak phosphatic shale member, Phosphoria Formation, Idaho, U.S.A. (Gulbrandsen, 1966).

SEAFLOOR PHOSPHATES

LOCATION	NO. OF SAMPLES	SAMPLE DESIGNATION
CAMPBELL PLATEAU, N.Z.	2	D134, F127
TASMAN SEAMOUNT, N.Z.	1	Z1037
AGULHAS BANK, S. AFRICA	1	AGULHAS
CALIFORNIAN CONTINENTAL MARGIN, U. S. A.	1	CALIFORNIAN NODULE
MABAHIS BANK, SAUDI ARABIA	1	MABAHIS

D134, phosphatised foraminiferal ooze, Snares Depression, Campbell Plateau, off New Zealand (Summerhayes, 1969).

F127, phosphatised foraminiferal ooze, Pukaki Saddle, Campbell Plateau, off New Zealand (Summerhayes, 1969).

Z1037, phosphatised foraminiferal ooze, Tasman Seamount, Tasman Sea, West of New Zealand (Summerhayes, 1969).

AGULHAS, glauconitic conglomerate, Agulhas Bank, off Southern South Africa (Parker and Siesser, 1972).

CALIFORNIAN NODULE, pelletal phosphorite, Forty Mile Bank, Californian Borderland (Dietz, Emery and Sheppard, 1942).

MABAHIS BANK, conglomeratic phosphorite, Mabahis Bank, off S. E. Saudi Arabia (Gerork'yan and Chugunnyy, 1969).

CHAPTER 2

GENERAL GEOCHEMISTRY

Introduction

In this chapter the geochemistry of the Moroccan phosphorite deposits is examined in detail in order to establish the source of the elements they contain, the partition of these elements between the mineral phases present, the major factors controlling the partitions, and the effect of weathering on the trace element assemblage. Such a detailed examination of seafloor phosphorites was thought necessary as it does not so far appear to have been attempted. Gulbrandsen (1966) provides a fairly comprehensive compilation of data on the phosphorites of the Phosphoria Formation. However, this deposit, though of marine origin, is now on land, and may have been subject to weathering. Also, the trace element data is only semi-quantitative. These two factors severely limit the value of any conclusions drawn regarding the original trace element assemblage. Likewise, a study of a similar deposit in Saudi-Arabia, undertaken by Reeves and Saadi concurrently with this research, has also proved of only limited value in elucidating element associations, probably because of extensive modification of the deposit by sub-aerial weathering.

This present study considerably improves upon and modifies the work of Summerhayes (1970) and other workers in elucidating the trace element controls in phosphorites, and also provides a great deal of good analytical data on a virtually unknown phosphorite occurrence.

The methods of investigation adopted for this study were evolved because the separation of a pure carbonate-apatite phase from these samples was found to be impossible (see appendix 4). This is almost certainly due to the cryptocrystalline nature of the samples. .

This chapter is divided into several sections for clarity of presentation. In Section A a comparison is made between phosphorite from each province. This has enabled conclusions to be drawn regarding the importance of the major phases, such as iron oxides, organic matter, clays, etc., in controlling the trace element assemblage, as each sample type contains variable amounts of each of these phases. This, together with computer calculated product-moment correlation coefficients and R-mode cluster analysis, presented in Section C, has enabled a fairly clear idea of major phase control of the trace elements to be obtained. In Section B a comparison of trace element abundances in the samples with those of crustal abundance has been used to evaluate the detrital contribution to the samples, and comparison with seawater abundances has provided information regarding the supply of elements from seawater. Section D presents the analysis of acid soluble fractions and acid insoluble residues of the samples which have been used to confirm element associations found by other methods, and to assess the relative contributions of elements adsorbed onto, and absorbed into, the mineral phases. Section E examines the role of iron phases and organic material in the government of trace element assemblages in general, and considers the theoretical aspect of such control. The conclusions of the section are applied to the Moroccan samples in support of the work presented in other sections. Finally, Section F examines the influence of glauconite on the geochemistry of the southern samples, and is followed by a summary of this chapter together with the final conclusions drawn.

The presence of many elements, such as the R.E.E., As, V, Mn, Sr, and Cr, in phosphorite rock in concentrations significantly above crustal abundance has frequently been reported (Swain, 1962; Cruft, 1965; Gulbrandsen, 1966; Summerhayes, 1970). A summary of published analysis is presented in table 2.1. High element concentrations have been ascribed to a variety of controlling factors, for example, the incorporation of R.E.E. into the carbonate-apatite lattice as a replacement for Ca^{2+} (Arrhenius and Bonatti, 1965; Cruft, 1965). Other elements which have been reported as occurring within the lattice of carbonate-apatite are As, Ba, Co, Cr, Cu, I, K, Mg, Mn, Ni, Pb, Si, Sn, Sr, S, U, V, Y, and Zn (McConnell, 1953; Arrhenius, Bramlette and Piccioto, 1957; Altschuler, Clarke and Young, 1958; Deer, Howie and Zussman, 1962; Cruft, 1965; Whippo and Murrowchick, 1967; Parker and Toots, 1970; Summerhayes, 1970; Reeves and Saadi, 1971; McConnell, 1973). Control of Zn, Cu, Ni, and V by organic carbon in Phosphoria Formation phosphorite has been suggested by Gulbrandsen (1966) and confirmed by Summerhayes (1970), who also adds Cr. Degens (1965) states that Ni, Co, Cu, and Pb are often considerably enriched in the pyritic and organic phases of sediments and may therefore occur in pyritic and organic inclusions within phosphorites. Manganese is well known for its association with iron oxide, which occurs in many Moroccan offshore samples and has also been found associated with the detrital fraction of Saudi Arabian phosphates by Reeves and Saadi (1971), who also suggest that Ba in the samples is controlled by silica precipitation. Stow (1969) has shown that in Florida Phosphates As is controlled by iron oxides, and to a lesser extent by organic carbon. Finally, Krauskopf (1956) has shown Pb, Cu, and Zn are easily adsorbed from solution by phosphates.

The above discussion serves to illustrate the wide variety of element controls possible in phosphorites. The major influences on the element assemblage are probably supply by detrital material, adsorption onto and complexing with organic material, incorporation into the carbonate-apatite lattice, coprecipitation or adsorption onto major authigenic phases such as iron oxides, calcite, and dolomite, and precipitation as sulphides in low Eh environments.

Analytical Methods

Unless otherwise stated, the element data presented in this thesis were obtained by x-ray fluorescence spectrometry (appendix 6). Phosphorus, magnesium, and uranium were also determined by other methods as a check on the reliability of the x-ray fluorescence analysis, P by classical analysis, Mg by atomic absorption spectrophotometry, and U by gamma counting. The agreement between the analytical techniques was excellent, being ± 5% for P; ±12% for Mg; and ± 3% for U.[*]

Sodium was determined by flame photometry on acid soluble fractions of the samples, as no significant contributions to Na were expected from phases other than carbonate-apatite. Potassium was determined on the same fractions, as a check on clay solubility (appendix 8).[*] Acid soluble fractions of the samples were analysed for elements other than Na and K by optical emission spectrography of the evaporated residues (appendix 7).[‡] Acid insoluble residues were analysed by x-ray fluorescence spectrometry (appendices 6 and 7).[×] Rare earth elements were determined by mass spectrography (appendix 9).[⊙] The analysis of glauconite was performed by atomic absorption spectrophotometry, after dissolution of the glauconite in an $HF/HClO_4$ acid mixture.

[*] See Addendum 1, 2, and 9.

[‡] " " 1.

[×] " " 3, 4, 5.

[⊙] " " 6.

SECTION A

Comparative Geochemistry of Offshore Moroccan Phosphorites

The mean values for the major and trace elements, and major mineral phases, from each province are presented in table 2.2. In comparing the element and mineral data from each province the mean values of each province are compared to the means of the northern phosphatised limestones. These samples are used as an arbitrary reference because of the closeness and even distribution of element and mineral data about the means compared to values for other provinces. Comparisons are not made to worldwide phosphorite averages because comprehensive mineralogical and petrographic data are available for the Moroccan samples, but for the worldwide phosphorite averages such ancillary data are lacking.

A comparison of the sample means for each element and mineral phase with those of the reference samples clearly shows significant differences between sample types. Table 2.3 presents a summary of the differences, which have been arbitrarily divided into groups; viz. those variables depleted or enriched by a factor of more than two, those definitely different, but to a lesser degree, and those not significantly different. Where the variability of the data was too great for meaningful assignment to one of these groups, the variable has been classified as being not significantly different.

The offshore southern samples contain more clay (K_20, $A1_20_3$), detrital materials (quartz,) , except for quartz in the southern pebbles, and Fe_20_3, than the reference samples. The trace elements Rb, Ba, V, Pb, As, and Mn are also enriched, suggesting the clays, other detritals and Fe_20_3 are important controls for these elements. That Ti may well be contained within the clay minerals in all Moroccan samples is indicated by fig. 2.1 which shows a very good relationship to exist between Ti and Al in these samples. Titanium is particularly high in the glauconitic conglomerates and matrix samples where it probably occurs within the glauconite lattice (Bentnor and Kastnor, 1965).

The high Cr content of these samples and the increased Y in matrix samples suggests this mineral could also be partially controlling Cr and Y. A similar glauconite-Cr association has been shown to occur in the sediments from the Moroccan continental margin (Summerhayes, 1970). In contrast, Bentnor and Kastnor (1965) found no such association in glauconite of similar age (Upper Cretaceous - Recent) from Israel, nor in a series of glauconites, ranging in age from Cambrian to Recent, from the U. S. A.

The enrichment of pyrite and organic carbon in the northern samples as a whole, relative to the onshore and southern samples, together with enrichment of Cu suggests these phases control this element, either directly by organic complexing, or indirectly by influencing Eh conditions, possibly causing precipitation of Cu as sulphide.

Carbonate-apatite seems to exert little influence on the trace element composition, unlike igneous apatite which often contributes quite markedly to the element assemblage of its host rocks.

Evidence is presented in chapter 5 to show that sub-aerial weathering of phosphate rock results in a lowering of the substitutional Sr^{2+}, Na^{+}, CO_3^{2-}, and SO_4^{2-} content of carbonate-apatites. The depletion of the first three of these species in the pebbles is probably a result of their exposure to sub-aerial weathering during their formation, and is thought to show that their formation was not accomplished solely within the marine environment. However, as the depletion is only very slight, though definitely significant, their period of exposure to weathering may have been relatively short. The remaining trace elements were probably little affected by this short exposure. The substitutional Na^{+}, Sr^{2+}, SO_4^{2-}, and CO_3^{2-} content of the southern matrix samples are close to those of the northern phosphatised limestones and are very similar to many phosphorites presently found in marine environments from several world locations. This indicates that the matrix was phosphatised in situ, and is not an advanced weathering product of the phosphate rock which formed the southern pebbles. Were this the case the substituents in the matrix would show some depletion relative to the northern phosphatised limestones. The enriched P_20_5, Na, $S0_4^{2-}$, Y, and Sr, and the depletion in calcite in the pelletal samples (table 2.3) is in keeping with their proposed mechanism of formation by phosphatisation and reworking of carbonate sediments (appendix 2). Disaggregation of a phosphatised sediment would result in re-exposure to the phosphatising medium, in this case sea water, and allow further phosphatisation of the calcite in the sediment, together with greater substitution of Na^{+}, Sr^{2+}, and SO_4^{2-}. That the lattice carbonate does not fall below 8%(1) during this re-exposure, supports the writer's suggestion that phosphatisation does not proceed to completion in a marine environment but stops at approximately 90% replacement of calcite by phosphate. The greatly increased Y in the pelletal samples may be an adsorption phenomenon, re-exposure of the disaggregated sediment to seawater causing increased phosphatisation and concomitant increase in substitution of Y for Ca.

(1) In this text lattice carbonate is expressed as a percentage by weight of the carbonate-apatite lattice which consists of CO_3^{2-}. All other data are expressed on a whole rock basis.

According to Parker and Toots (1970) this phenomenon of secondary enrichment is responsible for the high Y often associated with fossil bone material. The low V may be due to release of this element to the interstitial water of the sediment during early diagenesis and its loss, before reincorporation, during reworking.

The factors controlling the remaining elements (U, Zn, I, Ni) are not clear from the comparisons undertaken.

The effect of weathering on the onshore samples is seen by their depletion in K_20, calcite, organic carbon and the absence of detectable pyrite, together with a reduction in the carbonate-apatite lattice substituents, Sr^{2+}, Na^{+}, and CO_3^{2-} (table 2.3). However, the effects of the screening and water washing these samples received, prior to their analysis (appendix 2) may contribute to the depletion of the former phases. The low Fe content probably reflects the low Fe present or supplied to the original deposit. These small amounts of Fe may be bound within clay minerals, and may partially control the Mn. The origin of the enriched group Zn, Y, Ba, Cr, V, and I, is difficult to explain. Ba is possibly present as barite, the remainder possibly being within the weathering residue incorporated into clays or carbonate-apatite. The less enriched group of Cu, Ti, and Ni occurs with Al_20_3 and Rb suggesting they are also probably in the clay minerals.

Having compared the various provinces with regard to element and mineral abundances, some confirmation of the suggested element controls can be gained concerning the southern pebble samples by comparing the pebble samples from each conglomerate. The pebbles from sample 898, in most instances, are higher in P_20_5, Na, Sr, and are also higher in organic carbon and lower in Fe_20_3 than the remaining pebbles, the latter probably being due to a shorter exposure to an oxidising environment during formation. The clay and detrital contents are similar (table A.6.4). Comparing the two sets of samples shows that Mn is depleated, and U and V are enriched in the low Fe samples. This supports the suggested control of Mn by Fe_2O_3, and may indicate control of U and V by organic carbon, the carbonate-apatite lattice, or both.

Summary

The principal associations revealed by the intersample comparison are summarised below. It must be stressed that the associations found do not necessarily mean that of two apparently associated elements, one directly controls the other. Indirect or chance association is possible, for example associations may be caused by the variations in the proportions of major mineral phases and may be quite unrelated to any of the varying phases. However, the associations do provide a useful guide for further study.

Ti	associates with	clays and glauconite
Rb, Ba, Pb, V, As, Mn	associate with	clays, detritals, and iron oxides
Mn	associates with	iron oxides in southern pebble samples
Cr, Rb, and possibly Y	associate with	glauconite
Cu	associates with	organic carbon and pyrite in northern samples
Na, Sr, SO_4^{2-}, lattice CO_3^{2-}	associate with	carbonate-apatite in all samples
Y	associates with	carbonate-apatite in pelletal samples

Fig. 2.1

The variation of Ti with Al

in Moroccan samples

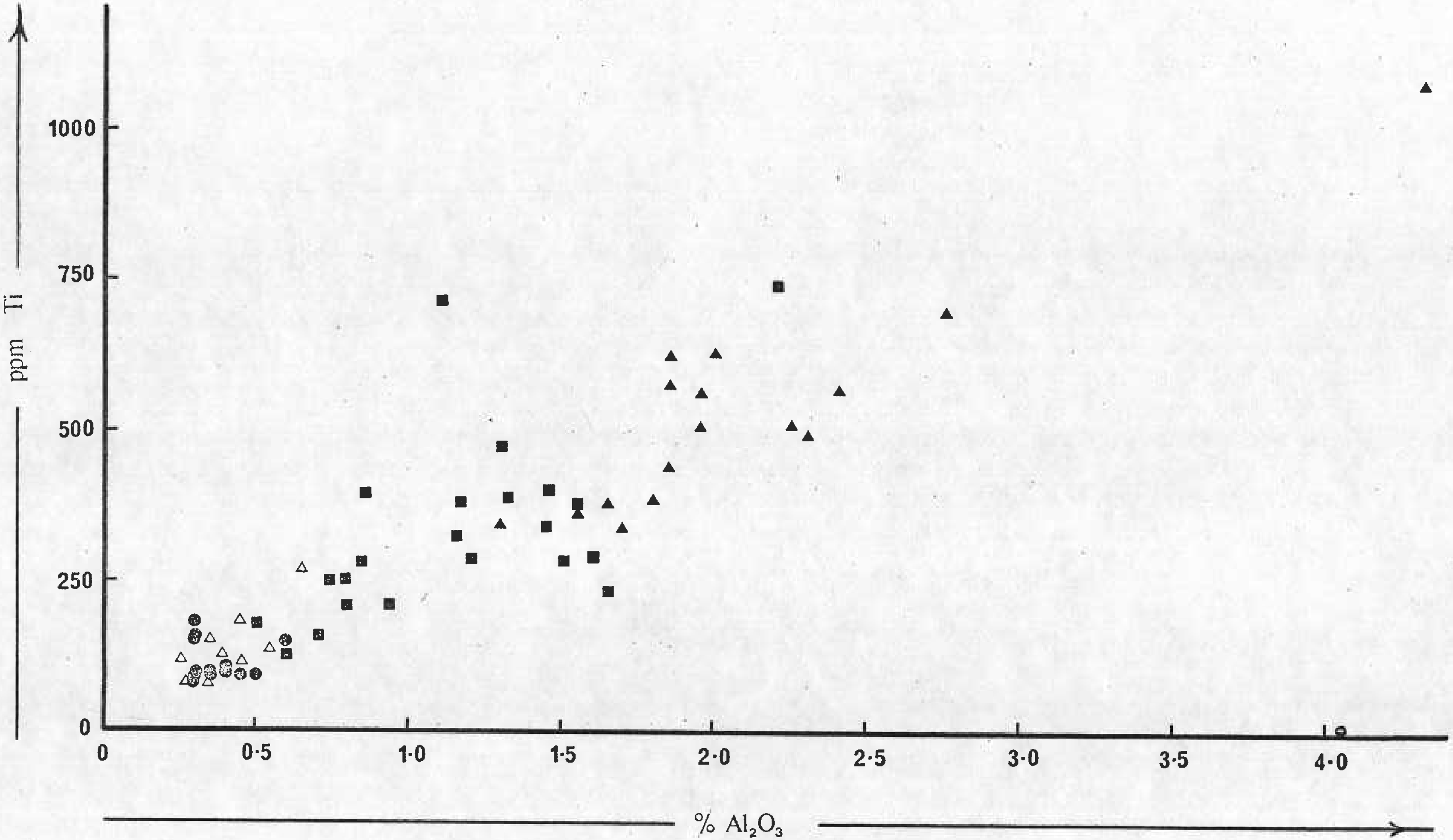

ppm Ti
1000
750
500
250
0
0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
% Al_2O_3

TABLE 2.1

Trace element abundances in phosphorites

sea water and the earths crust

ELEMENT	I	II	III	IV	V	VI
Y	33	0.13	-	0 - 50	30	pelletal ,onshore
Sr	375	81,000	1,900	1,800 - 2,000	1,000	pelletal
Rb	90	1,200	-	0 - 100	10	glauconitic
Zn	70	50	90	4 - 350	50	onshore
Cu	55	9	22	0 - 400	15	onshore
Ni	75	66	13	2 - 30	30	onshore
U	1.8	33	190	8 - 1,300	150	
Ti	4,400	10	476	100 - 3,000	400	onshore , northern
V	135	19	167	20 - 500	80	pelletal
Cr	100	2	285	7 - 1,600	30	onshore , glauconitic
Mn	950	4	428	0 - 10,000	100	onshore
Ba	425	210	100	1 - 1,000	50	northern
Pb	13	0.3	-	0 - 100	6	glauconitic
I	0.5	640	24	0 - 280	30	
As	1.8	26	21	0 - 190	30	onshore, southern pebbles

TABLE 2.2

Mean element concentrations and mineral contents of each sample province

SAMPLE PROVINCE	K_2O	Al_2O_3	P_2O_5	Fe_2O_3	Quartz	Calcite	Dolomite	Pyritic S	Organic Carbon	Na	[1] Lattice CO_3^{2-}	Lattice SO_4^{2-}	Y	Sr	Rb	Zn
Onshore Moroccan Samples	0.07	0.41	31.0	0.16	2.4	1.6	1.6	<0.1	0.15	0.48	4.6	1.92	230	950	15	240
Northern Phosphatised Limestones	0.15	0.37	18.3	0.54	1.8	26.2	1.7	0.44	0.61	0.74	8.5	1.50	23	1260	8.5	42
Northern Pelletals	0.13	0.36	26.2	0.77	2.0	8.0	1.5	0.56	0.76	1.04	8.4	2.35	130	2000	8.3	56
Southern Matrix Samples	2.10	1.95	16.5	8.6	3.1	9.0	1.1	<0.1	0.32	0.73	8.2	1.50	42	1130	50	40
Southern Pebble Samples	0.41	1.12	18.3	10.7	1.6	7.9	4.1	<0.1	0.21	0.68	7.8	1.50	16	940	18	54
Southern Conglomerates	1.75	2.00	16.2	8.7	4.6	6.7	2.8	<0.1	0.34	0.60	7.9	1.35	29	1090	47	49

[1] Expressed on a pure carbonate-apatite basis

TABLE 2. 2 Continued

SAMPLE PROVINCE	Cu	Ni	U	Ti	V	Cr	Mn	Ba	Pb	I	As
Onshore Moroccan Samples	31	42	118	140	115	154	27	49	5	64	<6
Northern Phosphatised Limestones	16	30	261	116	57	32	96	<4	5	32	20
Northern Pelletals	23	30	88	100	26	42	72	<4	6	19	17
Southern Matrix Samples	14	23	140	446	85	76	138	37	18	28	40
Southern Pebble Samples	13	31	74	320	135	28	196	20	9	34	77
Southern Conglomerates	14	24	157	520	90	68	125	72	19	28	42

TABLE 2.3

Enrichment and depletion of Moroccan samples

compared to the northern phosphatised limestones

	Onshore Samples	Pelletal Phosphorite	Southern Conglomerates	Southern Matrix Samples	Southern Pebbles
Enriched by a Factor >2:1	Y, Zn, Ba, Cr, V, I.	Y.	K_2O, Al_2O_3, Quartz, Fe_2O_3, As, Rb, Ti, Ba, Pb, Cr.	K_2O, Al_2O_3, Fe_2O_3, As, Rb, Ti, Cr, Ba, Pb.	K_2O, Al_2O_3, Fe_2O_3, As, Rb, Ti, Ba, Mn, V, Dolomite.
Enriched	Al_2O_3, P_2O_5, Rb, Cu, Ni, Ti.	Lattice Sulphate, P_2O_5, Na, Sr.	Mn, V, Dolomite.	Mn, Y, V, Quartz.	Pb.
Not Significantly Different	Quartz, Dolomite, Pb, Lattice Sulphate.	K_2O, Al_2O_3, Ba, Fe_2O_3, U, Rb, CO_3^{2-}, Ni, Zn, Cu, Ti, Cr, Mn, Pb, I, As, Dolomite, Pyrite, Organic C, Quartz.	Zn, Ni, I, U, Y, Lattice Sulphate.	Dolomite, Na, Zn, Ni, U, Sr, I, Lattice Sulphate, Lattice CO_3^{2-}	Lattice Sulphate, Ni, Zn, Cr, I, Y, Quartz, P_2O_5.
Depleted	Na, K_2O, Sr, U, Lattice CO_3^{2-}.		P_2O_5, Organic C, Na, Sr, Cu, Lattice CO_3^{2-}.	P_2O_5, Organic C, Cu.	Na, Sr, U, Cu, Lattice CO_3^{2-}.
Depleted by a Factor <1:2	Calcite, Pyrite, Organic C, Fe_2O_3, Mn, As.	Calcite, V.	Pyrite, Calcite,	Pyrite, Calcite.	Organic C, Pyrite, Calcite.

NB. Lattice Carbonate is expressed on a pure carbonate-apatite basis, and was not recalculated for inclusion in this table since it is examined in detail in chapter 5.

SECTION B

CONTRIBUTIONS TO THE ELEMENT ASSEMBLAGE OF OFFSHORE MOROCCAN PHOSPHORITES FROM SEAWATER AND DETRITAL MATERIAL

On the basis of their chemical and mineralogical analysis, the Moroccan offshore samples contain less than 10% detrital material, or less than 6% if quartz is excluded on the assumption that it does not significantly contribute to the overall element assemblage. Comparing the sample element abundances with crustal abundances (tables 2.1 and 2.2) it is clear that this small percentage of detrital material, if of average crustal abundance, can significantly contribute only to the Ti, Mn and Ba content of the samples, and to the Rb content of all but the glauconitic samples. Detrital material may also contribute up to 30% of the Cu and Cr and up to 20% of the Ni in all samples, and approximately 30% of the V in pelletal samples, but cannot account for any significant part of the Y, Sr, Zn, U, Pb, I, S, or As, or V in non-pelletal samples. It therefore seems likely that Ti, Rb and Ba are largely detrital in origin and probably associated with clay minerals (fig. 2.1), with additional amounts of these elements being incorporated from seawater into the glauconite within the southern conglomerates. If the glauconite is a replacement product of other detrital clay minerals, the entire contents of these elements could originally have been detrital. However, the uniform size, distribution, and shape, particularly the frequent occurrence of glauconite grains which obviously formed within foraminiferal tests, all suggest either nucleation and growth around now replaced clays of very small particle size, replacement of non-clay material, or perhaps spontaneous nucleation, as their method of formation. Thus a considerable part of the Ti, Rb, and probably Ba, they contain is probably derived from seawater, or possibly pore water, by absorption and adsorption during glauconite formation.

In the southern samples Mn may have a partially detrital origin, but appears to be controlled mainly by the Fe_2O_3, whereas in the northern samples it may be wholly detrital, as Fe_2O_3 in these samples is generally very low.

The comparison of element abundances to crustal abundances may, however, be misleading as it assumes that the detrital material supplied to the deposits contained elements at average crustal abundance levels. As a check on the validity of this assumption the element abundances have therefore been compared to their abundances in seawater (table 2.4). Following Nicholls (1967), enrichment or depletion by less than a factor of two between phosphorites and crustal abundance is not considered significant. A factor of 10,000 is used for comparisons of seawater abundances with those of crustal abundance after Tooms et al. (1969) and Summerhayes (1970). The results of the comparison are presented in table 2.4.

A comparison of element abundances in seawater, and in phosphorites, after both are ratioed to an arbitrary reference (crustal abundance), indicates two main groups of elements, those enriched in both seawater and phosphorites, relative to crustal abundance, and those depleted in both (table 2.4). The similarity of the groupings is striking (table 2.4). A large number of elements depleted in seawater are also depleted in the phosphorites, whilst another group is enriched in both. This supports the suggestion that seawater may be the major source of supply for these elements.

Comparison of Element Abundances in Moroccan Phosphorites to Worldwide Phosphorite Averages

Compared to worldwide phosphorite averages the element concentrations in the Moroccan phosphorites appear to be low (tables 2.1 and 2.2) though for the majority of elements the onshore samples are less depleted than the offshore samples.

In the northern phosphatised limestones Sr, Cr, and Mn are well below worldwide averages, whilst Zn, Cu, V, Ti, and Ba are all significantly down. Except for enrichment of Y and Sr, compared to worldwide averages, the pelletal samples are similar. These depletions may be due to the low content of scavenging phases, such as Fe_20_3, and the very low detrital content of these samples. The enrichment of Y and Sr is probably related to the re-exposure of these samples to seawater during their formation (appendices 2 and 3). In the onshore samples Y, Zn, and Cu are also enriched, whilst Ni is enriched in all samples. The enrichment of Ni in the offshore samples may be due to its concentration by organic carbon and pyrite (chapter 2, section E), phases which are virtually absent from many of the deposits upon which Swain's (1962) data is based. Why Cu and Zn are not also enriched is not clear.

The enrichment of As in southern samples compared to Swain's data, is probably related to the high concentrations of Fe_20_3 they contain.

The overall depletion in trace elements within the Moroccan samples may be due to the low detrital material they contain and in the northern samples to the virtual absence of scavenging phases. However, the fact that the onshore samples are less depleted than the offshore samples in nearly all elements, and are actually enriched in Y, Zn, Cu, and Ni, suggests that sub-aerial weathering of phosphorite rock produces an enrichment in their trace element content.

Summary

Detrital material is probably the main source of Ti, Ba, and Rb in the offshore samples, excepting the glauconitic samples where appreciable amounts of these elements may be derived by adsorption or absorption from seawater into glauconite. Manganese may have a partially detrital origin in the southern samples, but is probably wholly detrital in the northern samples. Detrital contributions to the Cu, Ni, and Cr content of the samples may occur, particularly in the southern samples where detrital material is much more abundant than elsewhere. The principal source of Sr, U, As, Zn, V, S, I, Cu, Ni, Pb, Cr, Y, and possibly part of the Mn, is seawater. The general level of element abundances in Moroccan samples is low compared to worldwide averages, and is probably partially due to a) the low level of trace element scavenging in the northern samples, b) the absence of organic carbon and pyrite in the southern samples due to the oxidising nature of the environment, c) the fairly low detrital content of the samples, particularly the northern samples, and partially because weathering of phosphorites appears to increase the trace element abundances of most elements originally present in the rock, and all Moroccan samples have been compared to data on weathered phosphorite deposits (Swain, 1962).

TABLE 2.4

A comparison of element enrichments
and depletions in Moroccan Phosphorites
relative to crustal abundances
and seawater abundances

Phosphorite Enriched>2:1	Sea Water Enriched>10:1	Phosphorite Depleted>2:1	Sea Water Depleted>10:1	Phosphorite "Normal"
Sr	Sr	Cu	Cu	
U	U	Ni	Ni	
I	I	Ti	Ti	
As	As	Ba	Ba	
		Mn	Mn	
S	S	Cr	Cr	
			Zn	Zn
			Ce	Ce
Pb			Pb	
	Rb			Rb
			Y	Y
			V	V

SECTION C

CORRELATION COEFFICIENTS AND R-MODE CLUSTER ANALYSIS OF MOROCCAN PHOSPHORITE DATA

Introduction

In order to examine inter-element associations on a more objective basis than inter-province comparison, or comparisons to crustal and seawater element abundances, product-moment correlation coefficients have been calculated for all pairs of elements and major mineral phases. Computation was carried out using an IBM 7094 computer using the program Taxon 2 (Howarth, 1966). The data for each sample province were treated separately. In addition, the computed correlation matrices were used to perform R-mode cluster analysis, which has assisted in interpreting the correlation matrices.

Following the approach of Chave and McKenzie (1961) the assumption is made that elements which are within the same mineral will correlate well, and also cluster together in the R-mode analysis. However, Chayes (1960, 1962) has pointed out that in closed data systems spurious correlations, particularly negative ones, are common, and especially so where the number of phases is small. In order to minimise the importance of such spurious correlations, negative correlations are not used. Virtually all the correlations discussed below are thought to be geologically meaningful, and are significant at the 1% level for the southern samples and at the 5% level for the onshore and northern samples, owing to their small number.

CORRELATION COEFFICIENTS

Onshore Samples - Table 2.5.a

Strong correlations exist, at the 5% level, between K, Fe, Al, Ti, quartz and dolomite. Both Ni and V correlate fairly strongly with Fe and K, with Ni also correlating with Al. Chromium shows a lesser correlation with Fe, and Rb a lesser correlation with K. Uranium and iodine show some correlation with phosphorus. Chromium, vanadium, manganese, and sodium all correlate with dolomite and Ti. Among the trace elements few correlations are apparent, the only significant ones being Cr with V, I with Y, Rb with Pb, and Ni with V.

The correlations found for the onshore samples probably no longer reflect the original associations within the samples, such associations having been extensively modified by weathering. The absence of pyrite and virtual absence of organic carbon and iron oxides means that probably only carbonate-apatite and clay minerals are exerting significant controls on the trace elements. The associations of Fe with clays and detritals suggest that little if any occurs as oxide and Fe therefore has no great independent effect on trace element abundances.

The correlations of dolomite with K, Fe, Ti, Al and quartz suggest that the Mg in these samples may exist primarily within clay phases, and may not be present only as dolomite. The correlations of Fe and Ti with clay and detritals suggest these elements are detrital in origin or bound within clays. The correlation of Rb, Ni, V, Cr and Mn with clays and the presence of Cr-V, Ni-V correlations suggests these elements are also associated with the clay phase possibly by adsorption from ground water during weathering. The Rb-Pb correlation may indicate that Pb is also in the clays though the absence of a Pb-clay correlation indicates the association may be statistical rather than geological. The association of Na with Ti and dolomite, i. e. Mg, is surprising as Na is known to be within the carbonate-apatite phase. The association is probably due to the negative Na-P correlation caused by weathering, whereby carbonate-apatite is concentrated, and Na simultaneously leached from the samples. The U-P correlation may indicate substitution of U within the carbonate-apatite lattice from which it is difficult to remove by weathering. The associations of Y, Cu, Zn, Ba and I are not clear.

Conclusions

Magnesium in the onshore samples is probably present within clay minerals as well as within dolomite. Clay minerals appear to control the levels of Rb, Ni, V, Cr, Mn (and Pb?) probably by adsorption from ground water during weathering. Uranium is probably in the carbonate-apatite, together with Sr and Na. Iron is probably mainly incorporated within the clay phase and exerts little independent control on minor elements, whilst Y, Cu, Zn, Ba, I are independent of other elements.

Northern Samples - Table 2. 5. b

In the northern samples, the apparently meaningful correlations between major elements and phases are confined to those of quartz with Ti, K with Al and Ti, and those between P, organic carbon, and pyrite. In contrast, correlations between major elements and minor elements are fairly well defined, with Rb, Mn, and U correlating, though not strongly, with K; Cu, Ni and Zn correlating with organic carbon and pyrite, the two latter elements also correlating with P, as do Cr, Y, Sr, and Na. Manganese, arsenic, and to a lesser extent, I, and Pb all correlate with Fe, and Mn and Cr correlate weakly with dolomite. Correlations among the trace elements occur between As, Mn, Pb, and I; As and Cr; and Zn and Ni.

The Al-K correlation supports the suggestion that illites are the major clay mineral in these samples. The correlation of dolomite with K suggests in these samples not all Mg is within the dolomite, and that Mg may be partially within the clay minerals or detritals.

The absence of any Fe-clay associations may indicate the presence of Fe at least partially as pyrite, and perhaps oxides, and adsorption onto such oxides would explain the correlation of As, Mn, Pb, and I with Fe. The inter-correlation of these elements supports the suggestion that they are all incorporated into the oxide phases.

The strong correlation of Ni and Zn with organic carbon and pyrite suggests their presence in these phases, either as sulphides or organic complexes, whilst the lesser correlation of Cu with these phases, and its correlation with Ti and quartz, suggests detrital contributions to Cu may be occurring in addition to the main control by organic carbon and pyrite. The correlation of organic carbon and pyrite with P may indicate a connection between reducing conditions and phosphatisation. This association is probably responsible for the association of Zn and Ni with P. The correlations of P with Y, Sr, and Na, and Y with Sr, probably reflect the presence of these elements in the carbonate-apatite phase in substitution for Ca. The correlation of Mn with K suggests a partial detrital origin for this element.

Conclusions

Free iron oxides appear to control the As, Mn, I, and Pb; organic carbon and pyrite control the levels of Ni, Cu and Zn, some detrital contributions to Cu and Mn also occurring, and carbonate-apatite is the principal control on Na, Sr, and Y. The clay content of the samples is principally responsible for the Rb content. The associations of V, Cr, Ba, and U, are not clear.

Southern Pebbles and Phosphatised Ferruginous Limestones - Table 2. 5. c

In the southern pebbles the correlations between major elements are limited to those of Al and quartz with K, and Al with Ti. Correlations of the trace elements Mn, V, Cr, Pb, and As with Fe are well defined, as are the inter-correlations of these trace elements. Sodium, strontium, and phosphorus also correlate well with each other. Other significant correlations between major and trace elements are those of Rb with K and Al, and Y with Al. Significant trace element correlations are probably restricted to those of Zn with V and Pb, and Ni with Zn and V.

The strong correlations of Cr, Mn, V, Pb, and As, with Fe, and those between these elements suggest control by adsorption onto iron oxides. The correlations of Zn, Ni, V and Pb suggest that Zn and Ni may also be controlled by this phase to some degree. Organic carbon appears to exert no influence as a control of trace elements, and P appears to influence only Na and Sr, almost certainly by their incorporation into the carbonate-apatite lattice in substitution for Ca. Rubidium is apparently controlled by the clay minerals (K, Al).

Conclusions

The iron oxide phase appears to control the levels of Pb, As, Mn, V, Cr and may exert some control on the levels of Ni and Zn. Y may be partially detrital in origin, and Rb probably wholly detrital and associated with clays, whilst the association of Cu, I, Ba, and U cannot be explained at present.

Glauconitic Conglomerates - Table 2.5.d

The correlations found in these samples are mainly a reflection of those occurring within the pebbles, e.g. the correlation of Mn and As with Fe, and so only associations apparently independent of pebble associations are discussed.

Rb is very strongly correlated with K whilst Cr is correlated to a lesser extent. Uranium correlates with organic carbon, whilst Ti correlates with dolomite.

The correlations of Cr and Rb with K probably indicate the presence of a considerable part of these elements in the glauconite phase within the matrix. The correlation of U with organic carbon is probably a reflection of the influence of the matrix, which contains more organic carbon than the pebble samples. This association is often found in phosphorites.

R-MODE CLUSTER ANALYSIS

Whilst correlation coefficients are useful as guides to the major controlling factors within the samples, the relative importance of each factor compared with any other is not easy to judge. To clarify the tables of correlation coefficients, cluster analysis was performed on each sample province, the clustering being computed from the complete correlation matrix for each province. Both weighted and unweighted pair group outputs were used, but since the outputs were virtually identical only the unweighted output is reproduced here. A weakness of clustering methods is that elements which are not similar in distribution to any other will be forced into one of the clusters produced and this may lead to apparently anomalous groupings. However, reference to the original correlation matrix from which the clusters were produced should enable a decision to be made concerning the correctness of the clustering of any apparently anomalous element.

Figs. 2.2.a - d represent the clustering produced for each sample group. Significance levels of association are presented on each diagram at either the 1% or 5% level as dotted lines. The relationships of elements are clearly demonstrated by the clusters and clearly reflect the influence of the major phases on minor elements.

The onshore samples (fig. 2.2.a) clearly show a strongly inter-correlated clay group discussed in the previous section. However, only V and Ni are now associated with the clay grouping indicating a more complex partitioning of the remaining elements than previously proposed.

In the northern samples (fig. 2.2.b) P appears to be the major influence on Cr. Vanadium and barium form a completely separate cluster, though they are only very weakly correlated, and the reason for this independence is not clear. Possibly these elements are associated with several phases. Uranium falls into the clay and detrital mineral cluster suggesting these phases may partially supply this element to the samples.

In the southern pebbles (fig. 2.2.c) the Y clusters independently of the clays, indicating its correlations with detritals to be less important than previously thought. The elements U, I, Cu, Y and Ba are all independent. Zn and Ni show a significant relationship but are not apparently dependent on any one phase.

The clusterings of the glauconite samples (fig. 2.2.d), whilst somewhat obscured by the complex composition of the samples, clearly indicates the close association of Cr and Rb with glauconite represented by K and Al. The Fe - V - As association is mainly a pebble influence. Y, U and Ba are seen to weakly correlate with detritals but not with clays. However, the general complexity of these samples makes their clusters dubious and no other conclusions concerning them may be drawn with confidence.

Product-moment correlation matrices for Moroccan samples

TABLE 2.5.a - Onshore samples

TABLE 2.5.b - Northern province samples

TABLE 2.5.c - Southern pebbles and phosphatised ferruginous limestones

TABLE 2.5.d - Glauconitic conglomerates

Onshore Samples
r = 0. 666 significant at 5% level
r = 0. 798 significant at 1% level

n = 9

	K	Fe	Ti	P	Al	Qtz	Py	Org C	Cal	Dol	Y	Sr	Rb	Zn	Cu	Ni	U	V	Cr	Mn	Ba	Pb	I	As	Na
K																									
Fe	.942																								
Ti	.912	.823																							
P	—	—	—																						
Al	.907	.878	.778	—																					
Qtz	.842	.660	.942	—	.740																				
Py	—	—	—	—	—	—																			
Org C	—	—	—	—	—	—	—																		
Cal	—	—	—	—	—	—	—	—																	
Dol	.876	.769	.974	—	.705	.956	—	—	—																
Y	—	—	—	—	—	—	—	—	—	—															
Sr	—	—	—	—	—	—	—	—	—	—	—														
Rb	.670	—	—	—	—	—	—	—	—	—	—	—													
Zn	—	—	—	—	—	—	—	—	—	—	—	—	—												
Cu	—	—	—	—	—	—	—	—	—	—	—	—	—	—											
Ni	.761	.840	—	—	.747	—	—	—	.701	—	—	—	—	—	—										
U	—	—	—	.720	—	—	—	—	—	—	—	—	—	—	—	—									
V	.825	.870	.758	—	—	—	—	—	—	.713	—	—	—	—	—	.667	—								
Cr	—	.688	.721	—	—	—	—	—	—	.708	—	.841	—	—	—	—	—	.852							
Mn	—	—	.777	—	—	.770	—	—	—	.883	—	—	—	—	—	—	—	—	—						
Ba	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—					
Pb	—	—	—	—	—	—	—	—	—	—	—	—	.709	—	—	—	—	—	—	—	—				
I	—	—	—	.797	—	—	—	—	—	—	.695	—	—	—	—	—	—	—	—	—	—	—			
As	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—		
Na	—	—	.669	—	—	—	—	—	—	.657	—	.748	—	—	—	—	—	.667	.933	—	—	—	—	—	

Northern Samples

n = 15

r = 0.514 significant at 5% level
r = 0.641 significant at 1% level

	K	Fe	Ti	P	Al	Qtz	Py	Org C	Cal	Dol	Y	Sr	Rb	Zn	Cu	Ni	U	V	Cr	Mn	Ba	Pb	I	As	Na
K																									
Fe	—																								
Ti	.555	—																							
P	—	—	—																						
Al	.749	—	—	—																					
Qtz	—	—	.686	—	—																				
Py	—	—	—	.598	—	—																			
Org C	.677	—	—	.578	—	—	.896																		
Cal	.621	—	.566	—	—	—	—	—																	
Dol	.560	.651	—	—	—	—	—	—	—																
Y	—	—	—	.702	—	—	—	—	—	—															
Sr	—	—	—	.955	—	—	—	—	—	—	.795														
Rb	.610	—	—	—	—	—	—	—	—	—	—	—													
Zn	—	—	—	.646	—	—	.711	.608	—	—	—	—	—												
Cu	—	—	.554	—	—	.797	.621	.623	—	—	—	—	—	—											
Ni	—	—	—	.539	—	—	.972	.707	—	—	—	—	—	.712	—										
U	.602	—	.806	—	—	—	—	—	.672	—	—	—	—	—	—	—									
V	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—								
Cr	—	—	—	.595	—	—	—	—	—	.563	—	—	—	.600	—	—	—	—							
Mn	.680	.907	—	—	—	—	—	—	—	.725	—	—	—	—	—	—	—	—	—						
Ba	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—					
Pb	—	.607	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	.542	—				
I	—	.597	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	.600	—	.661			
As	—	.919	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	.698	.795	—	.625	.538		
Na	—	—	—	.901	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	

Southern Pebbles and Phosphatised Ferruginous Limestones

n = 22 r = 0.537, significant at 1% level

	K	Fe	Ti	P	Al	Qtz	Py	Org C	Cal	Dol	Y	Sr	Rb	Zn	Cu	Ni	U	V	Cr	Mn	Ba	Pb	I	As	Na
K																									
Fe	—																								
Ti	—	—																							
P	—	—	—																						
Al	.585	—	.658	—																					
Qtz	.656	—	—	—	—																				
Py	—	—	—	—	—	—																			
Org C	—	—	—	.619	—	—	—																		
Cal	—	—	—	—	—	—	—	—																	
Dol	—	—	—	—	—	—	—	—	—																
Y	—	—	—	—	.619	—	—	—	—	—															
Sr	—	—	—	.851	—	—	—	.777	—	—	—														
Rb	.631	—	—	—	.539	—	—	—	—	—	—	—													
Zn	—	—	—	—	—	—	—	—	—	—	—	—	—												
Cu	—	—	—	—	—	—	—	—	—	—	—	—	—	—											
Ni	—	—	—	—	—	—	—	—	—	—	—	—	—	.835	—										
U	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—									
V	—	.577	—	—	—	—	—	—	—	—	—	—	—	.737	—	.650	—								
Cr	—	.624	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	.683							
Mn	—	.775	—	—	—	—	—	—	—	.580	—	—	—	—	—	—	—	—	.590						
Ba	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—					
Pb	—	.625	—	—	—	—	—	—	—	—	—	—	—	.622	—	—	—	.708	.800	.563	—				
I	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	.714			
As	—	.896	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	.668	.579	.711	—	.591	—		
Na	—	—	—	.926	—	—	—	.591	—	—	—	.918	—	—	—	—	—	—	—	—	—	—	—	—	

n = 16

Glauconitic Conglomerates

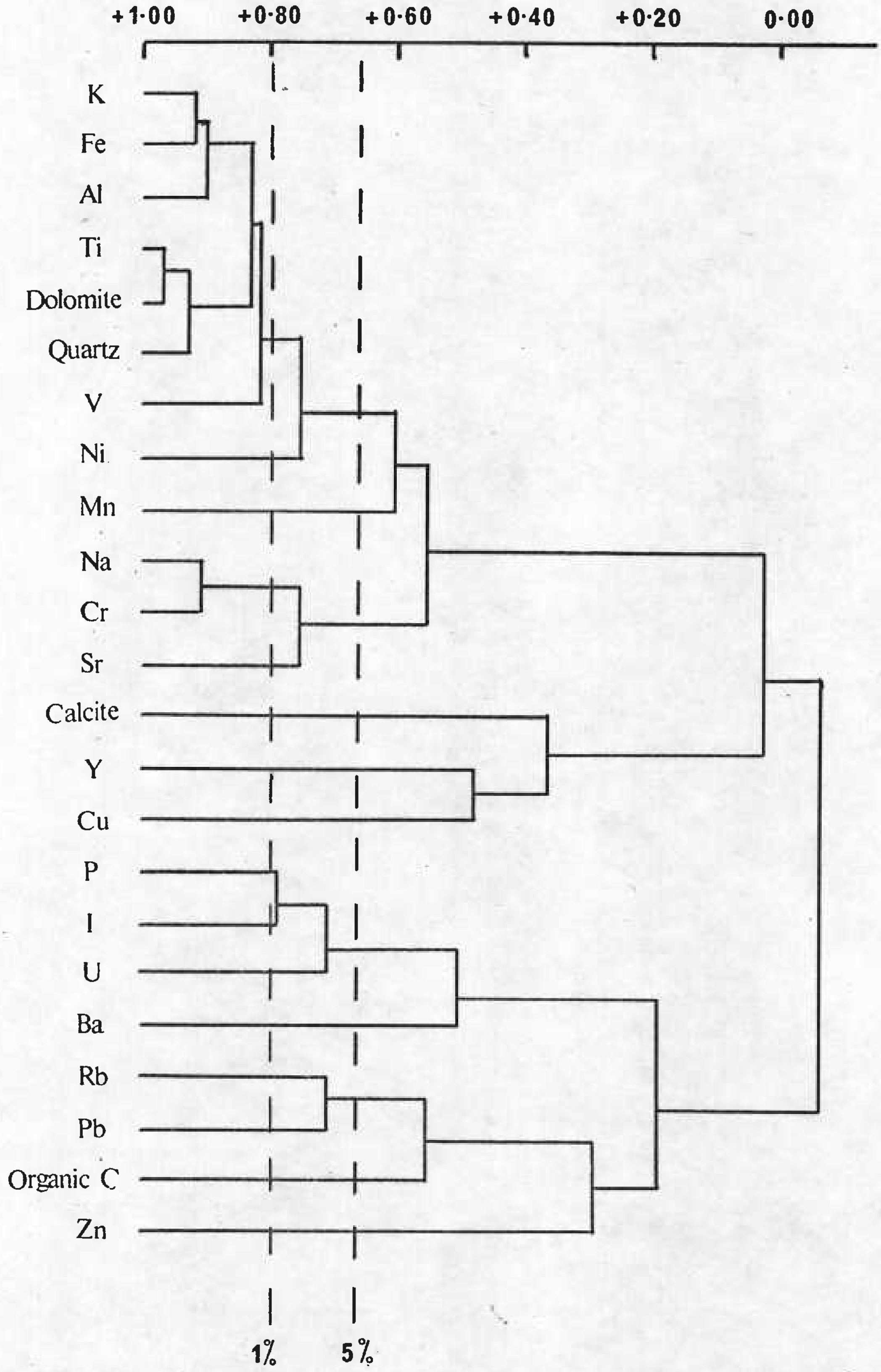
r = 0.623, significant at 1% level

	K	Fe	Ti	P	Al	Qtz	Py	Org C	Cal	Dol	Y	Sr	Rb	Zn	Cu	Ni	U	V	Cr	Mn	Ba	Pb	I	As	Na
K																									
Fe	—	—																							
Ti	—	—	—																						
P	—	—	—	—																					
Al	—	—	—	—	—																				
Qtz	—	—	—	—	—	—																			
Py	—	—	—	—	—	—	—																		
Org C	—	—	—	—	—	—	.838	—																	
Cal	—	—	—	—	—	—	—	—	—																
Dol	—	—	.720	—	—	.759	—	—	—	—															
Y	—	—	—	—	—	—	—	—	—	—	—														
Sr	—	—	—	.772	—	—	—	—	—	—	—	—													
Rb	.854	—	—	—	—	—	—	—	—	—	—	—	—												
Zn	—	—	—	—	—	—	—	—	—	—	—	—	—	—											
Cu	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—										
Ni	—	—	.742	—	—	—	—	—	—	—	—	—	—	—	.679	—									
U	—	—	—	—	—	—	—	.743	—	—	—	—	—	—	—	—	—								
V	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—							
Cr	.670	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—						
Mn	—	.646	—	—	—	—	—	—	.810	—	—	—	—	—	—	—	—	—	—	—					
Ba	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—				
Pb	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	.695	—	—	—	—			
I	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—		
As	—	.698	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Na	—	—	—	.740	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

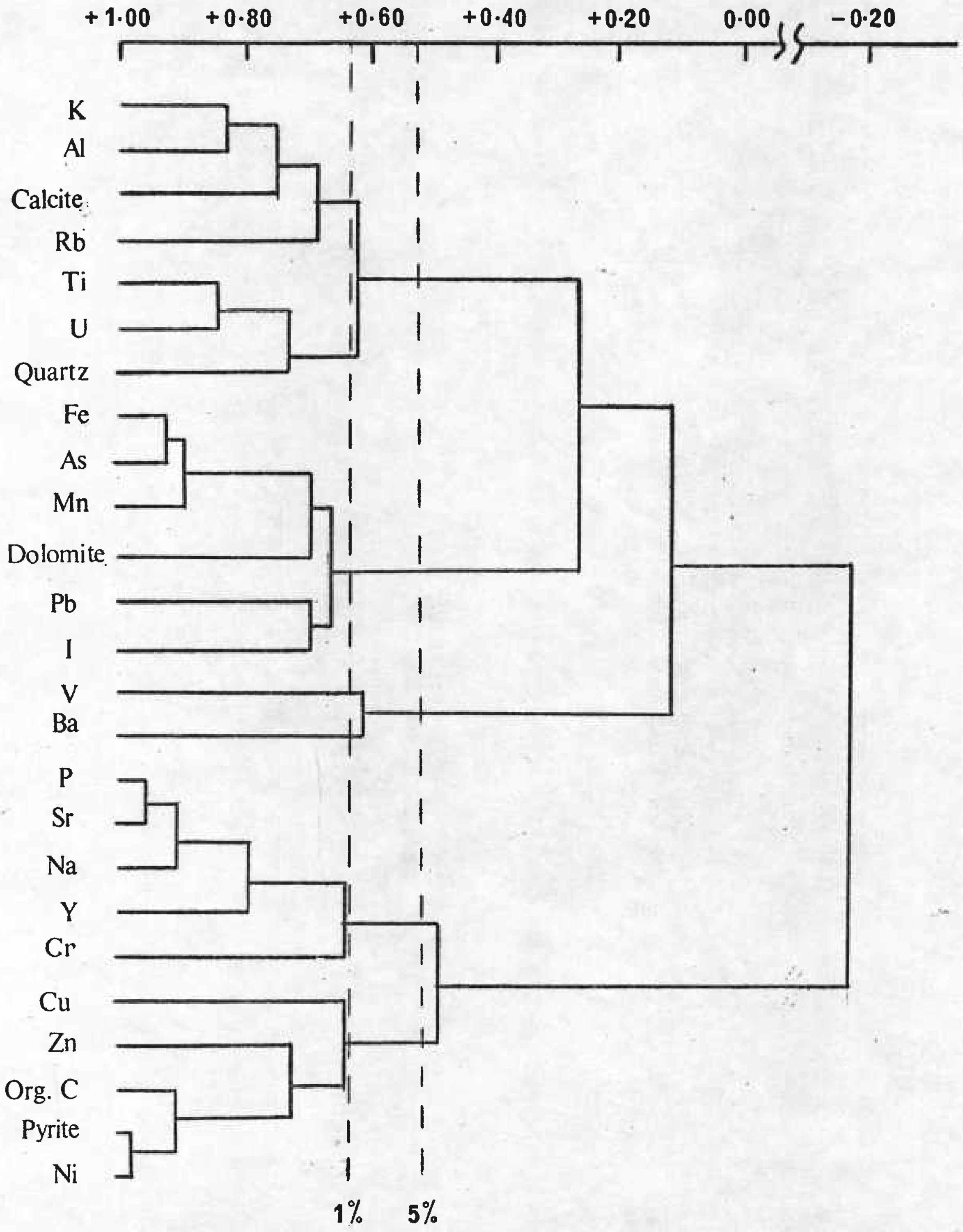
Unweighted pair group output for
R-mode cluster analysis

FIG. 2.2.a	Onshore samples
FIG. 2.2.b	Northern samples
FIG. 2.2.c	Southern pebbles and phosphatised ferruginous limestones
FIG. 2.2.d	Glauconitic conglomerates

Onshore samples

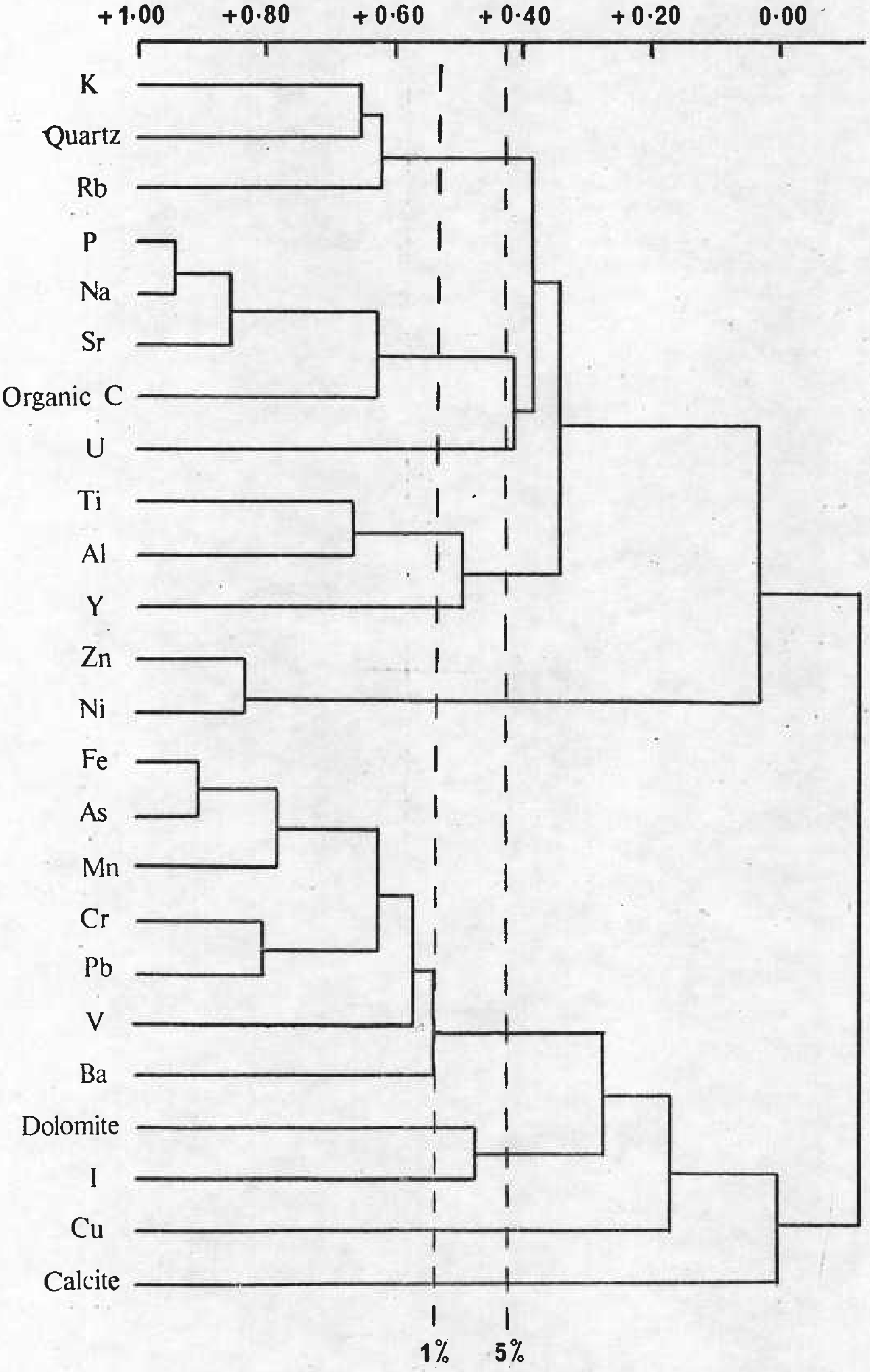


Northern samples

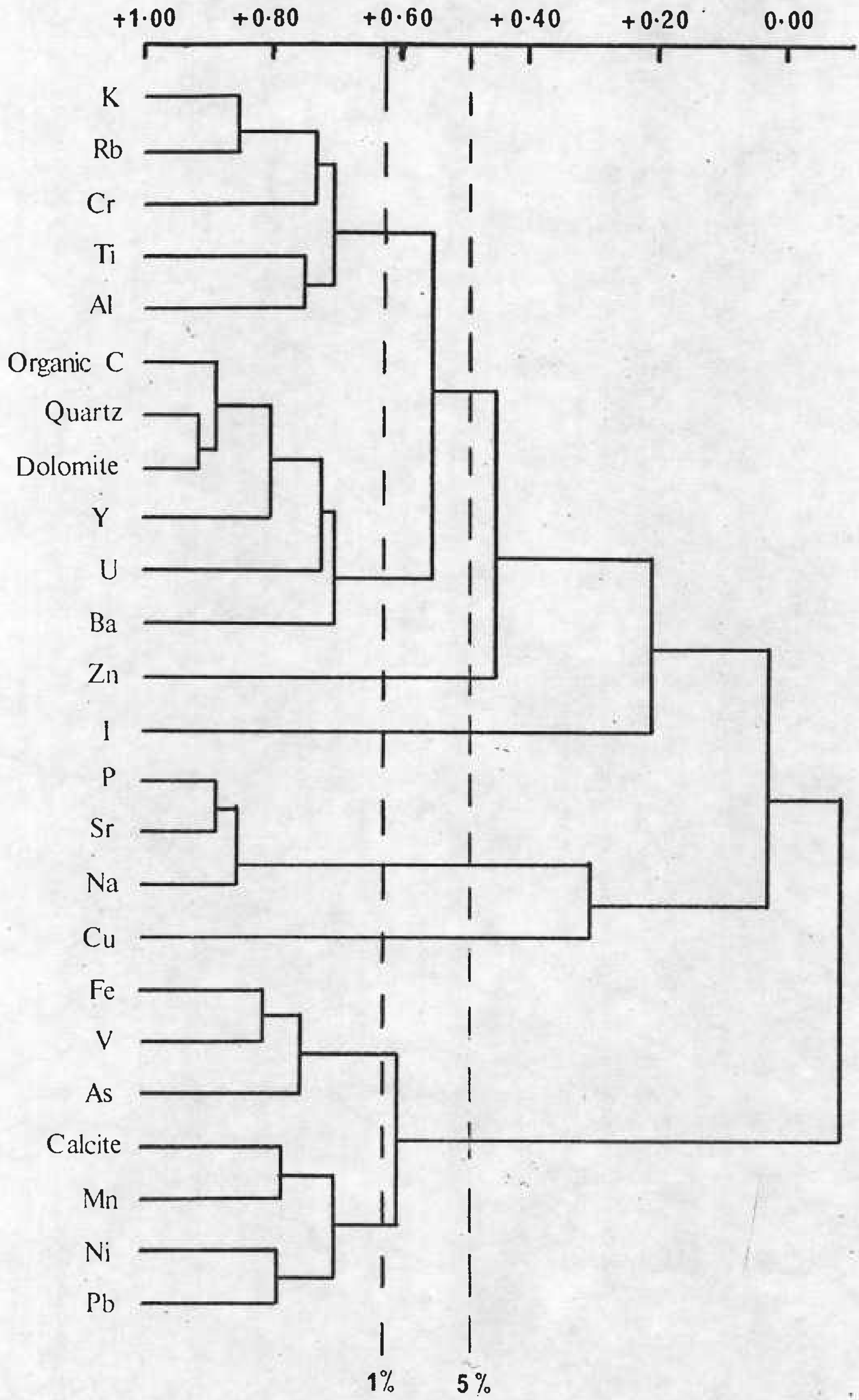


Southern pebbles and

phosphatised ferruginous limestones



Glauconitic conglomerates



SECTION D

THE ANALYSIS OF ACID INSOLUBLE RESIDUES AND ACID SOLUBLE FRACTIONS OF MOROCCAN PHOSPHORITES

Introduction

Confirmation of the proposed element associations, and an assessment of the relative importance of adsorption onto, and absorption into, mineral phases was attempted using the analysis of acid insoluble residues and acid soluble fractions. All samples were treated with 5% nitric acid, which readily dissolves carbonate-apatite and carbonate minerals. Both the acid insoluble residues and the acid soluble fractions were analysed, the former by x-ray fluorescence spectrometry, and the latter by emission spectrography, after evaporation of the residues to dryness. The dual analysis allowed a greater range of elements to be investigated than with either method used singly, and served as a check on the accuracy of each (appendix 7), and Addendum 3-5)

The precision of the methods was between 10% and 30% for the emission spectrography and approximately 10% for the x-ray fluorescence spectrometry, but depended upon the element and its concentration (appendices 6 and 7).

Results and Discussion

The solubilities of Al, K, and Fe in 5% nitric acid were low, (table 2.6) and usually less than 10% (except Fe in the northern samples). A water leach indicated that at least 30% of the acid soluble K was also water soluble, and probably represents ion exchangeable K. These results indicate that acid dissolution of clay minerals and Fe_20_3 is very limited. Since the clay and Fe_20_3 phases are fairly insoluble any trace elements which are also insoluble are probably incorporated within these phases, and any element which is soluble, but correlates strongly with these phases may well be adsorbed onto their surfaces.

The association of As with the Fe_2O_3 is supported by its similar low solubility (table 2.6). The element is most likely incorporated into the Fe_2O_3 in substitution for Fe. In addition, the high solubility of Mn together with its previously shown association with Fe_2O_3 suggests this element is adsorbed onto, rather than absorbed into, the Fe_2O_3 phase. The low solubility of Ti indicates its occurrence in an extremely stable form, probably as a lattice substituent within clay minerals (Bentnor and Kastnor, 1965; McRae, 1972). Ba has a similar low solubility in 5% nitric acid. It may also be incorporated into clay structures, where it can be very strongly bound (Degens, 1965), or may be incorporated into other detritals, or present as barite.

Zinc, copper and nickel are fairly soluble. As a microscopic examination of pyritic inclusions in several thin sections during treatment with nitric acid showed the pyrite to be at least partially soluble, and the organic carbon to be somewhat degraded by acid treatment, the high solubilities of these elements supports their association with these phases.

Chromium solubility varies considerably between provinces (table 2.6); it tends to be high in northern samples and low in southern samples. Chromium precipitates as $Cr(OH)_3$ in reducing environments (Rankama and Sahama, 1950; Tooms et al., 1969; Elderfield, 1970), and may occur in this form in the northern samples in association with reducing micro-environments. If so the high Cr solubility would be explained, as $Cr(OH)_3$ is acid soluble. The low solubility of Cr in the southern samples is probably due to its incorporation within either the Fe_2O_3 or the detrital minerals. The correlation of Cr with Fe_2O_3 (section C, chapter 2), and the fact that probably no more than 30% of the Cr is detrital (section B, chapter 2) suggest that the Cr is actually absorbed into the Fe_2O_3 in substitution for Fe. However, as the southern conglomerate and matrix samples have the lowest Cr solubility of all, the Cr may also be partially within the glauconite, as postulated in previous sections. The solubility of Cu, Ni and Mn is also at a minimum in the matrix suggesting they too may be partially incorporated into glauconite in the southern samples.

Yttrium is almost completely soluble in all samples, suggesting its incorporation into the carbonate-apatite lattice in substitution for Ca. Vanadium is very soluble in the onshore and northern samples, but mainly insoluble in the southern samples. This variability in its solubility makes any interpretation suspect. The high solubility in the northern samples may be due to its substitution, as VO_4^{3-}, within the carbonate-apatite lattice in place of PO_4^{3-}, whereas its lower solubility in southern samples is probably due to a great percentage being incorporated within insoluble Fe_2O_3 and clays. As in the case of Cr, its previously shown association with Fe_2O_3 (section C, chapter 2), coupled with its low acid solubility in the southern samples, suggests it is incorporated into, rather than adsorbed onto, the Fe_2O_3. The solubilities of Pb and I seem to be very variable, possibly due in part, in the case of Pb, to its being close to its detection limit in the samples analysed, and no conclusions can be drawn regarding their mode of occurrence.

TABLE 2. 6

Average element solubilities in
5% HNO_3 for the
Moroccan phosphorites

	Northern Limestones	Northern Pelletals	Glauconitic Conglomerates	Matrix	Southern Pebbles	Onshore
Cu	80	80	70	40	75	75
Ni	70	70	70	50	65	65
Zn	70	70	70	-	75	90
Mn	85	85	70	75	80	60
Cr	80	50	15	15	20	20
Pb	V	V	V	V	V	V
As	I	I	I	I	I	I
Ba	I	I	I	I	I	I
Y	S	S	S	S	S	S
Ti	I	I	I	I	I	I
V	S	S	35	80	V	S
Fe_2O_3	15	15	2	2	2	7
K_2O	20	20	10	10	20	20
Al_2O_3	10	10	10	10	10	10

Key:
V = Variable solubility
I = Insoluble
S = Very soluble

SECTION E

THE INFLUENCE OF IRON OXIDE, IRON SULPHIDE AND ORGANIC CARBON ON THE TRACE ELEMENT ASSEMBLAGE OF MOROCCAN PHOSPHORITES

Introduction

In the Moroccan phosphorites the principal trace element controls appear to be goethite, pyrite, and organic carbon. Their dominant influence probably rests upon their ability to concentrate, or scavenge, trace elements from seawater. In this section the theoretical ability of the iron phases to incorporate trace elements is examined in detail, together with the apparent influence of these phases on the overall trace element abundances of the samples.

A consideration of element adsorption from seawater onto sedimentary minerals and particulate matter requires a knowledge of at least three factors; (1) the speciation of the elements in seawater, (2) the charge on the adsorbing phase, and (3) the particle size of the adsorbing phase. In considering whether a particular element is adsorbed onto, or adsorbed into, a mineral phase, a further factor (4), the sizes of the incorporated species and the species it replaces, is also important. In partially re-crystallised replaced rock such as the Moroccan samples, the effect of the third factor cannot be evaluated. The paucity of data in the literature on the first two factors also severely restricts the usefulness of this approach. Sufficient data exist, however, for the adsorptive role of iron oxides to be investigated, and also for some useful discussion of the role of pyrite in this context.

1. Speciation of Elements in Seawater

Group I and II metals exist in seawater primarily as unassociated ions, complexing and ion pair formation being unimportant. The majority of transition elements in seawater exist as complex ions, owing to the presence of unfilled d orbitals and lone electron pairs; they are normally present in only one oxidation state. The probable speciation of many trace elements has been summarised by Goldberg (1965).

However, recent papers have modified a number of Goldberg's conclusions. Phillips and Williams (1966) have shown that the stability of several important trace elements towards the more polarising ligands is in the series $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. That Cu is very strongly complexed ion in seawater has been demonstrated by Slowey and Hood (1966) who found that most of the Cu in seawater is non-dialysable, and therefore complexed. Organic complexes must be important, as about 50% of Cu in seawater is extractable with chloroform (Slowey, Jeffrey and Hood, 1967). Williams (1969) concludes that 5-28% of Cu is organically complexed, possibly to lipids. Zirino and Yamomoto (1972) support Corcoran and Alexander (1964) in suggesting uncharged species are most important for Cu, and show theoretically that $Cu(OH)_2$ and $CuCO_3$, constitute 90% and 8% respectively of seawater Cu. These results differ from those of Goldberg (1965) who suggests Cu^{2+} and $CuSO_4$ are predominant: however, both Zirino and Yamomoto, and Goldberg, ignore organic complexing, which may invalidate their results.

Krauskopf (1956) considers Zn^{2+} and $ZnCl^+$ to be the dominant Zn speciation, whilst Goldberg differs slightly in favouring Zn^{2+} and $ZnSO_4$. However, Sillen (1961) stresses the role of uncharged species and is supported by Zirino and Yamomoto (1972), who show theoretically that $Zn(OH)_2$ and Zn^{2+} constitute 62% and 17% of zinc in seawater. These authors also suggest that Pb is mainly uncharged, existing as $PbCO_3$ (90%) and $PbCl^+$ (10%).

Vanadium is generally considered to be in seawater as VO_4^{3-} ions, which are possibly protonated (Krauskopf, 1956; Burton, 1966). These workers suggest polymeric species may be important, Krauskopf (1956) suggesting $H_3V_2O_{12}^{2-}$ may occur, and Burton (1966) showing sodium vanadate solutions at seawater pH contain a majority of $H_2V_4O_{13}^{4-}$ ions.

Manganese in seawater is divalent and has been suggested to exist as Mn^{2+} and $MnSO_4$ (Goldberg, 1965). , as $Mn(OH)_3^-$ and $Mn(OH)_4^{2-}$ (Sillen, 1961), and $MnHCO_3^+$ and $MnSO_4$ (Hem, 1972). Since Mn does not form strong complexes (Goldberg and Arrhenius, 1958; Phillips and Williams, 1966; Stark and Wallace, 1970), uncomplexed Mn^{2+} may be important.

Arsenic is generally accepted by most workers (Kanamori, 1965; Mason, 1966; Sevastyanov, 1967; Stow, 1969) as occurring as AsO_4^{3-} , $HAsO_4^{2-}$, or $H_2AsO_4^-$ and U as UO_2^{2+} complexed with carbonate to give a negatively charged species (Goldberg, 1965).

Chromium exists in two oxidation states in seawater Cr (III) and Cr (VI).

Chuecas and Riley (1966) conclude that Cr (III) is predominant and are supported experimentally by Elderfield (1970), whereas Fukai (1967) and Fukai and Vas (1967) find Cr (VI) is predominant. On purely theoretical grounds Goldschmitt (1954), Krauskopf (1956), Arrhenius and Bonatti (1965), Fukai and Huynh-Ngoc (1968), and Elderfield (1970) all conclude that Cr (VI) as CrO_4^{2-} should predominate. The major trivalent species is probably $Cr(H_2O)_4(OH)_2^+$, or more simply, $Cr(OH)_2^+$ (Elderfield, 1970).

The R. E. E. are characterised by d^o configurations in the ionic state and therefore probably exist mainly as uncomplexed ions in seawater (Riley and Skirrow, 1965).

TABLE 2.7

Trace element speciation
in seawater

ELEMENT	PRINCIPAL SPECIES IN SEAWATER
Ni	Ni^{2+}, $Ni(OH)_2$
Cu	Up to 50% as organic complexes, Cu^{2+}, $Cu(OH)_2$, and $CuCO_3$
Zn	$Zn(OH)_2$ 62%, Zn^{2+} 17%
Pb	$PbCO_3$ 90%, $PbCl^+$ 10%
V	$H_2VO_4^-$
Mn	Mn^{2+}, $Mn(OH)_3^-$, $Mn(OH)_4^{2-}$
Cr (VI)	CrO_4^{2-}
(III)	$Cr(OH)_2^+$
As	AsO_4^{3-}, $HAsO_4^{2-}$, $H_2AsO_4^-$
U	$UO_2(CO_3)_3^{4-}$
Y	Y^{3+}
Sr	Sr^{2+}, $SrCl^+$
I	I^-, IO_3^-
R.E.E.	R.E.E.$^{3+}$

2. Electrical Charge on Iron minerals

The electrical charge on particulate and colloidal material in seawater governs whether anionic or cationic species will be adsorbed. Stumm and Morgan (1972) state that all particulate matter in seawater is charged. Neihof and Loeb (1972 and 1974) go further and state that all particulate matter is negatively charged. The charge on particulate matter and mineral phases can be measured by determining the pH_{zpc} of the mineral (the pH at which all charge is neutralised). Results for such determinations on natural heamatite and goethite show considerable variation. Duval and Kurbatov (1952) conclude that hydrous ferric oxides are both anion and cation adsorbers, a conclusion supported by Joy, Watson and Compton (1964) after experimental study of Brazillian heamatite slimes. Amphoteric behaviour is shown by minerals close to their zero point of charge (the point at which the charge on the mineral is zero). A further study including Labradorian heamatite showed pH_{zpc} to be dependent upon particle size, and to vary between 4 and 6.9. In experimental studies of natural and artifical heamatite Johanson and Buchanan (1957) determined the pH_{zpc} to be 6.7 and 8.0 respectively, the latter decreasing to 6.5 on heating, whereas Parks (1962) determined pH_{zpc} of natural heamatite at 8.5. In two subsequent reviews, Parks (1965 and 1967) quotes values for pH_{zpc} of natural heamatite between 2.2 and 8.5, the majority of values being close to 6, and the pH_{zpc} of natural goethite between 3.2 and 9, again most values lying near 6. The data indicate the difficulties inherent in attempting to find the pH_{zpc} of iron oxides in the marine environment by measurement on geological material. As dehydration, dehydroxylation and increasing crystallinity would all be expected to decrease pH_{zpc} (Parks, 1965 and 1967), and since diagenesis would favour recrystallisation and possibly dehydration, it is suggested that natural goethite has a lower pH_{zpc} after diagenesis than when first precipitated, the pH_{zpc} being greater than 8 when initially formed.

In view of the preceding discussion, it is concluded that goethite in the marine environment is either close to its isoelectric point or carries a small positive charge, a conclusion in keeping with that of Krauskopf (1956), who has pointed out the efficiency of iron oxide in removing trace metals from seawater, and also of Mason (1966), who states that it is positively charged.

Discussion

On the basis of charge considerations discussed in the previous sections, it is likely that precipitation of goethite in the marine environment would be more likely to cause co-precipitation, or adsorption from seawater of V, Mn, As, Cr (VI), I, and U than of Cr (III), Cu, Ni, Zn, Pb, R.E.E. or group I or II elements. That such adsorption is probably occurring in the southern samples for V, As, Cr, and Mn, is shown by figs. 2.3 a - d, where the variation of these elements with the variations in Fe_20_3 are plotted. The association of Cr and As with Fe_20_3 has also been demonstrated by Kieth and Degens (1959) to occur in residual limonites from Pennsylvania. The correlations of I and U with Fe_20_3 are statistically non-significant, suggesting that other phases contribute some or all of these elements.

Whether co-precipitation or actual adsorption onto the goethite is more important in concentrating these elements is not known. Sevastyanov (1967) and Kanamori (1965) both indicate that As can be directly co-precipitated with iron; Burton (1966) and Krauskopf (1956) have shown V to be readily adsorbed onto colloidal Fe_20_3.

4. The Influence of Ionic Radii

A comparison of the ionic radii of Fe (III) with the radii of the elements associating with the Fe_20_3 may assist in deciding whether adsorption, or absorption and substitution for Fe, is the more important incorporating mechanism. Referring to table 2.8 it is clear that on size considerations alone the similarity to Fe (III) is in the order Cr (III), V, As, Mn, Cr (VI), I, and Pb. However, charge considerations indicate Cr (VI) to be the most probable species incorporated into the $Fe_2 0_3$, so Cr (III) must be disregarded.

From the comparison undertaken it is clear that V, As, and possibly Mn can be incorporated into $Fe_2 0_3$ in replacement for Fe. That V and As probably do so is shown by their low acid solubilities (section D, chapter 2), the high acid solubility of Mn indicates that it is adsorbed rather than absorbed. For Cr the charge and ionic radii considerations are at odds and therefore cannot satisfactorily explain the low acid solubility of Cr in the southern pebbles. The small ionic size of Cr (VI) may allow it to fit into interstital lattice positions within the goethite structure.

The statistically significant correlation of Pb with $Fe_2 0_3$ in both the northern samples and the southern pebbles, noted in section C, is not explained by the considerations of charge and size presented here. However, since the association occurs in both sample populations, and Pb in both populations correlates well with other elements almost certainly associated with $Fe_2 0_3$, its government by $Fe_2 0_3$ seems fairly likely. The discrepancy between the experimental results and charge and size considerations is unexplained.

TABLE 2.8

Six co-ordinate ionic radii for ions theoretically associated with Fe_2O_3

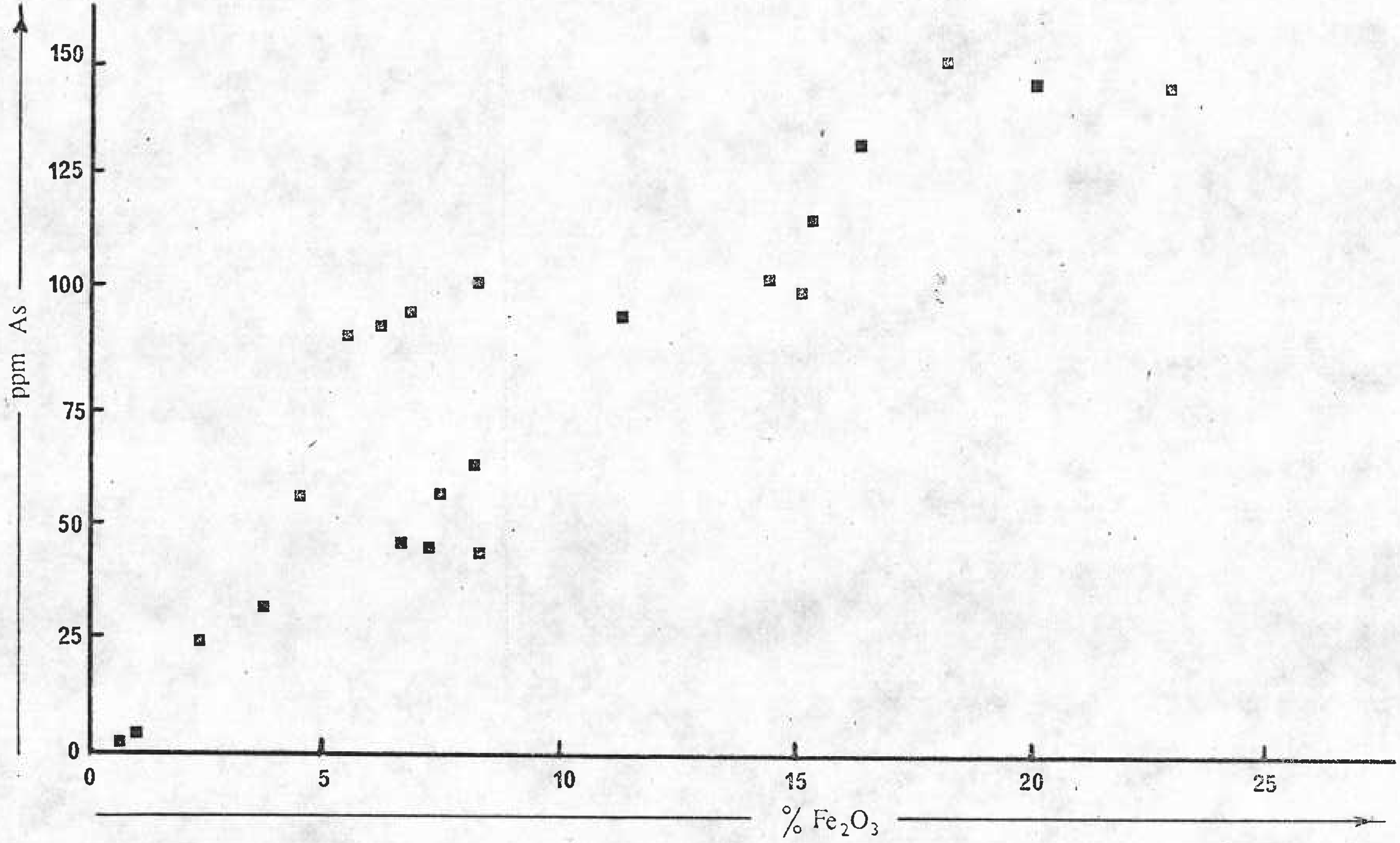
(Reproduced from Whittaker and Muntus (1970))

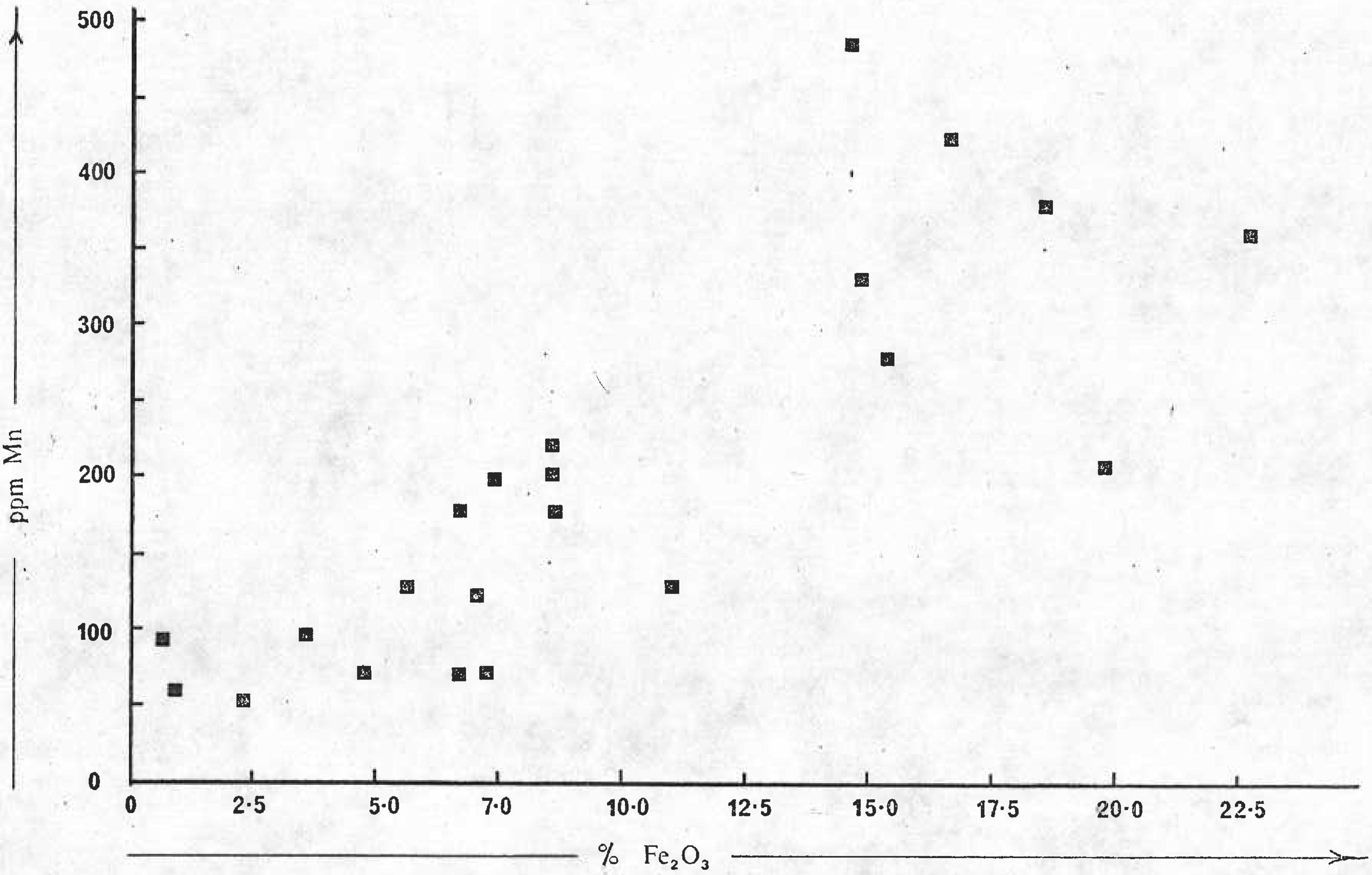
ELEMENT	VALENCY STATE	IONIC RADII (n.m)
Fe	III	0.073
V	V	0.062
Cr	III, VI	0.070, 0.043 (C.N. =4)
Mn	II	0.091
I	I, V	0.213, 0.103
As	V	0.058
Pb	II	0.126

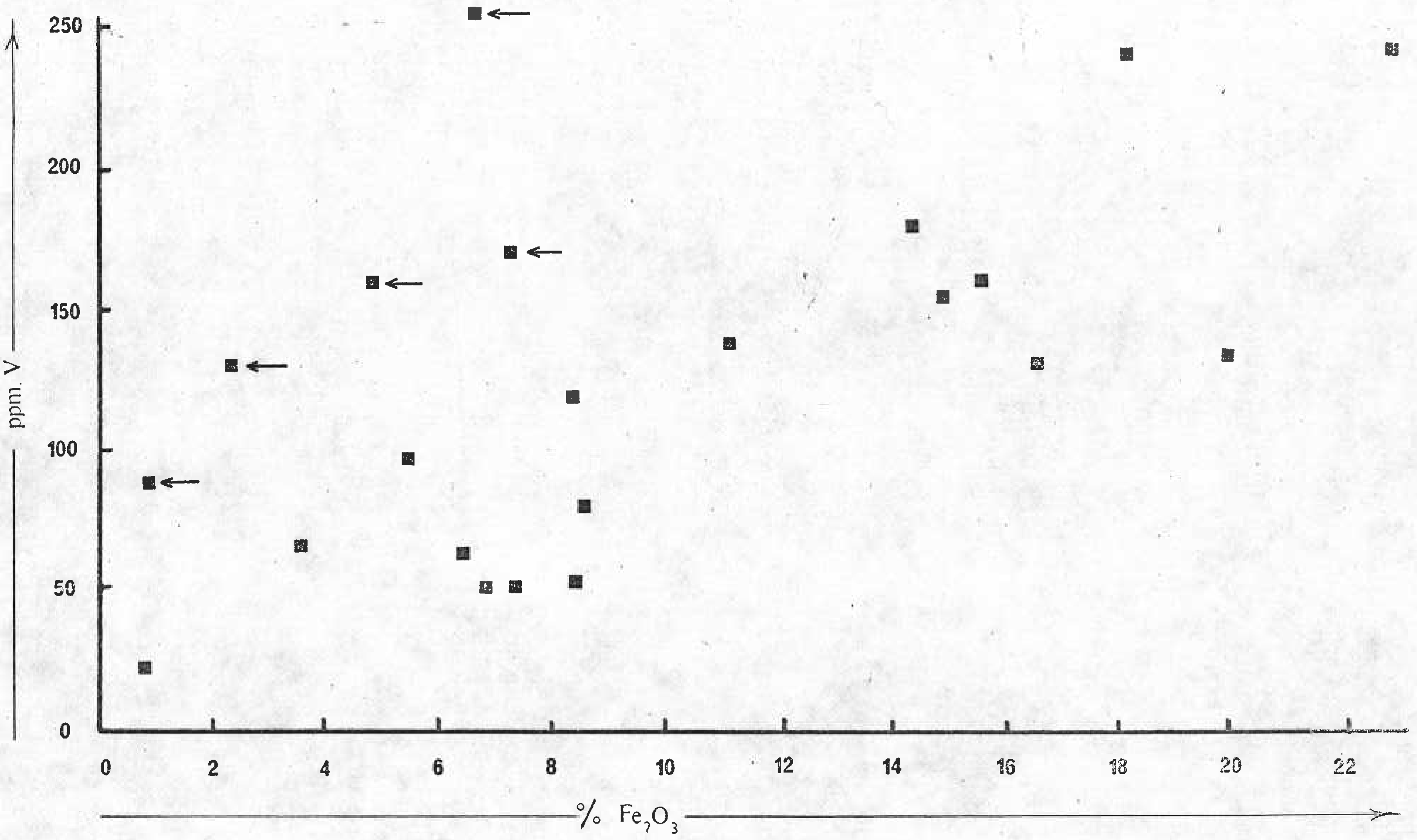
FIG. 2.3

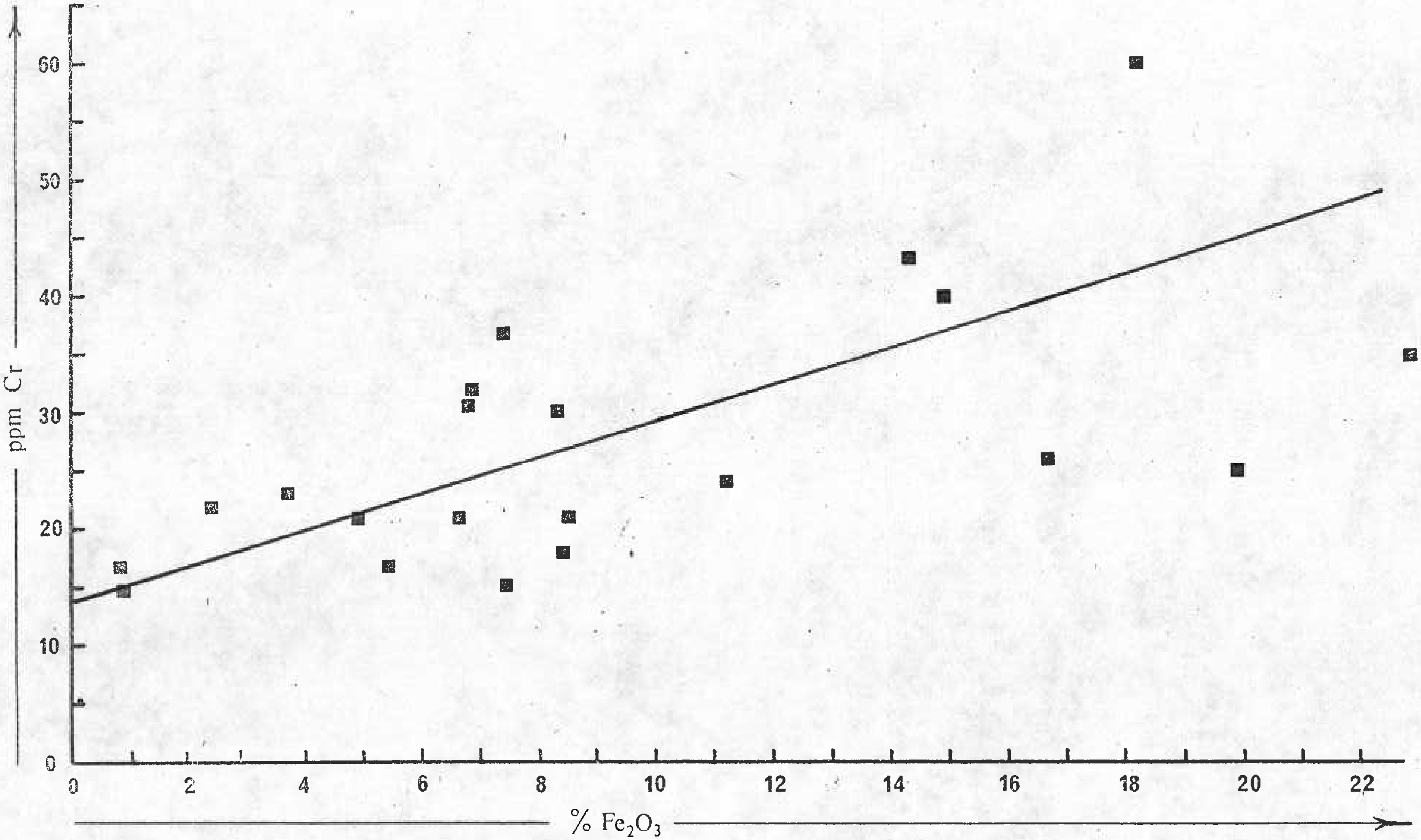
The variation of
As, Mn, V, and Cr with
Fe_2O_3 in southern pebbles

FIG. 2.3 a	As - Fe_20_3
FIG. 2.3 b	Mn - Fe_20_3
FIG. 2.3 c	V - Fe_20_3
FIG. 2.3 d	Cr - Fe_20_3


ppm As
150
125
100
75
50
25
0
0
5
10
15
20
25
% Fe_2O_3


ppm Mn
500
400
300
200
100
0
0
2·5
5·0
7·0
10·0
12·5
15·0
17·5
20·0
22·5
% Fe_2O_3


250
200
150
100
50
0
ppm. V
0
2
4
6
8
10
12
14
16
18
20
22
% Fe_2O_3



ppm Cr
60
50
40
30
20
10
0
0
2
4
6
8
10
12
14
16
18
20
22
% Fe$_2$O$_3$

The Influence of Pyrite on the Trace Element Assemblage

No data are available in the literature concerning the surface charge associated with sedimentary pyrite. Consequently the discussion of pyritic control of trace elements is restricted to a comparison of Moroccan pyrite with data from the literature.

In contradistinction to the results of the previous sections, As appears to be controlled by pyrite in the northern samples, (fig. 2.4 d) except in 966(1) where it is related more to Fe_20_3. The anomalous values of 966(1) were probably the reason for the previously assumed association of As in these samples with Fe_20_3. Bliskovskiy (1968) has shown pyritic control of As to occur in phosphate from the Soviet Union, and assigns a secondary role to organic carbon in this context. Similarly, Wells (1971) and Wells and Mullins (1973) find As in sulphide ore from Nevada, U. S. A. to be almost exclusively associated with the pyrite phase. According to Fliescher (1955) As in pyrite is present in true solid solution.

Zinc, copper, and nickel are strongly associated with pyrite and organic carbon in the northern samples (figs. 2.4 and 2.5). Nickel correlates significantly more strongly with both than either Cu or Zn. It is suggested that it is contained within the pyrite phase, in which it can extensively replace Fe (III), pyrite being an end member of the series Pyrite (FeS_2) - Bravoite ($FeNiS_2$) - Vaesite (NiS_2) (Hawley and Nicholls, 1961). Copper and zinc are, however, closer in ionic radii to Fe (III) than Ni (Whittaker and Muntus, 1970) and therefore might also be expected to substitute to at least the same degree. However, in the case of Cu, a stability constant for organic complexes of approximately 100 time that of either Ni or Zn (Beck, 1970), suggests it would rather complex with organic material, a suggestion supported by the existence of up to 50% of seawater copper as organic complexes (Slowey and Hood, 1966; Slowey, Jeffreys and Hood, 1967). Zinc is far less likely to be reduced in the marine environment than Ni on account of its much more strongly reducing nature and is therefore less likely to be incorporated within a partially covalent lattice structure such as pyrite.

The nickel, zinc, and copper (if any) present in the pyrite were probably originally derived from the organic matter supplied to the sediment, a suggestion supported by Kieth and Degens (1959) for other samples, these workers noting a common similarity between the trace element assemblages of pyrite and associated organic carbon in sediments.

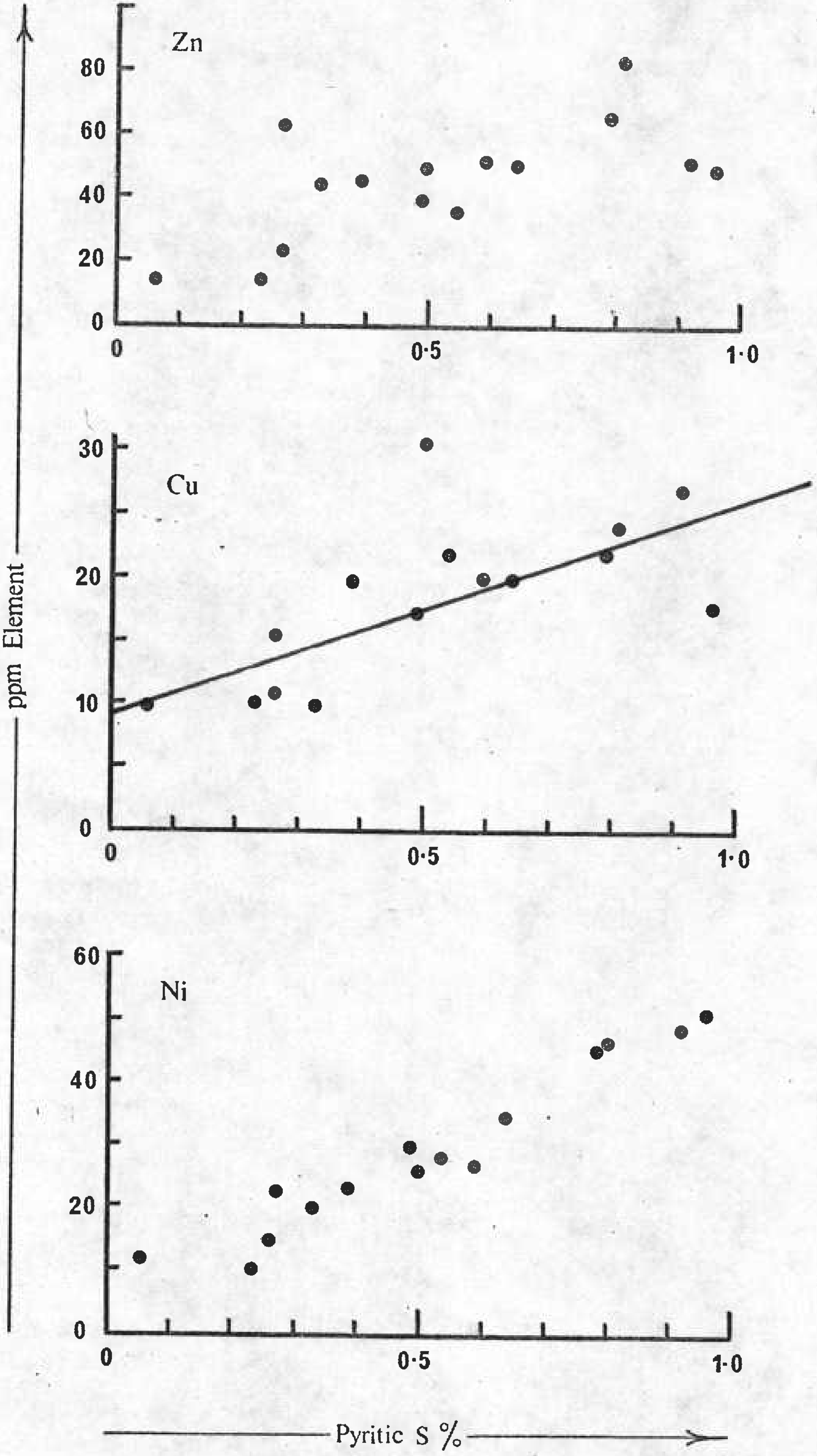
Several other elements (U, I, Cr, V and Pb) might be expected to occur in pyrite or be associated with organic carbon. Chromium and vanadium have been shown to occur to some extent in Cu, Zn, and Ni bearing pyrite (Gad, Catt and LeRiche, 1969; Fliescher, 1955; Nishiyama and Minato, 1971) and the association of Pb with sulphide minerals is well known. The association of U and I with organic carbon has frequently been demonstrated (Swanson, 1961; Price, et al. 1970). However, none of these elements appear to be influenced in any degree by organic carbon or pyrite, and their position in the pyritic northern samples is not clarified by this discussion.

FIG. 2.4

The variation of Zn, Cu,
Ni, and As with pyrite in
northern samples

(Pyrite expressed as % pyritic S)

FIG. 2.4 a	Zn - S
FIG. 2.4 b	Cu - S
FIG. 2.4 c	Ni - S
FIG. 2.4 d	As - S


Zn
80
60
40
20
0
0
0·5
1·0
Cu
30
20
10
0
0
0·5
1·0
Ni
60
40
20
0
0
0·5
1·0
ppm Element
Pyritic S %

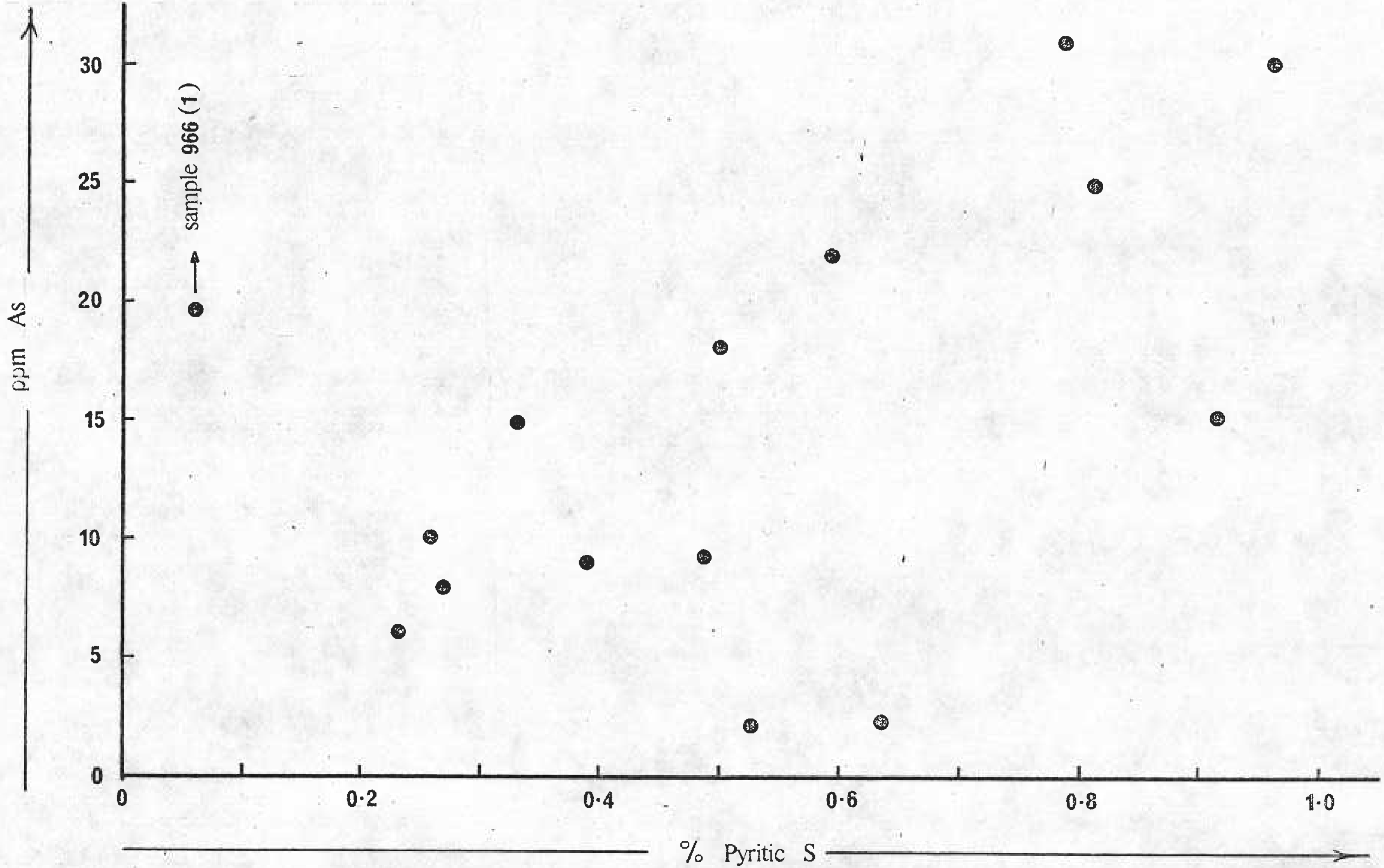
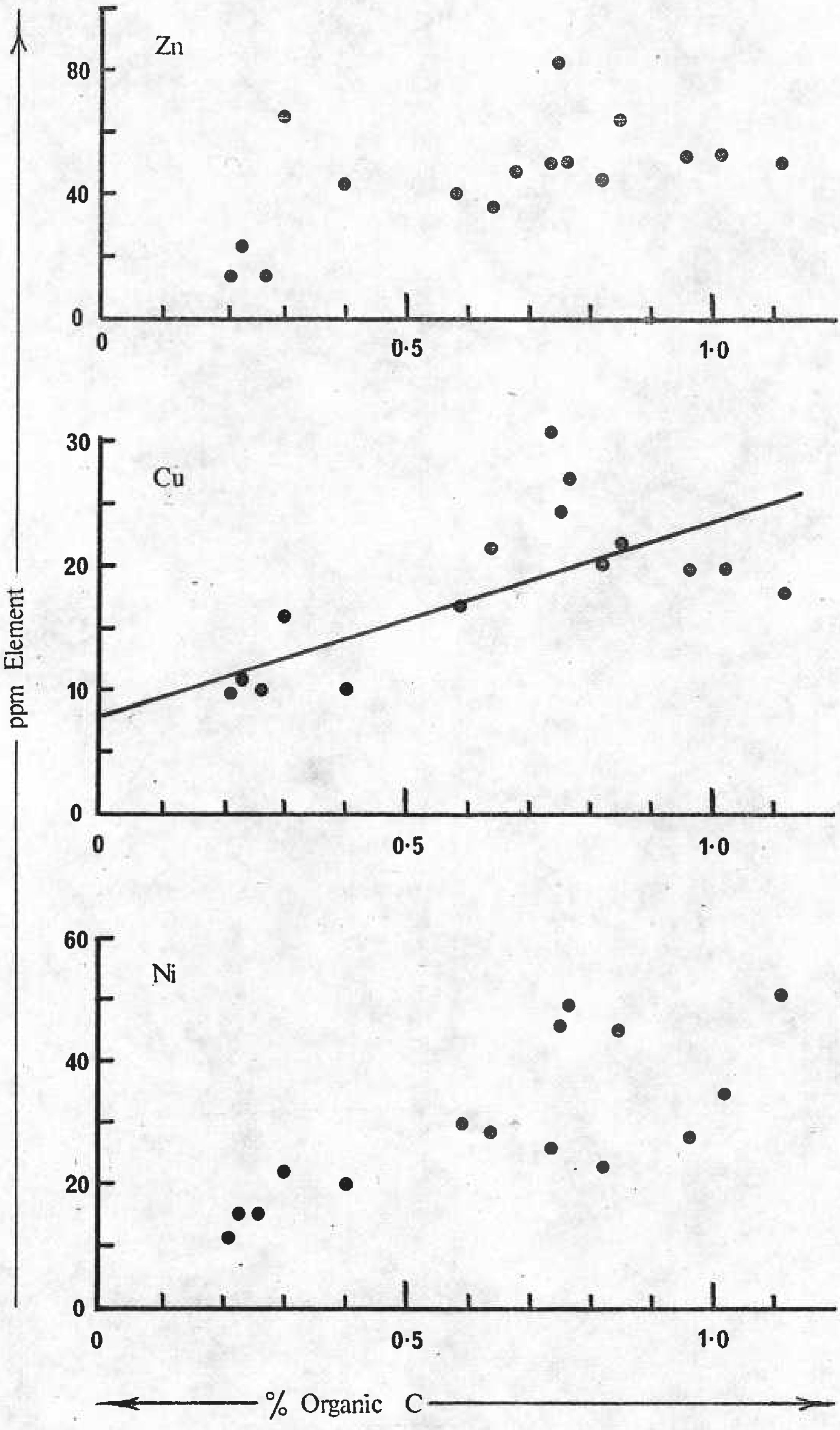

ppm As
30
25
20
15
10
5
0
sample 966 (1)
0
0·2
0·4
0·6
0·8
1·0
% Pyritic S

FIG. 2.5

The variation of Zn, Cu, and Ni with organic carbon in the northern samples

FIG. 2.5 a	Zn - organic carbon
FIG. 2.5 b	Cu - organic carbon
FIG. 2.5 c	Ni - organic carbon


Zn
80
40
0
0
0·5
1·0
Cu
30
20
10
0
0
0·5
1·0
Ni
60
40
20
0
0
0·5
1·0
ppm Element
% Organic C

Summary

Charge and ionic size considerations indicate that in the southern pebble samples and phosphatised ferruginous limestones V and As are incorporated into Fe_2O_3 in substitution for Fe, and that Mn is adsorbed onto this mineral. On theoretical grounds, Cr is expected to be adsorbed onto Fe_2O_3. However, this expectation is at odds with the experiment al result of section D, which indicates Cr to be strongly held within the goethite lattice. The conflict may be resolved either by postulating the incorporation of Cr (VI) within interstitial lattice sites and defects of the Fe_2O_3, or by incorporation not of Cr (VI), but of Cr (III), an ion virtually identical in size to Fe (III). Were this to be the case the principal speciation of Cr (III) in seawater assigned by Elderfield (1970) as $Cr(OH)_2^+$ may be incorrect, the association of Cr with Fe_2O_3 indicating Cr to be negatively charged in seawater. The principal speciation may therefore be CrO_2^- (Elderfield, 1970).

In the northern samples pyrite is shown to be the dominant control on Ni, by its incorporation of Ni in substitution for Fe(II). Copper is principally controlled by organic matter with which it forms strong complexes and Zn is distributed between these two phases.

The association of Pb with Fe_2O_3 in both the southern pebbles and the northern samples is at variance with the theoretical considerations presented here, but no explanation for this discrepancy is readily apparent.

SECTION F

THE INFLUENCE OF GLAUCONITE ON THE TRACE ELEMENT ASSEMBLAGE OF THE SOUTHERN PROVINCE SAMPLES

Introduction

Glauconite can contain appreciable quantities of trace elements, either within the lattice structure, or incorporated as heterogeneous inclusions. The extent to which trace elements may be incorporated into the lattice structure depends largely upon the number of expandable layers present (Hower, 1961; McRae, 1972). The range of element concentrations of several trace elements typically encountered within the glauconite (Bentnor and Kastner, 1965) are presented in table 2.9. It must be emphasised, however, that heterogeneous impurities may account for a considerable part of the trace elements apparently contained within glauconite. For example, concentrations of Ti up to 2000 ppm (Bentnor and Kastner, 1965; Speed, 1965) may be due to inclusions of rutile (Allen, 1937).

As the southern conglomerates contain between 20% and 30% of glauconite, this mineral may significantly contribute to the overall trace element assemblage of these samples. As assessment of these contributions has been made by the analysis of glauconite separated from three conglomerate samples.

Analytical Methods

Glauconite was separated from samples 877, 896(1), and 865 by magnetic separation, and was then purified with heavy liquids. Subsequent microscopic examination of the separated glauconite at high magnification showed it to contain virtually no recognisable impurities. Analysis of the glauconite for Zn, Cu, Ni, Ti, Cr, Mn, Pb, Fe, Ca, Mg, and Al was carried out using atomic absorption spectrophotometry. Analysis for the remaining elements Sr, V, Ba, K, and Si was done by direct reading emission spectrography.

Results and Discussion

The major element analysis of the glauconite (table 2.9) reveals a considerable content of impurity to be present. The CaO values are greatly in excess of the normal values for glauconite (approximately 0.2%), and are probably the result of considerable calcite or carbonate-apatite inclusions occurring within the glauconite. The low SiO_2 values, approximately one half the normal glauconite content, is probably the result of analytical error. Among the trace elements, analytical error may also account for the high Ni values, as the glauconite from sample 865 contains sufficient Ni to account for more than 100% of the Ni present within the whole rock sample. For the remaining elements the high Ti and Cr values confirm previous suggestions that glauconite almost entirely controls the Ti and also contributes significantly to Cr in these samples. Significant contributions to the Ba contents of these samples are also apparent.

TABLE 2.9

Element analysis of glauconite

Element	896(1)		877		865		Bentnor and Kastner (1965)[1]
	A	B	A	B	A	B	
CaO	12.0		9.1		12.0		0.2
K_2O	4.8		5.0		4.8		6.0
Fe_2O_3	19.4		23.7		28.0		24.0
SiO_2	19.1		19.1		26.0		50.0
MgO	7.4		4.7		4.5		2.0
Al_2O_3	4.6		4.9		5.2		7.0
Sr	450	7	180	6	320	11	50-250
Zn	36	15	15	9	18	14	
Cu	12	16	14	28	6	18	
Ni	51	43	42	54	117	100	
V	53	11	34	13	23	10	40-100
Cr	162	60	130	46	143	60	80
Mn	24	3	21	6	34	7	
Ba	33	23	74	37	110	25	40-90
Pb	11	12	12	18	14	21	
Ti	1050	81	1410	86	810	78	2000

A - element composition of glauconite

B - % contribution to total trace element abundance of whole rock sample

1. The major element analysis presented here represents an "average" analysis of typical glauconite based on these authors.

Discussion of the Trace Element Controls in Moroccan Phosphorites

1. Northern Samples:

In the northern phosphatised limestones and pelletal samples the association of Cu, Ni, and Zn with organic matter and pyrite is well defined. Nickel is most probably within the pyrite, where it replaces Fe. Zinc is probably partially within the pyrite, in substitution for Fe, and partially complexed with organic matter. Copper appears to be present mainly complexed with organic matter, although some may occur as chalcopyrite admixed with the pyrite. However, that approximately 20% of the Cu present in these samples may be of detrital origin is indicated by considerations of the content of detrital material present and the crustal abundance of Cu (section A). Furthermore, the intercept of the regression lines of the Cu-pyrite and Cu-organic carbon variation diagrams (figs. 2.4.b and 2.5.b) at approximately 8 ppm on the Cu axis indicates a 20%-25% contribution to these samples from phases other than pyrite and organic carbon.

Excepting detrital Cu, the original method of incorporation of these elements into the sediment may have been by complexing with organic matter, subsequent release during organic decay allowing incorporation into the sulphide phases. However, direct precipitation of these elements as sulphides cannot be ruled out. The original source of these elements was probably sea water, the lower enrichment of Zn compared to Cu and Ni during concentration in the samples possibly being due to its lower stability during complex formation.

Arsenic is also concentrated by the pyrite phase of the northern samples, with contributions from Fe_2O_3 being important mainly in sample 966(1) which contains 5% Fe_2O_3. The majority of non-pyritic Fe in these samples is probably authigenic Fe_2O_3, though the amounts are usually very small. Of the other elements manganese is probably partially detrital, within clay minerals, and partially controlled by adsorption onto the small quantities of free Fe_2O_3 present. As in the case of arsenic, the high Mn in sample 966(1), which contains high

Fe_2O_3 compared to other northern samples, confirms the role of adsorption as being of importance. Also, that Pb is associated with Fe_2O_3 in both the northern and southern samples is indicated by significant Pb-Fe_2O_3 correlation coefficients.

Barium, rubidium and titanium are mainly detrital in origin, the levels within the samples being commensurate with their content of detrital material, assuming that it contains these elements in amounts similar to their crustal abundances. The very low acid solubilities of both Ba and Ti could reflect their occurrence in stable phases probably mainly within clays.

Sodium and strontium are almost exclusively within the carbonate-apatite lattice in substitution for Ca. Yttrium is chemically similar to, and probably follows, the R.E.E. which also substitute for Ca in the carbonate-apatite lattice. The high acid solubility of Y suggests it does the same, as does the fact that both the R.E.E. and Y are enriched in Moroccan phosphorite relative to crustal abundance, but depleted in sea water.

Of the remaining elements V and U are enriched in samples 135, 959, 966(1) and 988(a). These samples also contain the least amounts of organic carbon and pyrite, and up to five times as much non-pyritic Fe_2O_3 as the remaining samples, i.e. up to 5% Fe_2O_3. The enrichment of V may be due to incorporation within this phase. The enrichment of U, however, is best explained in terms of the inclusion within these samples of uraniferous detrital collophane (chapter 3), with contributions occurring from organic matter and direct absorption by carbonate-apatite.

The modes of occurrence of I and Cr are not well defined. Some of the Cr is undoubtedly of detrital origin, and as the lowest Cr values occur in samples of highest Fe_2O_3, it suggests that the Cr is independent of the Fe. The associations of I appear to be random. Because I and Cr are often associated with organic matter in sediments and phosphorites, it is possible that these elements may originally have been incorporated into the sediments in this way. That they do not appear to associate with this phase may be due, in the case of I, to its early release from organic matter during diagenesis, and in the case of Cr to the obscuring effect of the detrital contributions.

2. Southern Pebble Samples:

The element associations in the southern pebble samples are less clearly defined than those in the northern province. This may be due to the virtual absence of pyrite and organic carbon, which may strongly influence the trace element concentrations.

Arsenic, lead, vanadium, chromium, and manganese are all strongly associated with iron oxides. This is shown by R-mode cluster analysis and correlation coefficients, and for As, Cr, and V, by their similar low acid solubilities. Manganese and lead are probably adsorbed onto the Fe_2O_3, whilst As, V and Cr are probably within the lattice structure. However, that an appreciable contribution to the Cr content of these samples is provided by detrital material is indicated not only by the comparisons between the detrital content of these samples and the crustal abundance of Cr (section A), but also by the interception of the regression line of the Cr-Fe_2O_3 variation diagram (fig. 2.3.b) on the Cr axis at approximately 14 ppm, suggesting that on average 30% of the Cr is not associated with the Fe_2O_3.

Rubidium, titanium, and barium are probably detrital, and mainly within clay minerals, their higher values in the southern pebbles, compared to the northern province, together with their higher clay content supporting this suggestion.

Sodium and strontium occur within the carbonate-apatite lattice in substitution for Ca. Yttrium has a high acid solubility and, as in other samples, probably also occurs within the carbonate-apatite lattice also in substitution for Ca.

The remaining elements appear independent of any particular major phase.

It is suggested that in the southern pebbles Cu is partially detrital whilst the remainder of the Cu, together with the Ni, Zn, U, and I may have originally been introduced by incorporation into organic matter as complexes. In addition, U may also have been directly absorbed from sea water by the carbonate-apatatite phase. The proposed organic control is supported by the residual amounts of organic material found in these samples and by the frequently observed association of these elements with organic matter. Such an association occurs in the northern samples for Cu, Zn, and Ni.

The absence of any present association of these elements with organic matter in the southern pebbles may be due to destruction of most of the organic material in the oxidising environment of formation, which probably released these elements from the organic material. Iodine may then have been adsorbed onto the positively charged Fe_2O_3 by virtue of its existence as an anion, whilst U was possibly partially lost to the sediment and partially incorporated into the carbonate-apatite phase. The Cu, Ni, and Zn, which exist in sea water as uncharged or cationic species were possibly partially adsorbed onto clay material, a mechanism which would explain their high acid solubilities.

3. Southern Conglomerate Samples:

Element associations are complicated in the southern conglomerates as a whole by the complex character and possible conflicting associations in the matrix and the pebbles, which were discussed in the previous section. Many element associations are reflections of those occurring in the pebbles, for example, the associations of Mn and As with Fe_2O_3. Associations which appear to be different are the association of Cr with glauconite and the detrital clay content of the matrix, Cr showing a significant correlation with these phases in the R-mode analysis. Analysis of separated glauconite shows that contributions of other elements to the samples by glauconite are significant for Ti and Ba.

4. Onshore Samples:

It has been suggested that the onshore samples formed in a similar way to the pelletal samples, but represent a more advanced stage of the process of phosphatisation and reworking. The original element associations were probably those now found in the offshore northern samples. However, they have probably been obliterated by extensive weathering.

In elucidating the present associations, R-mode cluster analysis and correlation coefficients have proved of little use, since 9 samples are far too few for good results to be obtained by these methods. Comparison with the northern province samples shows that the onshore samples are much higher in most trace elements (Cr, V, Zn, Cu, Ni, Rb, Ba, I and Y). If the original element abundances were similar to those in the northern offshore samples, these elements must have been concentrated during weathering. Substitution of V or increased Y into carbonate-apatite seems unlikely, since weathering removes most substituting species from the carbonate-apatite lattice. Adsorption onto clays, and possibly the carbonate-apatite, may well account for the concentration of these elements, though the former minerals are present in only very small amounts. Basically, the factors controlling the trace element concentrations of these samples have been too extensively modified to be clearly elucidated.

The methods presented in this thesis have defined the element associations within the samples well. Correlation analysis and cluster analysis appear very useful tools for elucidating such relationships and defining element controls. However, their use in isolation may lead to incorrect results. Ambiguous correlations may be produced in such complex systems as are found in nature, and verification of associations found by this method is advisable. Graphical plotting of data is useful as a check on computer correlations, although it must be emphasised that graphical plots suffer the same restrictions that are inherent in the calculation of correlation coefficients (cf. Chayes, 1960, 1962).

In spite of these limitations, the results of this work suggest that in the Moroccan offshore samples three phases predominate in controlling the trace element abundances. In the northern samples pyrite and organic carbon are most important with Fe_2O_3 playing a minor role. In the southern samples the situation is the reverse, with glauconite also contributing several elements, notably K, Ba, Ti, Rb, and Cr. The trace element contents of the onshore samples were probably similar to, and controlled by the same influences, as the present northern offshore samples, when the onshore samples were deposited. The major trace element control onshore now appears to be the clay fraction because of modification by weathering. The source of most of the trace elements in the samples was probably sea water. Titanium and barium were probably almost completely detrital, and Mn, Cr, Cu and Rb may be partially detrital in origin. These conclusions are summarised in fig. 2.6.

The influence of the carbonate-apatite phase on the total element variability of the offshore Moroccan phosphorites is not strong, only Na, Sr, SO_4^{2-} and lattice CO_3^{2-} being strongly governed, and probably U, R.E.E., and Y also being directly controlled, by carbonate-apatite. The numerous suggestions that other elements, e.g. Mn, K, As, V, Zn, I, Ba substitute within the lattice of marine, as well as igneous, apatite (Cruft, 1965; Whippo and Murrowchick, 1967; Tooms et al., 1969; Summerhayes, 1970) are not supported by the findings presented here. Since many of the possible substitutions have been suggested on the basis of theoretical considerations of ionic radii and charge, or analysis of deposits now on land and therefore weathered, they may not be applicable to phosphorite in offshore environments. It is suggested that the trace element content of phosphorites is largely controlled by the accessory phases (in the case of the offshore Moroccan phosphorites organic carbon, pyrite and iron oxide) and not by the apatite phase, as has been often suggested.

Direct comparison of data between phosphorites formed in oxidising and reducing conditions has been found useful in initially defining element associations in the offshore Moroccan phosphorites. This approach might usefully be applied to other deposits, if sufficient data and suitable reference deposits are available. Direct comparison of chemical data should not be undertaken, however, unless adequate petrographic and mineralogical data are available to ascertain the true modes of occurrence of elements such as Fe, S, Mg and Ca. Comparison with worldwide averages is not likely to prove valuable owing to the spread of data from which such averages are calculated, and the lack of ancilliary petrographic and mineralogical data.

The analysis of acid insoluble residues and acid soluble fractions has proved useful in confirming suspected element associations, and of some use in differentiating between adsorbed phases and those incorporated within the lattice of minerals. Selective and progressive chemical attack would probably be of greater use, if reliable methods could be developed. Refinement of such methods should enable adsorbed and substituting species to be clearly distinguished, as well as serving to reliably locate elements in particular phases, and would contribute greatly to the basic understanding of element controls in phosphorites. Such methods would be particularly suitable for application to land phosphorites, where element associations are much less well defined than in offshore samples, owing to the effects of weathering.

The main conclusions of this chapter are presented in fig. 2.6 and can be summarised as follows.

In the Northern Samples

i) Zn, Cu and Ni associate with pyrite and organic carbon, with 20% of the Cu being of detrital origin.

ii) As associates mainly with pyrite and organic carbon, with contributions from Fe_2O_3 where present.

iii) Pb and perhaps V appear to associate, though not strongly, with Fe_2O_3.

iv) Na, Sr, Y, R.E.E. associate with carbonate-apatite SO_4^{2-}.

v) Ba, Mn, Rb, and Ti are mainly detrital and within clays, with contributions to Mn occurring from Fe_2O_3 where present.

vi) U is associated with detrital collophane and carbonate-apatite and may also have been concentrated by complexing with organic carbon.

vii) Cr is partially detrital and may also have been concentrated by organic carbon.

viii) I does not appear to associate with any specific phase but may have been concentrated by organic carbon.

In the Southern Pebble Samples

i) As, Pb, V, Cr, and Mn associate with Fe_2O_3 with approximately 30% of the Cr and some of the Mn being of detrital origin.

ii) Rb, Ti and Ba are mainly detrital in origin and within clay minerals.

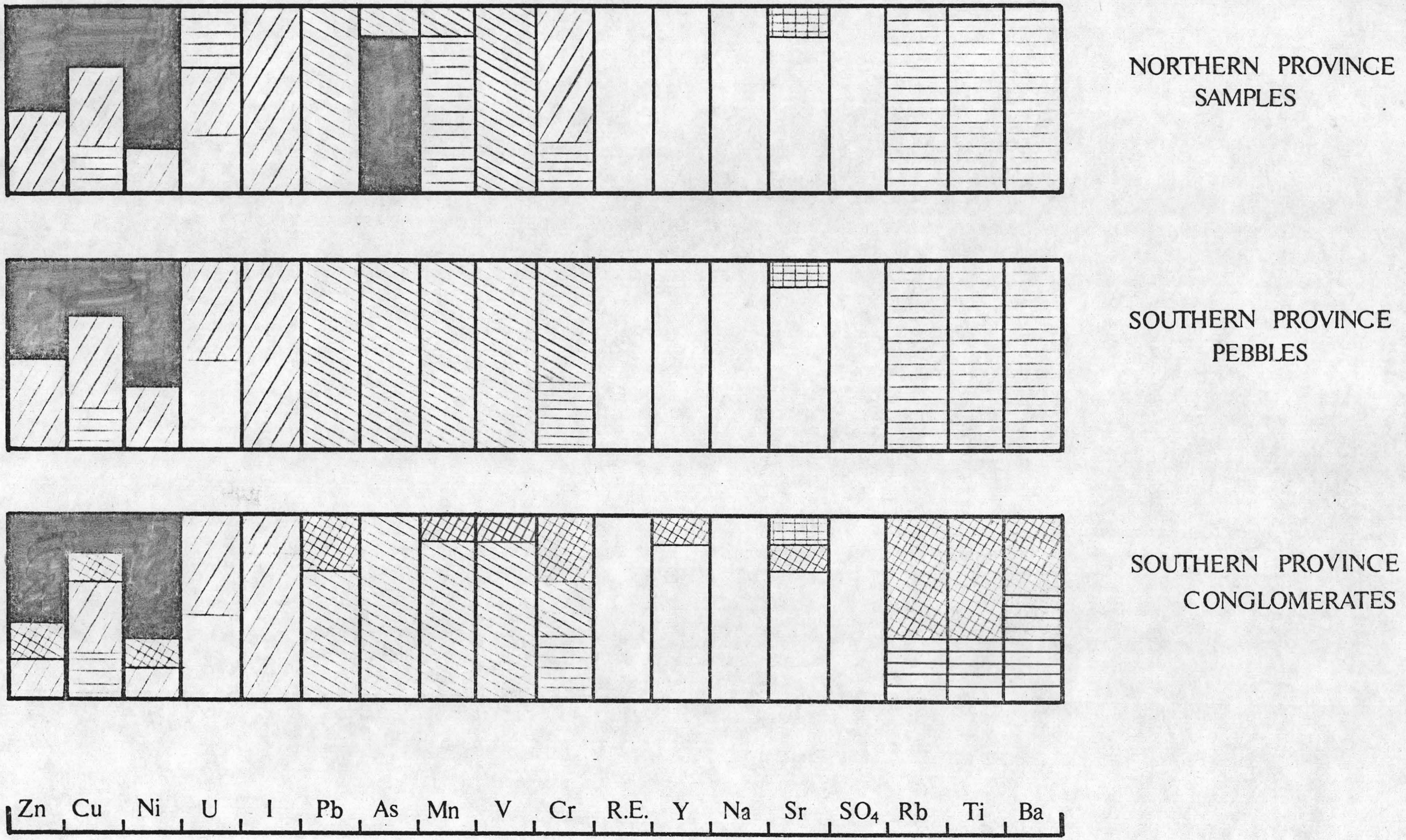
iii) Na, Sr, Y, R.E.E., and SO_4^{2-} are almost entirely associated with carbonate-apatite.

iv) Cu, Ni, Zn, U, and I appear to vary independently of any major phase, and were probably introduced into the samples by organic carbon and pyrite. In addition, 20% of the Cu is probably of detrital origin, and U is probably partially governed by carbonate-apatite.

In the southern conglomerates the associations and controls of the trace elements are in the main similar to those occurring in the pebble samples except for glauconite being the main influence on Ba, Ti and Rb, and having a considerable influence on Cr.

FIG. 2.6

Diagrammatic representation of the proposed original trace element controls in Moroccan phosphorites


NORTHERN PROVINCE SAMPLES
SOUTHERN PROVINCE PEBBLES
SOUTHERN PROVINCE CONGLOMERATES
Zn
Cu
Ni
U
I
Pb
As
Mn
V
Cr
R.E.
Y
Na
Sr
SO4
Rb
Ti
Ba

CHAPTER 3

URANIUM GEOCHEMISTRY

Introduction

The analysis of all samples for U was undertaken for three reasons.

Firstly, the development of undersea prospecting using submersible scintillation counters (Summerhayes et al., 1970) makes a study of the relationship between U and P desirable in order to assess whether a direct correlation exists between these two elements, in the offshore samples. The existence of such a correlation would enable the deposits to be assayed, and reserves calculated, without extensive sampling and analysis of the seabed. Such a method might also be applicable to other submarine deposits.

Secondly, the present use of airborne radiation detectors in phosphorite prospecting is based on the U content of the deposits (McKelvey, 1966). Removal, particularly rapid removal, of U during weathering would considerably reduce the possibility of detecting phosphate deposits by such methods, and might result in non-detection of extensively weathered (and therefore high phosphatic) deposits. Consequently weathering of U from phosphorites is examined by a comparison of offshore and onshore phosphorites.

Thirdly, U has been examined in order to assess the validity of the proposed mechanism of U incorporation into apatite, by the reduction of U VI in sea water to the less soluble U IV, and precipitation of the latter in the lattice of the carbonate-apatite (Altschuler et al., 1958).

Uranium occurs in phosphorites in concentrations well above its crustal abundance (Tooms et al., 1969). The majority probably substitutes for Ca^{2+} within the carbonate-apatite lattice (Inglesrud, 1948; Thompson, 1953 and 1954; McKelvey and Carswell, 1956; Altschuler et al., 1958; Sheldon, 1959; Ames, 1960; Tooms et al., 1969). The source of the U is sea water, where it occurs principally as the hexavelent uranyl ion UO_2^{2+}, usually strongly complexed to carbonate as $UO_2(CO_3)_3^{4-}$ (Mason, 1966). The removal from sea water is thought to involve reduction of hexavelent U to the less soluble tetravalent state, which is precipitated and incorporated into the carbonate-apatite (Altschuler et al., 1958; Kolodny and Kaplan, 1970). The frequently demonstrated correlation of U with organic carbon in phosphates (Swanson, 1961), sediments, and sedimentary rocks (Swanson, 1961; Baturin et al., 1967, 1971 ; Mo et al., 1973) supports this hypothesis. However, the occurrence of U VI in phosphate rock as a significant proportion of the total U content (Clarke et al., 1958; Kolodny and Kaplan, 1970) suggest uptake of U VI by direct adsorption may also occur (Cathcart, 1968a). This hypothesis is supported by Peacock and Taylor (1966) who report somewhat higher concentrations of U in phosphatised portions of the carboniferous limestone of Derbyshire and Yorkshire; by Cathcart (1968a), who showed U in United States coastal plain phosphorites to be higher in those samples longest exposed to sea water; by Kaneshima (1962) who found U in phosphorite on Ryukyu Island to be very low compared to older, continental deposits; and by Altschuler et al., (1958) who have shown that isolated fossil bones or phosphatic nodules may contain concentrations of U greatly in excess of surrounding strata.

Whether this uptake of U occurs by absorption into the lattice structure of carbonate-apatite, or by surface adsorption is not known. In the Moroccan samples tentative support for surface adsorption of U VI might be drawn from the rate of removal of U from the carbonate-apatite during sub-aerial weathering. A rate considerably in excess of the rate of removal of other substituting species, e.g. Na and Sr, might indicate considerable surface adsorption. Further, to evaluate the importance of reduction of U VI and precipitation, as a mechanism for the incorporation of U into phosphorites, a comparison is made between the highly oxidised southern samples and the reduced, northern samples. However, the fact that phosphates, and sediments, formed in reducing environments usually contain higher U than do those formed in oxidising environments (Sheldon, 1959; Arrhenius, 1963; Tooms et al., 1969) is not necessarily evidence in favour of the proposed reduction. Reducing conditions tend to be associated with finer grained deposits than oxidising conditions and higher U in reducing deposits may simply reflect the greater adsorptive capacity of the finer grained material. Comparisons between U concentrations in oxidising and reducing environments must therefore be made on samples of similar grain size if meaningful results are to be obtained. The great petrographic similarity between northern phosphatised limestones and many iron rich southern samples suggests that variations in U concentration due to grain size effects are probably absent, enabling a valid comparison to be made of their U contents in order to test the importance of reduction and precipitation, as opposed to surface adsorption, as a mechanism of U concentration in carbonate-apatite.

Results and Discussion

No correlation exists between the U and P content of the Moroccan samples. Consequently, no estimation of the grade of the deposits, or extent of reserves is possible by scintillation counting. However, since the majority of samples contain at least 100 ppm of U, the location of phosphorite is still possible by this method (Summerhayes et al., 1970). In order to further investigate the commercial viability of these deposits, seabed sampling and analysis must be used together with scintillation counting. The inability of counting to reveal P_2O_5 levels in Moroccan phosphorites does not necessarily mean that the method will not be useful elsewhere. Uranium and phosphorus have been shown to be generally proportional (though affected by weathering) in drill holes for phosphate exploration in Idaho (Hale, 1967). The absence of any comparable data for other deposits of similar environment means no general conclusions can be drawn. Each deposit will have to be treated independently.

A comparison between the U concentrations of onshore and offshore pelletal samples, after recalculation to pure carbonate-apatite, shows that no significant reduction in U content has occurred in the onshore samples. The recalculated onshore value of 150 ppm is close to that for the offshore samples of 146 ppm, and shows U to be extremely strongly held to the carbonate-apatite lattice. It also suggests surface adsorption of U VI is probably of little importance in concentrating U into phosphate rock. That U does not decrease during weathering validates the employment of radiation detectors in the exploration for phosphorite, irrespective of its age or weathering history.

A comparison of U concentrations between the oxidised southern pebbles and the reduced northern samples is complicated by the anomalously high U in five northern samples (135, 988(a), 959,1038, 1022(2)). For these samples some correlation exists between their U contents and the number, and degree of phosphatisation, of detrital collophane pebbles they contain (table 3.1), suggesting the collophane contains appreciable U, probably absorbed from sea water during reworking (c.f. Cathcart, 1968a) and is responsible for the anomalous values.

In the remaining samples from the northern province, the U concentrations are only 20% above those in the oxidised southern pebbles, suggesting that reduction of U VI to U IV may not be an important step in the incorporation of U into carbonate-apatite. However, the southern samples exhibit a strong inverse correlation (r= -0.88) between Fe and U, suggesting that U has been removed from these samples during their exposure to oxidising conditions.

It is suggested that organic material was responsible for the concentration of U in both provinces, prior to its incorporation into the carbonate-apatite lattice. However, in the southern province the prevailing oxidising conditions rapidly destroyed the organic material and oxidised the U to its more soluble U VI form, which was then lost from the sediment. The concomitant deposition of Fe during the loss of U resulted in their inverse correlation.

TABLE 3.1

Occurrence of detrital collophane
and anomalous U concentrations
in northern province samples

Sample No.	Uranium concentration (ppm)	*No. of detrital pebbles of collophane	Degree of phosphatisation
135	507	200	well phosphatised
1022(2)	483	100	very well phosphatised
959	369	80	not well phosphatised
988(a)	328	120	well phosphatised
1038	259	100	not well phosphatised
136	206	140	well phosphatised
Remaining samples	<150	<20	many grains possibly being phosphatised bone fragments

* No. of detrital pebbles of approximately modal size observed in 6 separate fields of view on each thin slide, with magnification of 50x. All comparisons were done by eye.

Summary and Conclusions

The mechanism of U incorporation into the Moroccan offshore samples appears to be partly a result of concentration and reduction of sea water U VI to U IV by organic material, followed by its incorporation in the carbonate-apatite lattice, and partly a result of incorporation of uraniferous detrital collophane. Surface adsorption of U VI seems unimportant. Direct absorption may also occur.

The absence of any U - P association in Moroccan phosphorites, as well as in those of the Phosphoria Formation (Swanson, 1961) suggests that the use of scintillation counters for seafloor phosphorite prospecting will reveal only the presence of phosphorite, and not its grade. Extensive sampling and analysis will be necessary in order to further define a deposit.

Weathering does not result in removal of U from the carbonate-apatite lattice of Moroccan phosphates, indicating that it is very strongly held. This phenomenon may be partly due to the high charge on the U IV and U VI ions, which makes its removal less energetically favourable than the removal of ions of lower charge, e.g. Sr^{2+}, Na^{+}. The widespread use of radiation detectors for phosphorite prospecting on land is thus not restricted by the weathering history of phosphorite deposits. Indeed extensively weathered deposits may well be easier to detect than recent ones, owing to the increase of phosphate during weathering, and the concomitant increase in U. As the effect of weathering on U in phosphorites has not been investigated before in this context, these findings must add greatly to the confidence in current prospecting methods.

CHAPTER 4

RARE EARTH ELEMENT GEOCHEMISTRY

Introduction

In view of recent discussions in the literature concerning La/Ce ratios in phosphorites, and whether such ratios parallel that of crustal abundance, i.e. are less than 1, or that of seawater abundance, i.e. are greater than 1 (cf. Goldberg, 1963, and Cook, 1972), it was thought desirable to obtain information on La/Ce ratios from the previously uninvestigated Moroccan sea-floor phosphorites. Two partially purified offshore samples have been analysed by Summerhayes (1970) and a further three partially purified (appendix 4) offshore and one onshore sample have been analysed by the writer. Also two world samples were analysed; F.127, a sea-floor phosphorite, was analysed by Summerhayes (1970), and a phosphate sample from a deposit in Jordan was analysed by the writer. These analytical data, together with data taken from the literature are used to help resolve the problem of La/Ce ratios in phosphorites. The analyses were all done by mass spectrography.

In addition to La and Ce, the remaining R.E.E. were examined in order to establish whether R.E.E. fractionation patterns in sea-floor phosphorites are in any way different to those found in land deposits, and whether the fractionations were similar to, or different from, that of seawater. Fractionations similar to that of seawater would suggest the elements are derived from that source, and thus help resolve the present uncertainty regarding the origin of these elements in sea-floor minerals (cf. Ehrlich, 1968, and Piper, 1972).

The R.E.E. fractionation patterns in offshore, onshore, and several world samples, were also compared in an attempt to assess whether or not sub-aerial weathering can induce changes in R.E.E. fractionations.

Finally, Ce was determined in a large number of offshore and onshore Moroccan phosphorites in order to assess the effect of weathering on the total R.E.E. abundances in phosphorites, and to examine whether the differences in the environment of deposition between the oxidised southern samples and reduced northern samples is reflected in the extent of R.E.E. substitution within the carbonate-apatite lattice.

RESULTS AND DISCUSSION

La/Ce Ratios

Until recently, the La/Ce ratio for phosphorites was thought to be less than one, paralleling that of crustal abundances (Goldberg, 1963; Schofield and Haskins, 1964). Several recent reports (Altschuler, Berman and Cuttitta, 1967; Fleischer and Altschuler, 1969; Summerhayes, 1970; Cook, 1972) suggest, however, that the ratio is in fact greater than one, the previous ratio being ascribed to analytical error, or to the inclusion of cerium bearing impurities or detrital material in the samples. Table 4.1 lists La/Ce ratios for seven partially purified Moroccan samples, together with a number of analyses of purified phosphorite taken from the literature. The ratios are very variable, even for samples from similar locations, probably owing to errors in the analytical methods employed in their determinations. However, all the ratios are greater than 1, thus paralleling the ratio in sea water, and supporting the suggestion that phosphorites derive their R.E.E.'s directly from sea water by absorption (Altschuler, et al., 1967; Piper, 1972).

TABLE 4.1

La/Ce ratios for 7 Moroccan phosphorites,

and several world phosphorites.

Sample	La/Ce Ratio	Reference
Bone Valley Formation, Florida, U.S.A.	1.24	Altschuler et al., (1967)
Phosphoria Formation, U.S.A.	1.85	"
Onshore Moroccan Phosphate (average of two samples)	1.56	"
New Zealand offshore nodule (F127), Campbell Plateau.	1.82	Summerhayes (1970)
Jordan phosphate	1.60	This work
Onshore Moroccan phosphate, K3	4.25	This work
Moroccan offshore phosphorites		
139(1)	1.93	Summerhayes (1970)
148	1.10	"
959	2.5	This work
1004	1.75	"
156(1)	1.16	"

Rare Earth Fractionation

The method of incorporation of the R.E.E.'s in marine deposits, particularly manganese nodules, has been widely discussed in the literature. Ehrlich (1968) suggested that detrital material of high R.E.E. concentration is the principal source of these elements in the marine environment. Arrhenius and Bonatti (1965) suggest submarine volcanism may be important in the distribution of R.E.E., on the basis of higher concentrations and greater fractionation of R.E.E. in pelagic apatite compared to shallow water apatite. However, manganese nodules having similar R.E.E. abundances occur both in active tectonic areas and non-active areas (Ehrlich, 1968), suggesting submarine volcanism is unimportant. Glasby (1970), Piper (1972), and Altschuler, Berman and Cuttitta, (1967) favour direct precipitation or absorption from sea water as the method of R.E.E. concentration in marine deposits, and support their suggestions with fractionation patterns very similar to those of sea water. Further support for this hypothesis is indicated by Parak (1973) who closely examined a number of highly phosphatic iron ores containing approximately 5000 ppm of R.E.E. and concluded that the bulk of the elements were in the carbonate-apatite crystal lattice, with only very minor amounts being present as inclusions of R.E.E. bearing minerals.

In fig. 4.1 the R.E.E. fractionation patterns of a number of phosphorites from a wide variety of world locations are presented as ratios of R.E.E. to seawater, plotted against atomic number. In addition, two samples representative of typical fractionation patterns have also been plotted as ratios to crustal abundance and to average shales. In all cases the R.E.E. were first ratioed to La to eliminate differences in absolute abundance between samples. The figures indicate that ratios to seawater yield reasonably smooth curves, suggesting that seawater is the main source of supply of

R.E.E. in phosphorites, with detrital material being of minor significance in this respect. The marked contrast between the ratios to seawater and those to crustal abundance and average shale in the two representative samples shown in figs. 4.1.1 and m also supports this view. The shale ratios are similar to that of crustal abundance, both exhibiting an enrichment in the heavy R.E.E. This similarity in trend and degree of fractionation suggests that terrestial detritus is the major contributor of R.E.E. in continental margin sediments.

Cerium enrichment in phosphorites compared to seawater, similar to those shown in figs 4.1.d, e, and k, have been ascribed, where observed in other phosphorites, to the incorporation of Ce bearing impurities (Tooms et al., 1969) or detrital material with La/Ce ratios less than one (Altschuler et al., 1967). However, the similarity of the R.E.E. fractionation patterns (excepting Ce) to that of seawater and other phosphorites, in the samples presented here, makes the latter explanation unlikely. As the Ce enrichment is not observed in any of the purified or partially purified phosphorites, or in extensively weathered, and therefore fairly high grade, gangue-free phosphorites, it may well be caused by the suggested Ce bearing impurities. However, as pointed out by Altschuler et al. (1967), many other factors may affect the fractionations of R.E.E. and the Ce enrichment may well be a manifestation of such unknown factors.

Virtually all the phosphorites presented here display a significant depletion of heavy R.E.E. compared to light R.E.E.'s. Similar fractionations among R.E.E. have been ascribed to the increasing stability with increase in atomic mass of R.E.E. organic and inorganic complexes (Goldberg, 1963). This explanation is supported by Krynov (1968) who has shown that the tendency of R.E.E. to precipitate from an alkaline environment is strongly influenced by the degree of complexing. Alternatively, Ronov (1967) suggests fractionation in sedimentary environments may be attributed to differences in hydrolysis parameters, a suggestion supported by Glasby (1970) on the basis of the similarity of hydrolysis parameters to R.E.E. distribution patterns in Indian Ocean manganese nodules. However, these factors are similar, both relating to complex formation. Which process, if either, is operative is unknown. Since both are probably manifestations of the decreasing ionic radii of the R.E.E.'s with increasing atomic number, and the consequent increase in effective ionic charge, it is probable that this decrease in ionic radii is the primary cause of R.E.E. fractionations in phosphorite.

No significant differences in R.E.E. fractionations were detected between land and seafloor phosphorites or between groups of samples of either category from different locations and environments. This suggests that fractionation patterns are unaltered by weathering. It also suggests that the carbonate-apatite lattice, and not the environment of deposition, is the controlling factor in the incorporation of R.E.E. into carbonate-apatite.

FIGURES 4.1 a - m.

Fractionation patterns of R.E.E. in phosphorites.
(For Analytical Data see Addendum 6).

On all diagrams the horizontal dotted line represents the R.E.E. concentrations in seawater ratioed according to the procedure adopted for the phosphorites:-

for figs. 4.1 a - k

$$\text{R.E.E. Ratio} = \frac{\text{(R.E.E.)/(La) in phosphorites}}{\text{(R.E.E.) in seawater}}$$

for figs. 4.1.1, 4.1.m.

$$\text{R.E.E. Ratio} = \frac{\text{(R.E.E.)/(La) in phosphorites}}{\text{(R.E.E.)/(La) in comparative material}}$$

comparative material being average shale, seawater, and crustal abundance.

Fig. 4.1.a. - 4.1.k. :-

Ratios of R.E.E. Concentrations to seawater (Høgdahl, 1967)

Present day seafloor phosphorites

Fig. 4.1.	a.	F127	(Summerhayes, 1970)
"	b	1004	
"	c	139(1)	(Summerhayes, 1970)
"	d	Californian Nodule (Goldberg, 1963)	

Present day land phosphorites

Fig. 4.1.	e	Eastern Europe composite sample (Semenov, 1962)	
"	f	Bone Valley phosphorite	(Altschuler et al., 1967)
"	g	Moroccan phosphorite	
"	h	Moroccan phosphorite	
"	i	Phosphoria Formation sample (Altschuler et al., 1967)	
"	j	Jordan phosphorite	
"	k	Bulgarian Composite sample (Alexiev, and Arnandov, 1965)	

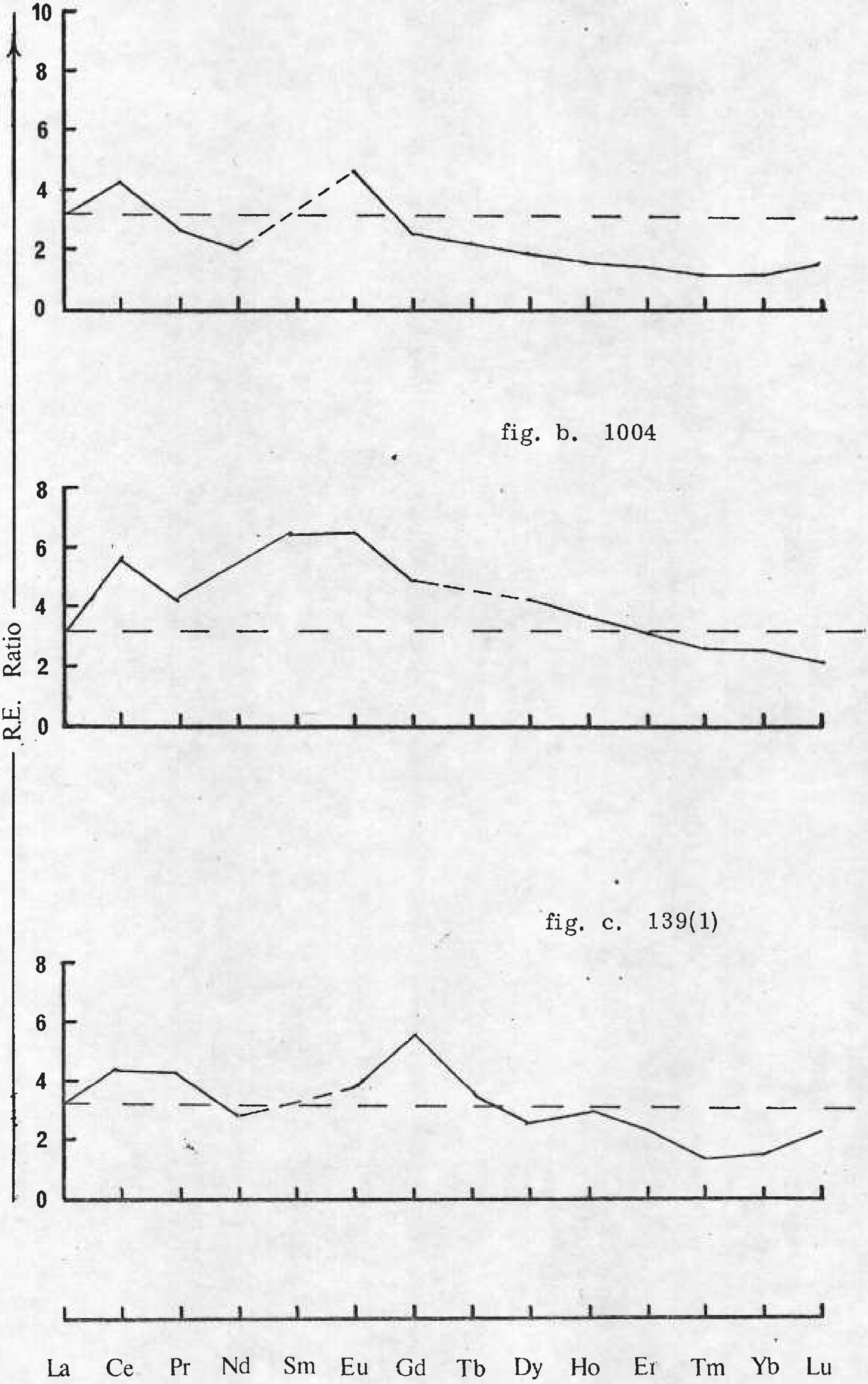


fig. a. F. 127

fig. b. 1004

fig. c. 139(1)

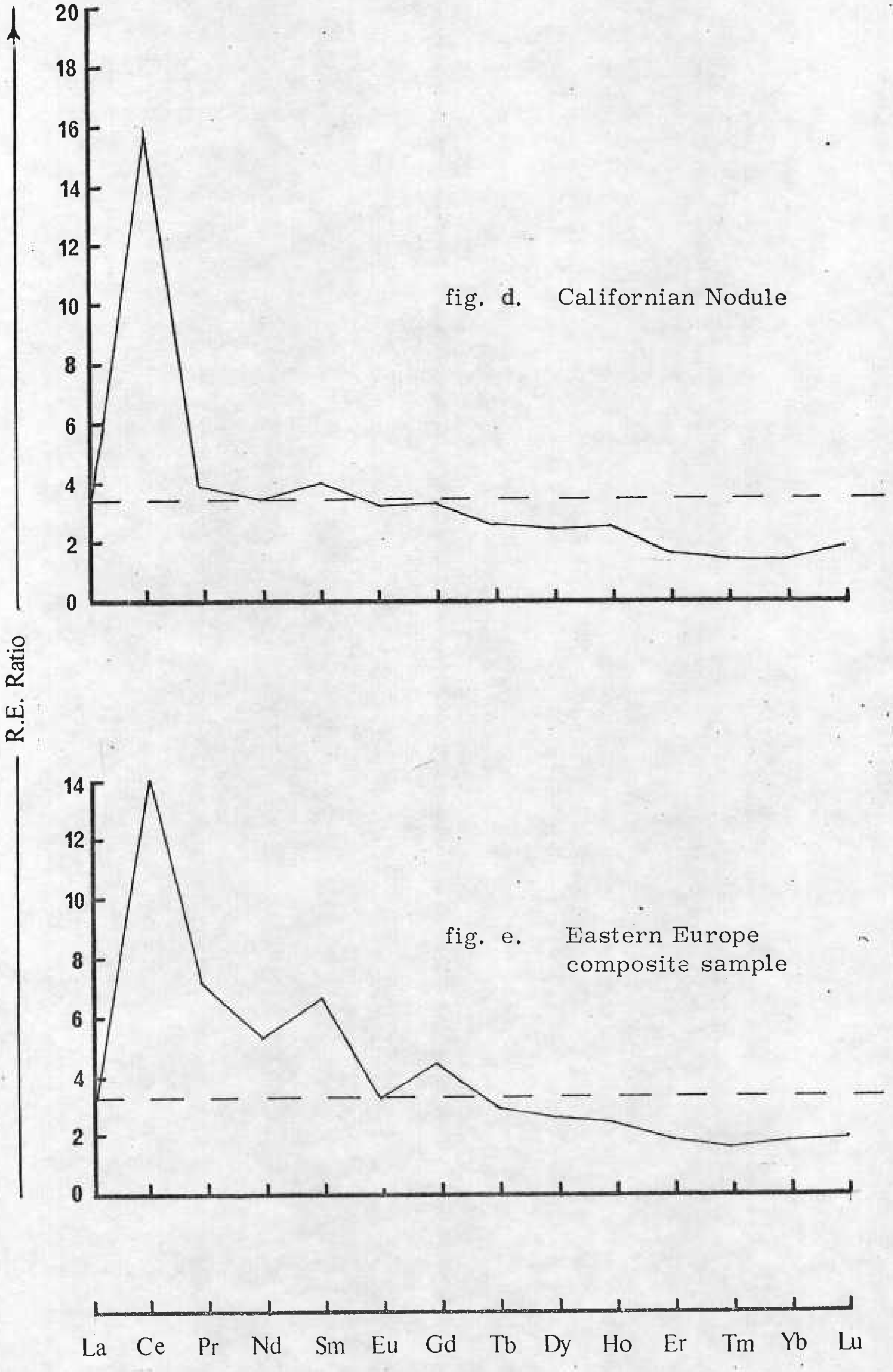
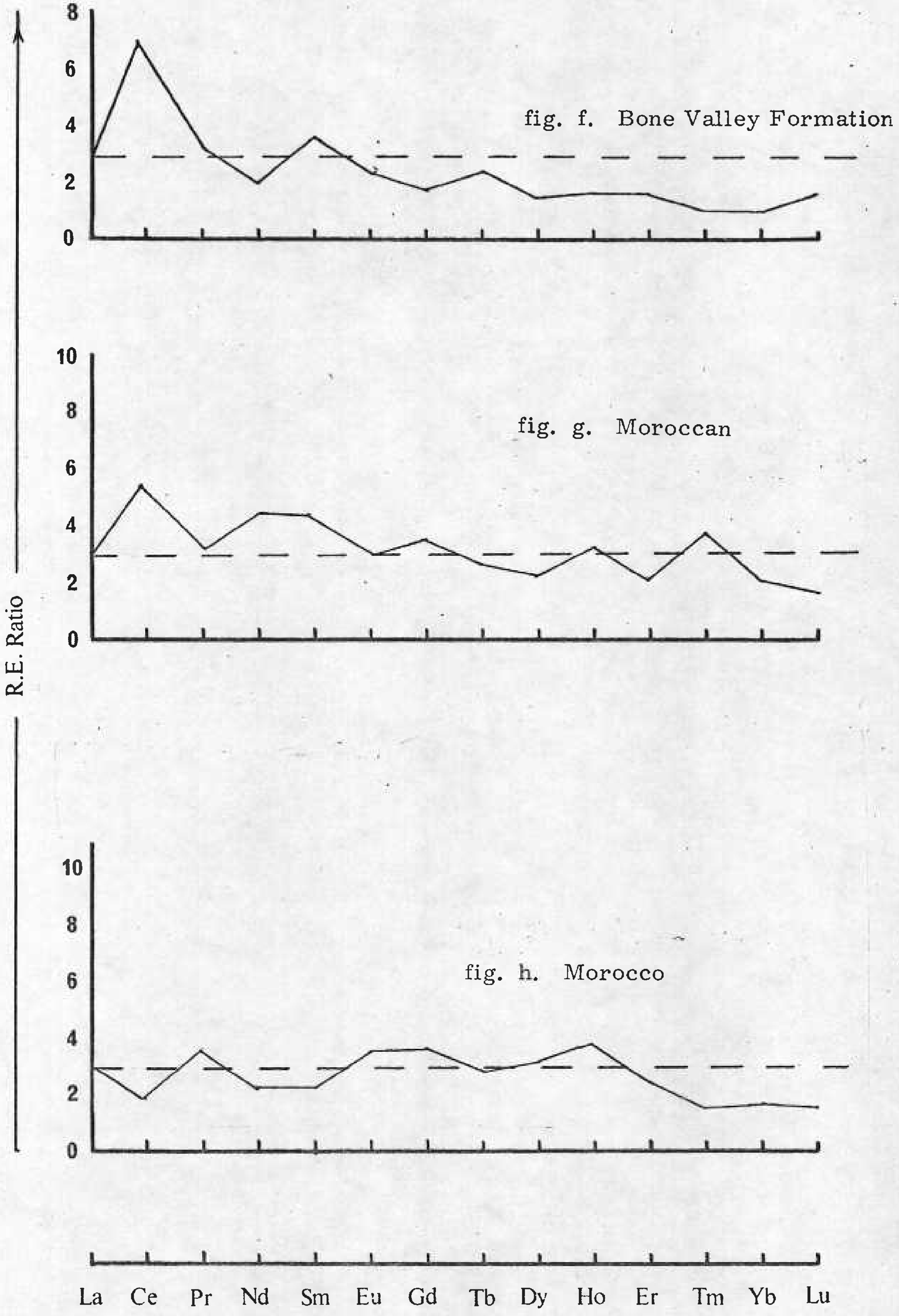


fig. d. Californian Nodule

fig. e. Eastern Europe composite sample


R.E. Ratio
fig. f. Bone Valley Formation
0
2
4
6
8
fig. g. Moroccan
0
2
4
6
8
10
fig. h. Morocco
0
2
4
6
8
10
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

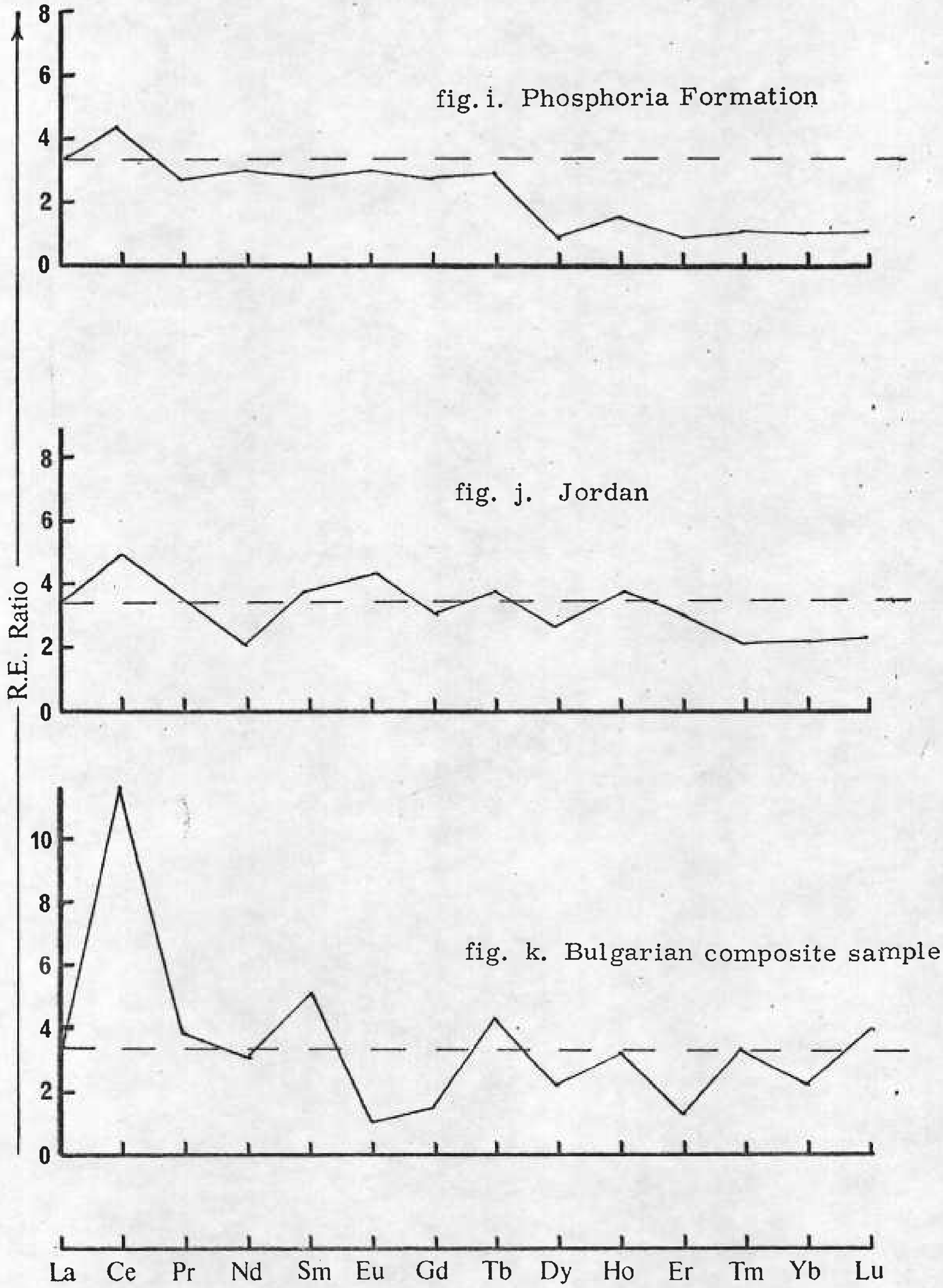


fig. i. Phosphoria Formation

fig. j. Jordan

fig. k. Bulgarian composite sample

Fig. 4.1.1

Moroccan Onshore Sample

A - R.E.E. ratio to average shale (Wildeman and Haskins, 1965)

B - R.E.E. ratio to sea water (Høgdahl, 1967)

C - R.E.E. ratio to crustal abundance (Mason, 1966)

D - R.E.E. ratio to average shale (Minami, 1935)

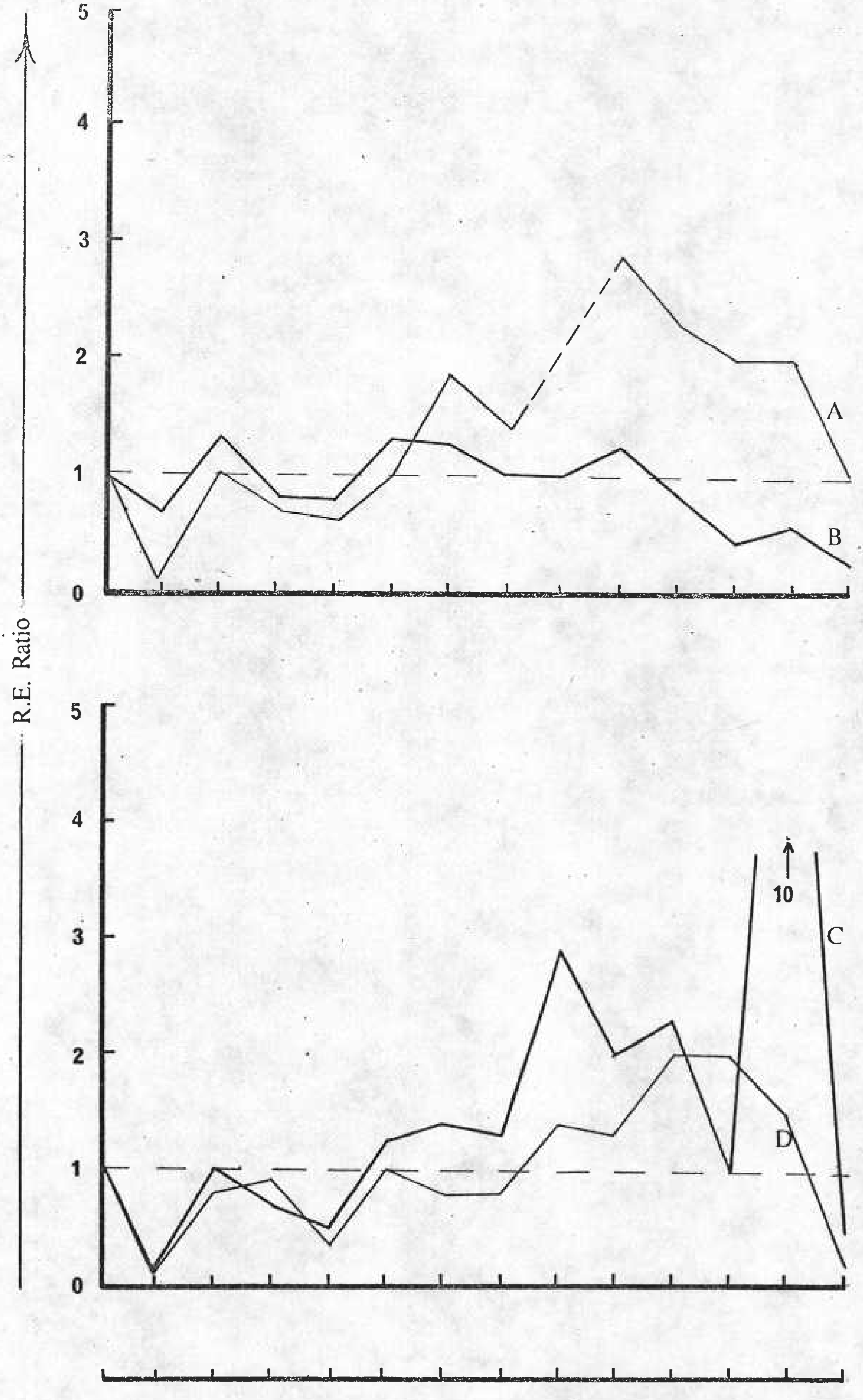

R.E. Ratio
5
4
3
2
1
0
A
B
5
4
3
2
1
0
10
C
D
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

Fig. 4.1.m

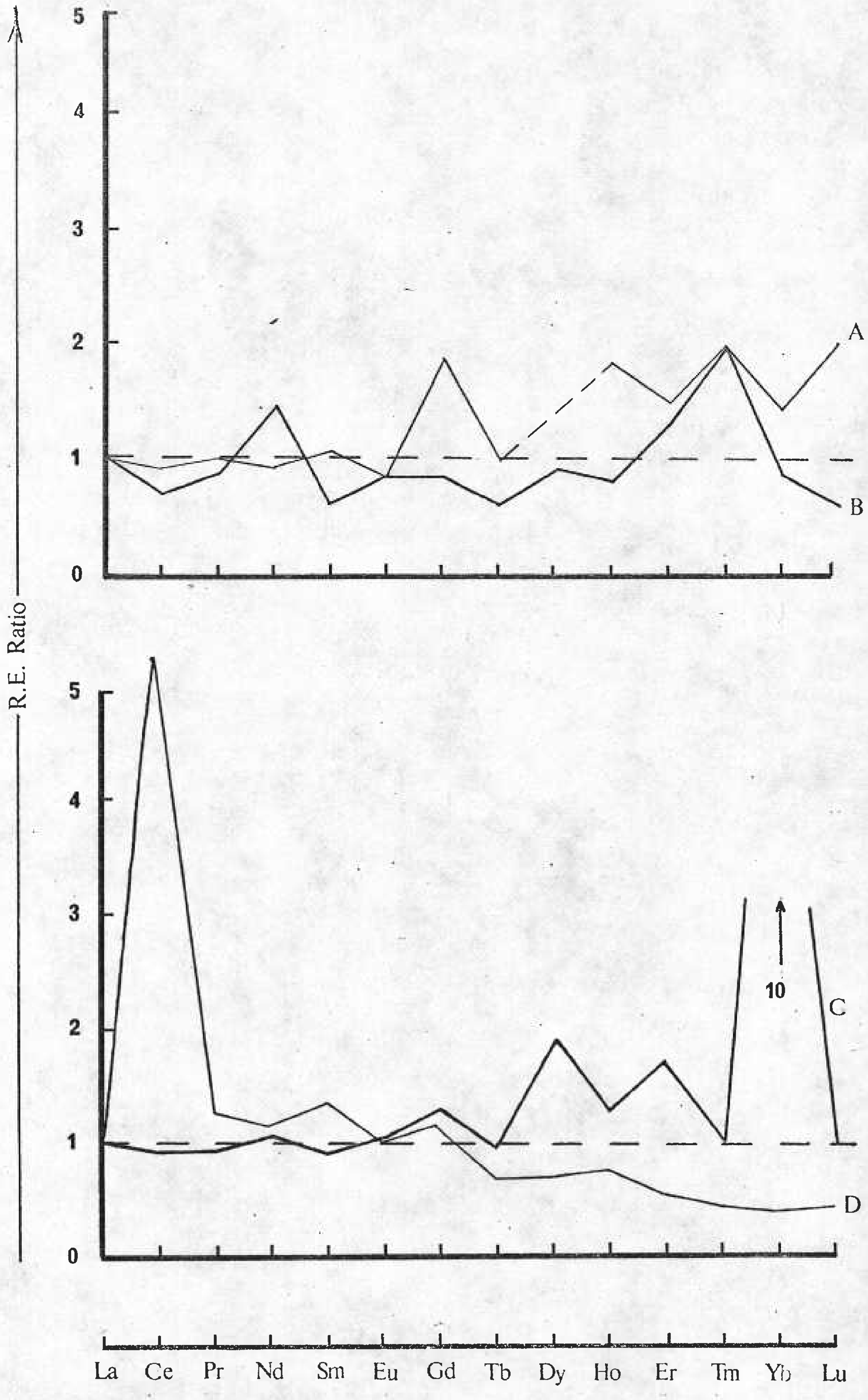
Californian Nodule

A - R.E.E. ratio to average shale (Wildeman and Haskins, 1965)

B - R.E.E. ratio to average shale (Minami, 1935)

C - R.E.E. ratio to crustal abundance (Mason, 1966)

D - R.E.E. ratio to sea water (Høgdahl, 1967)


R.E. Ratio
5
4
3
2
1
0
A
B
5
4
3
2
1
0
10
C
D
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

Regional Variations of R. E. E.

As there is little fractionation of R. E. E.'s in the Moroccan phosphorites, their regional variations can be represented in terms of values for cerium in samples from each province (table 4. 2). This is done because the concentrations of other rare earths could not be determined without the employment of time consuming techniques. The onshore samples are similar in R. E. E. fractionation patterns to the offshore samples, suggesting weathering has little effect on R. E. E. fractionation patterns. Recalculation of Ce concentrations to pure apatite for each province, however, indicates a depletion of some 40% in the onshore samples compared to the offshore northern province. This depletion is similar in extent to that of other substituting species noted in chapter 5. In view of the proposed mechanisms of formation of the phosphorite in the two provinces and the geochemical similarity between them, the assumption is made that the original R. E. E. abundances and fractionation patterns of onshore samples were similar to those now found in offshore samples, and the former now differ as a result of weathering. The R. E. E. concentrations in the southern samples are 20-30% lower than in the northern province (table 4. 2). Since the southern samples contain appreciably more detrital material than do the northern and onshore phosphates, Ehrlich's (1968) suggestion that detrital supply is paramount in R. E. E. supply to sediments is not supported. The reason for the lower Ce (and presumably R. E. E) concentrations in the southern samples may be related to their iron oxide content. If the R. E. E.'s exist as positive species in sea water, as seems likely (Riley and Skirrow, 1965), the presence of considerable concentrations of positively charged iron precipitates during formation of these samples may have reduced the ability of the carbonate-apatite to incorporate other positively charged species, because of electrostatic repulsion between the positive species. That Sr and Na substitution is also lower in the iron rich samples (chapter 5) supports this proposed mechanism, as the latter elements do exist as positive species in sea water.

TABLE 4.2

Cerium concentrations in Moroccan phosphorites

Location	Sample	Ce ppm	Average Ce ppm
Onshore Morocco	K3	65	60
	Y1	52	
	K1	65	
	S. D	60	
Offshore Northern Province	139(1)*	68	60
	966(2)*	72	
	959	59	
	1022(2)	59	
	1004 *	42	
Offshore Southern Pebbles	847(1)p1	47	43
	847(1)p2	42	
	896(1)p1	45	
	896(1)p2	36	
Offshore Southern Conglomerates	833	58	52
	896(2)	52	
	896(1)	46	

* pelletal samples

Summary and Conclusions

Sea water is the major source of R.E.E. in the phosphatic samples described here. The elements are either precipitated, or directly absorbed, from sea water into the carbonate-apatite phase during its formation. The Moroccan samples, and several world samples, show La/Ce ratios greater than one, supporting the above hypothesis. The distribution patterns of R.E.E. in onshore and offshore Moroccan samples also support the suggestion, and also indicate that sub-aerial weathering produces no apparent fractionation of R.E.E. These elements are, however, slowly removed by such weathering at the same rate as other ions (Na^+, Sr^{2+}, SO_4^{2-}, CO_3^{2-}) substituting in the carbonate-apatite lattice. A comparison of R.E.E. fractionation patterns found in Moroccan phosphorites and those from various offshore and onshore sites elsewhere indicate that some syngenetic process, and not weathering, must have been operative in other deposits to produce depletion of heavy lanthanons with respect to sea water, and the light lanthanons in some deposits. The mechanism of fractionation is not clear, but probably relates to the decrease in ionic radii of the R.E.E. with increasing atomic mass. Whether the environment of deposition of the R.E.E. is oxidising or reducing seems to exert little influence on their incorporation into the Moroccan phosphorites, the presence of iron oxide in the southern samples appearing to have more affect. The influence of the iron oxide is probably due to simple electrostatic repulsion between positively charged, precipitated, iron oxide and positively charged $R.E.E.^{3+}$ in sea water.

CHAPTER 5

SUBSTITUTIONAL CHEMISTRY OF CARBONATE-APATITE

Introduction

Virtually all published data pertaining to substitutions within the lattice structure of carbonate-apatite is concerned with deposits now on land, No systematic investigation of substitutions in present day seafloor samples has been published, and no comparison made of offshore and onshore deposits. Gulbrandsen (1970) has attempted to draw conclusions regarding the environment of deposition of carbonate-apatite from the substitutional CO_3^{2-} content of the Phosphoria Formation, but does so on a small scale using very limited data, and draws a conclusion with which the writer disagrees.

In this chapter the substitutions occurring within the carbonate-apatite lattice have therefore been examined in a large number of phosphorites from a wide variety of world locations, both onshore and offshore. In addition, data has been taken from the literature and compared to the data obtained by the writer. The reasons for this study were threefold. Firstly, in order to examine possible differences in substitution which might occur between samples from different deposits; secondly, in order to examine whether such differences, if they occur, are related to the environment of deposition and whether the effect the environment might have on the extent and degree of substitution can be useful as a paleo-environmental indicator; and thirdly, the comparison was undertaken to assess the effects of weathering on the substitutions.

To examine differences in degree and manner of substitution between deposits, all the Moroccan and world samples were compared with respect to Na, Sr, and substitutional CO_3^{2-} and SO_4^{2-}. Only non-pyritic samples were included in the examination of S substitution, the samples being chosen on the basis either of the iron oxide content (which was taken to indicate an oxidising environment if high), or petrographic examination, samples with observable pyrite being excluded from the comparison. In addition, data on Phosphoria

Formation phosphorites were taken from Gulbrandsen (1966), though data on S substitution were only used for those samples containing less than 1% organic matter and more than 2% iron oxide, as these samples were thought to contain little or no S present as pyrite. Data on Agulhas Bank phosphorites were taken from Parker (1971). In these latter samples pyrite was assumed to be absent on account of their high iron oxide content (up to 20%). The Phosphoria Formation and Agulhas Bank deposits were used for a comparison with Moroccan samples because of their contrasting depositional environments, that of the Phosphoria Formation being principally reducing, whilst that of the Agulhas Bank was principally oxidising. The effects of weathering on the substitutions was investigated by examining the relationship in all samples between the contents of P and substituents, and by comparing onshore and offshore Moroccan phosphorites, in particular the northern offshore samples. This has enabled weathering effects to be clearly seen, as the two sample populations were probably very similar in geochemistry when formed.

The principal substituting ions within the carbonate-apatite lattice are Na^{+}, Sr^{2+}, and Mg^{2+}, which replace Ca^{2+}, and CO_3^{2-} and probably SO_4^{2-}, which replace PO_4^{2-}.

The presence of Na and Sr in phosphorites in concentrations of up to 2% Na and 0.2% Sr have been widely reported (see Swain, 1962, Tooms et al., 1969; McConnell, 1973, for reviews). These elements are commonly stated to substitute for Ca within the carbonate-apatite lattice. Magnesium also occurs in phosphorites, both as dolomite and as a substituent for Ca in the carbonate-apatite lattice, where its presence in concentrations of up to 0.5% Mg are common (Lehr et al., 1967).

The fact that the carbonate ion, CO_3^{2-}, occurs within the carbonate-apatite lattice has been known for many years (Hausen, 1929), but its position as a substituent for phosphate ions, PO_4^{3-}, has only recently been settled beyond reasonable doubt (Lehr et al., 1967, McConnell, 1973). The mode of occurrence of S in phosphorites of marine origin is still in doubt. That S can substitute in the lattice of igneous apatite has been amply demonstrated by McConnell (1937), who showed apatite to be an end member of the series Apatite (41% P_20_5) - Wilkeite (21% P_20_5, 12% $S0_3$, 9% S_i0_2) - Ellastadite (20% $S0_3$, 17% S_i0_2), and by Vasileva (1958) who has reported appreciable S concentrations in igneous apatite from the U. S. S. R. However, the only work on S substitution within carbonate-apatite of marine origin is that of Gulbrandsen (1966) who suggests a coupled Na-S substitution within the lattice, on the basis of a linear Na-S relationship in certain selected samples from the Phosphoria Formation.

Analytical Methods

Sodium was determined by flame photometry of the nitric acid soluble fraction of the phosphorites, which consisted of carbonate-apatite, dolomite, and calcite (appendix 8). Sodium contributions from the carbonate minerals were not expected to be a significant portion of the total Na. Phosphorus was determined by a wet chemical method involving precipitation of P as a phosphomolybdate complex, and titration of the complex with standard alkaki. X-ray diffraction was used to determine lattice CO_3^{2-} (appendix 5), after the method of Gulbrandsen (1970). Strontium and sulphur were determined on whole rock samples by the use of x-ray fluorescence spectrometry (appendix 6).

Results and Discussion

Scatter plots of Na and Sr against P_20_5 (figs. 5. 1. a and 5. 1. b) indicate a strong positive correlation between these elements and the carbonate-apatite phase, for present day seafloor phosphates. This suggests that these elements are incorporated within the carbonate-apatite lattice. Bliskovskiy et al. (1967) have demonstrated similar relationships between Sr and P_2O_5 in a variety of primary phosphate deposits, and also conclude that Sr^{2+} substitutes for Ca^{2+} in the carbonate-apatite lattice of phosphorites. The iron rich samples (those from the Agulhas Bank and the Moroccan southern pebbles) are, however, somewhat lower in Na and Sr than the iron poor samples. This is probably not an effect of the depositional environment, as many of the iron poor samples contain little or no pyrite or organic matter, indicating that they may have formed in an oxidising environment. The observed depletion of Na and Sr may be explained on the basis of simple electrostatic repulsion. The presence of considerable quantities of positively charged colloidal iron oxide during phosphorite formation may inhibit the approach and substitution of positively charged Na^+ and Sr^{2+} ions within the carbonate-apatite lattice.

When the concentrations of Na and Sr in seafloor phosphorites are recalculated to a pure carbonate-apatite basis, they show a remarkable degree of uniformity, with iron rich samples being slightly lower in both elements. This suggests that a degree of substitution which is fairly sharply defined occurs in present day seafloor phosphorites, with approximately 1.6% Na and 3000 ppm Sr representing an approximate mean value for the maximum extent of substitution.

The samples from onshore locations presented here show a definite negative correlation between P_2O_5 and both Sr and Na (figs. 5.1.a, 5.1.b). Bliskovskiy et al. (1967) have noted similar relationships in some secondary phosphate deposits and have interpreted their findings in terms of deposition of secondary phosphate from Ca rich, Sr poor, continental Karst waters. A simpler, and more likely explanation is that both Na and Sr are removed from carbonate-apatite during weathering, together with accessory minerals such as carbonates and clays. The decrease of Na and Sr is therefore matched by a concomitant increase in P_2O_5, giving rise to a negative correlation.

The negative correlation between substitutional S and P_2O_5 (fig. 5.3), and the fact that all seafloor carbonate-apatite contains approximately 8% CO_3^{2-}, whilst onshore phosphorite is much lower, also supports the suggestion that it is weathering that reduces the concentration of lattice substituents in carbonate-apatite.

In fig. 5.2, Na concentrations are plotted against the extent of carbonate substitution in carbonate-apatite, represented by the mole ratio CO_3^{2-}/PO_4^{3-}. The solid line represents the regression line obtained using this method by Lehr et al. (1967) for over one hundred land samples. With few exceptions the samples presented here fall into two regions, with present day land samples falling near or on the line (within the limits of error, shown as dotted lines), whilst seafloor samples fall above the line by an average of 0.02 moles of Na. Samples from the Phosphoria Formation and the Agulhas Bank also fall above the line. It is suggested that samples plotting above the line contain excess Na over that required for a coupled $Na^+ - CO_3^{2-}$ substitution. This Na is probably present in a coupled substitution of $Na^+ - SO_4^{2-}$ for $Ca^{2+} - PO_4^{3-}$. That this is so is confirmed in fig 5.3 which indicates that a good positive correlation exists between S (i.e. substitutional SO_4^{2-}) and P in non-pyritic samples. Further confirmation of the proposed substitution is indicated in figs. 5.1.a and 5.3, which indicate a Na/S ratio of approximately one, which would be expected on the basis of charge considerations, if such a coupled substitution were present. When the substitutional SO_4^{2-}, and CO_3^{2-}, Na^+, and Sr^{2+}, contents of marine samples are recalculated to a pure carbonate-apatite basis, a surprising degree of similarity is shown for samples from such a wide variety of world marine locations. The phenomenon has already been noted for the substitutional Na and Sr in these samples. For the anions SO_4^{2-} and CO_3^{2-}, the data suggest that, as in the case of Sr^{2+} and Na^+, substitution occurs within fairly narrow concentration limits of approximately 8% CO_3^{2-} and 4% SO_4^{2-}.

The data on SO_4^{2-} and CO_3^{2-} contents in the carbonate-apatite lattice of land samples is similar to the data pertaining to Na and Sr. The higher the value of P_2O_5, i. e. the purer the carbonate-apatite, the lower is the substitutional SO_4^{2-} and CO_3^{2-} (fig. 5.3 and table A. 6. 4, the main analytical tables), indicating removal of both substituents during weathering.

The substitution of Mg for Ca in the lattice could not be investigated, owing to the difficulty of removing dolomite. However, the obvious incorporation of Sr into the lattice (fig. 5. 1. b) suggests an appreciable Mg substitution might also occur, as reported by Lehr et al. (1967).

The effects of weathering on the substituents within the carbonate-apatite lattice is deducible not only from the reciprocal relationships between P and lattice substituents, but also from a comparison of the present onshore and northern offshore Moroccan samples. The validity of this comparison rests on the assumption that both deposits were similar in geochemistry, or at least substitutional chemistry, when laid down. Justification of this assumption rests on the petrographic similarity of the onshore and offshore pelletal samples, and in addition, the data presented here on seafloor phosphorites, from a wide variety of world locations and environments, which indicate that they are all remarkably similar in substitutional chemistry. It therefore seems probable that the onshore deposits were also similar when first formed.

Comparing the onshore and offshore northern Moroccan samples after recalculation of substitutional species to a pure carbonate-apatite basis indicates that the onshore samples contain one half of the CO_3^{2-}, Na^+ and Sr^{2+} and approximately three-quarters of the SO_4^{2-} contained within the offshore samples. This suggests that weathering removes all the substituents, with SO_4^{2-} being removed more slowly than the other ions.

Source of the Substituents in Carbonate-Apatite

The only reasonable source for Na^{+} and SO_4^{2-} is sea water, from which these ions were probably incorporated by direct absorption. The majority of the Sr^{2+} was probably also derived from sea water, as the phosphates almost certainly formed by phosphatisation of calcareous sediments, and such samples of limestones as were obtained from the same areas as the phosphates contained less than 600 ppm Sr (Summerhayes,1970). Furthermore if the original calcite was a major contributor to the Sr content of the samples, poorly phosphatised samples would not show such a good Sr - P_2O_5 relationship as they do. Indeed a Ca - Sr relationship would be expected in such cases, but was not found. The CO_3^{2-} within the carbonate-apatite is probably a relic of the original carbonate sediments. Since none of the phosphates from present marine environments contain less than 8% substitutional CO_3^{2-}, this value probably represents the maximum extent of CO_3^{2-} replacement possible in the marine environment.

Summary and Conclusions

Virtually all present day seafloor phosphorites contain considerable quantities of substituents replacing Ca^{2+} and PO_4^{3-}. The major coupled substitutions are Na^{+} - CO_3^{2-} and Na^{+} - SO_4^{2-} replacing Ca^{2+} - PO_4^{3-}, with Sr^{2+} and Mg^{2+} also substituting for Ca^{2+}. These seafloor phosphorites exhibit a surprising degree of similarity in the quantities of substituents they contain, the usual values, expressed on a pure carbonate-apatite basis, being 1.6% Na, 3000 ppm Sr, 4% SO_4^{2-} and 8% CO_3^{2-}. The remarkable constancy of these substitutional levels indicates that they may represent the maximum substitutional levels possible within a normal marine environment.

The wide variety of trace element abundances and the occurrence of such Eh indicators as pyrite and iron oxides found in the phosphorites considered here testify to the wide variety of conditions in which these phosphates formed. That such a wide variety of samples from many world seafloor locations exhibit such similarities in substitution indicates that the environment of deposition plays little or no part in determining the extent or nature of the substitutions. These findings do not agree with those of Gulbrandsen (1970) concerning the Phosphoria Formation. Gulbrandsen attributes a slight but definite eastward increase in substitutional CO_3^{2-} within this formation to a slight easterly increase in temperature of the Permian Sea in which these phosphates formed. The writer suggests that these regional trends were in fact the result of progressively longer exposure of the deposit to weathering as the Permian Sea retreated westwards during the course of geologic time.

Land samples also exhibit the above substitutions, but to a lesser extent. Land deposits also exhibit a much greater range of substituent concentrations owing to the effects of weathering than do subsea deposits. Onshore samples, however, always contain lower substituent concentrations than do offshore samples. Moroccan onshore samples contain approximately one half as much Na^+, Sr^{2+}, and substitutional CO_3^{2-} as do the offshore pelletal phosphorites. This indicates that these species all weather at the same rate, assuming the present onshore samples were geochemically similar to the present offshore samples when formed. The great similarity of all the marine samples presented here indicates that this was very likely the case. However, the onshore Moroccan samples contain substitutional SO_4^{2-} in concentrations reduced only one half as much as the reduction in the other substituents. In addition, Phosphoria Formation samples (Gulbrandsen, 1966) contain substitutional SO_4^{2-} in concentrations which are often in excess of the substitutional CO_3^{2-} content. These facts suggest that substitutional SO_4^{2-} is removed from carbonate-apatite by weathering at only one half the rate of removal of the other substituting species. This is probably a result of the large ionic size of the SO_4^{2-} ion, which is 40% larger in diameter than CO_3^{2-}, and its tetrahedral configuration, CO_3^{2-} being planer.

The final weathering product of impure carbonate-apatite is francolite, a fluorapatite containing slightly more than 1% substitutional CO_3^{2-}, together with a few resistant accessory minerals, notably quartz. Such deposits form the world's major commercial phosphate sources.

Figs. 5.1.a and 5.1.b

Variation of Na and Sr content

in phosphorites with variation of P_2O_5

KEY TO FIGS. 5.1.a - 5.3

■	Southern Province Pebble Samples
○	Phosphoria Formation
○	Onshore World Samples
●	Northern Province
✱	Offshore World Samples
△	Onshore Moroccan Samples
▲	Southern Province Conglomerates

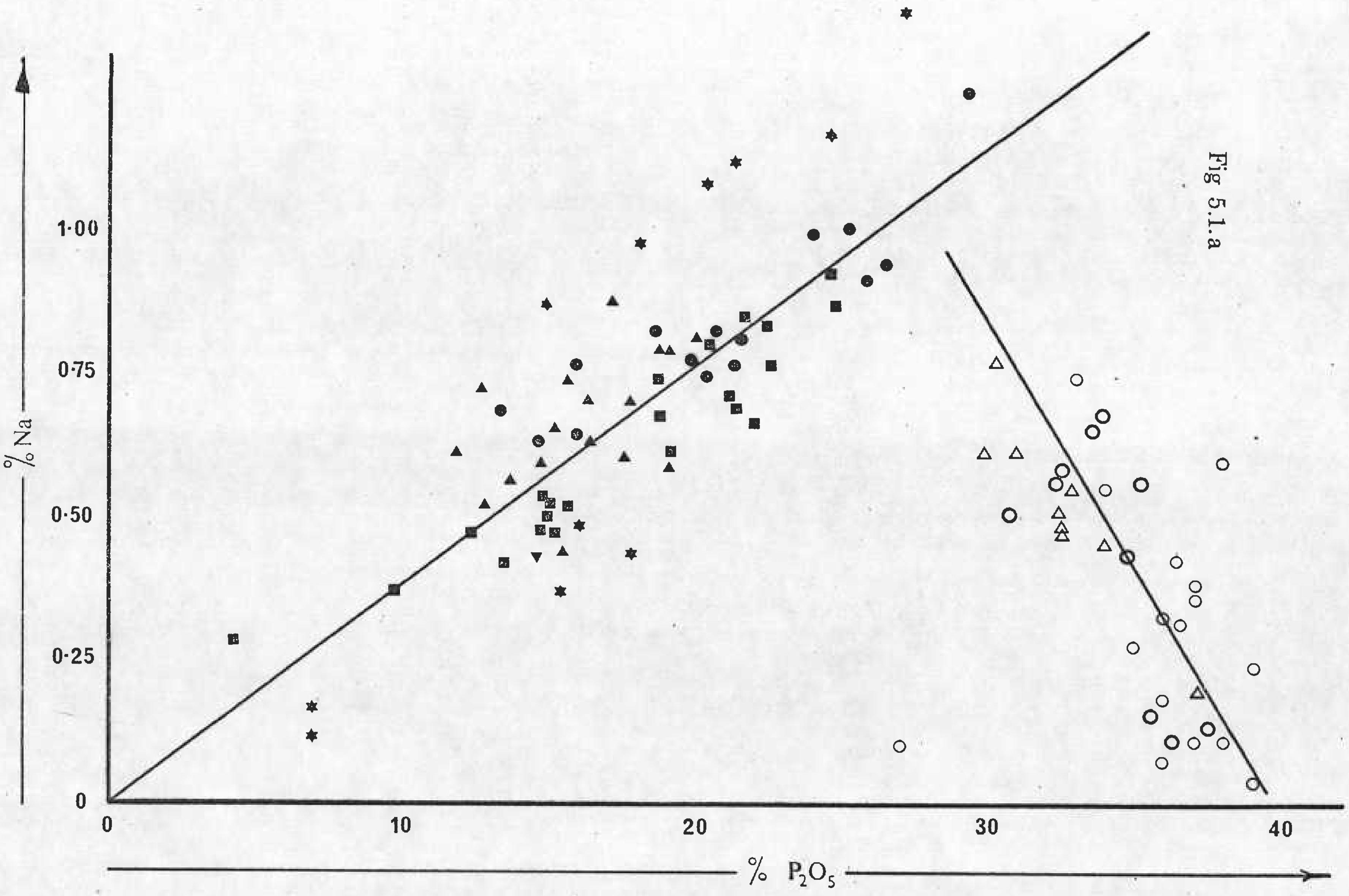


Fig 5.1.a

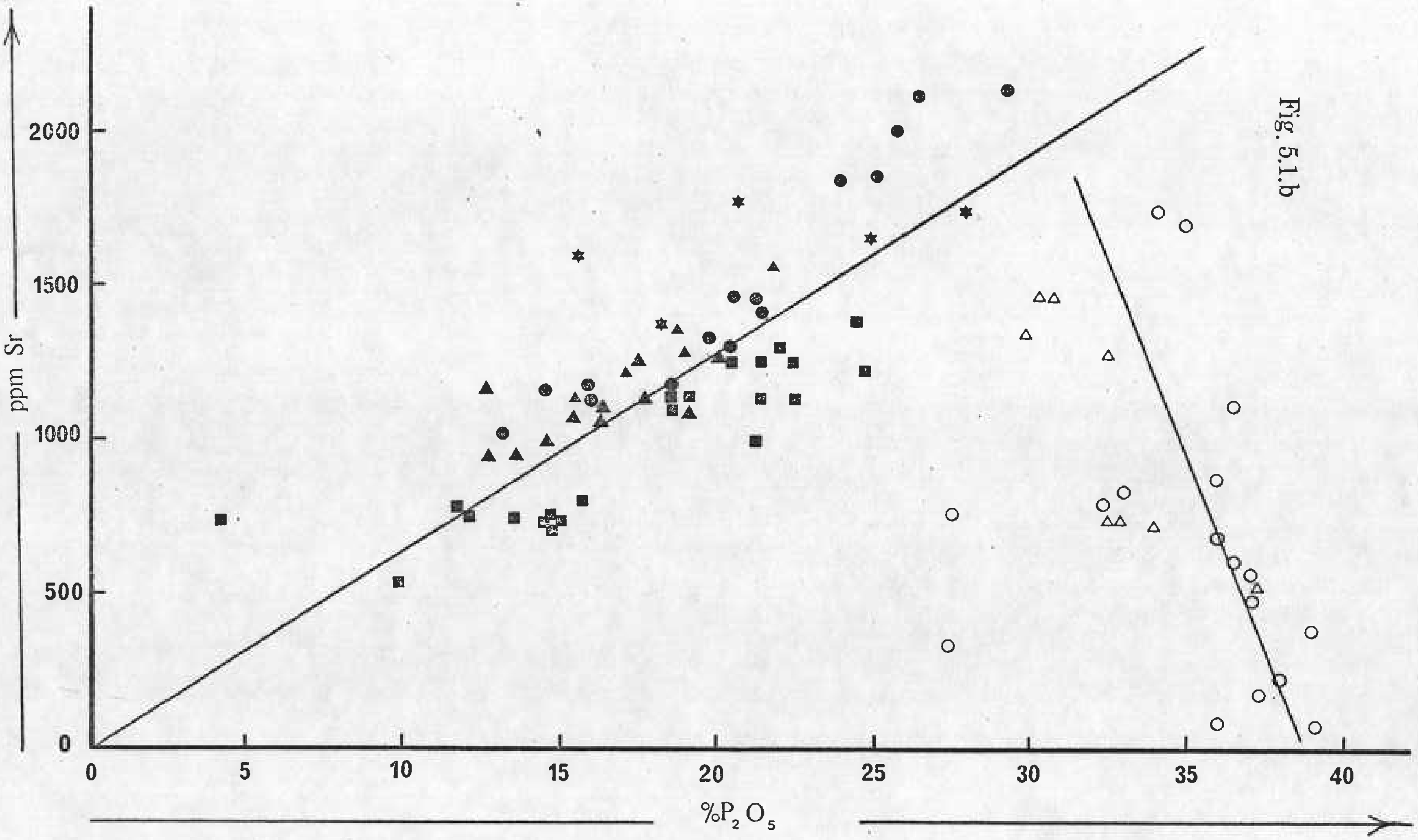


Fig. 5.1.b

Fig. 5.2

Variation of Na with CO_3^{2-} substitution

(expressed as the mole ratio $\frac{CO_3^{2-}}{PO_4^{3-}}$)

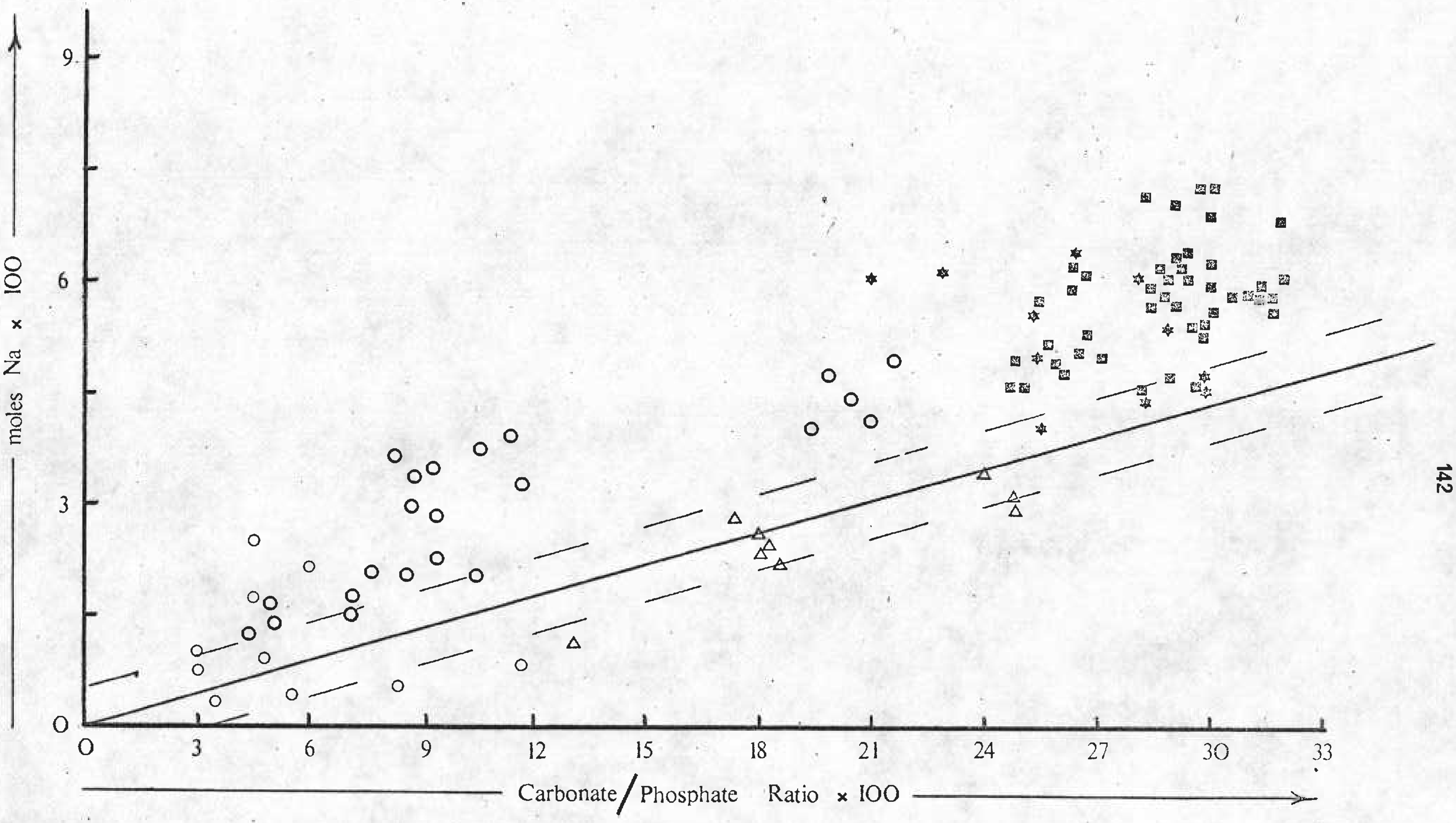
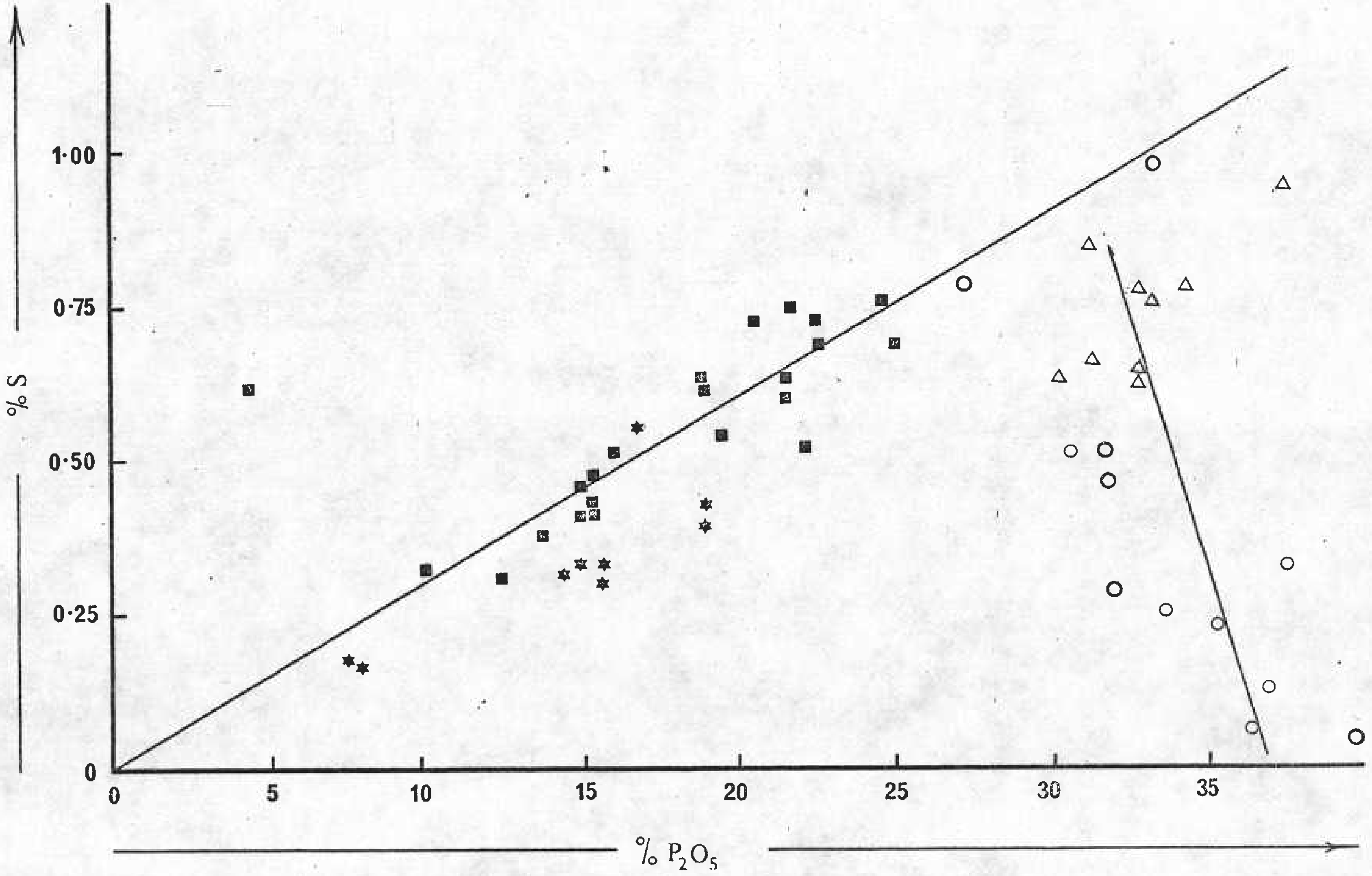

9
6
3
0
moles Na × 100
0
3
6
9
12
15
18
21
24
27
30
33
Carbonate/Phosphate Ratio × 100

Fig. 5.3

The variation of S with P_2O_5 in non-pyritic samples


% S
1·00
0·75
0·50
0·25
0
0
5
10
15
20
25
30
35
% P_2O_5

CHAPTER 6

PHOSPHORITE GENESIS

The development and refinement of theories proposed to account for phosphorite formation are well reviewed by Gulbrandsen (1969) and Tooms et al. (1969), among others, and only the three now considered by most workers to be viable are discussed here, viz. by the direct precipitation of carbonate-apatite from seawater (Kazakov, 1937; Emery, 1960; McConnell, 1966; Baturin, 1970, 1971, 1972), by phosphatisation of carbonate sediments (Ames, 1959, 1961; Peaver, 1967; Summerhayes, 1970; Parker and Siesser, 1972), and by the recycling and redeposition, by the action of both ground water and sub-aerial erosion, of P from sediments of low P content (Altschuler, 1965; Gilliland, in press).

Evidence for direct precipitation occurring in the marine environment was limited until the recent discovery of authigenic phosphorus concretions in organic rich sediments on the continental margin off Peru, Chile, and S. W. Africa. (Baturin, 1970, 1971, 1972; Summerhayes, 1973; Veeh et al. , 1973). The discovery of these concretions has been interpreted by these authors as indicative of the first stage of phosphorite formation. However, it has not yet been shown that these concretions in fact will form phosphorites, although this seems a strong possibility.

Other evidence cited in favour of direct precipitation as a method of phosphorite formation is 1) the pelletal form of many phosphorite deposits. However, this could well be caused by mechanical reworking of phosphatised carbonate sediments, as has occurred for the Moroccan pelletal samples; 2) the precipitation of carbonate-apatite under laboratory conditions, and also, in one instance, in nature where the brachiopod 'lingula' has been shown to have a shell of carbonate-apatite (McConnell, 1963). However, carbonate-apatite produced by precipitation under laboratory conditions frequently has been shown to be considerably different from natural carbonate-apatite (Trautz, 1960; Simpson, 1966, 1967, 1968a, 1968b; Termine and Posner, 1966, 1967). Furthermore, although the precipitation of carbonate-apatite in association with living organisms (the shell of lingula) has its counterpart in hydroxy-apatite, a mineral very similar to carbonate-apatite and the main component of teeth and bones, which form by precipitation, this merely serves to illustrate that complex organic reactions in cellular environments very different to that of seawater are needed to bring about the precipitation of apatite. Carbonate-apatite might precipitate from seawater if present at above saturation levels, although the high Mg concentration in seawater would make this unlikely. Unfortunately, the appropriate thermodynamic data for calculations of the solubility of carbonate-apatite in seawater are not available (Pytkowicz and Kester, 1967). Thus the theoretical calculations of Kramer (1964) and Roberson (1966) showing carbonate-apatite to be present at saturation levels or above may well be incorrect, a suggestion supported by McConnell (1965) on similar grounds. Indeed, Arrhenius (1963) showed apatite to be dissolving on the deep ocean floor, suggesting undersaturation.

The second mechanism of phosphate formation, by replacement of carbonate sediments rests on two observations: 1) the laboratory preparation, by calcite replacement, of carbonate-apatite very similar to natural carbonate-apatite (Ames, 1959, 1961; Simpson, 1966, 1967, 1968); and 2) the occurrence in nature of many obvious replacement phenomena particularly of foraminiferal oozes and tests (Dietz et al., 1942; Hamilton, 1956; D'Anglejan, 1968; Peaver, 1966, 1967; Summerhayes, 1970; Parker and Siesser, 1972; this work). The work of Ames (1959) suggests very low concentrations of phosphate can cause replacement, the lower limit being approximately 0.1 ppm. However, whether this concentration will cause replacement in normal natural systems is not definitely known, although the frequent occurrence of replacement in nature suggests it will, and on this basis Peaver (1967) points out that only waters in fjords, estuaries, and areas of upwelling contain greater than 0.1 ppm phosphate. However, carbonate replacement need not necessarily reflect interaction between carbonate minerals and phosphate rich waters, as concentrations of P within interstitial waters can reach values 50 to 100 times that in seawater (Brooks, Presley and Kaplan, 1968) indicating that such replacement could occur within the sediment. The source of this P is considered to be decaying organic material, and the common association of reducing conditions and phosphorite formation has been cited in support of this (Tooms et al., 1969; Riggs and Frease, 1965; D'Anglejan, 1968). However, phosphorites are also found in intimate association with Fe_20_3, indicating their formation within oxidising environments and probable early destruction of organic material before it can contribute significantly to the P content of the sediment. Thus such an organic supply of P is not essential to phosphorite formation.

The third mechanism of phosphorite formation at present proposed only for certain sections of the Bone Valley Formation in Florida, involves reworking of low grade phosphorite, or sediments of only average P abundance, by P dissolution and reprecipitation by groundwater, and erosion and concentration of the P by deposition in nearby quiet water marine environments (Altschuler, 1965). Extensive mass balance calculations (Gilliland, in press) indicate that this mechanism of formation could result in a deposit similar to the present Bone Valley Formation being formed in about 20 m. years even if the original level of P in the original sediment was of only average abundance ($<1\%$).

In view of the above discussion, it seems that direct precipitation of phosphorite from seawater is unlikely to be an important mechanism of phosphorite deposition in the oceans due to the difficulty of precipitating carbonate-apatite, and the low phosphate concentration in seawater. However, it may occur within sediments, where the concentration of phosphate can reach 100 times that in seawater (Brooks, Presley and Kaplan, 1968). Most phosphorites probably form by replacement of carbonate sediments, in esturine environments or areas of upwelling, where the phosphate content of seawater is greater than 0.1 ppm. Replacement also continues within sediments possibly faster than at the sediment-seawater interface, due to the high concentration of phosphate in the pore water.

Formation of Moroccan Phosphorites

It seems probable that the Moroccan phosphorites formed by replacement of carbonate sediments. This is indicated by the great petrographic similarity of many phosphorites to non-phosphatic limestones from the same or nearby sites; the wide variability in the phosphate content of the phosphatised limestones, the occurrence of highly phosphatic burrow margins, and to a lesser extent, pebble margins; and the phosphatisation of skeletal remains. The absence of an extensive phosphatisation of faunal remains is explicable in terms of the grain size of the microcrystalline matrix in which they are set. The matrix of very fine crystalinity would be more susceptible to phosphatisation than the larger faunal remains, owing to its greater area per unit mass. Exposure to a phosphatising medium after matrix phosphatisation might well cause faunal remains to be replaced, a phenomenon widespread in the pelletal phosphorites where re-exposure has occurred. The increase in phosphatisation towards the erosional horizons of pelletal phosphorite, and the phosphatisation of pebble margins indicates phosphatisation can occur long after lithification. Seawater was probably the major phosphatising medium for these sediments, most phosphatisation occurring soon after carbonate deposition, but continuing during diagenesis by utilisation of pore water phosphate. This mechanism is found by D'Anglejan (1968) to occur in sediments of the Californian continental shelf.

Other Subsea Phosphorites and their probable mechanism of formation

Phosphorites usually occur on continental margins, or offshore banks and guyots, at depth of less than 1000 m where sedimentation is slow or negligible. They are almost always found in association with high biological productivity, usually the result of upwelling phosphate rich seawater, although Summerhayes (1970) suggests that since most of this phosphorite is pre-recent, its association with present upwelling waters may be fortuitous, because of possible changes in ocean circulation patterns since their deposition. The occurrence of U. S. East coastal plane phosphorites was probably related not to upwelling, but to high biological productivity in esturine environments (Peaver, 1967).

Though seafloor spreading and continental drift must profoundly effect the oceanic circulation patterns, it is the writer's contention that present subsea phosphorites are young enough (often Eocene or Miocene) to have formed when ocean circulation patterns were very similar to those found today. The association between upwelling phosphate rich water and phosphorite deposits is therefore probably a genetic one, the high phosphorus concentration of these waters causing phosphorite deposition. In view of the discussion on the methods of phosphate formation in the previous section, it seems probable that phosphatisation of calcareous material is the major mechanism for phosphorite formation, with precipitation only being important in regions of exceptional P supply by organic material. That one mechanism is of much greater importance than the other is indicated by the remarkably constant levels of substitutional Na, Sr, SO_4^{2-}, and CO_3^{2-} found in all the sea floor phosphorites presented here. Were more than one formational mechanism operating such constancy would be difficult to envisage.

The relationship between upwelling and phosphorite is extensively reviewed by Gulbrandsen (1969), and has prompted workers (Summerhayes, 1970) to ask why widespread phosphorite deposition is not now occurring in these same areas. Recent data suggests deposits are in fact in the process of being formed, though on a very limited scale, in the organic rich sediments off the coasts of Chile and S.W. Africa. However, these instances are not conclusive proof of phosphorite formation on any large scale. Extensive phosphorite formation during the Tertiary era may have caused sufficient lowering of the phosphorus content of seawater so that deposition can now only occur in exceptionally favourable environments. However, mass balance calculations indicate that this is unlikely; assuming an average seawater concentration of 0.09 ppm P, an average river water concentration of 0.02 ppm P (Wedepohl, 1969) and a total water run-off of 2.7×10^{13} tons (Mason, 1966), then approximately

$$2 \times 10^{-8} \times 2.7 \times 10^{13} \times 70 \times 10^{6} \text{ tons} = 3.8 \times 10^{13} \text{ tons}$$

of P have reached the sea during a 70 million year period of the Tertiary. The total known reserves of Tertiary phosphate rock contained within commercial deposits total less than 10^{10} tons of phosphorus (Bateman, 1950; Shimkin, 1953; Gillson, 1960; Mero, 1965). Even allowing for a tenfold increase for undiscovered reserves, this is still only a fraction of the total phosphorus supplied to the ocean during the Tertiary era.

Summary and Conclusions

Phosphorite deposits form both by precipitation, probably within organic rich sediments, and by replacement of carbonate sediments, both processes operating in areas of high biological activity which are often the result of upwelling phosphate rich water. Of the two methods of formation, replacement is probably of much greater importance than direct precipitation, and probably formed the majority of the world's phosphate deposits. The former mechanism was responsible for the formation of the Moroccan deposits, both onshore and offshore which formed by replacement of calcareous sediments in areas of upwelling water. The relationship of upwelling and phosphorite occurrences is a genetic one, the upwelling water providing the phosphate for both the processes; and it seems probable that more phosphorite will be found in areas where upwelling, or high biological productivity is occurring, or has occurred in the past. The total offshore Moroccan reserves are estimated to be approximately 10^{10} metric tons[1] which are comparable in size to the land deposits. They are unlikely to be commercially viable in the foreseeable future, owing to their low grade, and the difficulties inherent in their recovery.

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[1] For calculation of reserves see Addendum 8

CHAPTER 7

SUMMARY OF MAIN CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Summary of Main Conclusions

1. The formation of the offshore Moroccan phosphorites appears to have been accomplished by phosphatisation of carbonate sediments, and this mechanism is probably responsible for the formation of the great majority of world phosphorite deposits.

2. Pelletal samples were formed by reworking of phosphatised carbonate sediments, with further phosphatisation occurring prior to, or during, resedimentation.

3. The conglomeratic southern samples were formed by uplift and erosion of phosphatised carbonate sediments, followed by redeposition in a phosphatised carbonate matrix. The uplift was probably related to the Oligocene Atlas orogeny.

4. The environment of formation of the northern pelletal samples, and most phosphatised limestones was slightly reducing and that of the southern conglomerates was probably neither reducing nor oxidising. However, within both sample types strongly reducing microenvironments were present. The formation of southern pebble samples was accomplished in environments varying from highly oxidising to neither oxidising nor reducing.

5. The main detrital minerals in the Moroccan deposits are quartz and illitic clay, though both are present in only minor amounts. Glauconite is abundant in the matrix of the southern conglomerates, and was probably formed in sediments adjacent to its present position.

6. The trace element content of the northern samples is controlled principally by organic carbon, pyrite (or pyrrhotite) and the carbonate-apatite crystal structure. Iron oxide (goethite) and glauconite are the main controls on the trace element geochemistry of the

southern samples, with pyrite and organic carbon contributing to this control in pebbles of low iron oxide content.

7. The trace elements found in the Moroccan phosphorites were derived principally from seawater.

8. The environment of formation in which phosphorite forms appears to have virtually no influence on the degree of substitution, within the carbonate-apatite lattice, of Sr, Na, SO_4^{2-} or CO_3^{2-}. The degree of substitution is probably affected only by the gross chemical composition of the water in which phosphorite forms. If such is the case, it may be possible to use the substituents in carbonate-apatite as indicators of a seawater or a fresh water environment of deposition.

9. The very great similarity in the concentrations of lattice substituents shown by the carbonate-apatite phase of all offshore phosphorites strongly suggests they have a common mechanism of formation, which was probably by phosphatisation of carbonate sediments.

10. Weathering removes all major lattice substituents from the carbonate-apatite lattice. Sulphate is removed at only half the rate of other substituents. Uranium, a minor substituent, does not appear to be removed by weathering.

11. The strong retention of U in carbonate-apatite during weathering validates the assumed ability of airborne radiation counters to locate phosphorites by detecting the radiation emitted by their U content. The age or weathering history of the deposit is not a factor which need be considered in using this prospecting technique.

12. Employment of towed scintillation counters for detecting subsea phosphorite will probably only yield information on the presence of a deposit, and not the grade of phosphorite, owing to the absence of any U - P correlation in such phosphorites.

13. R. E. E. fractionation patterns in phosphorites are not significantly affected by weathering, and therefore their fractionation patterns, which differ slightly from those of seawater, are probably the result of factors operating at the time of phosphorite formation. These factors are probably related to hydrolysis parameters, differences in these parameters between elements being due to their differing ionic radii.

14. The principal source of R. E. E. in phosphorites is seawater, and they are not related to detrital supply.

The main advances achieved by the presentation of this thesis are that it is the first extensive, detailed geochemical and mineralogical study of seafloor phosphorites, and that it presents considerable new data on a phosphorite deposit of which virtually nothing has been hitherto known. In addition, the factors controlling the geochemistry of a large number of elements in a seafloor phosphorite deposit are presented for the first time. It is also the first documented research on the effects of weathering on trace elements in phosphorites and lattice substituents in carbonate-apatite, as well as being the first documented discussion on the relevance of sub-aerial weathering to phosphorite prospecting. The comparisons made between a wide number of different seafloor phosphorite deposits adds substantially to the knowledge of such deposits, and has enabled completely new factors concerning formational crystal-chemistry of phosphorites to be elucidated.

Recommendations for Future Research

1. Accurate and complete major element and mineralogical analysis should be carried out on a wide variety of seafloor phosphorites to assist in defining their mechanism of formation. At present such data are rare.

2. A very detailed examination of the substitutional chemistry of the carbonate-apatite phase of a large variety of world seafloor and onshore phosphorite deposits may also help resolve the present conflict over their mechanism of formation, and lead to a clearer understanding of the true stoichiometry of marine carbonate-apatite.

3. Methods for the separation of the constituent phases should be developed, in order to assist in the examination of the geochemistry of phosphorites.

4. Electron microprobe analysis should be used to define fully the major element geochemistry of the Moroccan phosphorites, particularly with regard to glauconite and pyrite (pyrrhotite).

5. Phosphorite rock is the principal source of superphosphate fertiliser, and as several toxic elements, e.g. Ba, appear to be concentrated in phosphorite during weathering, further work on the effect of weathering on the trace element assemblage of phosphorites should be undertaken. Such work could probably be accomplished under laboratory conditions simulating the natural environment.

6. The effect of weathering in the sea should be investigated, as it appears to be responsible for the high U concentration found in the northern samples.

APPENDIX 1 - SAMPLE NUMBERING SCHEME

1) The onshore Moroccan samples are labelled with the initials of the name of the sample location, plus a number if more than one sample was obtained from any one location.

e.g. BG. 1. is sample 1 (of 2) from a deposit near Benguerir.

2) World samples are similarly labelled, either by the initial letter of their sample location, or by the original sample number assigned by the collector. Again, a number is added to indicate the number of samples from any location.

3) Offshore Moroccan samples are designated by the ship station number where they were obtained, plus a number in parenthesis to indicate if more than one sample was obtained at any station. In several cases subsamples of both matrix and pebbles were taken from southern conglomerates; these are identified by adding p. or c. to the main sample number to denote pebble and cementing matrix subsamples respectively. In order to differentiate between subsamples, a further number is added if more than one subsample of pebble or matrix was taken from each conglomerate.

e.g. 847(1)p2 represents one of two separate pebbles subsampled from one of several phosphate samples found at station 847.

APPENDIX 2 - SAMPLE DESCRIPTION AND PETROGRAPHY OF MOROCCAN PHOSPHORITES

Introduction

In this appendix a general description of the Moroccan samples is presented, together with a limited presentation of their petrography. This study was undertaken principally to assist in the elucidation of the geochemistry of the samples, and no attempt is made to present a detailed petrographic study of the offshore phosphorites. For a detailed petrographic study and discussion of the mechanism of formation of the samples the reader is referred to Summerhayes (1970).

Petrographic examination of the samples has proved useful in explaining the geochemistry of U, by relating its concentration in the northern samples to the occurrence of detrital collophane; of Zn, Cu and Ni also in the northern samples by the identification in these samples of extensive pyrite and organic carbon inclusions with which they are associated; and of S in all samples by noting the absence of any sulphides in S bearing samples.

Following McConnell (1950) and Summerhayes (1970) the term collophane is used here to denote isotropic, or virtually isotropic, carbonate-apatite.

Northern Province Samples (figs. A.2.1 a, b, and A.2.2)

Northern province samples were usually hand size, well rounded cobbles of phosphatised limestone, covered in a thin brown coating, probably of iron oxide. The rock texture was usually fine grained and massive, ranging in colour from almost black, to grey and brown.

In most samples, freshly fractured surfaces possessed a characteristic oily smell caused by organic material and became much lighter in colour on exposure to the atmosphere due to its oxidation. Five samples exhibited irregular bedding structures and a micro-conglomeratic, or pelletal, character and were composed of fine sand to pebble sized, sub-angular to well rounded fragments, very similar in appearance to the matrix. Sample 988 consisted of a well rounded cobble in which an outer light brown massive rock was partially surrounding a black, massive rock, both being of the same fine grained texture. These two rock types were separated and treated independently. These northern samples were often extensively bored, the borings usually being filled with material similar to the host rock.

Southern Province Samples (figs. A.2.3 a, A.2.3 b)

Southern province samples were generally more massive than the northern samples, raging from cobble to boulder size. They were rounded to sub-angular. Few of the samples were bored, and these not extensively. All samples were covered in a shiny brown coating of iron oxide, though it was often patchy. The samples were breccia type conglomerates containing pebbles of limestone, phosphatised limestone, ferruginous varieties of both, and sometimes chert. The pebbles, set in a phosphatised glauconitic micrite matrix, ranged in size from fine sand to large cobble, and in colour from grey to orange and brown.

The pebbles were almost always coated in a thin shiny brown iron oxide layer, were angular to rounded, and invariably fine grained in texture. Each sample contained all types of pebbles, though usually one size predominated. Sand sized glauconite was unevenly distributed through the matrix, and varied in quantity between samples, from abundant in 833 to sparse in 847(1). The matrix also varied within samples from mud to fine sand, and in colour from dark brown to light brown with occasional orange patches, possibly due to the presence of iron oxide. Small patches of soft white material, probably shell remains, occurred in the matrix of some samples and were identifiable as such in samples 898 and 896(1). Sample 847(1) contained a phosphatised sharks tooth (16.1% P_2O_5). The variation of matrix colour between samples is mainly due to differences in glauconite and organic carbon content.

Photographs of Moroccan offshore phosphorites

FIG. A.2.1 a	Northern phosphatised limestone 988
FIG. A.2.1 b	Northern phosphatised limestone 1022(2)
FIG. A.2.2	Northern pelletal sample 1004
FIG. A.2.3 a	Southern conglomerate 896 (1)
FIG. A.2.3 b	Southern conglomerate 898

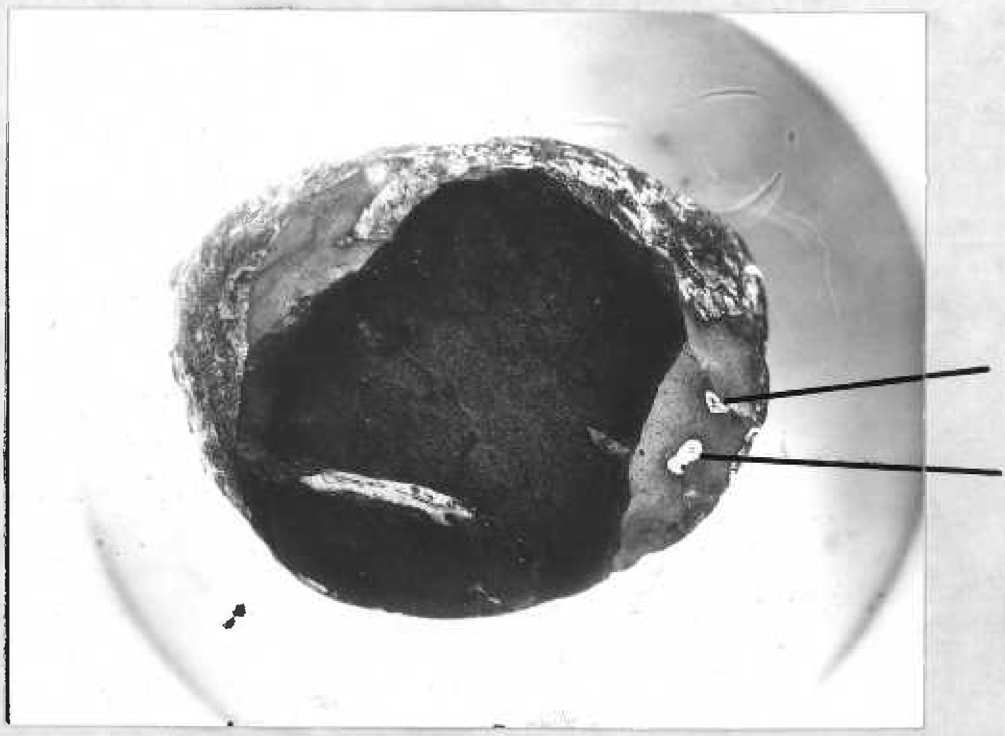
Fig. A.2.1 a

Sample 988. A composite northern phosphatised limestone clearly showing the two types of rock; 988(a) comprised of the light coloured outer material and 988(b) comprised of the inner black material. The colour difference is due to the much higher organic carbon and pyrite content of the inner material, and higher iron oxide content of the outer material. Several bore holes (arrowed) are visible in the outer section; the fillings are of calcite.

Fig. A.2.1 b

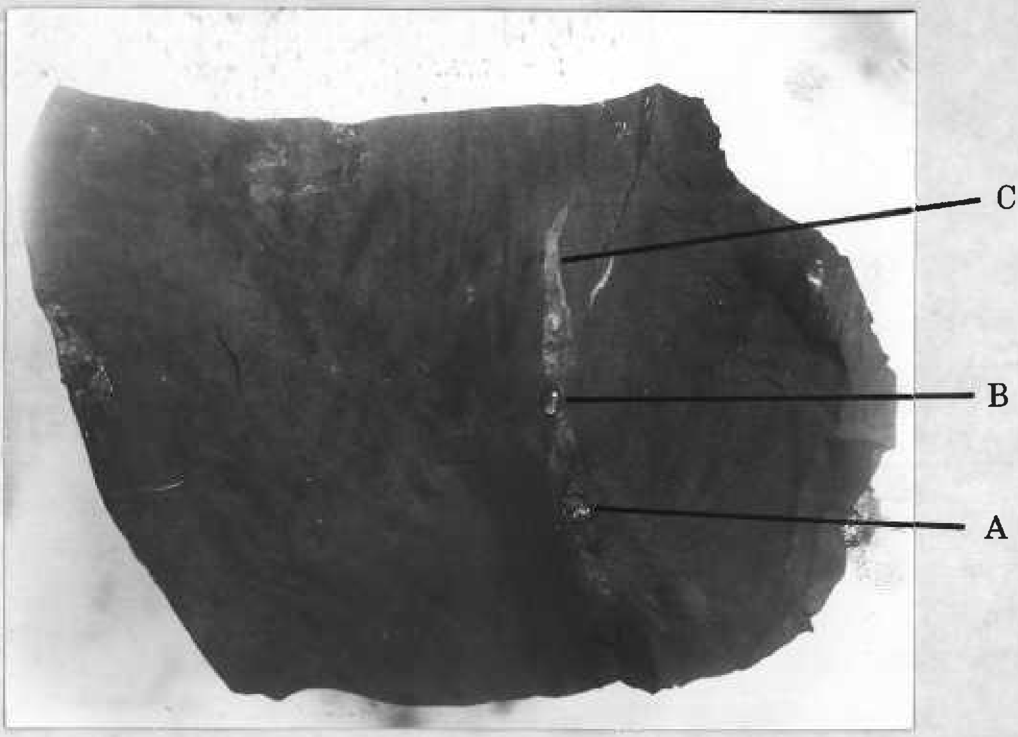
Sample 1022(2), a northern phosphatised limestone showing a fairly even texture. Two small bore holes filled with phosphatised calcite are visible (A and B) together with a rock fissure filled with sandy phosphorite (C). The apparent angularity of this sample is due to its being broken from a larger phosphorite nodule.

Fig. A.2.1 a



Scale = × $\frac{1}{2}$

Fig. A.2.1 b



Scale = × 1

Fig. A.2.2

Scale = × $\frac{1}{2}$

Sample 1004, a pelletal phosphorite showing the irregular bedding structures and assorted size and angularity of this type of phosphorite. The dark central band especially noticeable to the left of the photograph, is the remains of the original organic staining after lengthy atmospheric oxidation.

Fig. A.2.3 a Sample 896(1)

A section of a typical southern conglomerate showing the range of pebble size, angularity, and colour. The pebble coatings of iron oxide are clearly visible on many pebbles, and clearly discernable at A, where such a surface acts as a good light reflector. At B a replaced shell structure is clearly seen in close juxtaposition to unreplaced patches of soft calcareous material (C). At D and E borings within a pebble are visible, the filling at D being of slightly phosphatised carbonate, and at E being the same as the matrix, phosphatised glauconitic carbonate.

Fig. A.2.3 b Sample 898

This sample exhibits greater compositional variations within the matrix than 896(1) (fig. A.2.3 a). At C are patchy inclusions of red, presumably iron rich, phosphorite, which contains glauconite, and at D a patch area of soft calcareous material. At B are visible unreplaced fossil remains. The thin pebble coatings are most easily observable in the pebble at A.

Fig. A.2.3 a

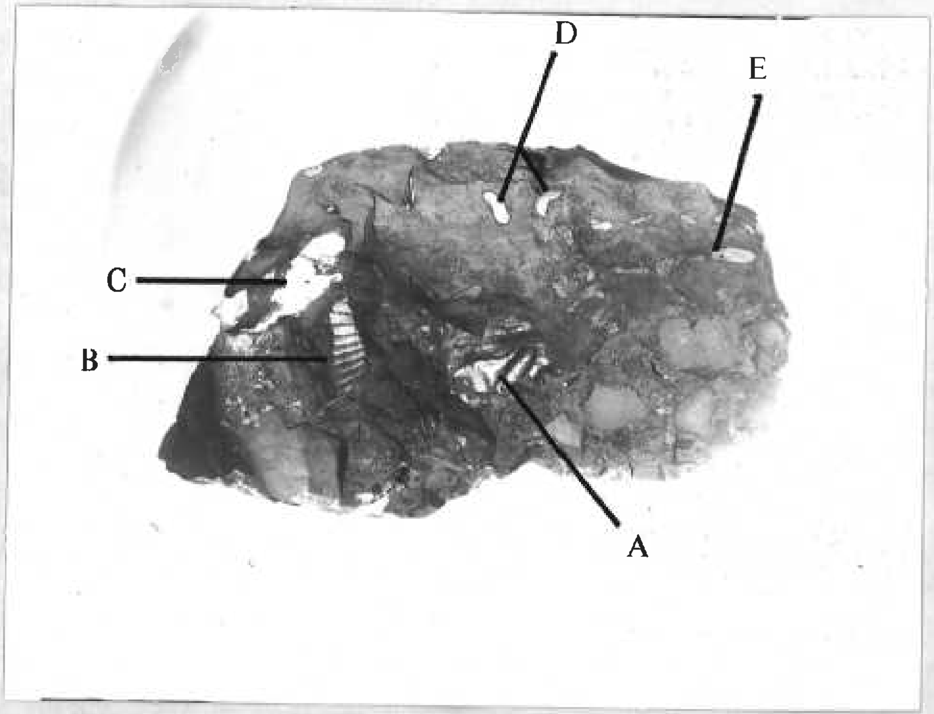


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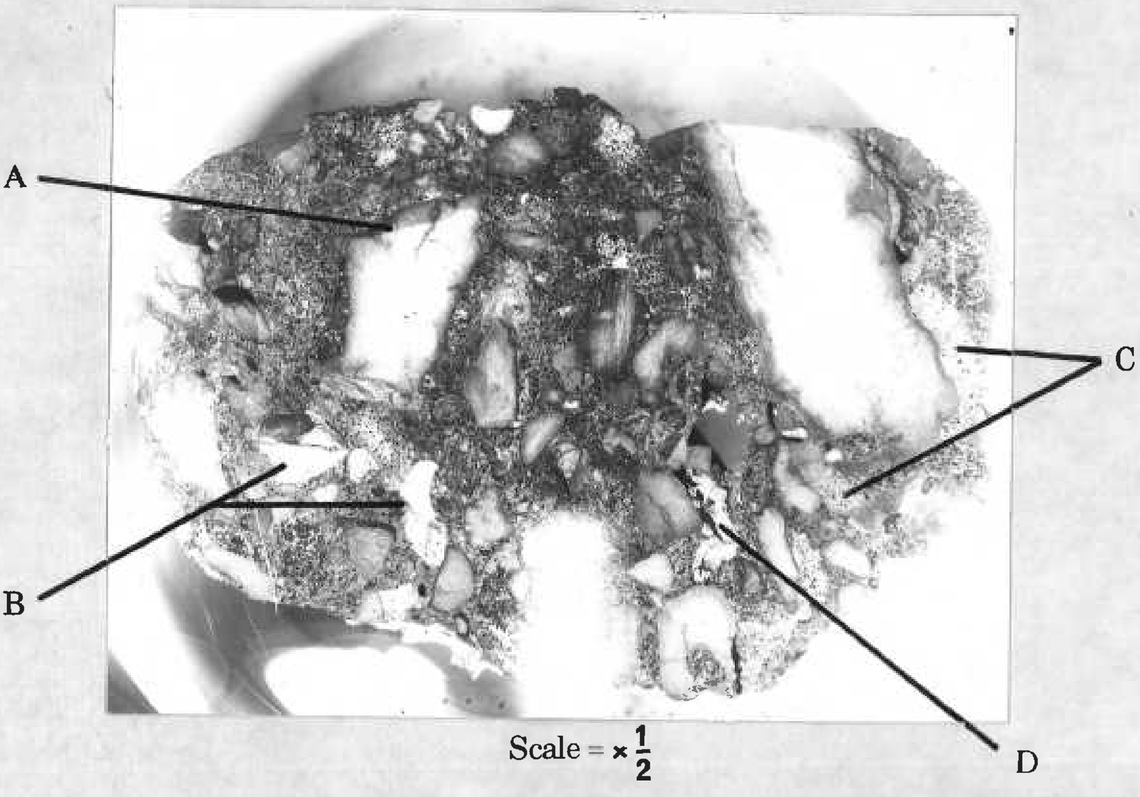
Fig. A.2.3 b



Scale = × $\frac{1}{2}$

Several samples from the southern province were non-conglomeratic (893, 847(2), 156(1), 156(2), 157, and 148). All except 847(2) were homogenous, orange, sub-angular hand sized cobbles of phosphatised, ferruginous limestone of fine grained texture. Sample 847(2) was different in being extensively fractured, the cracks and interstices of the rock being filled with glauconitic material similar to the matrices of other conglomerates.

Onshore Samples

These samples were all light grey sands with no other distinguishing macro characteristics. The texture and colour may be a result of water washing and screening of the samples prior to their arrival. They are fully described in later sections.

AGE DATA

All Moroccan offshore samples were examined for microfossils by Mr. J.D. Carter of Imperial College, and D. Fournie and F. Deres of SNPA, Pau, France, in order to determine their dates of formation. The two sets of data are not always in agreement and in most cases are only approximate, because of the scarcity of fossil remains. The ages are presented in table A. 2. 1.

The onshore samples were dated by C.E.R. Phos., Paris, France, except for three obtained from another source which were undated (table A. 2. 1).

Glauconite separated from glauconitic matrices of samples 877 and 848 were dated as Miocene by K/Ar methods (Summerhayes, 1970).

The range of possible ages obtained for the samples restricts their use in interpreting the geochemistry. No correlation has been observed between the ages of the samples and their geochemistry, and only a very poor correlation between their ages and present location on the continental shelf. (Bee, pers. com.) However, the dating of glauconite from the matrix of the southern samples indicates their age to be 11 - 12 million years (early Miocene) and shows that the matrix must have formed at that time or later. The dating of the pebble samples from the conglomerates as Eocene or Upper Cretaceous fits in well with their proposed method of formation (Summerhayes, 1970).

TABLE A.2.1

Ages of offshore and onshore Moroccan samples

Offshore Samples		AGES	
		Carter	Fournie and Deprès
135	NORTHERN PROVINCE	-	Tertiary
139		-	Tertiary
959		Eocene	-
966		Miocene	Upper Cretaceous-Eocene (Lutetian)
982		Upper Cretaceous	-
988		Early Tertiary	Upper Cretaceous-Eocene
1004		Upper Cretaceous-Low Tertiary	Upper Cretaceous-Eocene
1016		Eocene	Upper Cretaceous-Eocene
1022		Upper Cretaceous	-
1038		Upper Cretaceous	Upper Cretaceous-Eocene
152	SOUTHERN PROVINCE	Eocene	-
154		Early Eocene	-
833		Upper Cretaceous (Turonian)	Upper Cretaceous (Seromanian - Santonian)
847		Tertiary	-
865		-	Tertiary
877		-	Tertiary
883		Tertiary	Tertiary
896		Eocene	Tertiary
898		Tertiary	Tertiary
148		Eocene	-
156		Eocene	-
893		Paleocene-Eocene	-
Onshore Samples		AGE (DATA from C.E.R. Phos.)	
BG 1		Low Eocene (Thanetian)	
BG 2		" " (Montien)	
Y2		" " (Montien)	
EA		" " -	
K 2		" " (Ypresian)	

The offshore phosphorites can be divided into four groups on the basis of petrographic examination:

group 1, comprising glauconitic conglomerates found only south of Safi;

group 2, comprising phosphatised limestones found mainly in the northern province;

group 3, pelletal (micro conglomeratic) phosphorite found only in the northern province;

group 4, phosphatic ferruginous limestone, found mainly in the southern province.

As group 4 samples show considerable petrographic similarity to many phosphatic ferruginous limestones contained within the glauconitic conglomerates, they are discussed with those samples.

Group 1 - GLAUCONITIC CONGLOMERATES

Glauconitic conglomerates are composed principally of angular to rounded granules, cobbles, and pebbles of limestone, phosphatised limestone, ferruginous varieties of both, and occasionally chert. These are unevenly bedded in a matrix of partially phosphatised micrite containing sand size glauconite, silt size quartz, foraminiferal tests, patchy inclusions of iron oxides, and finely disseminated organic matter and clay.

Pebbles from samples 152 and 154 are of Eocene age (table A. 2. 1), and the similarity of many phosphatised limestone pebbles from the conglomerates to Upper Cretaceous and Eocene limestones from the same, or adjacent, sites suggests all the pebbles are of this age. The matrix of the conglomerates is either Miocene or younger depending on whether the glauconite it contains is authigenic or detrital. Pebble formation thus occurred well before conglomerate formation.

The Matrix, and Minor Matrix Inclusions

The matrix of these samples is poorly sorted with sandy, silty, and muddy areas being easily distinguished. The predominant phase is partially phosphatised micrite, mixed with calcite fragments, dolomite rhombohedra, quartz and sparse foraminiferal tests. The latter are usually unbroken and frequently filled with calcite; collophane and pyrite infillings are rare. The matrix is always turbid, probably because of admixed clays, organic matter, and iron oxides. Within a sample colour variations are very local between orange and dark brown, variations between samples being similar. Both variations probably result from changes within the sample of iron oxide, clay, and possibly organic matter.

The matrices contain much sand size glauconite but they are never actually glauconitised. This possibly indicates a change of environment after glauconite formation, and before lithification of the matrix. The glauconite grains are predominantly sand size, sub-angular to rounded, poorly sorted, and unevenly distributed through the matrices. That some grains formed as internal foraminiferal casts, or by replacement of foraminiferal test, is indicated by their present appearance as foraminiferal tests. Between 10% and 20% of the glauconite grains are oxidised, some completely, others around their margins, suggesting that the grains formed in mildly reducing conditions, and were later oxidised for a brief period. Some grains show truncated oxidised margins where the grain has broken after oxidation. No grains were observed which were oxidised after fracture (and therefore exhibiting oxidised fracture zones). This suggests that oxidation of the grains occurred soon after their formation, and stopped before they had undergone any appreciable reworking or transportation. The low incidence of broken grains, their angularity, and the poor sorting in general all suggest their local origin.

It is suggested that the glauconite formed within sediments adjacent to the area containing the pebbles. Before consolidation of the sediments they were disturbed, and the glauconite transported to the area containing the pebbles. This would account for the oxidation observed in some glauconite grains, oxidation occurring before transportation. If the areas were adjacent the small number of broken grains could be accounted for. The presence of glauconite in the matrix does not therefore indicate the occurrence of reducing conditions within the matrix during its formation.

Quartz is fairly common as angular to sub-angular, fine sand to silt size particles suggesting a calm water environment of deposition. Their angularity and size suggest derivation from a nearby source, and incorporation into the sediment before significant reworking or transportation occurred. Samples further from the present coast contain less quartz than inshore samples, indicating that the eroding coastline was probably the original source of quartz.

Foraminiferal tests vary widely in abundance, though they are never abundant. Samples from the upper slope and outer shelf contain more foraminiferal tests than do those from mid- and inner-shelf areas. The tests are usually unbroken and never phosphatised suggesting, as do the quartz contents of these samples, that deposition occurred in a calm water environment. Foraminiferal infillings are usually calcite and occasionally collophane or pyrite. The presence of pyrite (and therefore presumably organic carbon) suggests that significant contributions to the trace element abundance of the matrix samples may occur from these phases, as in the case with the northern province samples.

Major Matrix Inclusions

The remaining matrix inclusions vary widely in size and consequently the term pebble is used throughout this thesis to include all size ranges occurring in the southern samples, unless a specific size, e. g. cobble, is referred to.

The main types of pebble are:-

1) Calcareous siltstone grading to silty limestone, and usually with few or no fossils. These pebbles were invariably non-phosphatic.
2) Phosphatic and non-phosphatic foraminiferal limestone, with widely varying abundances of foraminifera.
3) Phosphatic and non-phosphatic limestones, the latter principally microcrystalline calcite, both containing few or no fossils, but with widely varying amounts of iron oxide.
4) Collophane, often with iron oxide impurities.
5) Glauconitic foraminiferal limestone.
6) Chert.
7) Composite pebbles, e.g. detrital collophane within a limestone pebble.

The first four rock types were common and were found in all the samples, whereas the remainder were neither common, nor observed in all samples.

The phosphatic pebbles showed widely varying degrees of phosphatisation both within a conglomerate and between conglomerates. However, the even phosphatisation of most pebbles suggest phosphatisation occurred before their formation by phosphatisation of an unconsolidated or partially lithified carbonate sediment. The phosphatic margins on some pebbles indicate a second period of exposure to phosphatisation after pebble formation when penetration by the phosphatising medium was difficult, and therefore slow, before incorporation into the matrix. Phosphatisation during incorporation into the matrix would be expected to result in a great majority, if not all, pebbles showing a phosphatised margin. That phosphatisation of the pebble margins did not occur during matrix formation is shown by the presence of unphosphatised limestones, the random distribution of phosphatised pebble margins, and the absence of any correlation between pebble and matrix phosphatisation.

Iron rich margins around ferruginous pebbles were not uncommon but were not observed around non-ferruginous pebbles. The ferruginous and phosphatic margins sometimes coincided, but not with sufficient regularity for a connection to be suggested. The iron content varied considerably between pebbles, with phosphatic pebbles usually containing more than non-phosphatic varieties. Apart from the incidence of enriched margins the iron distribution of the pebbles was homogeneous in all but two samples (156(1) and 157). These two samples are somewhat different to the remaining ferruginous limestone samples in showing a fine bedding structure in which phosphatisation and iron content increase towards each bedding horizon. They contain abundant dolomite rhombohedra which according to Rooney and Kerr (1967) may indicate formation within a lagoonal environment. They also contain round 'blobs' of calcite, presumably unphosphatised organic remains, as well as fewer foraminifera than the other limestones. The even distribution of foraminifera within each bed suggests that each bed was deposited in a similar environment, and also suggests that the layering may be the result of interruption of sedimentation. Additionally, it is suggested that phosphatisation was very rapid after sedimentation and continued to act after sedimentation ceased, causing higher phosphate at the top of the bedding horizons. The higher iron oxides towards the surface of each horizon suggests phosphatisation and oxidation were concomitant, and that the iron in these samples may well be authigenic.

Within the pebble margins of a limited number of pebbles a banding phenomenon was observed similar to that reported by D'Anglejan (1967) in phosphatic sands off Baja California. In the Moroccan samples it is apparently caused by inward migration, or destruction within the pebble margins, of organic and pyritic material. Only non-ferruginous pebbles exhibit banding suggesting that partial penetration of the pebbles by an oxidising medium may be its cause, owing to the destruction within the margin of the organic and pyritic material. The complete oxidation of ferruginous pebbles precludes banding by such a mechanism. Extensive inclusions of pyrite and organic matter occur in many non-ferruginous samples, the pyrite usually as foraminiferal infillings, the organic carbon often as disseminated "stringers" of material.

Bore holes in the pebbles are uncommon but where they do occur the borehole margins are usually much more phosphatic and pyritic than the remainder of the pebble. They are often filled with material different to that of the matrix, indicating that the phosphatisation and reduction of the borehole margins occurred before the incorporation into the present matrix.

The presence in sample 898 of a phosphatised limestone pebble containing a borehole filled both with detrital collophane and phosphatised limestone more phosphatic than the sample matrix indicates a maximum of four periods of phosphatisation may have occurred in the southern province, viz. phosphatisation of the original pebble which was then bored; phosphatisation of the detrital collophane deposited in the borehole; phosphatisation of the carbonate sediment which also filled the borehole; and finally phosphatisation of the present conglomerate matrix in which the samples are set. The four periods of phosphatisation represent a maximum number concordant with the data, the actual number may be less. However, in view of the considerable changes in environment thought to have occurred during the formation of the southern conglomerates (Summerhayes, 1970), interruption of phosphatisation seems extremely likely.

Group 2 - PHOSPHATIC LIMESTONES

These are divided by Summerhayes (1970) into three main subgroups; phosphatic limestones, phosphatic limestones containing detrital collophane of coarse silt to sand size and phosphatised limestones containing detrital limestone fragments, often with detrital collophane inclusions. However, detailed quantitative examination of the northern samples suggests that these divisions are artificial, since no clear dividing line exists between the three categories. The varying contents of detrital collophane and limestone probably reflects a variation in distance from the detrital source within a single deposit. Consequently, in this thesis the northern phosphatised limestones have been treated as one rock type.

These samples are of Upper Cretaceous-Eocene age, except possibly for 966(2) which may be of Miocene age (table A. 2. 1) indicating their formation occurred at the same time as the formation of the southern pebbles.

The matrix of these samples is partially phosphatised microcrystalline calcite and is structureless and turbid, varying in colour from pale yellow to orange and brown, probably because of admixed iron oxides, organic matter, and clays. Phosphatisation is uniform throughout the samples except near boreholes where it is usually more intense, and in sample 135 where it is patchy. Boreholes are rare, however, and usually filled with either sandy or pelletal phosphorite. This indicates a maximum of three periods of phosphatisation for the northern samples, viz. phosphatisation of limestones, lithification and then boring by marine organisms; the production of collophane grains by phosphatisation either of partially phosphatised limestone or carbonate sediment; and finally deposition of the collophane in a borehole together with newer phosphatised calcareous sediment. The actual number may be less than three, if, for example, the borehole filling is detrital material derived from an earlier period of phosphatisation.

Quartz is present as angular to sub-angular silt size grains, as in samples from other areas, and probably was derived from the nearby coastline. Its sparse abundance suggests a quiet water formational environment for these samples. Silt sized, angular to subangular detrital limestone also occurs in some phosphatised limestones, and in all the phosphatic limestones occur recrystallised rhombohedra of dolomite, and possibly calcite. Sub-angular to rounded detrital collophane pebbles are present in most of these samples but vary widely in abundance. Approximate estimations of their frequency has indicated a correlation between their number and the U concentration of the northern samples (table 3. 1).

All the phosphatised limestones contain abundant foraminiferal tests, which are usually unbroken, and only rarely phosphatised, confirming the formation of these samples in a quiet water environment. Infillings are usually calcite, but collophane and pyrite infillings are not uncommon.

Pyrite and organic carbon also exist in large concentrations in the margins of some boreholes and also as diffuse inclusions unrelated to foraminifera, the number of such inclusions varying widely between samples. The presence of these inclusions, the reduced borehole margins, and the general "organic" smell of many of the freshly fractured samples testify to the general reducing nature of the depositional environment of many of these samples.

Treatment of a number of the larger pyritic inclusions with dilute nitric acid showed them to be fairly soluble, and therefore probably more akin to pyrrhotite than pyrite. However, in the absence of definite analytical data, the term pyrite is used to indicate all iron sulphide phases identified.

Group 3 - PELLETAL PHOSPHORITE

Pelletal phosphorites are of Upper Cretaceous-Eocene age (table A. 2. 1) and consist of a matrix of partially phosphatised, unevenly bedded carbonate, containing granule to sand size, poorly sorted, phosphatic pellets and foraminifera, sand and silt size quartz and finely divided and disseminated iron oxides.

The Matrix and Minor Matrix Inclusions

The matrix is partially phosphatised microcrystalline calcite showing irregular erosional horizons, indicative of formation in moderate to shallow water environments, containing truncated foraminifera and pellets. The erosional horozons, which are often iron stained, separate thin beds varying from poorly sorted sand to muddy sand and are usually graded from top to bottom. Differences in phosphate and iron oxide content are apparent between the top and remainder of each bed, the top being more phosphatic and ferruginous. Pyrite inclusions are common as foraminifera infillings as well as diffuse "blobs" in which pyrite and organic carbon are intimately associated. They rarely occur within the top section of any bed.

The iron staining at many erosional horizons, together with the occurrence of pyrite and organic carbon inclusions throughout the matrix, excepting the erosional horizons, suggests rapid and periodic changes of environment. Reducing conditions probably prevailed during the initial deposition of each bed. Cessation of sedimentation, compaction and erosion probably occurred in an oxidising environment. Quartz is rare in these samples, occurring as angular to sub-angular silt and fine sand, suggesting, as in the other groups, probable derivation from a nearby source such as the coast. Foraminifera are almost completely phosphatised and usually contain collophane infillings, though infillings of calcite and pyrite are not uncommon. The phosphatisation of the foraminifera within the pelletal samples probably occurred during their re-exposure to seawater during disaggregation of the original phosphatised sediment (Summerhayes, 1970). The initial phosphatisation bypassed the foraminifera, perhaps because phosphatisation of the micro-crystalline calcite utilised all available phosphorus. However, during the second period of phosphatisation, the unphosphatised foraminifera were attacked and phosphatised. The foraminifera in these samples are largely unbroken.

Pellets

The pellets are principally collophane, and range from angular to rounded in shape. Regular ovoids and oolitic pellets are also present, the pellets vary in colour from light brown and orange to dark brown and are often turbid, possibly due to admixed iron oxide and clay. The complete range of pellets is found in each conglomerate. The presence of oolitic pellets suggests concretionary growth may play some part in pellet formation. However, since only 10% of pellets exhibit oolitic structure it is probably only of minor importance.

The most likely method of formation of these samples is suggested by Summerhayes (1970), who considers them to be intraformational conglomerates, formed by disaggregation and reworking within a phosphatising medium of partially phosphatised carbonate sediments. However, in order to account for the degree of angularity of some of the pellets, and the presence of truncated foraminifera and pellets within the bedding horizon of these samples, the original sediments must have undergone considerable compaction, and subsequent erosion during the formation of each bed. The conclusion that reworking has occurred supports similar conclusions based on the geochemistry of these deposits presented in chapters 2 and 5, and by the fact that the pellets are usually more phosphatic than the matrix, as would be expected if the pellets had been phosphatised twice, but the matrix only once.

Considerable organic material (and possibly pyrite, is apparently present within the pellets, where it appears as stringers of black material. However, it is frequently absent from pellet margins, suggesting re-exposure to seawater has destroyed the organic material by oxidation.

ONSHORE SAMPLES

The petrography of these samples could not be examined directly as they had been screened and water washed prior to their arrival. The deposits have been extensively reviewed elsewhere (Cayeux, 1941; Salvan, 1952; Vise, 1953) and the petrography and mode of formation are summarised from these authors.

The samples are of Eocene age (table A. 2. 1). The usual texture of the onshore deposits is of well sorted sand, the main phase being pelletal collophane, often with calcite or quartz nuclei. The pellets often exhibit oolitic structures, thought to be mechanically induced. Accessory phases are quartz, often similar in size to the collophane pellets and foraminifera which occur both in the collophane grains and in the cementing calcite matrix. The pellets are thought to form in an offshore region of high biological productivity and were subsequently transported to a shallow depositional area where they were well sorted, mixed with quartz, and deposited.

Summary

The petrographic study presented here has assisted in understanding some aspects of the geochemistry of the Moroccan samples.

Within the northern samples the identification of pyrite (or more probably pyrrhotite) and organic carbon confirms the general reducing nature of the environment in which they were formed. It has also assisted in clarifying the factors controlling the abundances of Zn, Cu and Ni, which are strongly related to these phases (chapter 2) and helped clarify the substitutional chemistry of S.

Also within the northern pelletal samples the presence of iron staining at erosional horizons has enabled apparent discrepancies in Fe and S analysis to be resolved and indicated that the iron oxide content of these samples is probably authigenic.

The correlation of U and detrital collophane in the northern samples (chapter 3) has enabled its apparently anomalous behaviour to be explained by its incorporation into the samples in the form of uraniferous collophane.

Petrographic analysis of the southern samples has been less useful in understanding their geochemistry than in the northern samples. However, the presence of organic matter and pyrite in some non-ferruginous pebbles, suggests that these phases may have been present in ferruginous pebbles during their early stages of formation before oxidation, where they may have contributed to the trace element assemblage. The problem of defining the redox conditions under which the matrix was formed because it contains indicators of both oxidising (iron oxides) and reducing conditions (glauconite), is resolved by the identification of the glauconite as not truly authigenic.

APPENDIX 3 - MINERALOGY

Introduction

X-ray diffraction studies of the Moroccan samples have been undertaken in order to evaluate their mineralogy and its regional variations. The data obtained have assisted in elucidating the geochemistry of the samples, particularly with regard to the phases containing Mg and K, and has helped clarify the role of glauconite in influencing the trace element abundances of the southern conglomerates.

The major mineral phases have been identified by a comparison of the Moroccan sample diffraction patterns with published tables and reference patterns. Owing to the presence of clay minerals other than glauconite in only very small quantities, their definite identification has not been possible from diffraction patterns of whole rock samples alone. Consequently diffraction patterns of acid insoluble residues have been used to assist in their identification, these diffraction patterns also being useful in confirming the presence of goethite in some samples and in delineating the type of glauconite present in others. In order to further clarify the identification of the clay minerals, the K/Al, K/Si, and Al/Si ratios of the samples have been compared to values from the literature for a number of well defined clay minerals.

Analytical Methods

Calcite, dolomite, and quartz concentrations in the samples have been obtained by comparing the areas under their main diffraction peaks with the main peak areas of a number of Moroccan phosphorites chosen as arbitrary standards (appendix 5). The methods were only semi-quantitative, as no internal standards were used. However, the similar nature of the standards and the samples analysed, the standardised sample preparation, and the fact that all the samples were run within a very short space of time on the same diffractometer, have resulted in an accuracy and precision of an acceptable level.

Duplicate analysis indicated precision to be good, and the accuracy is thought to be good enough for valid comparisons of the data to be made.

X-ray methods of mineral identification were used in preference to chemical methods for two reasons. The method of Silvermann (1952) for estimating free carbonate minerals by their selective dissolution in alkaline tri-ammonium citrate solution was not reproducible, and proved unreliable in completely removing all carbonate minerals (appendix 4). This is probably due to the existence of calcite and carbonate-apatite (and perhaps dolomite) in a microcrystalline form in which one phase, carbonate-apatite, is unreactive towards the leaching agent. Acid leaches followed by determination of Ca and Mg on the leachate was not feasible as carbonate-apatite is acid soluble, and leachable Mg from clays may reinforce the Mg leached from dolomite. However, samples containing very low clay contents, but high concentrations of Mg, were used to check the x-ray determinations of dolomite, as in such samples virtually all Mg is present in the dolomite. Experimental details of the semi-quantitative mineralogical determinations are presented in appendix 5.

Mineralogy of Major Mineral Phases

The major mineral phases identified within the Moroccan samples are carbonate-apatite, calcite, dolomite, quartz, and goethite.

The diffraction pattern of carbonate-apatite agrees extremely well with those published by Cathcart (1968b) and Milton and Bennison (1968). The carbonate-apatite diffraction patterns of the offshore samples are, however, considerably less well developed than those of the onshore deposits, or any other land sample, the onshore and world samples invariably yielding sharper and better resolved diffraction patterns. This suggests that sub-aerial weathering of carbonate-apatite may be accompanied by a recrystallisation of the lattice to a more ordered structure. The carbonate-apatite content of the samples, calculated from chemical data (table A. 6. 4) ranges from 12% to 90% of the total rock, most values lying in the range 30% to 70%. The pelletal samples are noticeably higher in carbonate-apatite than the remaining northern samples, supporting their suggested mechanism of formation by disaggregation and reworking of phosphatised carbonate sediments within a phosphatising environment (appendix 2).

Calcite is found in nearly all samples, the ranges in its concentration being considerable (table A. 3. 2). Except for sample M. E. A. which contains 17% calcite, the contents of the onshore samples are low ($<$ 5%). This may be due to removal of the mineral during weathering or may simply reflect the effects of the screening and water washing to which these samples had been subjected. The northern samples show a distinct division into pelletal and non-pelletal samples on the basis of their calcite contents, because of the increased phosphatisation of the former during their formation. Pelletal samples contain between 7% and 14% calcite, non-pelletal samples are between 20% and 40%, with only one sample (988(a)) being intermediate between the two groups, with 14% calcite. The calcite contents of the southern samples are lower than those in the northern samples, probably because of the dilution of the calcite in the former by iron oxide, detrital material and glauconite.

Using the method of Goldsmith et al. (1958, 1961), the $MgCO_3$ content of the calcite in all samples was found to vary between 4% and 8% by weight, yielding a Ca/Mg ratio between 12 and 25. This is within the range for foraminifera given by Degens (1965), but below that given for inorganic precipitates of calcite. This supports the suggestion that the microcrystalline calcitic matrix of the Moroccan phosphorites, noted in appendix 2, is a reworked foraminiferal carbonate sediment and is not an inorganic chemical precipitate.

In the offshore samples the distribution of dolomite is considerably different from that of calcite. There is little difference between pelletal and non-pelletal samples (1%-3% dolomite) suggesting phosphatisation of dolomite may not have occurred. The southern province samples contain little more of this mineral (1%-5%) than do the northern samples. However, pebbles from the conglomerates 896(1) and 896(2) have a considerably higher concentration of dolomite than other pebbles, suggesting a different depositional environment, possibly lagoonal (Rooney and Kerr, 1967). However, no petrographic evidence such as bedding structures or high detrital content is apparent for such an environment. Dolomite concentrations in the onshore samples are low, with several samples containing no detectable dolomite ($<1\%$), probably because of its removal by weathering, or by screening and water washing.

The quartz content of the northern province and southern pebble samples is in the range 1%-4%, except for sample 865p1, which contains 30.7% quartz, indicating deposition near a detrital source. That the former samples are fairly phosphatic (table A.6.4) whilst the latter is very low in phosphate (4.2% P_2O_5) is in keeping with many previous observations that phosphorites form only in regions of low sedimentation. The glauconitic conglomerates, and in particular the southern matrix samples have fairly high quartz contents (2%-8%) compared with the remaining samples. The quartz contents of the former decrease with increase of the distance of the conglomerate from the present coastline, suggesting a coastline similar in location to the present one may have been its original source.

Goethite was tentatively identified in the x-ray diffraction patterns of most pebble samples and a number of the glauconitic conglomerates. However, the patterns were usually poorly defined and in most cases only the two main reflections were visible, so no quantitative determinations were possible. In order to make the identification more precise, diffraction patterns were taken of the acid insoluble residues of the samples in which the presence of goethite was suspected. Goethite was identified in the acid insoluble residues of all southern pebbles, phosphatic ferruginous limestones, and conglomerate samples except 865p1 and 898p3, which contained very low iron oxide concentrations as whole rock samples (table A. 6. 4). Although identification was tentative in some cases, most of the residues gave diffraction patterns sufficiently strong and well defined to make a positive identification possible (fig. A. 3. 1). The presence of goethite in the residues is surprising in view of its usual high acid solubility. However, the orange colour of the residues, together with the fact that the percentage of insoluble material was usually consistent with the goethite being insoluble (table A. 3. 1) support the x-ray diffraction results. Unfortunately insufficient material was available for the preparation of acid insoluble residues of the matrix, so the apparent occurrence of iron oxides in these samples (appendix 2) could not be confirmed.

Mineralogy of Clay Minerals

The presence of small quantities of clay minerals in most samples was indicated by chemical analysis, and in many cases by x-ray diffraction patterns. When compared with an analysis of a typical illite (Degens, 1965) the concentrations of K_2O and Al_2O_3 in the samples suggest a clay content of 3% for northern province samples, and 6% for non-glauconitic southern samples. These low concentrations have meant that only tentative identifications have been possible. X-ray diffraction patterns of acid insoluble residues have been used to assist in these identifications.

Glauconite is present in the matrix of all the southern conglomerates. Burst (1958a, and b), and later Hower (1961) have proposed similar classification systems for glauconite based upon structural and chemical considerations. Bentnor and Kastner (1965) stress the importance of structural as opposed to chemical data in such classifications, but propose broadly the same groupings as the previous authors.

The diffraction patterns of the glauconitic conglomerates all showed peaks at 10Å and 4.5Å which were fairly symmetrical. This indicates the glauconite is of the disordered type (Burst, 1958a and b; Hower, 1961; Bentnor and Kastnor, 1965). According to Hower (1961), this type of glauconite has a structure composed of mixed "illite and expandable montmorillonite" layers containing 10% to 20% of the latter. As the ability of glauconite to incorporate foreign ions as impurities is largely a function of the number of expandable montmorillonite layers present (Hower, 1961), the presence in the samples of disordered glauconite which is not capable of incorporating large concentrations of foreign ions, suggests that it would not contribute significantly to the trace element assemblage of the samples.

When analysed as whole rocks, few of the northern and onshore samples showed detectable peaks attributable to clay minerals. Where such peaks were visible they occurred at 10Å. By contrast, except for samples 896(2)p1, 896(2)p2, and 148, all southern samples showed definite, though in most cases, small peaks at 10Å. These peaks indicate the presence of a mica group mineral. Several glauconitic conglomerates also showed peaks at 14Å indicating the possible presence of montmorillonite or chlorite.

In an attempt to obtain more information on the clay mineralogy, a number of samples representing each province and rock type were leached in 5% HNO_3 for 30 minutes, and the residue was examined by x-ray diffraction. In all samples peaks at 10Å were visible, which were strengthened over those in samples showing 10Å peaks as whole rock. Mica group minerals may therefore occur in the northern and onshore samples as well as the southern samples. The 14Å peaks shown by some samples (883, 833, 896(1), and 896(2)) disappeared entirely on acid treatment. Since chlorites are partially soluble in acid (Brown, 1961) it may be that chlorites are present.

The results obtained from the x-ray diffraction studies at best only suggest the clay minerals present. However, a comparison of the K/Al, Al/Si and K/Si ratios of known clay minerals with the ratios found in the samples has enabled some of their identifications to be clarified. Such an approach suffers from the variability in clay mineral composition and also assumes that only one clay mineral is constituting the majority of the clay fraction, an assumption which may well be incorrect. Nevertheless, element ratios have been averaged from a number of literature sources (Bentnor and Kastnor, 1965; Degens, 1965; Porrenga, 1967; Mason, 1966; Speed, 1965) and the averaged ratios are presented in table A. 3. 3. Ratios for each sample province are also included, and were derived graphically.

For the northern and onshore samples the main clay mineral appears to be illitic, despite the rather low K/Si ratio for the onshore samples. The K/Al and K/Si ratios found in the southern samples supports the suggested presence of illites, since high K is an illite characteristic (Degens, 1965; McRae, 1972). The identification of illite as the predominant clay mineral apart from glauconite is in keeping with the findings of Weaver and Wampler (1972) who have shown that illite is the predominant clay mineral in a large number of phosphorite deposits.

Summary and Conclusions

The sparse detrital content of all samples except those of the southern matrix, indicates their formation within an environment of low sedimentation. The correlation between distance from the present coastline and quartz content of the southern conglomerates suggests the original source of quartz in the matrix of these samples may have been a coastline similar in location to the present one. The higher detrital content of the southern matrix compared to all other samples is also probably due to their deposition near to a coastline.

The presence of goethite in the southern pebbles indicates the oxidising nature of their depositional environment. That goethite in these samples has been shown to be insoluble in acid has allowed some clarification to be made of the relative contributions to the trace element assemblage of the iron rich samples by elements adsorbed onto and those included in this particular phase (chapter 2).

The low calcite content of pelletal samples, compared to other northern samples, provides confirmation of their proposed mechanism of formation (Summerhayes, 1970) whereby phosphatised carbonate sediments were disaggregated into pellets, re-phosphatised, and then reincorporated within the sediment. The re-phosphatisation results in a lowering of the calcite content due to its replacement by phosphate.

The presence in the samples of sufficient concentrations of dolomite to account for all the Mg present, suggests that the amount of Mg contained within the carbonate-apatite lattice is very small and certainly less than 0.25% (fig. A. 5. 2).

The identification of illite as the main clay mineral, apart from glauconite, explains the levels of K in the samples, whilst the presence of disordered glauconite, which cannot contain appreciable concentrations of impurities, suggests its contribution to the trace element assemblage of the conglomerates is small. The high glauconite content of the matrices of the southern conglomerates may reflect an original high level of clay material within the sediment, as glauconite can be a diagenetic modification of other clay minerals (Burst, 1958a and b; Hower, 1961; Degens, 1965; Speed, 1965; Mason, 1966; McRae, 1972).

Fig. A.3.1

X-ray diffraction pattern of the acid insoluble residue of sample 847(1)p

$CO_{K\alpha}$ radiation

Range 300

Zero suppression 6.8

Time constant 2

Scan speed $1^{\circ} 2\theta$ per min

The indexed peaks are the principal reflexions of goethite, $Fe_2O_3.H_2O, . nH_2O$


RELATIVE INTENSITY
100
50
0
061
250
151
160
240
221
211
140
121
111
021
130
120
110
020
QUARTZ
CLAY
70
60
50
40
30
20
10
DEGREES 2θ

TABLE A.3.1

A comparison of theoretical
and experimental acid solubilities
of Moroccan samples

KEY

A - Theoretical % of acid insoluble residue assuming Fe_2O_3 is insoluble

B - Theoretical % of acid insoluble residue assuming Fe_2O_3 is soluble

SAMPLE NO.	% ACID INSOLUBLE RESIDUE		
	A - THEORETICAL	B - THEORETICAL	EXPERIMENTAL
847(1)p1	28	8	31,38
p2	10	5	18
p3	12	5	40
p4	15	7	17
865 p1	37	36	45
p2	19	12	23
896(1)p1	28	5	37
p2	14	7	22
p3	20	11	18
896(2)p1	20	4	24
p2	19	4	25
898 p1	16	10	18
p2	17	10	15
p3	11	10	22
p4	11	9	10
p5	14	9	19
148	9	5	7
156(1)	26	8	32
156(2)	16	7	22
157	23	8	25, 30
847(2)	16	5	20, 23
893	20	3	21

TABLE A. 3. 2

Calcite, dolomite, and quartz contents
of onshore and offshore Moroccan samples

Sample No		Quartz	Calcite	Dolomite			Quartz	Calcite	Dolomite
135	Northern Phosphatised Limestones	3.9	27.0	1.7	847(1)p1	Southern Pebble Samples	1.3	10.8	2.8
136		1.3	23.2	1.8	p2		1.3	10.1	2.0
959		2.3	31.5	2.4	p3		2.3	10.2	2.5
966(1)		1.0	31.0	4.4	p4		1.2	9.8	2.0
988(a)		1.2	14.1	1.9	865 p1		30.7	38.0	1.7
988(b)		1.2	26.4	1.3	p2		2.3	8.0	7.8
1016		1.8	21.7	1.9	896(1)p1		2.0	7.7	4.8
1022(1)		1.5	24.4	1.3	p2		1.3	9.1	11.5
1022(2)		1.9	39.1	3.1	p3		2.5	9.8	10.5
1038		1.7	23.6	1.8	896(2)p1		0.5	7.9	8.9
					p2		1.2	7.7	6.1
139(1)	Northern Pelletal Samples	2.2	9.5	2.2	898 p1		1.3	4.1	1.5
139(2)		2.0	13.6	1.7	p2		1.9	5.7	1.5
966(2)		1.6	<1.0	1.8	p3		3.5	4.5	2.2
982		2.3	8.4	1.8	p4		1.6	8.8	1.9
1004		1.8	7.1	1.4	p5		2.0	9.5	1.5
152	Southern Glauconitic Conglomerates	6.4	9.1	4.5	148	Southern Non-Conglomerates	1.8	12.7	2.2
154		5.0	4.3	1.7	156(1)		1.3		5.6
155		4.8	8.8	5.0	156(2)		1.0	4.7	1.7
833		4.5	4.2	3.0	157		1.0	8.2	7.4
847(1)		2.3	4.5	1.3	847(2)		1.0	4.3	2.8
865		7.6	4.8	4.0	893		1.5	3.2	10.4
877		6.2	5.0	2.8					
883		3.5	3.0	1.4	847(1) c1	Southern Conglomerate Matrix	2.6	8.4	0.6
896(1)		3.2	10.2	2.1	896(2) c1		5.2	13.6	2.0
896(2)		3.0	11.8	1.0	898 c1		2.4	10.6	1.0
898		2.2	7.9	1.9	c2		2.7	6.8	1.0
					c3		2.8	5.9	1.0

Table 3.2. ctd.

Sample No	Quartz	Calcite	Dolomite
K1	1.5	<1.0	< 1.0
K2	2.5	1.0	1.0
K3	2.0	3.5	1.0
Y1	2.0	1.0	<1.0
Y2	3.0	4.5	1.5
SD	3.0	<1.0	<1.0
BG1	4.5	<1.0	2.5
BG2	12.0	4.0	4.5
MEA	2.0	17.0	<1.0

Precision on	Calcite	1.0%
	Dolomite	1.0%
	Quartz	0.5%

as determined by duplicate analysis

TABLE A. 3. 3

K/Al, K/Si, and Al/Si
ratios for clay minerals and Moroccan samples

Sample Type	Element Ratios		
	K/Al	K/Si	Al/Si
Onshore	1/3	1/6	1/1
Northern	1/2	1/4	2/3
Glaucomitic Conglomerate	3/2	2/7	1/7
Southern Non-Conglomeratic	1/2	1/6	1/4
Southern Pebble	1/2	1/6	1/4
Literature Averages			
Illites	1/3	1/4	1/1
Illitic Glauconite (ordered)	2/1	1/4	1/6
Kaolinites	<1/10	<1/10	1/1
Montmorillonites	<1/10	<1/10	1/2
Chlorites	<1/10	<1/10	1/1

APPENDIX 4 - SEPARATION OF PHOSPHATIC ROCK INTO CONSTITUENT PHASES

Geochemical investigations of trace elements, and substitutions, in the carbonate-apatite phase of phosphatic rocks is obviously best carried out on purified carbonate-apatite. This phase must be separated by methods unlikely to affect its geochemistry.

Heavy liquid separations have been used to separate the carbonate-apatite phase of coastal sediments (D'Anglejan, 1967) and igneous apatite (Gulbrandsen et al., 1966), but this method was not particularly effective for the offshore Moroccan samples. This was probably because of the intimate admixture of microscopic and submicroscopic impurities such as clays, and because the phosphatisation of limestones to produce carbonate-apatite seems to result in the formation of a solid solution of carbonate-apatite in limestone, impossible to separate by normal means. No reports of the separation by heavy liquid techniques of a carbonate-apatite phase from impure phosphatised limestones containing large amounts of carbonate minerals were found in the literature. Indeed, Emigh (1967) considers such separations to be impossible, for reasons similar to those given here. Fairly pure quartz was separated from two samples (877, 898) in the course of attempts to obtain a carbonate-apatite fraction and this was quantitatively estimated during the separations and used to check the accuracy of the x-ray determinations of quartz in other samples. Despite producing only minor increases in the purity of the carbonate-apatite phases of the samples, a number of samples were treated with heavy liquids to separate quartz, and as much extraneous material as possible, prior to the analysis of the samples for R.E.E.'s by mass spectrography (chapter 4).

Chemical methods of removing free carbonate minerals were attempted. Acid leaches (Hirst and Nicholls, 1958), including acetic acid, were tried but proved unsuccessful because of dissolution of phosphate. Silverman's method (Silverman et al., 1952) has been widely used to remove free carbonates from phosphate rock (Lehr et al., 1967) but only for samples containing relatively small percentages of carbonate minerals. The method was successful for some Moroccan samples but unsuccessful, despite several separate treatments, for the majority, and was therefore not used.

The inability to effect good separations on all samples resulted in all analyses being performed on whole rock samples. The carbonate minerals are not expected to contribute significantly to the overall geochemistry, except possibly for Mg, Sr, Zn, Ca and Ba (Chester, 1965); however Sr is easily shown to be associated with the apatite phase. Quartz is not expected to contribute to the trace element geochemistry.

APPENDIX 5 - X-RAY DIFFRACTION ANALYSIS

All Moroccan and most world samples were analysed by x-ray diffraction in order 1) to determine the major mineral phases, 2) to provide semi-quantitative estimates of the amount of each phase, in order to help refine the geochemistry of the phosphorites, and 3) to quantitatively estimate the extent of carbonate substitution within the carbonate-apatite lattice.

Sample Preparation

All samples were ground under alcohol in a McCrone Mill with alumina grinders for 10 minutes to reduce their particle size to approximately 10 microns. They were then dried at 60°C, broken up in a pestle and mortar and run as cavity mounts on a Phi lips Proportional Counter X-Ray Diffractometer, fitted with a horizontal goniometer.

Operating Conditions

The operating conditions used varied with the nature of the samples and the data to be obtained. For the identification of major mineral phases the following instrumental parameters were employed:

Scan speed	2° 2θ/min.
Scan range	4°-65° 2θ
Time constant	2
Chart speed	3 cm/min
Radiation	$Cu_{K\alpha}$ for most samples,

with $Co_{K\alpha}$ being employed for samples of high iron content.

For the semi-quantitative estimation of the mineral phases, and for the estimation of the extent of carbonate substitution the instrumental parameters were:

Scan speed	1^{o} 2θ/min
Scan range	25^{o}-34^{o} 2θ
Time constant	4
Chart speed	4 cm/min
Radiation	$Cu_{K\alpha}$ for most samples,

with $Co_{K\alpha}$ being employed for samples of high iron content.

The employment of $Co_{K\alpha}$ radiation for samples of high iron content reduces the background and improves the quality of the trace.

Semi-quantitative Estimation of Major Phases

Quartz:

A standard graph was prepared (fig. A. 5. 1) by plotting the area of the main quartz peak against the total silica content of those samples which contained very little clay material, estimated on the basis of their chemical analysis ($< 0.2\%$ K_20, $<0.4\%$ Al_20_3). Also plotted were two samples from which quartz had been separated and estimated by heavy liquid separations (samples 877, 898). This graph was used to determine quartz in all samples. Replicate determinations yielded a precision of 1% of SiO_2 at the 95% confidence level.

Dolomite:

The determination of dolomite was similar to that of quartz. The northern province and onshore samples contain little clay, estimated on the basis of their chemical analysis, ($< 0.21\%$ K_20 $<0.60\%$ Al_20_3) and thus these samples cannot contain significant Mg within the clay phase. Any Mg contained in the sample will exist as dolomite, or as a substituent within the apatite phase. Since the latter contributions are probably small, the Mg0 content of these samples were used to construct a standard graph (fig. A. 5. 2) of Mg0 against dolomite peak area from which the dolomite content of the remaining samples were determined.

Runnells (1970) points out that the solid solution variation of dolomite leads to little error in such determinations utilising the main dolomite peak.

The formula for dolomite is $Mg_x Ca_{1-x} CO_3$, the ideal formula being $Mg_{0.5} Ca_{0.5} CO_3$ (Degens, 1965). The true Mg/Ca ratio for these samples is unknown and an assumption is made that the dolomite is solely $MgCO_3$ for the purposes of this thesis. The validity of this assumption is questionable, but since variations of Mg/Ca ratio within the samples is not thought large, such an assumption allows an internally consistent set of dolomite values to be obtained which, while subject to systematic error, are useful in defining the mineralogy and geochemistry of the samples.

Calcite:

A standard graph was plotted (fig. A. 5. 3) of the main calcite peak area against the total CO_2, less substitutional CO_2, of the samples with MgO values <0.8% MgO. This graph was used to obtain all calcite values. The method rests upon the fact that samples containing <0.8% MgO cannot contain more than 0.8% CO_2 within a dolomite phase and thus all carbon dioxide, apart from that in the lattice, must be within calcite. The method is justified by the standard graph and by the fact that deviations from the standard line are directly proportional to the MgO content of the sample. Replicate determinations yield a precision of 1% of calcite at the 95% confidence level.

It has been pointed out by Chave (1952), and later by Goldsmith et al. (1958, 1961) and Runnells (1970), that the substitution of Mg within the calcite lattice can appreciably affect the intensity of the main calcite peak and lead to serious errors in quantitative x-ray diffraction studies. However, if all samples contain approximately equal, or low concentrations, of Mg no significant error is introduced by the presence of Mg.

The data of Goldsmith (1961), relating the d spacing giving rise to the calcite main peak to the mole % of $MgCO_3$ in solid solution within calcite, has been used to estimate the $MgCO_3$ content of the calcite found in the Moroccan samples. In both offshore and onshore samples the calcite contained between 4 mole % and 8 mole % $MgCO_3$, an amount and variation insufficient to cause errors in excess of those already inherent in the methods employed (Runnells, 1970).

Estimation of Lattice Carbonate within the Carbonate-Apatite Lattice

The method of Gulbrandsen (1970) was used. The method relies upon a direct linear relationship existing between the length of the a-axis of the carbonate-apatite crystal structure and its carbonate ion content. The c-axis is relatively unaffected by the substitution. The variation in the a-axis with variation of carbonate ion is measured by the variation in the separation of the 300 and 210 peaks of the carbonate-apatite x-ray diffraction spectra. The measured separation is substituted into the experimentally derived relationship:-

$$\% \; CO_2 \text{ by weight in lattice} = 185.0 - 25.574\,x$$

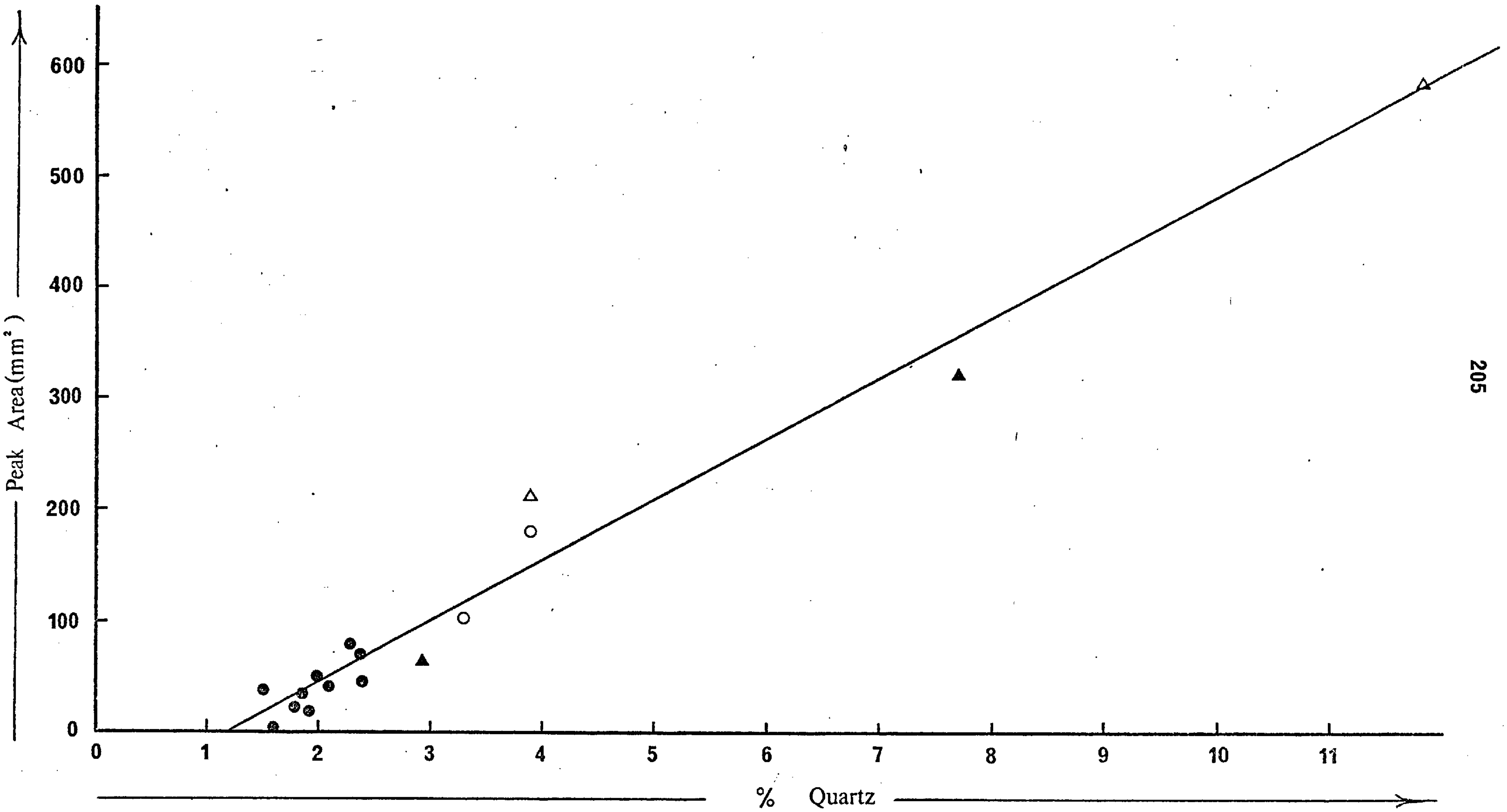
where x is the separation of the 300 and 210 peaks in degrees 2θ, measured with $Cu_{K\alpha}$ radiation

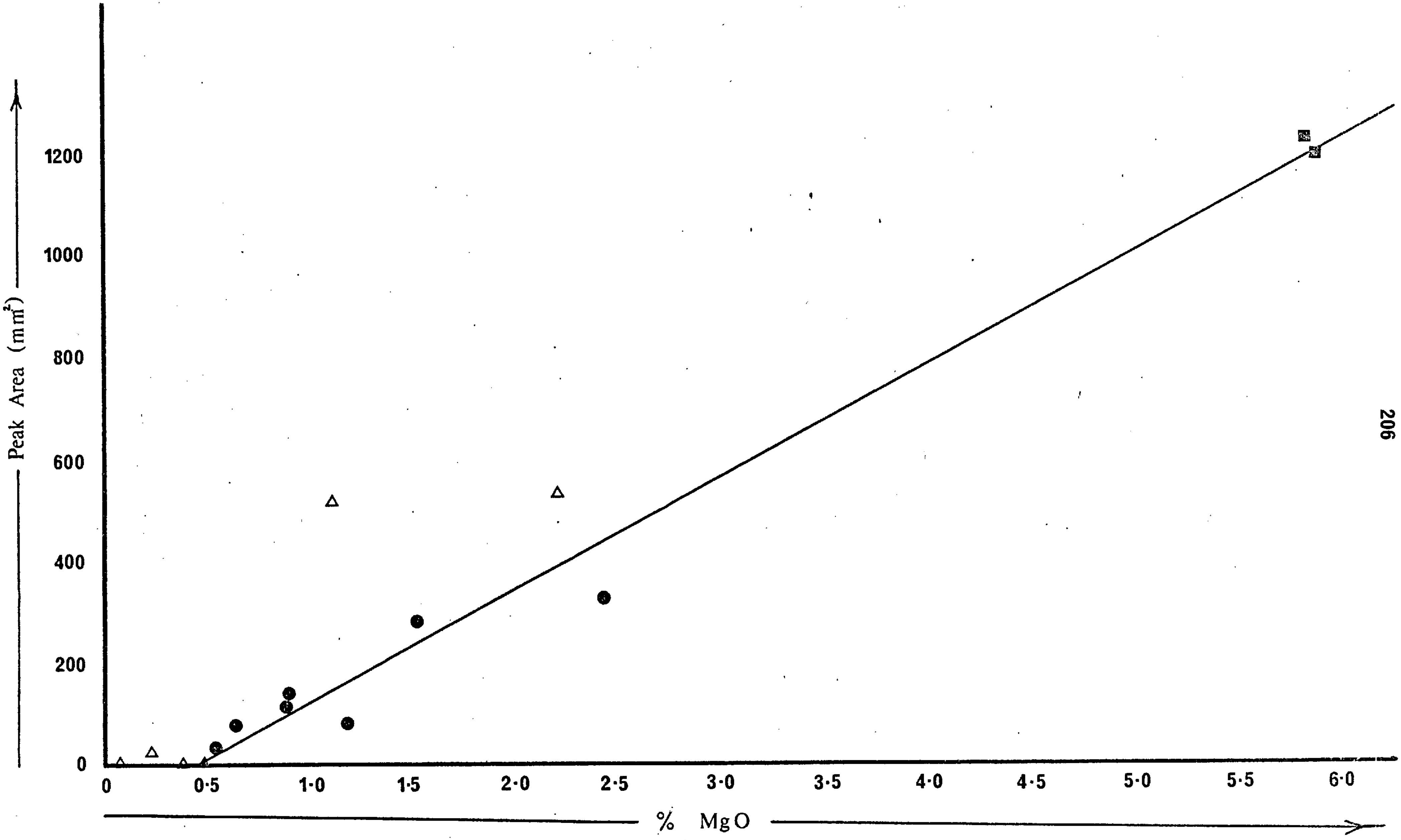
Duplicate runs on all samples were performed. The precision being within that quoted by Gulbrandsen, as ± 0.5% of substitutional CO_2 at the 95% confidence level.

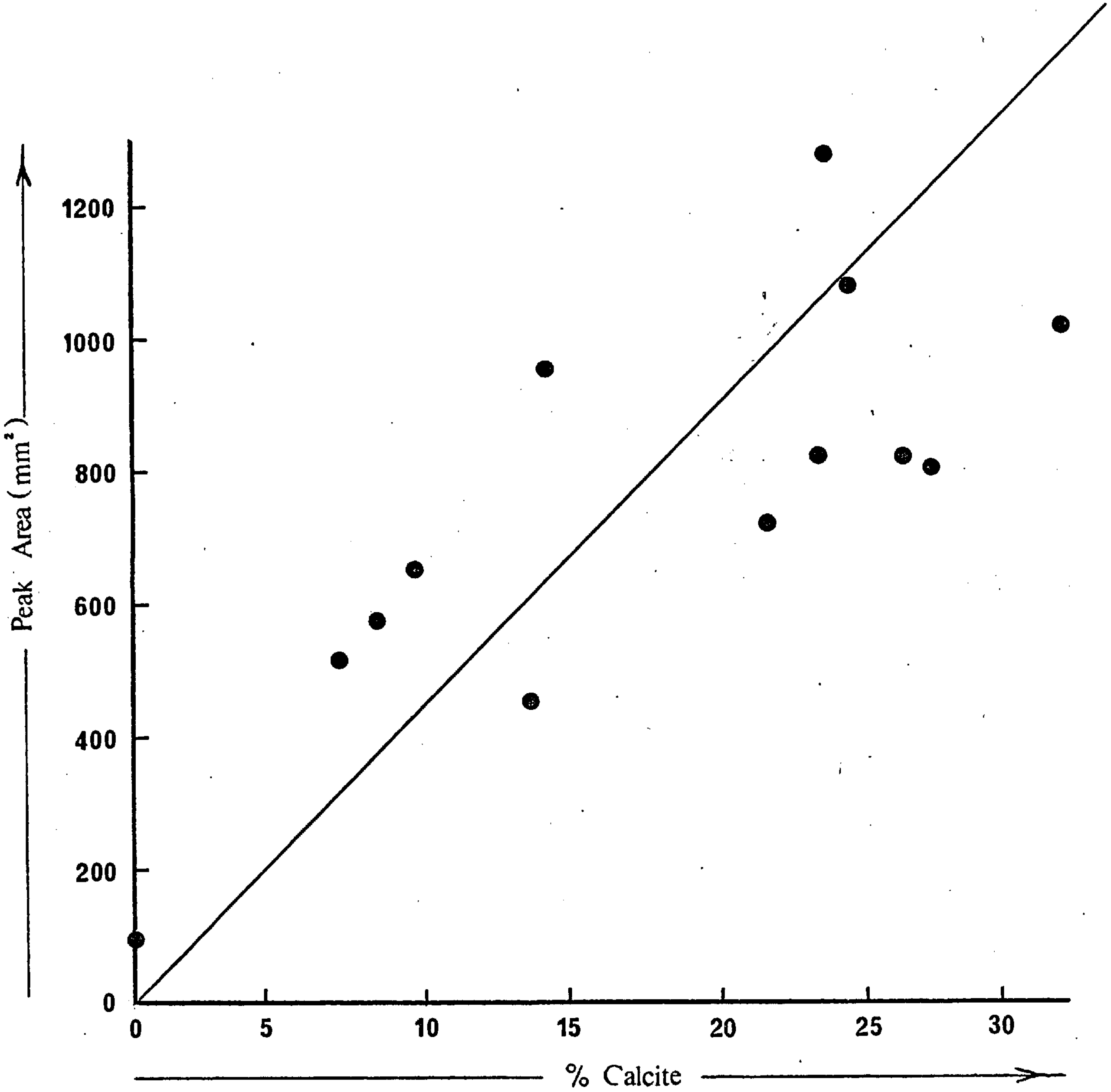
Figs. A.5.1 Standard graph for quartz determinations

A.5.2 Standard graph for dolomite determinations

A.5.3 Standard graph for calcite determinations


Peak Area (mm²)
0
100
200
300
400
500
600
0
1
2
3
4
5
6
7
8
9
10
11
% Quartz


Peak Area (mm^2)
1200
1000
800
600
400
200
0
0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
5·0
5·5
6·0
% MgO


Peak Area (mm²)
1200
1000
800
600
400
200
0
0
5
10
15
20
25
30
% Calcite

APPENDIX 6 - X-RAY FLUORESCENCE ANALYSIS

Most of the analyses in this thesis were done using a Phillips PW 12/12 24 Channel Automatic X-ray Fluorescence Spectrometer at Edinburgh University. A comparison of two methods of analysis - Reynolds (1963), and Andermann and Kemp (1958) - were carried out at the time the analyses were performed. The results are presented in table A. 6. 4., the main analytical tables.

1) Major Element Analysis

Difficulties in analysis caused by differing mass absorption coefficients, chemical bonding, crystal environment, and structural effects between samples, and between samples and standards, are eliminated by the use of a fusion method of sample preparation.

0.400g. of sample were fused with 0.400g. of Lanthanum Oxide and 3.200g. of Lithium Tetraborate for 4 hours at 1200°C in carbon crucibles. The resulting glass bead was ground for two minutes in a tungsten carbide tema mill and then pressed into a pellet with a boric acid backing using a pressure of 15 tons psi. 10 samples were prepared and analysed in duplicate as a check on precision. The elements Ca, K, Fe, Mg, Si, Al, and P were analysed using a 2 k.w. chromium tube. Instrumental conditions varied between elements.

Standards used in major element analysis

The standards used consisted of 9 different rock samples, previously well analysed, four of which were phosphates. The samples were also mixed in various proportions and analysed in order to show if the original analyses were inaccurate. In no case was this found to be the case, mixtures of standards always falling on the line. Table A. 6. 1. lists the standards used.

TABLE A. 6. 1.

Standard Rock Samples used in

X-ray fluorescence analysis

MAJOR ELEMENT STANDARDS

National Bureau of Standards Rocks	120(a)	Florida Phosphate
	1(a)	Argillaceous limestone
	1(b)	" "
	88(a)	Dolomitic limestone
University of Edinburgh Internal Standard	E1	
(Analysts G.R. Angell, D. Strong)	E2	
United States Geological Survey Samples	22	Phosphoria Formation Phosphate
(Gulbrandsen, 1966)	41	
	47	

TRACE ELEMENT STANDARDS

United States Geological Survey Standard Diabase	W-1	
" " " " " Granite	G-2	
United States Geological Survey Standard Rock	AGV-1	
" " " " " "	DTS-1	
" " " " " "	GSP-1	
National Bureau of Standards Standard Sample	98(a)	Plastic Clay
" " " " " "	89	Lead-Barium Glass
" " " " " "	1(b)	Argillaceous Limestone

2) Minor Element Analysis

Minor element analysis is subject to serious errors if allowance is not made for variation in mass absorption between samples, and in any sample at different wavelengths. Two methods are available to correct for this effect, if computational corrections cannot be applied.

a) Reynolds Method (1963). This depends upon the measurement of the intensity of the Compton Scatter line from the incident radiation, which is proportional to the mass absorption coefficient of the sample at the wavelength of the incident radiation. Measurement of the intensity of the Compton Scatter line in each sample prior to analysis allows a simple correction factor, proportional to the size of this line, and hence the mass absorption of the sample, to be established for all analyses line intensities. The disadvantage of the method is that the mass absorption coefficient is wavelength dependent and the method is therefore only strictly applicable to the wavelength region near that of the incident radiation.

b) Andermann and Kemp (1958) have shown that at any particular wavelength the use of peak/background ratios obviates any further correction being necessary for mass absorption coefficients, since the background intensity is related to the mass absorption coefficient.

A comparison of these methods for all minor elements analysed indicates that Reynolds method was best in the region $12^{\circ}/2\theta$ to $75^{\circ}/2\theta$ where mass absorption coefficients change rapidly with wavelength. The elements I, Y, Sr, Rb, U, Zn, S, Cu, Ni, As, and Pb, were analysed in this region. Only for Mn at $95^{\circ}/2\theta$ was the ratio method found superior.

For Ti, Ce, V, Cr, and Ba a simple line minus background intensity was found to yield the best results. These elements were measured at angles between $85^{\circ}2\theta$ and $125^{\circ}2\theta$ in the long wavelength region of the spectrum.

Sample Preparation

The samples, previously prepared as 80 mesh powder, were ground under alcohol for ten minutes in a McCrone Mill with agate grinders. The resulting powder was dried at 110° for four hours, mixed in an agate pestle and mortar for 10 minutes and then pressed into a pellet with a boric acid backing. These pellets were run in the machine.

Some samples consisted of insufficient material to make pellets. These were analysed as powdered samples. Since Reynolds method is inapplicable to powders, the method of Andermann and Kemp was used.

A 2kw Tungsten tube was used to analyse for Y, Sr, Rb, Ti, U, Pb, As, V, Cr, Mn, Cu, Ni, Zn, Ba, and I.

The eight standards used for determination of these minor elements are listed in table A. 6. 1. Recommended values for the U. S. G. S. standards were used (Fleischer, 1969; Flanagan, 1969, 1970).

The instrumental conditions used in the analyses are given in table A. 6. 3.

Precision of the Major and Minor Analysis

Ten sample duplicates were prepared and analysed for both major and minor elements. The precision of the analyses were found from these duplicates to be good, and are listed in table A. 6. 2.

TABLE A. 6. 2.

Precision of major and minor element analyses

MAJOR ELEMENTS		TRACE ELEMENTS		
			PRESSED DISCS	POWDERS
CaO	0.8	Y	1.5	2
K_2O	0.01	Sr	15	20
Fe_2O_3	0.05	Rb	1	2
SiO_2	0.20	Cu	1	3
Al_2O_3	0.50	Ni	2	4
P_2O_5	1.0	Zn	2	5
MgO	0.15	Ti	10	100
S	0.04	U	4	6
		Cr	2	3
		Mn	5	5
		Pb	1.5	3
		I	10	20
		As	4	4
		Ba	2	5
		V	2	5

MAJOR ELEMENTS - precision expressed as ± % of oxide

MINOR ELEMENTS - precision expressed as ± ppm of element.

TABLE A.6.3.

Instrumental conditions for minor element analysis

(For Major Elements see Addendum 7)

Bk = Background

F = Flow Counter

S = Scintillation

L - B = Line - Background Method

Rey = Reynold's Method

Ratio = Andermann and Kemp's Method

ELEMENT	LINE	BK. 1	BK. 2	VACUUM	COLLIMATER	k. V	m. A
Ce	111.8 $L_{\beta1}$	117.5		✓	COARSE	80	24
Y	23.85 $K_{\alpha1}+K_{\alpha2}$	23.30	24.51	-	FINE	80	24
Sr	25.20 $K_{\alpha1}+K_{\alpha2}$	24.51	25.90	-	"	"	"
Rb	26.70 $K_{\alpha1}+K_{\alpha2}$	25.9	27.11	-	"	"	"
Zn	41.86 $K_{\alpha1}+K_{\alpha2}$	41.21	-	-	"	"	"
Cu	45.08 $K_{\alpha1}+K_{\alpha2}$	45.61	-	-	"	"	"
Ni	48.72 $K_{\alpha1}+K_{\alpha2}$	48.00	-	-	"	"	"
U	26.23 $L_{\alpha1}$	25.80	-	-	"	"	"
Ti	86.20 $K_{\alpha1}$	84.50	-	✓	F	80	24
V	123.40 $K_{\alpha1}+K_{\alpha2}$	121.00	- -	"	"	"	"
Cr	107.20 $K_{\alpha1}$	105.50	-	"	"	"	"
Mn	95.32 $K_{\alpha1}$	98.00	-	"	"	"	"
Ba	128.90 $L_{\beta1}$	132.00	-	✓	F	80	24
Pb	28.28 $L_{\beta1}+L_{\beta2}$	27.85	28.70	-	"	"	"
I	12.42 $K_{\alpha1}+K_{\alpha2}$	11.80	13.00	-	"	"	"
As	34.03 $K_{\alpha1}+K_{\alpha2}$	33.40	34.60	-	"	"	"
S	75.80 $K_{\alpha1}+K_{\alpha2}$	73.00	-	✓	"	"	"

ELEMENT	CRYSTAL	COUNTER	% INTERFERENCES	METHOD (pellets)	METHOD (powders)
Ce	LiF(220)	F + S	6.3% Nd not corrected for	L - B	-
Y	LiF(200)	S	29.6% Rb on Y	Rey	RATIO
Sr	"	"		"	"
Rb	"	"	2.1% U on Rb	"	"
Zn	"	"	-	"	"
Cu	"	"	-	"	"
Ni	"	"	-	"	"
U	"	S	-	"	"
Ti	"	S + F	-	L - B	L - B
V	LiF(220)	"	2.15%Ti on V	"	"
Cr	"	"	5.5%V on Cr	"	"
Mn	"	"	-	RATIO	RATIO
Ba	"	F + S	0.5% Cr on Mn ignored	L - B	L - B
Pb	LiF (200)	S	-	Rey	L - B
I	"	"	-	Rey	RATIO
As	"	"	70% Pb on As	Rey	RATIO
S	PET	F + S	-	Rey	-

TABLE A.6.4.

Main analytical tables

Sample No.		CaO	K_2O	Fe_2O_3	SiO_2	P_2O_5	MgO	Al_2O_3	Na	CO_2	ORGANIC CARBON	PYRITIC SULPHUR	LATTICE CO_3^{2-}	LATTICE SO_4^{2-}
135	NORTHERN PHOSPHATISED LIMESTONES	47.8	0.17	0.57	3.9	18.6	0.85	0.30	0.82	17.1	0.40	0.33	8.5	1.65
136		51.2	0.11	0.42	1.9	19.8	0.90	0.35	0.77	15.5	1.02	0.64	8.1	1.71
959		48.7	0.12	0.43	3.3	16.0	1.20	0.30	0.64	19.4	0.23	0.26	8.7	1.38
966(1)		47.3	0.12	5.00	1.6	14.6	2.20	0.35	0.64	20.7	0.21	0.06	8.2	1.26
988(a)		50.6	0.19	1.75	2.5	15.9	0.95	0.50	0.76	11.2	0.30	0.27	8.7	1.38
988(b)		50.0	0.10	0.67	1.7	20.4	0.65	0.30	0.74	16.6	1.12	0.96	8.3	1.77
1016		50.0	0.13	0.79	1.8	21.3	0.95	0.35	0.76	15.3	0.85	0.79	8.2	1.83
1022(1)		49.1	0.11	0.26	1.5	20.6	0.65	0.30	0.84	16.1	0.64	0.54	8.9	1.53
1022(2)		52.0	0.21	1.07	2.9	13.3	1.55	0.60	0.68	22.7	0.28	0.23	8.2	1.14
1038		48.9	0.13	0.64	2.0	21.5	0.90	0.35	0.81	16.0	0.77	0.92	8.2	1.83
139(1)	NORTHERN PELLETAL SAMPLES	48.8	0.13	0.82	2.4	25.2	1.10	0.30	1.00	11.0	0.96	0.59	8.1	2.15
139(2)		48.6	0.15	0.97	3.0	24.0	0.85	0.40	0.99	11.9	0.74	0.50	8.6	2.06
966(2)		50.3	0.12	0.78	2.3	29.3	0.90	0.45	1.24	6.9	0.75	0.81	8.2	2.55
982		46.8	0.10	0.57	2.3	25.8	0.90	0.30	0.91	10.2	0.58	0.49	8.3	2.22
1004		48.7	0.14	0.70	2.4	26.5	0.71	0.40	0.94	9.3	0.82	0.39	8.3	2.28
152	SOUTHERN CONGLOMERATES	31.6	1.87	8.80	17.2	12.9	4.70	1.85	0.52	12.0	0.58	0.28	8.1	1.11
154		29.2	2.15	8.20	20.0	14.7	2.80	2.75	0.59	6.7	0.61	0.37	8.2	1.35
155		31.7	1.38	5.50	16.3	12.7	3.60	4.3	0.72	10.9	0.42	0.02	8.0	0.96
833		32.2	2.43	10.20	17.3	16.4	2.95	2.4	0.70	7.2	0.75	0.71	7.7	1.41
847(1)		37.8	1.33	10.90	10.3	19.1	2.70	1.3	0.59	7.3	0.24	0.00	8.1	1.62
865		30.9	1.77	8.00	20.6	13.7	3.90	1.95	0.56	10.0	0.62	0.33	7.5	1.17
877		32.2	1.85	8.75	18.7	15.2	3.35	1.85	0.65	9.1	0.46	0.00	8.2	1.14
883		35.1	2.6	7.10	17.5	17.8	2.95	2.3	0.70	7.8	0.37	0.21	7.7	1.35
896(1)		39.1	0.99	9.30	9.2	17.6	2.90	1.85	0.60	11.3	0.33	0.00	7.5	1.53
896(2)		36.3	1.55	12.65	9.6	16.4	2.50	1.95	0.63	10.1	0.21	0.00	7.8	1.35
898		40.7	1.34	6.50	10.5	20.1	2.20	1.55	0.81	8.9	0.43	0.26	8.7	1.74

Sample No.		Y	Sr	Rb	Zn	Cu	Ni	U	Ti	V	Cr	Mn	Ba	Pb	I	As
135	NORTHERN PHOSPHATISED LIMESTONES	30	1170	8	43	10	20	507	178	79	29	104	<4	5	26	15
136		17	1330	8	53	20	35	206	94	29	32	34	"	<3	<5	<6
959		27	1130	9	23	11	15	369	143	63	43	73	"	8	83	10
966(1)		33	1160	9	15	10	12	142	125	50	6	239	"	12	94	75
988(a)		35	1190	10	64	16	22	328	95	76	35	125	"	9	28	8
988(b)		8	1300	7	50	17	51	108	94	20	28	64	"	3	25	30
1016		16	1450	10	66	22	45	103	93	38	33	55	"	4	18	31
1022(1)		21	1460	10	38	22	29	109	85	25	32	46	"	<3	9	4
1022(2)		13	1010	9	15	10	10	483	148	40	29	116	"	4	15	6
1038		33	1410	7	51	27	49	259	100	158	28	103	15	<3	5	15
139(1)	NORTHERN PELLETAL SAMPLES	103	1860	10	53	20	28	84	100	29	51	65	<4	<3	18	22
139(2)		76	1840	8	50	31	26	96	110	23	33	108	"	6	10	18
966(2)		134	2130	8	82	24	46	129	94	34	58	65	"	10	<5	25
982		237	2000	6	40	17	30	71	94	19	34	74	"	7	59	9
1004		99	2120	11	46	20	22	60	102	23	33	50	16	6	<5	9
152	SOUTHERN CONGLOMERATES	28	950	47	37	10	22	154	575	68	82	120	73	13	16	6
154		36	990	61	54	9	16	149	695	70	94	105	63	16	25	38
155		28	1180	38	70	25	227	171	1080	98	30	4109	140	12	20	20
833		42	1100	60	41	17	24	192	565	83	80	75	87	24	10	56
847(1)		21	1100	44	55	15	31	122	347	84	38	150	30	10	63	40
865		30	950	44	39	10	21	170	561	72	75	140	133	19	19	59
877		34	1070	53	49	15	24	195	620	75	84	100	60	20	21	45
883		29	1130	78	43	15	17	181	496	54	73	157	58	14	14	5
896(1)		28	1250	34	45	15	24	133	438	103	53	150	28	17	38	43
896(2)		24	1040	35	54	13	28	112	505	148	71	182	40	24	47	75
898		38	1270	21	60	13	49	155	363	143	66	67	240	23	29	50

Sample No.		CaO	K_2O	Fe_2O_3	SiO_2	P_2O_5	MgO	Al_2O_3	Na	CO_2	ORGANIC CARBON	PYRITIC SULPHUR	LATTICE CO_3^{2-}	LATTICE SO_4^{2-}
847(1)c	SOUTHERN MATRIX	33.4	2.26	9.65	13.5	15.7	2.28	1.65	0.74	8.8	0.23	0.30	8.2	1.17
896(2)c		38.3	1.60	6.50	13.8	17.2	1.65	2.00	0.87	10.4	0.31	0.00	7.1	1.50
898c1		37.3	1.58	11.40	11.4	11.9	2.45	2.25	0.61	14.2	0.17	0.20	8.2	1.56
898c2		36.8	2.37	8.10	13.7	19.1	2.30	1.80	0.79	7.9	0.26	0.61	8.3	0.63
898c3		36.5	2.45	7.50	13.2	18.8	1.85	1.70	0.79	7.8	0.19	0.30	8.9	1.44
847(1)p1	SOUTHERN PEBBLES	36.2	0.49	19.90	6.5	15.1	3.30	0.85	0.47	11.1	0.18	0.00	7.1	1.38
847(1)p2		45.3	0.35	5.45	3.6	21.3	2.05	0.80	0.69	12.8	0.20	0.00	7.4	1.86
847(1)p3		43.6	0.32	6.45	4.3	18.7	2.40	0.85	0.68	13.4	0.13	0.10	7.6	1.62
847(1)p4		44.4	0.45	8.50	4.8	21.1	1.95	1.32	0.70	11.9	0.13	0.10	7.2	1.74
865p1		33.2	0.42	0.72	34.7	4.2	0.80	1.10	0.28	18.1	0.21	0.40	7.2	0.60
865p2		37.9	0.71	6.85	10.3	18.7	4.85	2.20	0.75	10.2	0.17	0.00	7.2	1.20
896(1)p1		33.3	0.31	22.80	3.5	13.5	3.55	1.15	0.42	13.1	0.20	0.00	7.1	1.13
896(1)p2		39.6	0.55	7.40	4.9	14.9	5.55	1.50	0.50	18.7	0.22	0.00	7.8	1.20
896(1)p3		40.4	1.00	8.40	8.5	14.8	5.70	1.60	0.53	17.2	0.25	0.00	7.7	1.35
896(2)p1		36.6	0.22	15.50	3.2	15.0	4.25	0.80	0.53	14.7	0.13	0.00	7.4	1.26
896(2)p2		34.1	0.15	14.90	3.5	14.8	4.60	0.75	0.48	16.5	0.11	0.00	7.1	1.20
898p1		41.8	0.51	6.70	7.5	22.3	2.36	1.55	0.84	8.7	0.36	0.00	7.9	2.13
898p2		39.2	0.45	7.25	7.9	21.5	2.35	1.45	0.85	7.8	0.28	0.00	8.6	1.71
898p3		45.0	0.99	0.92	7.5	24.5	2.45	1.45	0.93	8.4	0.34	0.00	8.3	2.22
898p4		44.2	0.38	2.32	7.5	24.8	1.95	1.20	0.87	8.4	0.37	0.00	7.5	2.00
898p5		42.3	0.58	4.85	7.2	20.3	2.30	1.30	0.81	11.2	0.21	0.00	8.6	2.15
148	SOUTHERN NON-CONGLOMERATE	48.3	0.25	3.65	3.8	19.2	1.55	0.70	0.62	15.1	0.34	0.10	7.2	1.65
156(1)		33.4	0.55	18.10	5.8	15.8	4.50	1.16	0.52	10.5	0.13	0.00	8.2	1.50
156(2)		43.3	0.36	8.35	6.0	22.0	2.60	0.95	0.66	8.9	0.45	0.00	8.3	1.50
157		34.6	0.25	14.30	6.4	12.1	7.65	1.65	0.47	18.0	0.21	0.00	8.6	0.90
847(2)		42.6	0.39	11.10	4.1	22.5	1.80	0.60	0.76	8.0	0.17	0.00	7.8	2.01
893		36.2	0.16	16.60	2.3	9.8	8.65	0.50	0.37	21.5	0.12	0.00	7.4	0.99

Sample No.		Y	Sr	Rb	Zn	Cu	Ni	U	Ti	V	Cr	Mn	Ba	Pb	I	As
847(1)c	SOUTHERN MATRIX	29	1130	56	58	10	24	183	373	68	55	130	<4	24	20	56
896(2)c		40	1220	45	44	13	<3	157	630	63	64	145	48	18	26	25
898c1		32	790	43	91	17	61	73	510	127	71	258	18	24	44	81
" c2		50	1290	55	53	17	12	142	380	86	84	83	83	18	28	22
" c3		59	1360	53	54	13	17	135	337	84	88	77	37	15	23	14
847(1)p1	SOUTHERN PEBBLES	14	740	23	61	21	49	78	282	134	25	193	55	5	80	145
" p2		9	1000	14	70	16	65	433	202	97	17	124	40	<3	<5	90
" p3		14	1100	14	70	19	47	75	400	64	21	172	<4	10	"	92
" p4		6	1140	15	70	18	42	170	390	80	21	170	"	14	20	102
865p1		23	730	14	21	6	9	114	718	23	17	104	"	5	18	<6
" p2		27	1130	29	37	11	6	61	747	51	31	125	"	9	19	47
896(1)p1		18	750	18	67	11	35	40	325	242	35	330	112	33	70	144
" p2		9	780	21	26	10	18	81	286	50	15	202	<4	9	141	46
" p3		9	740	21	27	8	16	78	296	54	18	202	37	7	132	43
896(2)p1		24	750	16	35	12	6	52	254	160	52	287	72	21	44	114
" p2		25	720	17	36	11	6	53	269	154	40	329	72	11	<5	99
898p1		22	1250	18	83	23	112	95	375	256	32	71	30	9	49	95
" p2		30	1260	20	70	6	24	75	400	170	36	71	<4	10	46	56
" p3		13	1390	21	31	16	17	215	341	89	15	65	"	<3	<5	<6
" p4		5	1220	17	45	13	39	125	291	129	22	61	"	6	37	27
" p5		17	1280	25	85	4	57	57	474	160	21	71	18	7	48	57
148	SOUTHERN NON-CONGLOM-ERATES	14	1120	11	41	13	24	285	159	66	23	100	<4	3	23	32
156(1)		21	800	25	104	16	94	241	385	240	60	374	32	49	308	151
156(2)		11	1300	14	40	17	32	251	202	120	30	213	<4	<3	60	64
157		29	780	13	77	14	51	38	233	184	43	486	"	20	50	100
847(2)		14	1130	20	62	14	35	169	138	139	24	127	25	12	35	91
893		7	530	13	34	12	28	32	180	130	26	425	317	<3	43	131

Sample No.		CaO	K_2O	Fe_2O_3	SiO_2	P_2O_5	MgO	Al_2O_3	Na	CO_2	ORGANIC CARBON	PYRITIC SULPHUR	LATTICE CO_3^{2-}	LATTICE SO_4^{2-}
K1	ONSHORE (NORTHERN) DEPOSIT	50.9	0.05	0.11	2.10	33.9	0.40	0.30	0.45	3.7	0.18	0.00	5.6	2.25
K2		50.2	0.06	0.13	2.90	32.8	0.45	0.40	0.54	4.5	<0.1	0.00	5.3	2.15
K3		49.5	0.07	0.16	3.15	32.4	0.40	0.45	0.47	5.5	0.21	0.00	5.4	2.20
MEA		51.5	0.09	0.21	3.10	25.9	0.55	0.55	0.41	11.1	0.05	0.00	5.4	1.42
Y1	ONSHORE (SOUTHERN) DEPOSIT	51.5	0.04	0.10	1.90	32.5	0.50	0.25	0.48	4.4	0.27	0.00	5.6	1.82
Y2		49.8	0.08	0.17	3.40	30.8	0.75	0.35	0.61	5.1	0.22	0.00	7.0	1.84
BG1		47.4	0.08	0.20	4.50	29.9	1.15	0.45	0.61	5.2	0.19	0.00	7.0	1.80
BG2		42.6	0.13	0.23	11.8	24.0	2.15	0.65	0.60	7.8	0.08	0.00	6.7	1.95
SD		49.3	0.04	0.09	2.10	37.1	0.05	0.35	0.20	2.1	0.13	0.00	4.1	2.73

Sample No.		Y	Sr	Rb	Zn	Cu	Ni	U	Ti	V	Cr	Mn	Ba	Pb	I	As
K1	ONSHORE (NORTHERN) DEPOSIT	320	720	12	200	58	39	115	83	63	117	25	78	4	106	<6
K2		310	730	6	215	33	21	118	130	75	143	21	53	3	109	"
K3		323	720	9	220	29	46	111	114	74	136	16	63	11	115	"
MEA		250	640	10	295	31	75	103	140	135	137	20	15	5	16	"
Y1	ONSHORE (SOUTHERN) DEPOSIT	95	1290	62	264	24	33	119	116	74	143	24	65	7	45	"
Y2		134	1460	9	410	27	36	109	150	153	234	33	53	9	31	"
BG1		129	1350	5	200	29	49	131	180	128	204	38	26	3	5	"
BG2		229	1150	8	200	25	64	101	270	145	205	42	46	4	5	"
SD		253	530	12	168	20	16	133	83	49	54	25	43	3	105	"

APPENDIX 7 - ANALYSIS OF ACID SOLUBLE FRACTIONS AND ACID INSOLUBLE RESIDUES OF MOROCCAN PHOSPHATES

The analysis of acid soluble fractions and acid insoluble residues was undertaken in an attempt to confirm the trace element associations indicated by other methods, and to differentiate between elements absorbed and adsorbed onto the mineral phases present in the Moroccan phosphorites.

The methods used here were developed in preference to the use of atomic absorption spectrophotometry because of the interferences caused by both calcium and phosphorus in the latter method.

Sample Preparation

5.00 g of each sample were leached with 40 cm^3 of 5% nitric acid for approximately 30 minutes, and then filtered using Whatman 542 filter paper. The residue was washed with distilled water, dried and weighed, and set aside for analysis.

The filtrates were evaporated to small bulk in conical flasks, and then transferred to vitriosil crucibles and evaporated to dryness. The evaporates were ground to powder in agate pestles and mortar, and stored in desiccators. The standards used in analysing the acid soluble fractions were treated by this method, in order to eliminate any specific adsorption effects of the conical flasks or vitriosil containers.

Analysis of Acid Soluble Fractions

The samples were mixed in a ratio of 1:1 with graphite, hand packed into the electrode cups, pinholed in the centre and heated in a bunsen flame for ten seconds. The samples were then arced on a Hilger-Watts Large Quartz Spectograph at a current of seven amps at two hundred and forty volts for sixty seconds. A three step spectrum was recorded for each sample on photographic plate. In addition, a seven step spectrum of sample U. S. G. S. 22, containing added iron was exposed on each plate to provide a spectrum for plate calibration. The sample was also used as a check on precision. The majority of the samples burned very smoothly, those that did not being repeated until they did. Line densities were measured from the photographic plates, converted to intensities and background corrections applied.

Standards were prepared using specpure calcium phosphate base together with the requisite weights of analar compounds. Two series of standards were prepared to reduce errors in preparation caused by too great an element/base ratio.

Analysis of Acid Insoluble Residues

Acid insoluble residues were analysed by x-ray fluorescence spectrometry according to the procedure described for whole rock samples in appendix 6. Previously analysed phosphorite samples of high iron content were used as standards.

Precision of Analysis

No internal standards were used in the optical spectrography. Preliminary investigations during development of the method indicated that no significant increase in precision was obtained with Pd, Ge, or In internal standards. A comparison of precision on line intensities with and without internal standards is presented in table A. 7. 1. These results were obtained by replicate exposures of one sample on a single plate. The overall precision of the analysis was somewhat poorer, though acceptable, and is presented in table A. 7. 2 together with the analysis lines used, and their observed sensativity.

The precisionsof the x-ray fluorescence analysis of the acid insoluble residues was found to be good, though a little poorer than that obtained for the whole rock samples. The precision for each element are presented in the table A. 7. 2.

TABLE A. 7. 1

Precision of optical emission spectrography
with and without internal standards

Element	% - Precision with and without Internal Standards					
	No Internal Standard	Pd	Ge 3039Å	Ge 3269Å	In 3039Å	In 3256Å
Al	5	4	20	21	15	9
Cr	9	10	7	24	7	8
Cu	13	15	7	28	8	10
Fe	10	10	8	26	9	9
Si	37	32	36	47	35	33
V	12	9	12	27	17	15
Pb	27	27	23	29	21	21

TABLE A.7.2

Sensitivity, precision and working lines for emission spectrography of acid soluble fractions

Precision of x-ray fluorescence analysis of acid insoluble residues

Element	Emission Spectrography			X-Ray Fluorescence
	Sensitivity (ppm)	Analysis Line (Å)	Precision (%)	Precision (ppm)
Al	20	3082.1	22	800
Ba	30	3071.6	-	5
Cr	8	4274.0	12	4
Cu	3	3247.5	11	2
Fe	100	2966.9	14	600
Mn	30, 10	4034.0, 4055.5	15	5
Ni	8	3446.0	-	3
Pb	2	2833.0	10	
Si	200	2881.0	44	4000
V	15	3282.0	16	3
Zn	5	3183.4	-	3
Ti	-			20
I	-			15
Y	-			13
As				6

Precision of Emission Spectrography is expressed as ± x% of element level observed.

Precision of X-Ray Fluorescence is expressed as ppm of element.

APPENDIX 8 - DETERMINATION OF ACID SOLUBLE Na AND K

Acid soluble Na and K were determined by flame photometery using an E.E.L. Flame Photometer.

100 m.g. of sample were leached in a Whatman 542 filter paper by 40 cm^3 of 10% HNO_3. The filtrates were made up to 50.0 cm^3 in standard flasks. This solution was sprayed directly for K determinations, and at 10 times dilution for the Na determinations. Distilled water standards were used for both Na and K, as development work showed that neither the acid nor the calcium phosphate produced any significant interference. Every tenth sample was followed by a blank determination. The precision calculated using 12 replicate determinations of sample F127 was better than ± 7% of determined value for Na, and ± 15% of determined value for K, and was mostly ascribable to batch variations.

A comparison of the values obtained by the writer, and those from Gulbrandsen (1966) for three Phosphoria Formation samples is presented in table A.8.1. Agreement is excellent for two samples (U.S.G.S. 22 and 41). A replicate determination of U.S.G.S. 47 indicates an error in the value quoted by Gulbrandsen (1966).

TABLE A. 8. 1

A comparison of Na analysis
with literature values

TABLE A. 8. 1.

Sample No.	This work	Gulbrandsen (1966)
U.S.G.S. 22	5950	5930
U.S.G.S. 41	2920	2970
U.S.G.S. 47	2490 2510	4160

all values expressed as ppm of element.

APPENDIX 9 - MASS SPECTROGRAPHY

Solid source spark mass spectrography was used principally for the analysis of R. E. E. in the Moroccan phosphorites. However, a large number of other elements were also analysed during this investigation of the R. E. E.'s, in order to examine more fully the applicability of the technique to the analysis of phosphorites in general.

Five samples were analysed using an M. S. 7 Mass Spectrometer at Manchester University under the guidance of Dr. G. D. N. Nicholls. The usual sample preparation method, by fusion of the sample with a base containing internal standard (Nicholls et al., 1967) was not employed, owing to the immiscibility of phosphates with the base usually employed. Instead, a dry mixing method was adopted for the introduction of the internal standard, and is described in detail below. Although it has a lower precision (~30%) than the fusion method normally employed, this was considered sufficiently good for the purposes of this thesis.

Sample Preparation

All samples were reduced to a particle size of less than 10 microns by grinding under alcohol in a McCrone Mill for 20 minutes. The samples were then dried at 60° C and broken up with a pestle and mortar. Two samples of Ringsdorff spectrographic graphite were similarly treated to check contamination, which was found to be negligible. The samples were then mixed in a 1:1 ratio with Ringsdorff spectrographic graphite containing a known quantity of Re internal standard (approx 20 ppm Atomic). The mixing was done under alcohol in a plastic phial for 20 minutes. After drying the mixture was pressed into electrodes with a steel die, at a pressure of 15 tons/per sq. inch. These electrodes were then inserted into the machine and analysed.

Calculation of Results

The ionic spectra of each sample were recorded on Ilford Q2 spectrographic plates. Each plate was exposed in fifteen different positions, each exposure being a logarithmic increase of the previous one. The exposures, measured in nano-coulombs, varied from 1 to 1000, the former requiring only about 2 seconds, the latter many hours. The line densities recorded on the plate were measured by microdensitometer. The density of each measured line was compared to the density of the internal standard line, the ratio of the two lines being used to calculate the ppm of the elements by substitution in the formula:-

$$C_E = \frac{C_S \times E_S \times I_S}{E_E \times I_E \times R}$$

where

C_E = Element concentration in the electrode analysed (ppm atomic)

C_S = Concentration of internal standard element (ppm atomic)

E_E = Exposure in nano-coulombs required to give a line of chosen density for a chosen isotope of the element

E_S = Exposure in nano-coulombs required to give a line of the same chosen density for a chosen isotope of the standard element

I_E = Isotopic abundance of chosen isotope of element

I_S = Isotopic abundance of chosen isotope of standard

R = A correction factor introduced as a measure of total recording sensitivity of the element line when compared to the sensitivity of the standard line

The ratio E_S/E_E is determined graphically to reduce errors. The exposures of the element and the standard are plotted along the log axis of log-linear paper against line density plotted on the linear axis, and the ratio E_S/E_E determined from the separation of the lines at an arbitrary density of 0.80 (Nicholls, et al. 1967). Isotope lines used in the analysis were carefully chosen to be free of interference, and each sample was run in duplicate. The precision of duplicates was within 30% for the rare earth elements, and for most other elements the precision was similar.

As a further check on accuracy several elements were determined from the same plate using different isotope lines. The results (table A. 9. 1) were poor for Ge, possibly due to interference on the 70 Ge line, but were acceptable for the remaining elements. The values obtained by mass spectrography were also compared to values obtained by x-ray fluorescence spectrometry and neutron activation analysis (table A. 9. 2). A number of discrepancies between the methods is apparent, and in view of the increasing use of mass spectrography for the analysis of geological materials, further investigation of its applicability in this regard is therefore considered to be worthwhile.

CRITIQUE OF MASS SPECTROGRAPHY

It must be emphasised that these samples were analysed by a method differing from that recommended by Nicholls, et al., (1967), and this probably accounts for a considerable portion of the error involved in the method. However, other errors are thought to be common to both the method employed here, and to the fusion method.

A source of error in the analytical method adopted by the writer is the preparation of the Re bearing graphite base by dry mixing of a Re compound and graphite, followed by dry mixing of this base with sample. In neither case can complete homogenisation be accomplished. In order to overcome these errors the Re base was prepared by evaporation of a standard Re solution onto a known quantity of graphite, followed by thorough mixing and then slow evaporation at room temperature. This base was also wet mixed, under alcohol, with the samples to be analysed and dried slowly at room temperature before being pressed into electrodes. Unfortunately these precautions do not seem to have seriously reduced the analytical error as reported by Nicholls, et al. (1967). The occurrence of two separate phases, one containing an internal standard for elements contained in the other may well be the main reason for this. For good accuracy and reproducibility the Re base must be incorporated into the actual phase being analysed. This can only be done using a fusion technique. Phosphates form a low viscosity melt with $Li_2B_40_7$, and future analysis of phosphates should entail the preparation of a Re containing base of $Li_2B_40_7$, and fusion of the base and sample.

A possible source of inaccuracy but not imprecision is the employment of specpure $KRe0_4$ in the preparation of the base. The stoichiometry of specpure materials is not guaranteed.

The measurement and use of line densities may be subject to error. Long exposures inevitably produce much broader lines than short exposures, because of the instrumental fluctuations during the several hours required for long exposures. This means that the density of the long exposures are less than they should be. Consequently the slope of the line drawn on the plots of exposure against density are in error and less steep than they should be, both for standard lines and element lines. Since the lines are plotted on logarithmic paper this results in an incorrect ratio for the line densities and hence exposures (E_S/E_E).

Fluctuations in the strength of the ion beam may result in errors in the exposure measurements. Automatic sample adjusters which produce a steadier beam can considerably improve the standard graphs produced. This suggests fluctuating ion beams are not accurately measured by the meter in use on the MS 7. The fact that line densities produced by long exposures can fluctuate between wide limits supports this contention.

Some uncertainty may be involved in the values assigned to the correction factors (R-values) used in the calculations. Glasby (1970) found that the original R-values were in error by a factor of approximately 3, and the possibility exists that some are still incorrect; for example, the R value of Ti may be incorrect, as Summerhayes (1970) found that Ti determined by mass spectrography was considerably in excess of spectrographic values, and the writer finds the same for mass spectrographic and x-ray fluorescence determinations of Ti. Furthermore, were all R values correct some periodicity would be expected in their values, since they are governed by only the mass and charge of the ions, if selective volatilisation and matrix effects are absent. However, even the rare earths show deviations from such expected periodic behaviour. Further doubt on their validity is cast by their having been determined empirically on mixtures of specpure chemicals, the stoichiometry of which is not guaranteed.

Further analysis of geological material could undoubtedly be improved by 1) the use of analar compounds of Re for internal standards, and re-determination of R values, 2) employing a fusion technique for sample preparation; for phosphates a suitable fusion would be $Li_2B_40_7$, 3) introduction of the Re standard to the base by use of Re solutions subsequently evaporated, to ensure an even distribution of Re in the base, 4) the use of photocell detectors in place of photographic plates, to minimise errors in exposure measurements, 5) the use of automatic sample adjusters to ensure a steady ion beam, though this may be unnecessary if 4) is implemented.

TABLE A. 9. 1

Duplicate element determinations

by matched pairs of isotope lines

SAMPLE NO.	^{52}Cr	^{53}Cr	^{58}Ni	^{60}Ni	^{69}Ga	^{71}Ga	^{70}Ge	^{74}Ge	^{86}Sr	^{88}Sr	^{137}Ba	^{138}Ba
156(1)	28	26							172	206	3.2	3.6
1004	40	140			2.2	3.0	4.0	1.7				
959			8	8					285	320	3.5	2.0
JORDAN	98	60			0.8	2.0	3.0	0.6	154	120	6	6

(All values in ppm)

TABLE A. 9. 2

A comparison of element concentrations obtained by x-ray fluorescence spectrometry, mass spectrography, and neutron activation analysis.

	SAMPLE 1004			SAMPLE 156(1)			SAMPLE 959			SAMPLE JORDAN			SAMPLE K3		
	X.R.F.	M.S.	N.A.A.‡	X.R.F	M.S.	N.A.A.‡	X.R.F	M.S.	N.A.A.‡	X.R.F.	M.S.	N.A.A.‡	X.R.F	M.S.	N.A.A.‡
Y	99	72		21	2.4		27	20		11	16		323	112	
Sr	2120	680		800	186		1130	300		1580	134		720	140	
Rb	11	2.2		25	12		9	1		7	2		9	0.6	
Zn	46	40		104	22		23	26		120	42		220	50	
Cu	20	28		16	14		11	34		62	44		29	38	
Ni	22	3		94	4.4		15	8		15	3		46	4	
U	60	42	47	241	54		370	180		91	8		111	50	80
Ti	102	1044		385	1440		143	1160		90	1580		114	3000	
V	23	10		240	4.2		63	54		56	18		74	56	
Cr	33	142		60	27		43	86		71	80		136	138	
Ba	16	6		32	3.4		< 4	2.8		30	6		63	12	
Pb	6	< 1		49	2		9	3		5	0.4		11	1	
I	< 5	480		308	760		83	820		58	260		115	1360	
As	9	28		151	38		10	22		< 6	32		< 6	7	
Sc		6.6	3.1								3.4	2.4			
Ce	59	12	39				59	3.2		48	2.4	47	65	8	58
Sm		9	3.5								0.7	1.6		3.4	7.4
Eu		2.2	2.1								0.24	1.1		1.6	3.7
Lu		0.36	3								0.2	4		3.2	9.0

X.R.F. - X-ray fluorescence spectrometry
M.S. - Mass spectrography

N.A.A. Neutron activation analysis (All values in ppm)

‡ (Performed by A. Aspinell, Dept Nuclear Physics Bradford University)

BIBLIOGRAPHY

ALEXIEV, E., ARNANDOV, B., 1965: Rare Earths, Uranium and Thorium in Certain Bulgarian Phosphorites. Trudy Vurkhu Geolog. Na Bulgariia 5, p.69 (in Bulgarian).

ALLEN, V.T., 1937: A study of Missouri Glauconite. Am. Miner. 22, p.1180.

ALTSCHULER, Z.S., 1965: Precipitation and Recycling of Phosphate in the Florida Land-Pebble Phosphate Deposits. U.S. Geol. Surv. Prof. Paper 525-B, p.91.

ALTSCHULER, Z.S., CLARKE, R.S., YOUNG, E.J., 1958: Geochemistry of Uranium in Apatite and Phosphorite. U.S. Geol. Surv. Prof. Paper 314-D, p.45.

ALTSCHULER, Z.S., BERMAN, S., CUTTITA, F., 1967: Rare Earths in Phosphorites - Geochemistry and Potential Recovery. U.S. Geol. Surv. Prof. Paper 575-B, p.1.

AMES, L.L., 1959: The Genesis of Carbonate Apatites. Econ. Geol. 54, p.829.

AMES, L.L., 1960: Some Cation Substitutions during the Formation of Phosphorites from Calcite. Econ. Geol. 55, p.354.

AMES, L.L., 1961: Anion Metosomatic Replacement Reactions. Econ. Geol. 56, p.521.

ANDERMANN, G., KEMP, J.W., 1958: Scattered X-Rays as Internal Standards in X-Ray Emission Spectroscopy. Anal. Chem. 30, p.1306.

ARRHENIUS, G.O., 1963: Pelagic Sediments. In: M.N. Hill (Ed.), The Sea, Interscience, New York, p.655.

ARRHENIUS, G.O., BRAMLETTE, M.N., PICCIOTTO, E., 1957: Localisation of Radioactive and Stable Heavy Nuclides in Ocean Sediments. Nature (London) 180, p.85.

ARRHENIUS, G.O., BONATTI, E., 1965: Neptunism and Volcanism in the Oceans. Progress in Oceanography 3, p.7.

BATEMAN, A.M., 1950: Economic Mineral Deposits. J. Wiley & Sons, New York, 912 pp.

BATURIN, G.N., 1970: Authigenic Phosphate Concretions in Recent Sediments of the S.W. African Shelf. Doklody 189, p.227.

BATURIN, G.N., 1971: Formation of Marine Phosphorite on the Ocean Floor. Nature (Phys. Sci.) 232, p.61.

BATURIN, G.N., KOCHENOV, A.V., SHIMKUS, K.M., 1967: Uranium and Rare Metals in Sediments of the Black and Mediterranean Seas. Geochem. Int. 4, p.29.

BATURIN, G.N., KOCHENOV, A.V., SENIN, Yu M., 1971: Uranium Concentration in Recent Ocean Sediments in Zones of Rising Currents. Geochem. Int. 8, p.

BATURIN, G.N., MERKULOVA, K.I., CHALOV, P.I., 1972: Radiometric Evidence for Recent Formation of Phosphatic Nodules in Marine Shelf Sediments. Mar. Geol. 13, M 37.

BECK, M.T., 1970: Chemistry of Complex Equilibria. Van Nostrand Reinhold Company, London, 285 pp.

BENTNOR, Y.K., KASTNER, M., 1965: Notes on the Mineralogy and Origin of Glauconites. J. Sed. Pet. 35, p. 155.

BLISKOVSKIY, V.Z., EFIMOVA, V.A., ROMANOVA, L.V., 1967: The Strontium Content of Phosphorites. Geochem. Int. 4, p. 1186.

BLISKOVSKIY, V.Z., ROMANOVA, L.V., SMIRNOVA, A.I., YEDAKOVA, L.M., 1968: Arsenic in Phosphorites. Geochem. Int. 5, p. 592.

BROOKS, R.R., PRESLEY, B.J., KAPLAN, I.R., 1968: Trace Elements in the Interstitial Waters of Marine Sediments. Geochem. et Cosmochim. Acta, 32, p. 397.

BROWN, G., (Ed.), 1961: The X-Ray Identification and Crystal Structure of Clay Minerals. Mineralogical Soc. (Clay Minerals Group), London, 1961, 544 pp.

BURST, J.F., 1958a: Mineral Heterogeneity in Glauconite Pellets. Am. Miner. 43, p. 481.

BURST, J.F., 1958b: Glauconite Pellets; their mineral nature and applications to stratographic interpretations. Am. Ass. Petrol. Geol. Bull. 42, p. 310.

BURTON, J.D., 1966: Some Problems concerning the Marine Geochemistry of Vanadium. Nature 212, p. 976.

BUSHINSKIY, G.I., 1964: On Shallow Water Origin of Phosphorite Sediments; in Developments in Sedimentology 1, p. 62. Van Straaten, L.M.J.U. (Ed.), Elsevier, Amsterdam.

CATHCART, J.B., 1968a: Phosphate in the Atlantic and Gulf Coastal Plains. Proc. 4th Forum Geol. Ind. Miner, Austin, Texas, Mar 14-15, Univ. Texas Bur. Econ. Geol. p. 23.

CATHCART, J.B., 1968b: Texture and Composition of Outcropping Phosphorite in the Turayf Region, Northern Saudi Arabia. U.S. Geol. Surv. Prof. Paper 600-C, p. 4.

CAYEUX, L., 1941: Etudes des Gites Mineraux de la France; Les Phosphats de Chaux Sedimentaires de France (metropolitaine et d'outremer), 2, Serv. Carte Geol. de France (Paris).

CHAVE, K.E., 1952: A Solid Solution between Calcite and Dolomite. J. Geol. 60, p. 190.

CHAVE, K.E., MACKENZIE, F.T., 1961: A Statistical Technique Applied to the Geochemistry of Pelagic Muds. J. Geol. 69, p.572.

CHAYES, F., 1960: On Correlation between Variables of Constant Sum. J. Geophys. Res. 65, p.4185.

CHAYES, F., 1962: Numerical Correlation and Petrographic Variation. J. Geol. 70, p.440.

CHESTER, R., 1965: Differentiation of Reef and Non-Reef Carbonates. Bull. Am. Soc. Pet. Geol. 49, p.258.

CHUECAS, L., RILEY, J.P., 1966: The Spectrophotometric Determination of Chromium in Sea Water. Anal. Chim. Acta, 35, p.240.

CLARKE, R.S., ALTSCHULER, Z.S., 1958: Determination of the Oxidation State of Uranium in Apatite and Phosphorite Deposits. Geochim. et Cosmochim. Acta, 13, p.127.

COOK, P.J., 1972: Petrography and Geochemistry of Phosphate Deposits of N.W. Queensland. Econ. Geol. 67, p.1193.

CORCORAN, E.F., ALEXANDER, J.E., 1964: The Determination and Distribution of Copper in Sea Water. Bull. Mar. Sci. Gulf Caribbean 14, p.594.

CRUFT, E.F., INGAMELLS, C.O., MUYSSON, J., 1965: Chemical Analysis and the Stoichiometry of Apatite. Geochim et Cosmochim. Acta, 29, p.581.

D'ANGLEJAN, B.F., 1967: Origin of Marine Phosphorites off Baja California, Mexico. Mar. Geol. 5, p.15.

D'ANGLEJAN, B.F., 1968: Phosphate Diagenesis of Carbonate Sediments as a Mode of in situ Formation of Marine Phosphorites: Observations in a Core from the East Pacific. Can. Jour. Earth Sci. 5, p.81.

DEER, W.A., HOWIE, R.A., ZUSSMAN, J., 1962: Rock Forming Minerals, Vol. 5, Non-Silicates. Longmans, London, pp. 323-335.

DEGENS, E.T., 1965: Geochemistry of Sediments. A Brief Survey. 342 pp. Prentice-Hall, Inc. Englewood Cliffs, New Jersey.

DIETZ, R.S., EMERY, K.O., SHEPARD, F.P., 1942: Phosphorite Deposits on the Sea-floor off Southern California. Bull. Geol. Soc. Amer. 53, p.815.

DUVAL, J.E., KURBATOV, M.H., 1952: Adsorption of Cobalt and Barium Ions by Hydrous Ferric Oxide at Equilibrium. J. Phys. Chem. 56, p.982.

EHRLICH, A.M., 1968: Rare Earth Abundances in Manganese Nodules. Unpublished Ph.D. thesis, Massachusetts Institute of Technology, 225 pp.

ELDERFIELD, H., 1970: Chromium Speciation in Sea Water. Earth and Plan. Sci. Letters 9, p.10.

EMERY, K.O., 1960: The Sea off Southern California. J. Wiley & Sons, New York, 366 pp.

EMIGH, D.G., 1967: Petrology and Origin of Phosphorites. Intermountain Assoc. Petrol. Geol. Annu. Field Conf., Guidebook 15, p. 99.

FLANAGAN, F.J., 1969: U.S.G.S. Standards. II - First Compilation of data for the New U.S.G.S. Rocks. Geochim. et Cosmochim. Acta, 33, p. 81.

FLANAGAN, F.J., 1970: Sources of Geochemical Standards II. Geochim. et Cosmochim. Acta, 34, p. 121.

FLEISCHER, M., 1955: Minor Elements in some Sulphide Minerals. Econ. Geol. 50, p. 970.

FLEISCHER, M., 1969: U.S.G.S. Standards. I - Additional data on Rocks G-I and W-I (1965-1967). Geochim. et Cosmochim. Acta, 33, p. 65.

FLEISCHER, M., ALTSCHULER, Z.S., 1969: The Relationship of the Rare Earth Composition of Minerals to Geologic Environment. Geochim. et Cosmochim. Acta, 33, p. 725.

FUKAI, R., 1967: Valency State of Chromium in Sea Water. Nature 213, p. 901.

FUKAI, R., VAS, D., 1967: A Differential Method of Analysis for Trivalent and Hexavalent Chromium in Sea Water. J. Oceanogr. Soc. Japan, 23, p. 298.

FUKAI, R., HUYNH-NGOC, L., 1968: Studies on the Chemical Behaviour of the Radionuclides in Sea Water, I. General considerations and study of the precipitation of trace amounts of Cr, Mn, Fe, Co, Zn, Ce. I.A.E.A. radioactivity of the sea, no. 22.

GAD, M.A., CATT, J.A., LE RICHE, H.H., 1969: Geochemistry of the Whitbian (Upper Lias) Sediments of the Yorkshire Coast. Proc. Yorkshire Geol. Soc. 37, p. 105.

GEVORK'YAN, V.KH., CHUGUNNYY, YU,G., 1964: A New Find of Accumulations of Phosphate Concretions in the Indian Ocean. Doklady, 187, p. 230.

GILLSON, J.L., (ed.), 1960: Industrial Minerals and Rocks. Am. Inst. of Mining Metalurgical and Petrol. Engineers.

GLASBY, G.P., 1970: The Geochemistry of Manganese Nodules and Associated Pelagic Sediments from the Indian Ocean. Unpubl. Ph.D. Thesis, Imperial College, London, 673 pp.

GOLDBERG, E.D., 1965: Minor Elements in Sea Water. In Chemical Oceanography, vol. 1, Riley, J.P., Skirrow, G, (ed.), London, Academic Press, 163 pp.

GOLDBERG, E.D., ARRHENIUS, G.O., 1958: Chemistry of Pacific Pelagic Sediments. Geochim et Cosmochim. Acta, 13, p. 153.

GOLDBERG, E.D., KOIDE, M., SCHMITT, R.A., SMITH, H.V., 1963: Rare Earth Distribution in the Marine Environment. Jour. Geophys. Res. 68, p.4209.

GOLDSCHMITT, V.M., 1954: Geochemistry. Clarendon Press, Oxford, 730 pp.

GOLDSMITH, J.R., GRAF, D.L., 1958: Relation between Lattice Constants and Composition of the Ca-Mg Carbonates. Am. Miner. 43, p. 84.

GOLDSMITH, J.R., GRAF, D.L., HEARD, H.C., 1961: Lattice Constants of the Calcium-Magnesium Carbonates. Am. Miner. 46, p.453.

GULBRANDSEN, R.A., 1966: Chemical Composition of Phosphorites of the Phosphoria Formation. Geochim. et Cosmochim. Acta, 30, p. 769.

GULBRANDSEN, R.A., 1969: Physical and Chemical Factors in the Formation of Marine Apatite. Econ. Geol. 64, p. 365.

GULBRANDSEN, R.A., 1970: Relation of CO_2 Content of Apatite of the Phosphoria Formation to Regional Facies. U.S. Geol. Surv. Prof. Paper 700-B, p.9.

GULBRANDSEN, R.A., KRAMER, J.R., BEATTY, L.B., MAYES, R.E., 1966: Carbonate-Bearing Apatite from Faraday Township, Ontario, Canada. Am. Miner. 51, p. 819.

HALE, L.A., 1967: Phosphate Exploration using γ Radiation Logs, Dry Valley, Idaho. Intermountain Assoc. Petrol. Geol. Annu. Field Conf., Guidebook 15, p. 147.

HAMILTON, E.L., 1956: Sunken Islands of the Mid-Pacific Mountains. Geol. Soc. Amer. Memo. 64, 97 pp.

HAUSEN, H., 1929: Die Apatite deren chemische Zusammensetzung und ihr Verhältnis zu den physikalischen und morphologischen Eigenschaften. Acta Acad. Abö, math.-phys., 5, 62 pp.

HAWLEY, J.E., NICHOL, I., 1961: Trace Elements in Pyrite, Pyrrhotite, and Chalcopyrite of Different Ores. Econ. Geol. 56, p.467.

HEM, J.D., 1972: Chemical Factors that Influence the Availability of Fe and Mn in Aqueous Systems. Geol. Soc. Amer. Bull. 83, p.443.

HIRST, D.M., NICHOLLS, G.D., 1958: Techniques in Sedimentary Geochemistry - (1) Separation of Detrital and Non-Detrital Fractions of Limestones. J. Sed. Pet. 28, p.468.

HØGDAHL, O., 1967: Distribution of the Rare Earth Elements in Sea Water. Central Institute for Ind. Res., Oslo, Nato grant 203, Semi Annual Prog. Rept., No.4.

HOWARTH, R.J., 1966: Taxon 2. Numerical Taxonomy Package, Fortran IV. Program (unpublished), Imperial College, Univ. London.

HOWER, J., 1961: Some Factors concerning the Nature and Origin of Glauconite. Am. Min.. 46, p.313.

INGLESRUD, I., CHOCHOLAK, J., STEPHAN, E.F. et al., 1948: Chemical Processes to recover U from Phosphate Rock. U.S. Atomic Energy Comm., B.M.I.-JDS-126, 29 pp.

JOHANSEN, P.G., BUCHANAN, A.S., 1957: An Application of the Microelectrophoresis Method to the Study of the Surface Properties of Insoluble Oxides. Aust. J. Chem. 10, p.398.

JOY, A.S., WATSON, D., COMPTON, R.W.G., 1964: Collector Adsorption and Surface Charge Density. Trans. A.I.M.E. 229, p.5.

KANAMORI, S., 1965: The Geochemistry of Arsenic in Natural Waters, III. The Significance of Ferric Hydroxide Precipitates in the Stratification of Arsenic in Lake Waters. J. Earth Sci. Nagoya Univ. 13, p.46.

KANESHIMA, K., 1962: Geochemistry of the Phosphate Rocks in the Ryukyu Islands. (1) Content and Behaviour of Zn in the Phosphate Rocks. Nippon Kagaku Zasshi 83, p.1007, (Japanese, English Summary).

KAZAKOV, A.V., 1937: U.S.S.R. Sc. Inst. Fertilisers and Insect Fungicides Trans. 142, p.95, (in English).

KEITH, H.L., DEGENS, E.T., 1959: Geochemical Indicators of Marine and Freshwater Sediments. In Researches in Geochemistry, No.1, P.H. Ableson (ed.), p.38.

KOLODNY, Y., KAPLAN, I.R., 1970: Carbon and Oxygen Isotopes in Apatite CO_2 and Coexisting Calcite from Sedimentary Phosphorite. J. Sed. Pet. 40, p.954.

KRAMER, J.R., 1964: Sea Water Saturation with Apatites and Carbonates. Science 146, p.637.

KRAUSKOPF, K.B., 1955: Sedimentary Deposits of Rare Metals. Econ. Geol. 50th Anniversary Vol., p.411.

KRAUSKOPF, K.B., 1956: Factors Controlling the Concentration of Thirteen Rare Metals in Sea Water. Geochim et Cosmochim. Acta, 9, p.1.

KRAYNOV, S.R., 1968: Aspects of the Occurrence and Migration of Niobium, Beryllium and Rare Earths in Natural Alkaline Waters. Geochemistry, p.315.

LEHR, J.R., McCLELLAN, G.H., SMITH, J.P., FRAZIER, A.W., 1967: Characterisation of Apatites in Commercial Phosphate Rocks. Colloque International sur les Phosphates Mineraux Solides, Toulouse, 16-20 Mai, p.29.

MASON, B., 1966: Principles of Geochemistry, 3rd edition, J. Wiley & Sons, New York, 329 pp.

McCONNELL, D., 1937: The Substitution of SiO_4 and SO_4 Groups for PO_4 groups in the Apatite Structure: Ellestadite, The End Member. Am. Miner., 22, p. 977.

McCONNELL, D., 1950: The Petrography of Rock Phosphates. Jour. Geol. 58, p. 16.

McCONNELL, D., 1953: Radioactivity of Phosphatic Sediments. Econ. Geol. 48, p. 147.

McCONNELL, D., 1963: Inorganic Constituents in the Shell of the Living Brachiopod Lingula. Geol. Soc. Amer. Bull. 74, p. 363.

McCONNELL, D., 1965: Precipitation of Phosphates in Sea Water. Econ. Geol. 60, p. 1059.

McCONNELL, D., 1966: Shallow Water Phosphorites. Econ. Geol. 61, p. 967.

McCONNELL, D., 1973: Apatite. Springer-Verlag, Wien, New York, 111 pp.

McKELVEY, V.E., 1966: Successful New Techniques in Prospecting for Phosphate Deposits. Aust. Mining 58, p. 10.

McKELVEY, V.E., CARSWELL, L.D., 1956: Uranium in the Phosphoria Formation. U.S. Geol. Surv. Prof. Paper 300, p. 483.

McRAE, S.G., 1972: Glauconite: a Review. Earth Science Reviews 8:4, p. 397.

MERO, J.L., 1965: The Mineral Resources of the Sea. Elsevier, New York, 312 pp.

MILTON, C., BENNISON, A.P., 1968: Phosphate Nodules from the Wills Point Formation, Hopkins County, Texas. U.S. Geol. Surv. Prof. Paper 600B, p. 11.

MINAMI, E., 1935: Gehalte an seltenen Erden in europaischen und japanischen Tonschiefern: Nachr. Gesell. Wiss. Göttingen, ser. IV, N.F. 1, no. 14, p. 155.

MO, T., SUTTLE, A.D., SACKETT, W.M., 1973: Uranium Concentrations in Marine Sediments. Geochim. et Cosmochim. Acta, 37, p. 35.

MURRAY, J., RENARD, A.F., 1891: Deep Sea Deposits, In: Thompson, C.W., (Ed.), Report on the Scientific Results of the Voyage of H.M.S. Challenger. Eyre and Spottiswood, London, 5, p. 391.

NEIHOF, R.A., LOEB, G.I., 1972: Surface Charge of Particulate Matter in Sea Water. Limnol. and Oceanog. 17, p. 7.

NEIHOF, R.A., LOEB, G.I., 1974: Dissolved Organic Matter in Sea Water and the Electric Charge of Immersed Surfaces. J. Mar. Res. 32, p. 5.

NICHOLLS, G.D., 1967: Trace Elements in Sediments: An Assessment of their Possible Utility as Depth Indicators. Marine Geol. 5, p. 539.

NICHOLLS, G.D., GRAHAM, A.L., WILLIAMS, E., WOOD, M., 1967: Precision and Accuracy in Trace Element Analysis of Geological Materials using Solid Source Spark Mass Spectrography. Anal. Chem. 39, p. 584.

NISHIYAMA, T., MINATO, T., 1971: Minor Elements in some Sulphide Minerals (1) Pyrite and Chalcopyrite from the Shakanai Mine. Min. Geol. (Soc. Min. Geol. Jap.) 21, p. 418.

PARÁK, T., 1973: Rare Earths in the Apatite Iron Ores of Lappland, together with some Data about the Sr, U, and Th Content of these Ores. Econ. Geol. 68, p. 210.

PARKER, R.J., 1971: The Petrography and Major Element Geochemistry of Phosphorite Nodule Deposits on the Agulhas Bank, South Africa. S. Africa Nat. Com. Oceanogr. Res., Bull. 2, p. 1.

PARKER, R.B., TOOTS, H., 1970: Minor Elements in Fossil Bone. Geol. Soc. Amer. Bull. 81, p. 925.

PARKER, R.J., SIESSER, W.G., 1972: Petrology and Origin of some Phosphorites from the South African Continental Margin. J. Sed. Pet. 42, p. 434.

PARKS, G.A., 1965: The Isoelectric Point of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems. Chem. Rev. 65, p. 177.

PARKS, G.A., 1967: Aqueous Surface Chemistry of Oxides and Complex Oxide Minerals. Isoelectric Point, and Zero Point of Charge. In Equilibrium Concepts in Natural Water Systems, R.F. Gould (Ed.), p. 121.

PARKS, G.A., DE BRUYN, P.L., 1962: The Zero Point of Charge of Oxides. J. Phys. Chem. 66, p. 967.

PEAVER, D.R., 1966: The Estuarine Formation of United States Atlantic Coastal Plain Phosphorites. Econ. Geol. 61, p. 251.

PEAVER, D.R., 1967: Shallow Water Phosphorites. Econ. Geol. 62, p. 562.

PHILLIPS, C.S.G., WILLIAMS, R.J.P., 1966: Inorganic Chemistry, Vol. II, Clarendon Press, Oxford, 683 pp.

PIPER, D.Z., 1972: Rare Earth Elements in Manganese Nodules from the Pacific Ocean. In Ferromanganes Deposits on the Ocean Floor, p. 23, D.R. Horn (Ed.) National Science Foundation, Washington, D.C.

PORRENGA, D.H., 1967: Glauconite and Chamosite as Depth Indicators in the Marine Environment. Mar. Geol. 5, p. 495.

PRICE, N.B., CALVERT, S.E., JONES, P.G.W., 1970: The Distribution of Iodine and Bromine in the Sediments of the Southwestern Barents Sea. J. Mar. Res. 28, p. 22.

PYTCOWICZ, R.M., KESTER, D.R., 1967: Relative Calcium Phosphate Saturation in Two Regions of the North Pacific Ocean. Limnol. and Oceanogr. 12, p. 714.

RANKAMA, K., SAHAMA, T., 1950: Geochemistry. University of Chicago Press, 912 pp.

REEVES, M.J., SAADI, T.A.K., 1971: Factors Controlling Deposition of Phosphate Bearing Strata. Econ. Geol. 66, p. 451.

REYNOLDS, R.C., 1963: Matrix Corrections in Trace Element Analysis by X-Ray Fluorescence: an Estimation of the Mass Absorption Coefficient by Compton Scattering. Am. Miner. 48, p. 1133.

RIGGS, S.R., FREAS, D.H., 1965: A.I.M.E. preprint No. 65H84, 17 pp.

RILEY, J.P., SKIRROW, G., 1965: Chemical Oceanography. Academic Press, London, 732 pp.

ROBERSON, C.E., 1966: Solubility Implications of Apatite in Sea Water. U.S. Geol. Surv. Prof. Paper 550-D, p. 178.

RONOV, A.B., BALASHOV, Y.A., MIGDISOV, A.A., 1967: Geochemistry of the Rare Earths in the Sedimentary Cycle. Geochem. Int. 4, p. 1.

ROONEY, T.P., KERR, P.F., 1967: Mineralogical Nature and Origin of Phosphorite, Beaufort County, North Carolina. Bull. Geol. Soc. Am. 78, p. 731.

RUNNELLS, D.D., 1970: Errors in X-Ray Analysis of Carbonates due to Solid Solution Variations in Composition of Component Minerals. J. Sed. Pet. 40, p. 1158.

SALVAN, H.M., 1952: Phosphates. In Geologie des Gites Mineraux Marocains. Int. Geol. Congr., 19th, Algiers, Monogr. Regionales Ser. 3, Maroc No. 1.

SCHOFIELD, A., HASKIN, L., 1964: Rare Earth Distribution Patterns in Eight Terrestial Materials. Geochim. et Cosmochim. Acta, 28, p. 437.

SEMENOV, E.I., KHOLODOV, V.N., BARINSKII, R.L., 1962: Rare Earths in Phosphorites. Geochemistry 5, p. 501.

SEVAST'YANOV, V.F., 1967: Redistribution of As during the Formation of Fe-Mn Concretions in Black Sea Sediments. Dokl. Akad. Nank, S.S.S.R. 166, p. 172.

SHELDON, R.P., 1959: Geochemistry of Uranium in Phosphorites and Black Shales of the Phosphoria Formation. U.S. Geol. Surv. Bull. 1084-D, p.83.

SHIMKIN, D.B., 1953: Minerals - A Key to Soviet Power. Harvard University Press, Cambridge, Massachusetts, 463 pp.

SILLEN, L.G., 1961: The Physical Chemistry of Sea Water. In Oceanography, Sears, M. (Ed.), Internat. Oceanogr. Cong. New York, Am. Acad. Adv. Sci. Pub. 67, p.549.

SILVERMAN, S.R., FUYAT, R.K., WEISER, J.D., 1952: Quantitative Determination of Calcite Associated with Carbonate-Bearing Apatites. Am. Min. 37, p.211.

SIMPSON, D.R., 1966: Effects of Magnesium on the Formation of Apatite. Am. Miner. 51, p.205.

SIMPSON, D.R., 1967: Effect of pH and Solution Concentration on the Composition of Carbonate-Apatite. Am. Miner. 52, p.896.

SIMPSON, D.R., 1968a: Substitutions in Apatite: I. Potassium Bearing Apatite. Am. Miner, 53, p.432.

SIMPSON, D.R., 1968b: Substitutions in Apatite: II. Low Temperature Fluoride-Hydroxyl Apatite. Am. Miner. 53, p.1953.

SLOWEY, J.F., HOOD, D.W., 1966: The Chemistry and Analysis of Trace Elements in Sea Water. Ann. Rept. A.E.C. Contract No - AT(40-1) - 2719, Texas, A. and M. Report 66-2F.

SLOWEY, J.F., JEFFREY, L.M., HOOD, D.W., 1967: Evidence for Organic Complexed Copper in Sea Water. Nature 214, p.377.

SPEED, D.P., 1965: Formation of Vermicular Pellets in New Zealand Glauconites. Am. Miner. 50, p.1097.

STARK, J.G., WALLACE, H.G. (Ed.): Chemistry Data Book. London, John Murrey, 1970, 109 pp.

STOW, S.H., 1969: The Occurrence of As and Colour Causing Components in Florida Phosphate Rock. Econ. Geol. 64, p.667.

STUMM, W., MORGAN, J.J., 1970: Aquatic Chemistry: An Introduction Emphasising Chemical Equilibria in Natural Waters. New York, Wiley-Interscience.

SUMMERHAYES, C.P., 1969: Marine Geology of the New Zealand Subantarctic Sea Floor. N.Z. Oceanogr. Inst. Mem. 50, N.Z. Dep. Sci. Ind. Res. Bull. 190, 91 pp.

SUMMERHAYES, C.P., 1970: Phosphate Deposits on the Northwest African Continental Shelf and Slope. Unpublished Ph.D. Thesis, Imperial College, Univ. London, 282 pp.

SUMMERHAYES, C.P., 1973: Phosphate in Sediments off S.W. Africa. Nature 243, p.509.

SUMMERHAYES, C.P., HAZELHOFF-ROELFZEMA, TOOMS, J.S., SMITH, D.B., 1970: Phosphorite Prospecting using a Submersible Scintillation Counter. Econ. Geol. 65, p. 718.

SWAINE, D.J., 1962: The Trace Element Content of Fertilisers. Commonwealth Agr. Bureau Tech. Comm. No. 52, Farnham Royal, England, 306 pp.

SWANSON, V.E., 1961: Geology and Geochemistry of Uranium in Marine Black Shales. U.S. Geol. Surv. Prof. Paper 356-C, p. 67.

TERMINE, J.D., POSNER, A.S., 1966: Infra red Analysis of Rat Bone: Age Dependency of Amorphous and Crystalline Mineral Fractions. Science 153, p. 1523.

TERMINE, J.D., POSNER, A.S., 1967: Infra red Absorption of Carbonate-Apatite. Science 155, p. 607.

THOMPSON, M.E., 1953: Distribution of Uranium in Rich Phosphate Beds of the Phosphoria Formation. U.S. Geol. Surv. Bull. 988-D, p. 45.

THOMPSON, M.E., 1954: Further Studies on the Distribution of Uranium in Rich Phosphorite Beds of the Phosphoria Formation. U.S. Geol. Surv. Bull. 1009-D, p. 107.

TOOMS, J.S., SUMMERHAYES, C.P., 1968: Phosphatic Rocks from the North-West African Continental Shelf. Nature 218, p. 1241.

TOOMS, J.S., SUMMERHAYES, C.P., CRONAN, D.S., 1969: Geochemistry of Marine Phosphate and Manganese Deposits. Oceanogr. Mar. Biol. Ann. Rev. 7, p. 49.

TRAUTZ, O.R., 1960: Crystallographic Studies of Calcium Carbonate Phosphate. Ann. New York Acad. Sci. 85, p. 145.

VASILEVA, Z.V., 1958: Sulphur Bearing Apatites. Geochemistry 4, p. 464.

VEEH, H.H., BURNETT, W.C., SOUTAR, A., 1973: Contemporary Phosphorites on the Continental Margin of Peru. Science 181, p. 845.

VISE, L., 1953: Les Facies Phosphates, Rev. Inst. Franc. Petr. Ann. Combus. Lique. 7, p. 87.

WEAVER, C.E., WAMPLER, J.M., 1972: The Illite-Phosphate Relationship. Geochim. et Cosmochim. Acta, 36, p. 1.

WEDEPOHL, K.H., (Ed.) 1969: Handbook of Geochemistry. Springer-Verlag, Wien, New York.

WELLS, J.D., 1971: The Association of Gold and Arsenic with Pyrite; Cortez and Carlin Mines, Nevada. Econ. Geol. 66, p. 1270.

WELLS, J.D., MULLENS, T.E., 1973: Gold Bearing Arsenian Pyrite determined by Micro-probe Analysis, Cortez and Carlin Gold Mines, Nevada. Econ. Geol. 68, p. 187.

WHIPPO, R.E., MURROWCHICK, B.L., 1967: The Crystal Chemistry of Some Sedimentary Apatites. Trans. Soc. Min. Eng. 238, p.257.

WHITTAKER, E.J.W., MUNTUS, R., 1970: Ionic Radii for Use in Geochemistry. Geochim. et Cosmochim. Acta, 34, p.945.

WILDEMAN, T.R., HASKIN, L., 1965: Rare Earth Elements in Ocean Sediments. Jour. Geophys. Res. 70, p.2905.

WILLIAMS, P.M., 1969: The Association of Copper with Dissolved Organic Matter in Sea Water. Limnol. and Oceanogr. 14, p.156.

ZIRINO, A., YAMOMOTO, S., 1972: A pH dependent Model for the Chemical Speciation of Cu, Zn, Cd, and Pb, in Sea Water. Limnol. Oceanogr. 17, p.661.

ADDENDUM 1

Analytical methods employed for the determination of total CO_2, Organic C, and Pyritic S.

Carbon dioxide present as carbonate was determined by acid hydrolysis. Organic carbon was determined by difference between total carbon and carbonate carbon. Pyritic sulphur was determined by difference between total sulphur, determined by X-ray fluorescence, and substitutional sulphur.

I. TOTAL CARBON DETERMINATIONS

Total carbon was determined by combustion of a known weight of sample in a stream of oxygen and measurement of the volume of CO_2 produced with a Leco Carbon Analyser. The sample weight was accurately known and generally in the range 0.100 - 0.300 g. Standard samples of mild steel containing 0.928%C were run after every fifth sample in order to maintain a good instrument calibration. Every tenth sample was duplicated. The mean error of the determinations was ± 4% of determined value.

II. CARBONATE DETERMINATIONS

Carbonate was determined as CO_2 by hydrolysis of the samples with dilute nitric acid and measurement of the volume of the resulting gas with a Leco Carbon Analyser. The accurately known sample weight was generally in the range 0.100 - 0.300 g. Twelve duplicate determinations gave a mean error of ± 2.5% of determined CO_2.

III. PYRITIC SULPHUR DETERMINATIONS

The determination of pyritic S rested upon the assumption that any S not present in substitution for P would be present as sulphide phases, and also that in all samples a direct linear relationship exists between their amount of substitutional S and their P content.

Variation diagrams of total S, determined by X-ray fluorescence, and both Na and P_2O_5 (fig. 5.3.) were plotted for all southern pebble samples. These were assumed to contain no sulphide phases as they formed in highly oxidising environments. Lines of best fit were drawn to pass through the data points and the origin. The deviations from the best fit line of the remaining data, when plotted on the same variation diagrams, was taken to represent the S present in sulphide phases. The values of pyritic S obtained from each variation diagram are presented in table ADDENDUM 1. Confirmation of the validity of the method was obtained by comparing the determined pyritic S with the amount of pyrite observable in thin sections of all northern samples. The two methods were in strict agreement when compared on a hierarchical basis of sulphur values.

TABLE ADDENDUM 1 - COLUMN HEADINGS

Column A - Pyritic S determined from Na - S plots

" B - " " " " Na-P_2O_5 plots

" C - P_2O_5 determined volumetrically

" D - P_2O_5 " by X-ray fluorescence

" E - K_2O determined by X-ray fluorescence

" F - Acid Soluble K_2O determined by Flame photometry.

TABLE ADDENDUM 1

SAMPLE	A(%)	B(%)	C(%)	D(%)	E(ppm)	F(ppm)
135	0.30	0.33	18.6	17.5	1700	290
136	0.67	0.64	19.8	20.0	1100	300
139(1)	0.61	0.59	25.2	27.2	1500	360
139(2)	6.50	0.50	24.0	25.0	1500	420
959	0.25	0.26	16.0	17.1	1200	215
966(1)	0.04	0.06	14.6	14.8	1800	565
966(2)	0.80	0.81	29.3	28.0	1200	420
982	0.51	0.49	25.8	27.5	1000	-
988(a)	0.20	0.27	15.9	15.5	1900	410
988(b)	1.05	0.96	20.4	22.2	1000	300
1004	0.50	0.39	26.5	26.2	1400	350
1016(2)	0.88	0.79	21.3	20.5	1300	275
1022(1)	0.49	0.54	20.6	20.1	1100	265
1022(2)	0.12	0.23	13.3	11.8	2100	495
1038(2)	0.97	0.92	21.5	22.0	1300	325
152	0.22	0.28	12.9	12.5	18700	2050
154	0.25	0.37	14.7	14.0	27500	3730
155	0.00	0.02	12.7	13.2	13800	1800
833	1.00	0.71	16.4	16.5	24300	2650
847(1)	0.11	0.00	19.1	17.2	13000	1745
865	0.31	0.33	13.7	14.7	17700	2120
877	0.00	0.00	15.2	15.4	18500	2230
883	0.08	0.21	17.8	18.5	26000	2432
896(1)	0.10	0.00	17.6	18.5	9900	1325
896(2)	0.00	0.00	16.4	17.3	15500	1300
898	0.25	0.26	20.1	21.2	13400	1670
847(1)C	-	0.30	15.7	15.0	22600	2335
896(2)C	0.00	0.00	17.2	18.2	16000	-
898C1	-	0.20	11.9	12.0	15800	1445
" C2	-	0.61	19.1	19.3	23700	1810
" C3	-	0.31	18.8	20.0	24500	1865

TABLE ADDENDUM 1 (continued)

SAMPLE	A	B	C	D	E	F
847(1)p1	0.11	0.00	15.1	16.2	4900	650
" p2	0.11	0.00	21.3	23.7	3500	600
" p3	0.11	0.10	18.7	18.3	3200	600
" p4	-	0.10	21.1	21.4	4500	-
865 p1	-	0.40	4.2	3.3	4200	340
" p2	-	0.00	18.7	19.6	7100	1260
896(1)p1	0.07	"	13.5	13.4	3100	625
" p2	-	"	14.9	15.7	5500	-
" p3	-	"	14.8	14.5	10000	-
896(2)p1	0.03	"	15.0	15.0	2200	540
" p2	-	"	14.8	16.0	1500	-
898 p1	-	"	22.3	22.0	5100	940
" p2	-	"	21.5	19.5	4500	750
" p3	0.10	"	24.5	24.8	9900	770
" p4	0.00	"	24.8	26.5	3800	685
" p5	-	"	20.3	20.6	5800	1035
148	0.21	0.10	19.2	18.8	2500	540
156(1)	0.12	0.00	15.8	17.5	5500	990
156(2)	0.03	"	22.0	24.3	3600	795
157	0.00	"	12.1	12.6	2500	540
847(2)	0.15	"	22.5	23.3	3900	710
893	0.07	"	9.8	10.0	1550	240
K1			33.9	34.0	500	155
K2			32.8	31.2	600	125
K3			32.4	33.0	700	275
MEA			25.9	24.9	900	110
Y1			32.5	33.7	400	90
Y2			30.8	32.0	800	170
BG1			29.9	30.5	800	145
BG2			24.0	23.8	1300	60
SD			37.1	39.8	400	65

ADDENDUM 2

Determination of MgO by Atomic Absorption Spectrophotometry and X-Ray Fluorescence Spectrometry.

The MgO determinations done by X-ray fluorescence were usually low (table A.6.4.) and in the case of the onshore samples approached the detection limit of the method. MgO was therefore independently determined by atomic absorption spectrophotometry in order to check the fluorescence values.

Samples were prepared by leaching 0.200g of sample overnight in 20cm^3 of 10% HNO_3 and spraying the resulting solution on a Perkin-Elmer 404 A.A. Spectrophotometer. Standards were made up in 1 Molar HNO_3. A nitrous oxide-acetylene flame was used and 1% La added to all samples to suppress interferences.

A comparison of the values obtained by the two methods is given in table ADDENDUM 2.

TABLE ADDENDUM 2. A comparison of MgO determined by atomic absorption spectrophotometry and X-ray fluorescence spectrometry.

SAMPLE	A.A.	X.R.F.	SAMPLE	A.A.	X.R.F.
135	0.82	0.85	847(1)p1	2.59	3.30
136	0.70	0.90	" p2	1.85	2.05
959	1.17	1.20	" p3	2.30	2.40
966(1)	1.90	2.20	" p4	1.90	1.95
988(a)	0.40	0.95	865 p1	-	0.80
988(b)	0.60	0.65	" p2	4.40	4.85
1016	0.70	0.95	896(1)p1	3.40	3.55
1022(1)	0.65	0.65	p2	5.50	5.55
1022(2)	1.25	1.55	p3	5.63	5.70
1038	0.70	0.90	896(2)p1	4.40	4.25
			" p2	4.55	4.60
139(1)	0.80	1.10	898 p1	2.00	2.36
139(2)	0.75	0.85	" p2	2.22	2.35
966(2)	0.70	0.90	" p3	1.90	2.45
982	0.80	0.90	" p4	2.05	1.95
1004	0.71	0.70	" p5	1.52	2.30
152	4.13	4.70	148	1.47	1.55
154	-	2.80	156(1)	4.05	4.50
155	3.55	3.60	156(2)	2.25	2.60
833	2.60	2.95	157	6.48	7.65
847(1)	2.22	2.70	847(2)	1.62	1.80
865	3.53	3.90	893	7.63	8.65
877	2.94	3.35			
883	1.80	2.95	K1	-	0.40
896(1)	2.40	2.90	K2	0.38	0.45
896(2)	2.00	2.50	K3	0.29	0.40
898	1.65	2.20	MEA	0.30	0.55
			Y1	-	0.50
847(1)C	1.60	1.65	BG1	1.03	1.15
898C1	1.89	2.45	BG2	2.07	2.15
" C2	1.44	2.30	S.D.	-	0.05
" C3	1.37	1.85			

TABLE ADDENDUM 3

The percentage of soluble and insoluble material in all samples analysed as acid soluble fractions or acid insoluble residues. The following samples were not analysed owing to the small quantity of sample available: 896(2)C, 847(1)p4, 896(1)p2, 896(1)p3, 896(2)p2, 898p1.

SAMPLE	%Insoluble	%Soluble	SAMPLE	%Insoluble	%Soluble
135	14	86	898C1	27	73
136	17	83	" C2	30	70
959	11	89	" C3	25	75
966(1)	8	92			
988(a)	12	88	847(1)p1	34	66
988(b)	13	87	" p2	18	82
1016	11	89	" p3	40	60
1022(1)	15	85	865 p1	45	55
1022(2)	18	82	" p2	23	77
1038	4	96	896(1)p1	37	63
			896(2)p1	24	76
139(1)	9	91	898 p2	15	85
139(2)	10	90	" p3	22	78
966(2)	10	90	" p4	10	90
982	8	92	" p5	19	81
1004	12	88			
			148	7	93
152	33	67	156(1)	32	68
154	32	68	156(2)	22	78
155	31	69	157	27	73
833	34	66	847(2)	21	79
847(1)	32	68	893	21	79
865	37	63	K1	5	95
877	37	63	K2	7	93
883	34	66	K3	8	92
896(1)	26	74	MEA	8	92
896(2)	28	72	Y1	3	97
898	24	76	Y2	5	95
			BG1	8	92
847(1)C	32	68	BG2	15	85
			S.D.	5	95

TABLE ADDENDUM 4 - ANALYTICAL RESULTS OF ANALYSIS OF ACID SOLUBLE FRACTIONS. (all values are ppm)

SAMPLE	Cu	Ni	Zn	Mn	Cr	Pb	V	Fe	Al	Si
135	11	18	53	81	23	2	350	660	820	10
136	18	40	50	<10	14	d	39	330	250	10
959	16	14	18	88	10	12	200	1600	740	2100
966(1)	5	7	15	220	<8	5	45	1350	370	240
988(a)	14	11	49	127	28	2	700	430	740	1500
988(b)	14	32	44	52	28	2	67	1250	590	140
1016	19	33	54	45	27	d	41	780	430	40
1022(1)	25	21	42	<10	47	2	28	760	690	600
1022(2)	12	11	10	85	16	6	115	900	1250	840
1038	16	43	38	111	28	3	150	840	680	1300
139(1)	19	28	55	82	32	d	65	1220	740	380
139(2)	32	20	61	89	24	"	25	880	880	740
966(2)	17	35	74	45	16	"	70	530	290	200
982	-	-	-	-	-	-	-	-	-	-
1004	25	19	33	47	27	2	70	650	680	100
152	8	25	29	160	d	5	68	1900	1250	920
154	16	21	48	175	13	10	60	2300	2000	1600
155	9	120	65	>200	d	26	110	1100	2000	3700
833	17	18	39	40	8	24	190	2100	1400	1700
847(1)	12	29	21	165	11	5	85	1800	1700	1030
865	8	15	42	>200	17	20	74	1900	3400	900
877	10	24	40	120	31	14	97	340	530	330
883	8	15	37	140	<8	8	68	1200	870	130
896(1)	12	9	62	180	<8	13	66	1400	1000	520
896(2)	8	28	49	190	<8	33	123	2000	2500	880
898	10	38	50	52	d	16	175	1700	1300	940
847(1)C	12	41	-	20	11	3	97	1800	200	1250

TABLE ADDENDUM 4 (continued)

SAMPLE	Cu	Ni	Zn	Mn	Cr	Pb	V	Fe	Al	Si
898C1	21	75	-	>200	<8	36	80	1900	1800	2100
" C2	23	26	-	68	11	30	120	1600	1250	180
" C3	16	27	-	77	17	20	112	1800	2000	920
847(1)pl	18	55	63	>200	d	2	144	1100	600	330
" p2	19	67	59	170	<8	3	23	420	340	200
" p3	17	47	74	155	d	2	65	600	550	660
865pl	5	13	25	140	14	3	42	1000	590	980
" p2	14	10	36	100	d	4	43	1300	870	690
896(1)pl	13	27	74	>200	d	16	115	15	920	60
896(2)pl	10	8	30	>200	10	4	185	1200	780	1100
898p2	3	28	76	33	12	15	220	-	1600	1800
" p3	4	27	44	47	<8	3	68	500	900	620
" p4	5	45	42	60	d	3	142	1800	2200	2000
" p5	3	63	58	54	d	3	136	800	920	660
148	12	27	38	82	10	6	120	940	840	230
156(1)	8	112	90	200	20	21	69	1600	860	85
156(2)	10	40	27	>200	<8	3	205	1350	900	1130
157	14	41	68	>200	<8	3	111	1600	860	2100
847(2)	17	38	57	153	13	3	67	1800	890	1150
893	13	34	39	>200	d	3	38	1650	350	260
K1	42	27	185	32	31	<2	78	20	260	850
K2	38	22	190	18	33	3	120	120	470	15
K3	30	38	205	10	26	d	126	30	300	35
MEA	27	54	154	15	25	d	115	130	530	10
Y1	14	27	285	18	25	d	142	40	260	760
Y2	31	61	315	25	31	6	200	40	500	80
BG1	26	35	225	33	54	3	186	170	630	20
BG2	20	28	310	24	58	3	194	230	860	300
S.D.	14	12	200	20	45	d	97	110	580	1300

TABLE ADDENDUM 5

Element concentrations in acid insoluble fractions of Moroccan phosphorites.

All data in ppm.

SAMPLE	Y	Zn	Cu	Ni	Ti	V	Cr	Mn	Ba	I	As
898	24	83	23	75	1400	240	250	170	840	58	200
152	14	39	12	28	1750	66	185	152	170	18	10
833	24	41	14	15	2100	110	210	35	260	16	190
865	11	41	8	16	1650	73	168	127	280	24	150
898p4	10	100	43	78	2500	260	185	160	18	85	240
847(1)p1	6	51	25	78	760	290	56	187	140	35	330
" p2	3	140	36	140	1600	270	63	124	210	-	470
847(2)	2	85	27	55	560	143	75	131	112	15	560
BG1	190	200	53	110	1600	110	380	60	230	34	-
K1	450	670	330	158	1550	123	330	100	1400	106	-
1022(1)	7	54	24	77	450	23	53	34	14	72	24
988(a)	27	123	39	86	760	42	48	131	10	112	72
139(1)	97	48	97	147	1200	3	97	65	20	136	231

ADDENDUM 6

Rare earth element analysis of phosphorites, shales, crustal abundance, and sea water were taken from the following sources:

COLUMN HEADING AND SOURCE	AUTHOR
1 - Bone Valley phosphorite	Altschuler, et al. (1967) (data presented as ratios to La)
2 - Moroccan phosphorite	
3 - Phosphoria Formation	
4 - 1004	Offshore Moroccan samples presented in this work
5 - 959	
6 - 156(1)	
7 - MOROCCAN (K3)	This work
8 - JORDAN	
9 - F127	Summerhayes (1970)
10 - 139(1)	
11 - 148	
12 - Californian Nodule	Goldberg, et al. (1963) (presented as ratios to La)
13 - Eastern Europe, average of 23 samples	Semenov, et al (1962)
14 - Bulgaria, average of 13 samples	Alexiev and Arnadouv (1965)
15 - Crustal Abundance	Mason (1966)
16 - Average Shale, average of 60 shales from Europe and Japan	Minami (1935)
17 - Average Shale, average of 40 American Shales	Wildeman and Haskin (1965)
18 - Seawater	Høgdahl (1967)

TABLE ADDENDUM 6 - RARE EARTH ELEMENT DATA.

	1*	2*	3*	4	5	6	7	8	9	10	11	12*	13	14*	15	16	17	18
La	1.00	1.00	1.00	21	8.0	3.1	34	3.8	41.4	48.5	3.81	1.0	76.5	1.00	30	18.3	39.1	0.0034
Ce	0.81	0.64	0.54	12	3.2	2.7	8	2.4	22.4	25.9	3.48	1.83	175	1.43	60	47	76.4	0.0012
Pr	0.21	0.21	0.12	5.8	-	1.1	8.6	0.76	6.32	12.3	0.71	0.26	37.4	0.22	8.2	57	10.4	0.00064
Nd	0.47	1.39	0.69	31	-	4.7	22	1.8	18.9	35.6	2.52	1.02	141	0.82	28	23.5	37.2	0.0028
Sm	0.18	0.24	0.10	9.0	-	-	3.4	0.7	-	-	-	0.20	29.4	0.20	6.0	6.4	6.99	0.00045
Eu	0.03	0.04	0.03	2.2	-	-	1.6	0.24	2.56	2.45	-	0.050	4.15	0.01	1.2	1.05	1.96	0.000130
Gd	0.10	0.27	0.14	7.4	-	-	8.4	0.78	39.3	20.0	3.24	0.27	33.0	0.12	5.4	6.3	6.08	0.00070
Tb	0.03	0.04	0.03	-	-	-	1.4	0.22	1.31	2.48	-	0.038	4.86	0.06	0.9	2.55	1.30	0.00014
Dy	0.10	0.23	0.08	8.4	-	-	9.8	0.78	6.20	10.2	-	0.22	21.0	0.15	3.0	4.4	-	0.00091
Ho	0.03	0.07	0.03	1.8	-	-	2.6	0.26	1.18	2.74	-	0.059	4.19	0.06	1.2	1.2	1.40	0.00022
Er	0.14	0.18	0.07	5.5	-	-	7.0	1.0	4.06	8.95	-	0.16	12.6	0.09	2.8	2.45	4.01	0.00087
Tm	0.01	0.08	0.02	0.86	-	-	0.7	0.13	0.53	0.91	-	0.019	1.40	0.06	0.5	0.20	0.58	0.00017
Yb	0.05	0.17	0.07	3.6	-	-	4.4	0.54	2.51	4.43	-	0.12	14.1	0.18	3.4	2.60	3.40	0.00082
Lu	0.02	0.02	0.01	0.36	-	-	3.2	0.20	0.51	0.82	-	0.021	2.11	0.05	0.5	0.64	0.60	0.00015

All in ppm except for 18, which is expressed as ppb.

* Normalised to La.

TABLE ADDENDUM 7

Conditions used for major element analysis by X-ray fluorescence.

ELEMENT	LINE	VACUUM	COLLIMATOR	k.V.	m.A.	CRYSTAL	COUNTER
Ca	$K\alpha1$	✓	F	40	16	PET	FLOW
K	"	✓	F	60	24	PET	"
Fe	"	✓	F	60	24	LiF(220)	"
Si	"	✓	C	60	24	PET	"
Mg	"	✓	C	40	32	ADP	"
P	"	✓	F	60	24	PET	"
Al	"	✓	C	60	24	PET	"

All majors were done using a 2Kw Cr Tube.

ADDENDUM 8

CALCULATION OF MOROCCAN OFFSHORE PHOSPHORUS RESERVES

The calculation of the total phosphorus present in the Moroccan offshore deposits is extremely difficult in the absence of strict stratographical control, and at best will be correct to an order of magnitude only. In calculating the extent of offshore phosphorus the following assumptions are made:

(1) that phosphorite outcrops along the shelf only in those areas from which it was dredged, and outcrops and underlies the shelf to a width of 10km (Summerhayes, 1970). The outcrop length is approximately 60km in the southern province and 40km in the northern province. The area of phosphorite occurrence is therefore approximately 1000km^2;

(2) that the phosphorite is of an average P content equal to the average of all offshore samples analysed here (8.4% P);

(3) that the average density of the phosphorite is 2.8, a typical value observed during their a attempted purification by heavy liquid separation;

(4) that the deposits are of an average thickness of 10m, a thickness in keeping with typical onshore deposits, e.g. the Phosphoria Formation.

The total offshore reserves of P are therefore

$$1000 \times 10^6 \times 10 \times \frac{84}{100} \times 2.8 \text{ tons} = 2.4 \times 10^{10} \text{ metric tons.}$$

ADDENDUM 9 - A COMPARISON OF U BY X-RAY FLUORESCENCE AND γ COUNTING

The offshore Moroccan samples show no correlation between their U and P_2O_5 contents. In order to make certain that this was not due to incorrect analysis for U twelve samples, representing the total range of U values found in the samples, were checked by γcounting. To make sure that no γ radiation was contributed by ^{40}K, a γ ray spectrum was run overnight on sample 896(1). No ^{40}K was detected. Approximately 5g of each of the samples were weighed into separate hard glass bottles and the total radiation count for two separate 1 hour periods were determined for each sample. The mean error of the recorded counts was ± 3%. Within the limits of error all but the two samples lowest in U plotted on a straight line graph of ppm U against counts, confirming the analysis of U by X-ray fluorescence to be good. The results are presented in table ADDENDUM 9.

TABLE ADDENDUM 9

SAMPLE	893	898p5	1016	1022(1)	896(1)	847(2)	136	1038	988(a)	959	135
U by X.R.F.	32	57	103	109	133	169	206	259	328	369	507
γ COUNTS	37	106	169	171	204	266	308	387	489	559	796