A

T H E S I S

entitled

PHOSPHATE DEPOSITS ON THE NORTHWEST AFRICAN CONTINENTAL SHELF AND SLOPE

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ABSTRACT

Phosphatic Limestones and Phosphorites outcrop extensively on the northwest African continental margin. Off Morocco these are Upper Cretaceous, Eocene and Miocene while off the Spanish Sahara they are Lower Pliocene. Cessation of Phosphorite formation after the Pliocene may reflect climatic and attendant sedimentological changes. The Oligocene appears to have been, over the entire region, a period of uplift and erosion which may relate to postulated cessation or slowing of Atlantic seafloor spreading.

Phosphatic surficial sediments, always found in the vicinity of rock outcrops, are concentrated in a shelf edge belt and in patches on the shelf. Phosphate is concentrated in sand sized detrital grains of phosphorite and forms, in effect, placer-type concentrates. There is no relation between sediment phosphate and upwelling of nutrient-rich water. The sands are relict from low Pleistocene sealevel stands and are in part buried by a later silt blanket prominent at mid shelf depths off Morocco but absent from the Sahara. Differing phosphatic facies are defined using multi-element geochemical mapping techniques.

The presence of a widespread Recent authigenic iron-manganese mineral phase among relict sands in regions of low organic productivity is disclosed mainly using geochemical techniques. Glauconite is locally forming within the sediments but much is undoubtedly detrital. Quartz is the only major detrital mineral phase.

The uraniferous character of the phosphatic rocks and sediments permits their detection by submersible scintillation counter.

The economic viability of these deposits is suspect owing to the low grade of both rocks (usually $< 20\%$ P_2O_5) and sediments (usually $< 5\%$ P_2O_5) and their concentration mainly at water depths > 300 ft.

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INTRODUCTION

Submarine phosphorites were initially found as nodules on the Agulhas Bank off the South African coast during the Challenger Expedition of 1873-76 (Murray and Renard, 1891). They have subsequentally been reported from many parts of the globe and are widely regarded as being of considerable potential economic interest particularly in regions adjacent to developing countries where onshore phosphate deposits are rare (Mero, 1965, 1966; McKelvey, 1963, 1967; Tooms, 1967, a and b; U.N. Secretary-General Report, 1968; Overall 1968, a and b). Despite this encouraging interest very few offshore phosphate deposits have been systematically investigated in any detail; the particularly well studied examples are those off the Californian coast (Dietz, Emery and Shepard, 1942, d'Anglejan 1967) and off South Africa (Cayeux, 1932, Parker, 1970).

Phosphorite is a general term used to describe sedimentary deposits of marine origin composed mainly of carbonate-apatite, a calcium phosphate mineral which forms authigenically in shallow water marine environments. Usually phosphorite pellets or nodules are found in water depths less than 1000m on offshore banks, continental shelves and marginal plateaux in regions where sedimentation is very slow or negligible. Continental shelf phosphorites are generally pelletal; deeper deposits are nodular or massive. Geographically they appear to be most concentrated along the western coasts of continents, and lie more or less between the 40th parallels (McKelvey, 1963, 1967; McKelvey and Chase, 1966; Sheldon, 1964), but it must be stressed that the recovery of marine phosphorite and its identification are quite accidental and this distribution may be apparent rather than real (van Andel, 1965). Of particular interest is the association of known sea-floor phosphorites with regions of upwelling nutrient rich currents, especially noteworthy where upwelling phenomena are associated with current

divergence (Kazakov, 1937; Macpherson, 1945; Brongersma-Sanders, 1957; McKelvey, 1963). Owing to the prevailing global hydrospheric and atmospheric circulation patterns, divergent upwelling occurs mainly on the west coasts of landmasses in the middle latitudes where McKelvey (1963) reports the most extensive phosphorite deposits and it was widely thought that these oceanographic phenomena and authigenic phosphate mineral formation were causatively related. Paradoxically, although there is an observed association between the occurrences of sea-floor phosphorites and the phenomena associated with upwelling currents, most of the phosphorites are not in fact geologically young.

As is well known the western coast of north Africa is a region of active divergent upwelling, the intensity of which increases south from Morocco towards the Spanish Sahara, and which is attributed to the influence of the north-east trade winds (cf. Jones and Folkard, 1968, Defant, 1961). Phosphorites were first reported from off the Moroccan coast near Safi by Murray and Chumley (1924) and anticipated on an extensive scale by McKelvey (1963, 1967; McKelvey and Chase, 1966). However, nothing was known of the nature, distribution, age or origin of these deposits, nor, for that matter, if they were authigenic deposits more or less in situ or detrital deposits derived by erosion of the extensive phosphorite deposits known inland in both the Spanish Sahara and Morocco. Bearing in mind the logistics problem involved in investigating any further distant deposit it was decided that the long term potential economic interest justified a detailed investigation of this supposed deposit, and should also contribute knowledge which might aid in the exploration and eventual exploitation of other deposits in economically more favourable locations.

It was also hoped that, were Recent phosphorites to be found in this environment, as might be expected from a situation where divergent upwelling of highly productive water occurred off moderately arid coasts where Recent

detrital sedimentation was expected to be low or negligible, that the poorly understood mechanisms of authigenic phosphate mineral formation might be studied.

The geochemistry of present marine phosphorites has rarely been considered but in view of the potential use of these rocks in the manufacture of fertilisers and elemental phosphorus, and also because of the feasibility of the by-product extraction of vanadium (Krauskopf, 1955), uranium (Barr, 1955), fluorine (McKelvey, 1967) and the rare-earth elements (Ryabtchikov, Senyavin and Skylarenko, 1958) the geochemistry of these samples is of more than academic interest. From the petrogenetic viewpoint the possibility that the major and minor element geochemistry of phosphorites will reflect the milieu from which they formed makes appraisal of the geochemistry of phosphorites essential and accordingly it was decided that a reconnaissance geochemical survey of the phosphorites should also be undertaken.

Because, at commencement of the project in October 1967, very little was known of the marine geology of the northwest African continental margin, this survey could not be confined merely to phosphate distribution but had to first establish the regional geology and structure as well as the nature of the sediment cover. As a result the present work represents a reconnaissance geological and geochemical survey of the submerged part of the northwest African continental margin in which special emphasis is placed on the nature and distribution of phosphatic rocks and sediment. In principal the project objectives are:-

1) to define the regional sedimentation patterns and establish sediment facies distribution using sedimentological and geochemical techniques;

2) to determine the nature and distribution of phosphatic sediment components with particular reference to the possibility that they may presently be forming;

3) to determine the geological structure of the continental margin and define the structural setting of outcropping phosphatic rocks;

4) to determine the age and petrography of different phosphate-rock facies and ascertain their origins;

5) to investigate the geochemistry of phosphatic rocks with a view to establishing the physico-chemical conditions under which they may have been deposited;

6) to assess the economic potential of offshore phosphate deposits and to investigate different prospecting methods with a view to speeding up the presently laborious exploration techniques of classical oceanography.

In order to achieve these broad aims, the writer planned a series of reconnaissance traverses each some 60 miles long oriented at ninety degrees to the coast, and about 100 miles apart along an 800 mile stretch of the northwest African coast between Rabat, Morocco, in the north, and the northern Mauritanian border in the south. Seven traverses were successfully completed from R.R.S. John Murray in January and February 1968 (Fig. 1). Dredge samples were collected from depths between 28 and 1300m in areas where previously obtained continuous seismic reflection profiles indicated probable outcrops of bedrock. In addition, unconsolidated sediment samples were collected at intervals along the traverses across the whole width of the shelf and parts of the upper continental slope. A total of twenty rock and 103 sediment samples were obtained from the seven traverses. As reported by Tooms and Summerhayes (1968) a number of phosphatic limestones and phosphorites were discovered, and were found to be particularly common off south central Morocco between Al Jadida and Agadir where they were associated with apparently placer type phosphatic sediments.

In view of these general findings it was decided that the area likely to

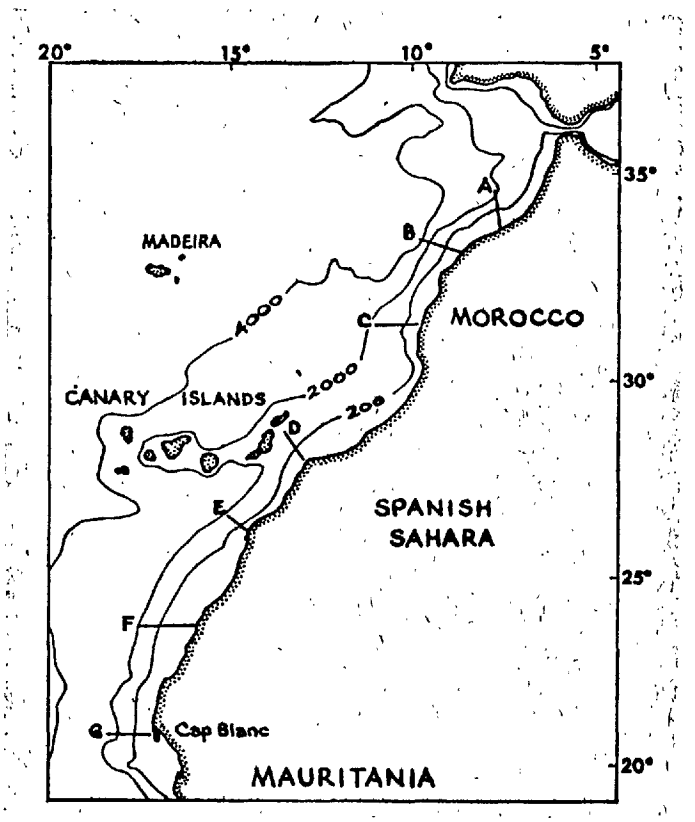


Fig.1.
Location of reconnaissance sampling traverses across the north-west African continental margin : 1968 R.R.S.John Murray cruise.

yield the most phosphatic material for detailed follow up study was the Moroccan coast between Al Jadida (Cap Blanc) and Agadir. Accordingly the writer drew up a second cruise plan designed to allow detailed sampling in the immediate vicinity of those traverses which had yielded numbers of phosphatic samples, and further more closely spaced reconnaissance traverses, at about 20 mile intervals, along the entire Moroccan coast between Agadir and Rabat between which limits the onshore Cretaco-Tertiary phosphatic province is contained.

Nineteen continuous seismic reflection and sampling traverses were successfully completed from R.R.S. John Murray in January and February 1969(Fig.2a). Initially the present project was restricted to a study of Saharan traverses (2b) and the southernmost group (numbers 1 - 8) of Moroccan traverses between Safi and Agadir. The South Moroccan group of samples containing glauconitic sediments and a notably glauconitic facies of phosphorite, differed distinctly from the north Moroccan group studied contemporaneously by Nutter (1969, unpublished D.I.C. thesis, University of London). There are also profound differences between the geological structure of the two regions, the southernmost being within the High Atlas zone, the northern being in the realm of the stable Moroccan Meseta, which made this division of effort desirable. Following completion of the preliminary survey of structure, sediment texture and sedimentary phosphate distribution off north Morocco by Nutter (1969) the present study was expanded to complete the regional petrographic survey of phosphatic rocks and the regional geochemical reconnaissance mapping of superficial sediment along the entire Moroccan coast.

The sampling techniques and equipment used being standard, and previously described in detail (cf. Nutter, 1969, and for a discussion of the free-fall coring technique, Glasby, 1970), they are not described in this work.

Results of these investigations are presented in two main sections. In

section (1) the superficial sediments of the northwest African continental margin are examined. The sedimentation history is deduced and the distribution, character, provenance and dispersal of phosphatic components is discussed. The facies distribution of non-carbonate (principally detrital) sediment components is determined using geochemical techniques and the distribution of different facies is discussed in relation to the genesis of the phosphatic deposits.

In section (2) the geological structure and development of the northwest African continental margin is discussed in relation to the age and distribution of phosphatic rock samples. The petrographic character and geochemistry of these samples is examined to ascertain the environmental conditions under which they may have formed. The genesis of marine carbonate-apatite deposits is reviewed and, finally, a successful investigation into the potential of scintillation counting as a remote sensing prospecting method for subsea phosphate deposits is described and the economic potential of the phosphatic deposits is discussed.

Except in the case of certain indicated routine analytical work carried out mainly by the technical support staff of the Applied Geochemistry Research Group, Imperial College, or by other laboratories, this thesis embodies entirely the result of the writer's own research or observation.

Fig.2a Location of sample sites off Morocco; sample numbers are given at traverse ends, and intervenimg samples(not numbered on the figure) are sequentially numbered along each traverse; exceptions are on traverse 2 where 817 follows 815, and on traverse 13 where 982 is adjacent to 1007.

Bathymetry south of Safi drawn by the writer, and north of Safi drawn by Nutter (1969) from soundings provided by D.Roberts of N.I.O. ; depths in metres; shelf edge defined approximately by 150 m isobath.

Traverses 21,15 and 5 correspond with A,B and C in Fig.1. and were sampled from R.R.S.John Murray in 1968; all other samples were collected from R.R.S.John Murray in 1969.

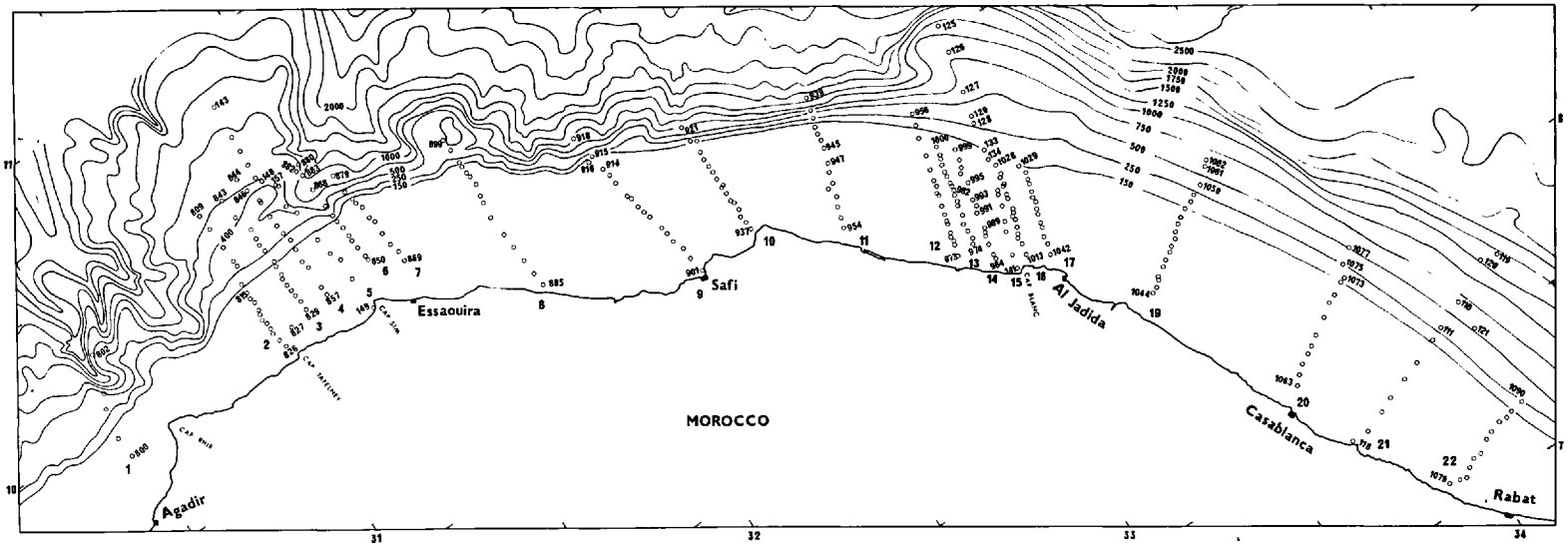
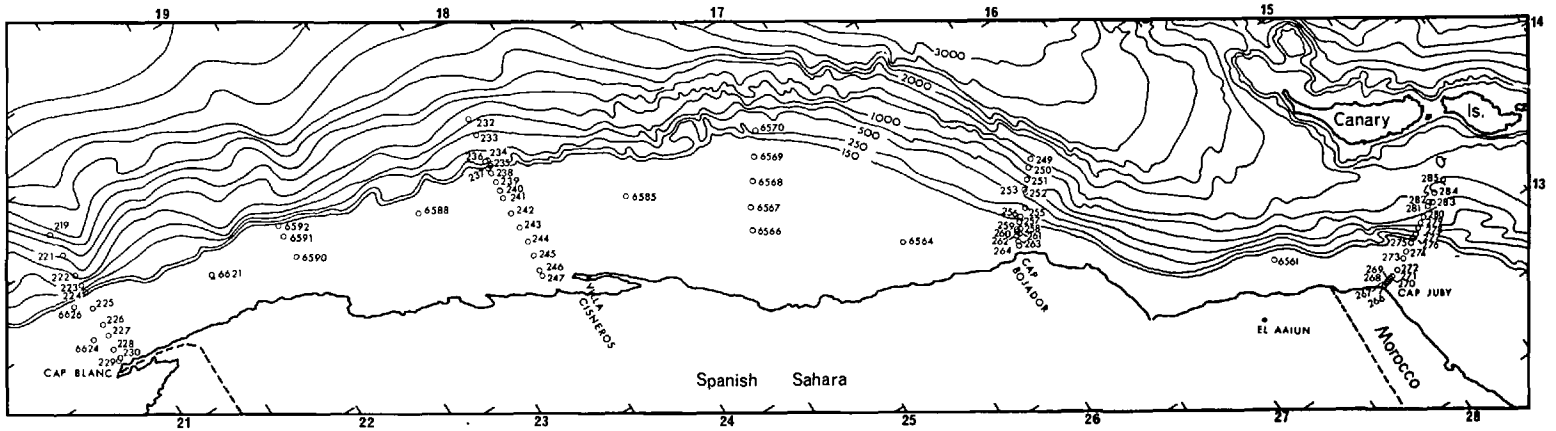


Fig.2b.

Location of rock and sediment sample sites off the Spanish Sahara; Sta.236 and 253 are camera stations; samples prefixed 6 were collected from R.R.S.Discovery and were provided by N.I.O.

The traverses correspond with D,E,F and G in Fig.1. Bathymetry north of lat 24°N is taken from Bosshard (Unpub.PhD.thesis,Univ.London,1968);that to the south was contoured by the writer from soundings on Admiralty Hydrographic Chart 3251. Depths are in metres.



SECTION 1.

SEDIMENTS OF THE NORTHWEST AFRICAN CONTINENTAL SHELF AND SLOPE

CHAPTER 1

SEDIMENT TEXTURE AND MINERALOGY

1.1 Introduction

Textural and mineralogical characteristics of some northwest African shelf and slope sediments have been broadly investigated in order to establish the regional pattern and history of sedimentation in this region. Some knowledge of the regional framework of sedimentation is desirable to aid in the interpretation of the distribution and origin of the sedimentary phosphate discussed in Chapter 2. Moreover, the sediment characteristics must be known if the extent and character of the phosphate deposit is to be calculated in terms of economic potential. First the distribution of different sediment types is assessed, then the mineralogy investigated broadly in terms of the regional and intra-sediment distribution of the major mineral phases which are biogenic skeletal debris, detrital mineral and rock fragments, and glauconite. Finally, some clues as to the physico-chemical conditions of the environment which may be of relevance to authigenic apatite formation are obtained from observations of sediment colour, redox potential and organic carbon content. This study is concerned with detailed analysis of selected samples and general analysis of all samples from the study area. All total samples are at present the subject of detailed textural and mineralogical studies by Dr. J.D. Milliman of Woods Hole Oceanographic Institution.

Previously published sediment reconnaissance studies on the shelf off Casablanca by Matthieu (1968), between Cap Rhir and Cap Juby by Navarro (1947), between Cap Juby and Cap Bojador by De Llarena (1950) and between Gibralter and Cap Blanc in the Spanish Sahara by McMaster and Lachance (1969) have assisted in the interpretation of these new data. Admiralty records

are the main source of data for the continental slope.

In broad outline, mixed carbonate-detrital sands and some muds prevail on the Moroccan shelf, carbonate rich sands on the Saharan shelf, and muds and biogenic oozes on the continental slope.

1.2 Analytical Methods

Sampling and analytical methods are described in detail in Appendix 1 and only a brief resume is given below. Samples were collected using Shipek grabs, pipe-dredges, piston corers, gravity corers or free-fall corers. Dredges were used where rugged topography was indicated on echo-sounding traces and, with cores, on the continental slope for sampling at depths where grab samples were likely to wash out during retrieval. Cores were collected only from the continental slope.

Textural analyses of selected samples were effected using standard techniques in which the distribution of sand sized components ($>63\mu$) was determined at 1 phi intervals into Wentworth grades by dry sieving, while silt and clay were determined by a settling tube method. Pebbles and shells coarser than 1 cm diameter were not included in these analyses but the very coarse sand fraction was enlarged to incorporate granules, small pebbles and large shell fragments all of which had to be less than 1 cm across. On the basis of their sand, silt and clay contents, these samples were classified as sands, muddy sands or muds (cf. Nutter, 1969, Fig. 3.1) using a technique developed by van der Linden (1967). As the boundaries between these grades are 70 per cent and 30 per cent sand respectively, this allows easy visual correlation with unanalysed samples. In order to obtain a qualitative assessment of sediment texture distribution, all other samples were classified into these same categories by visual comparison with analysed samples. Although it is realised that visual analyses of this nature are

not ideal they are here regarded, and have elsewhere been used (cf. Emery and Gould, 1958), as adequate for reconnaissance purposes.

Carbonate analyses were carried out using a titrimetric method on both total samples and size fractions of selected samples but not on cores with the exception of the uppermost core sample. Visual inspection prior to and after acid treatment of the samples showed the dissolved components to be mainly biogenic skeletal debris.

Certain samples of shelf sediments also contain in their coarser fractions, a few lithic carbonate fragments derived by erosion of local limestone; these too were dissolved in this analysis. Calcium phosphate is also readily soluble in the dilute HCl used and all carbonate values were therefore corrected for phosphate.

Organic carbon was determined titrimetrically using a method based on Schollenberger (1927) (AGRG. Tech. Comm. 32) and although results are lower than obtained by a combustion method, no correction has been applied since the data are internally consistent. According to Trask (1939) the total organic matter within the sediment is expected to be higher than the organic carbon by a factor of 1.8 but this conversion has not been applied in this study.

Binocular microscope analyses were made of the mineral component distribution in different size grades of selected sediments before and after dissolution of the carbonate constituents by leaching in 25% vol. acetic acid. The clay fractions of selected sediments were subjected to X-ray diffraction analyses to establish their mineralogy and separated glauconites were similarly examined.

On board ship, immediately after collection, Eh measurements were made on cores and surface samples collected during 1968. Some deep sea photographs

were also taken during this 1968 reconnaissance cruise.

1.3 Sediment Texture: Morocco

1.3.a Regional Pattern (Fig.I.3.I.).

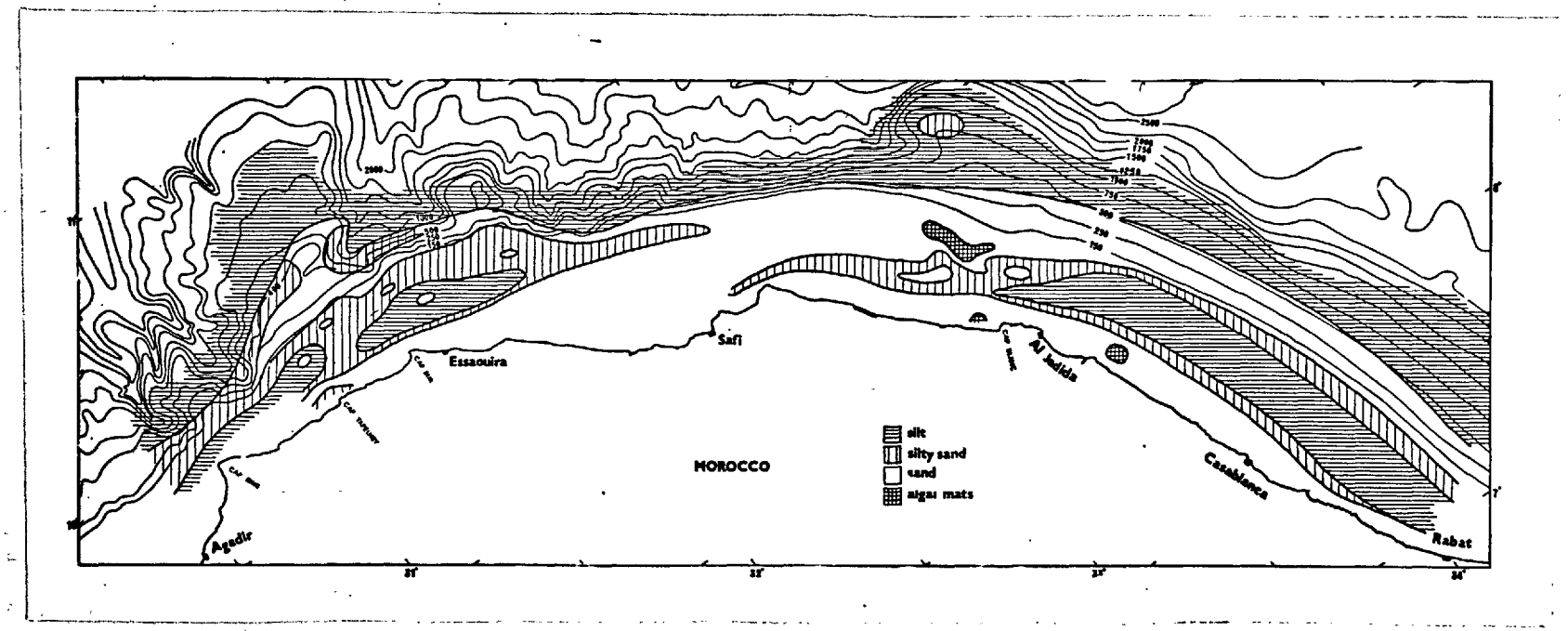
In order better to ascertain the regional framework of sedimentation, results obtained in this study on the region south of Safi are discussed throughout with data obtained by Nutter (1969) using comparable techniques, from the Safi-Rabat region. As Nutter (op. cit.) demonstrated, a prominent silt and silty sand belt occupies most of the shelf north of Al Jadida but to the south it is considerably reduced and represented only by an inner shelf silty sand zone which does not extend further south than Safi. Discontinuous with this, in the present study area, is a further silt and silty sand belt which occupies almost the entire mid and outer shelf between Essaouira and Agadir, becoming restricted to the outer shelf between Essaouira and Safi, north of which it is not recorded. Patches of sand are recorded from these belts in the rugged and rocky shelf regions off Cap Blanc and Cap Sim.

There are two major sand belts, both relatively narrow, one on the innermost shelf adjacent to the coast and another on the outermost shelf and uppermost slope. Both zones appear continuous from Rabat to Cap Tafelney. Between Cap Blanc and Essaouira, sands also occupy much of the mid shelf area between the two silt belts. Although there is no outer shelf sand belt, off Agadir, outer shelf and upper slope sediments are coarser than those at mid shelf depth or deeper on the slope.

Seaward of the outer shelf and upperslope coarse sand zone, the slope is almost everywhere mantled by silt except off Cap Sim where, over a prominent ridge, there is a well developed sand and muddy sand salient.

Fig.I.3.I.

Distribution of main sediment types off Morocco : data from north of Safi taken from Nutter (1969).



1.3.b Cores (Fig.2.2.2.and 2.2.3)

Cores collected from different depths on the continental slope penetrated up to about 1½metres into predominantly silty sediment. Visual appraisal (Fig.2.2.2.) shows there to be no appreciable textural variation in cores 143,802,803 or 811. Conversely, core 809 shows an abrupt transition from a silt at surface to a shelly silty mud in which are molluscan fragments reaching 0.5cm.dia. The remaining cores, although predominantly silt, contain sand or silty sand horizons the lower boundaries of which are frequently sharp. Graded bedding with upward decrease in grain size is seen within these horizons

Three cores (1049, 1052, 1082) were obtained from the mid shelf silt belt off north Morocco and in the two longest cores (1052 = 1.45 metres; 1082 = 1.57 metres) Nutter (op. cit.) observed a facies change from silt at surface to coarse shelly silt at the base of the core. Assuming the coarser deposit to represent some period during the Holocene transgression (commencing 16-14000 years before present according to Milliman and Emery 1968), then a sedimentation rate of about 1 cm./100 years is suggested for the silt belt.

1.3.c Sediment thickness

Sediment cover and thickness on the shelf have been estimated from P.D.R. and C.R.S.P. records (Chapter 5, this study; and Nutter, 1969). The shelf appears tobe arocky, and in places ruggedly rocky platform with only a thin veneer of sediment never exceeding 20m. in thickness except off Agadir. Between Al Jadida and Cap Tafelney sediments appear to be ponded between rock ridges on the mid and outer shelf. Locally in the Cap Sim silt belt up to 16m. of sediment were recorded by P.D.R. although nearshore this decreased to 2m. and on the outer shelf was even less. In the northern silt belt Nutter's P.D.R. records show the accumulation of up to 11m. of sediment. As shown by the distribution of rock outcrops and from seismic profiles

(Chapter 5) the thickness of Recent sediment on the slope off Cap Sim is extremely variable, being reduced to a veneer over and in the vicinity of the ridge on the slope off Cap Sim.

1.3.d Algal Mats

Further information regarding sedimentation rates is given by the incidence of algal mats on the inner and mid shelf on either side of the northern silt belt near Al Jadida. These mats, with living surface layers, encrust rock outcrops protruding through the thin veneer of sediment. At these sites, sedimentation is virtually non existent. The significance of algal mats, which have not previously been reported from this region, is discussed in the section on Spanish Saharan sediments.

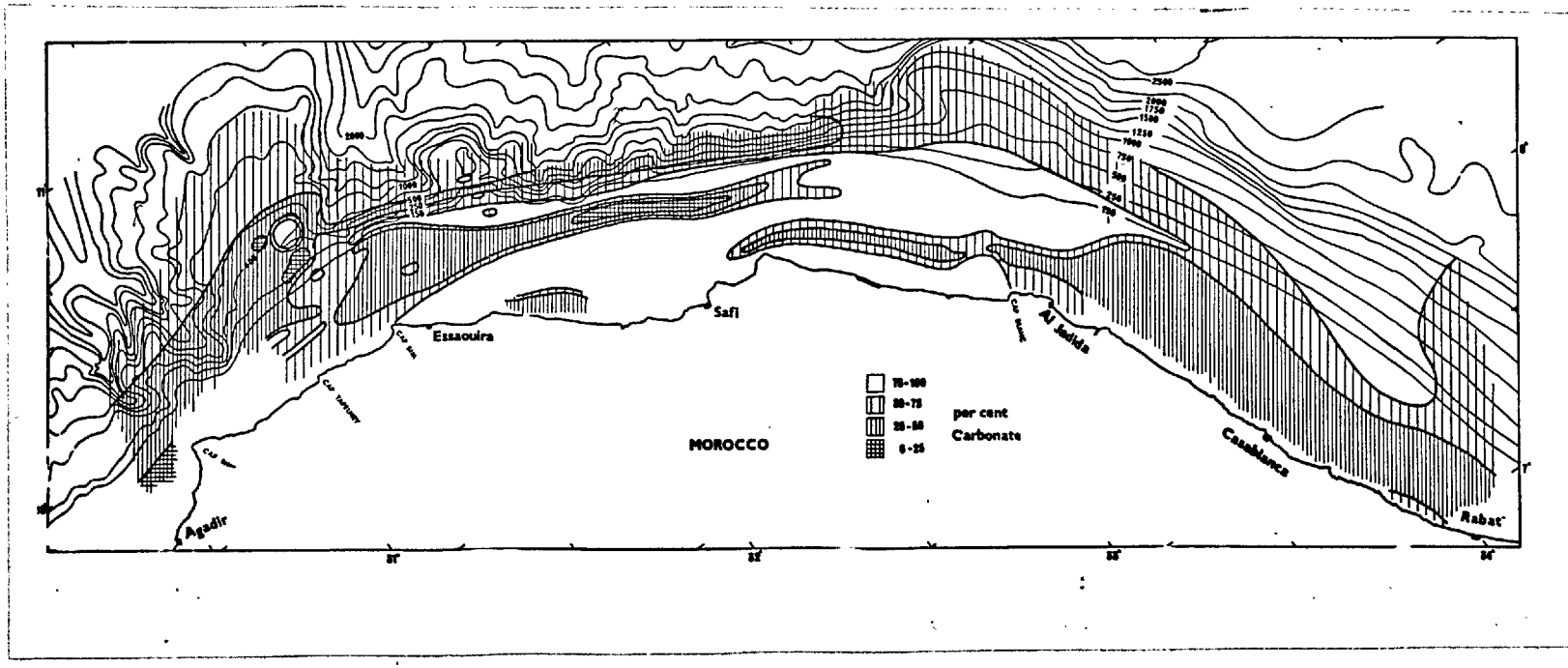
1.4 Mineralogy: Morocco

1.4.a Regional Carbonate Distribution (Fig. 1.4.1)

Carbonate constituents are distributed in belts subparallel to the continental margin. Classifying sediments with less than 50% $CaCO_3$ as carbonate poor, and the rest as carbonate rich, facilitates discussion of the distribution of this mineral phase. Correlation between carbonate and grain size distributions are apparent from comparison of Figs. 1.3.1 and 1.4.1. Both continental shelf silt belts coincide more or less exactly with carbonate poor zones although the carbonate poor zone associated with the southern belt continues among outer shelf sands for some distance beyond the northern end of the silt belt. The inner shelf sand belt appears to be moderately enriched in carbonate (50-75%) north of Al Jadida and south of Safi, and greatly enriched in carbonate (75-100%) between these towns. Mid shelf sands between the two silt belts from Essaouira to Al Jadida are carbonate rich (75-100%) as are the outer shelf and uppermost slope sands. By contrast,

Fig.I.4.I.

Distribution of carbonate in sediments off Morocco : data from north of Safi given by Nutter (1969).



outer shelf and upper slope sands north of Al Jadida tend to be only moderately enriched in carbonate (50-75%) while south of Essaouira the outer shelf and slopesands and muddy sands are dominantly carbonate poor. Silts on the continental slope are moderately enriched in carbonate (50-75%) over most of the area with the notable exception of a carbonate enriched salient off Casablanca and a carbonate poor zone along the uppermost slope off Safi and on parts of the upper slope south of Safi.

In general terms then, shelf and upper slope sands are carbonate rich except off Cap Sim, and shelf silts are carbonate poor; slope silts are moderately carbonate rich and locally uppermost silts are carbonate poor, particularly south of Safi. This regional correlation between carbonate content and texture is graphically expressed using the median diameters of samples for which accurate textural analyses were available (Fig. 1.4.2). Although there is some degree of scatter, carbonate rich sediments are coarser than carbonate poor samples. Therefore the supply of carbonate material can influence the resultant grain size and the textural characteristics of the environment may not necessarily reflect the size distribution of non carbonate, detrital components. This possibility is examined below.

1.4.b Size Fraction Analysis

A series of samples from different sites across the continental shelf and slope off Cap Sim were chosen to illustrate specific features of the phosphate distribution (Chapter 2). Textural analyses of these samples, which also represent all sediment zones except the inner shelf sands, are here examined to ascertain the granulometric character of these zones. Also examined are the data and conclusions presented by Nutter (1969) from the north Moroccan shelf. Histograms representing grain size distributions in samples from traverse 5 are given in Fig. 1.4.3.

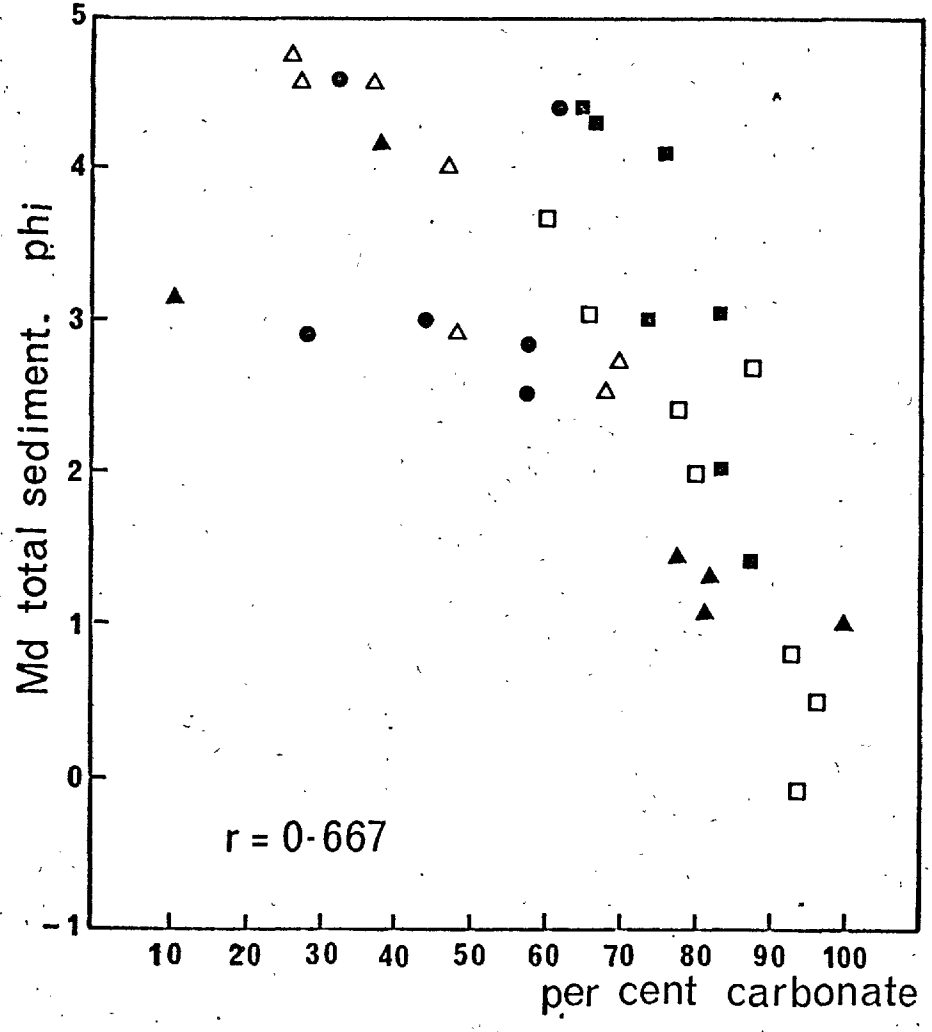


Fig.I.4.2. (LEFT). Variation of median diameter with carbonate content.

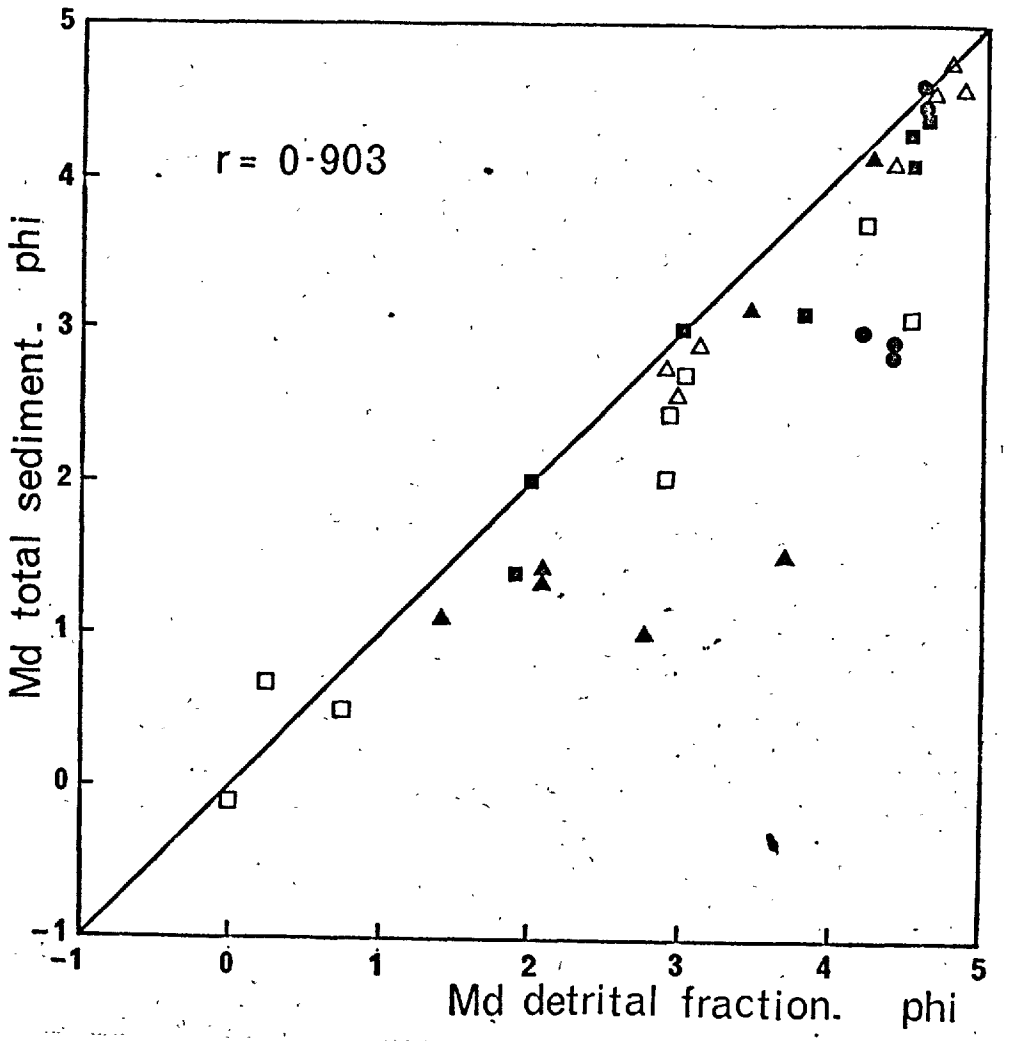


Fig.I.4.5.(RIGHT).Comparison of granulometric properties of the detrital fraction and the total sediment.

Correlation coefficients (r) refer to Fig.I.4.5.A. ; trav.5 = ⊙ ; trav. 10 = ▲ ; trav. 14 = □ ; trav. 15 = ■ ; trav. 22 = △

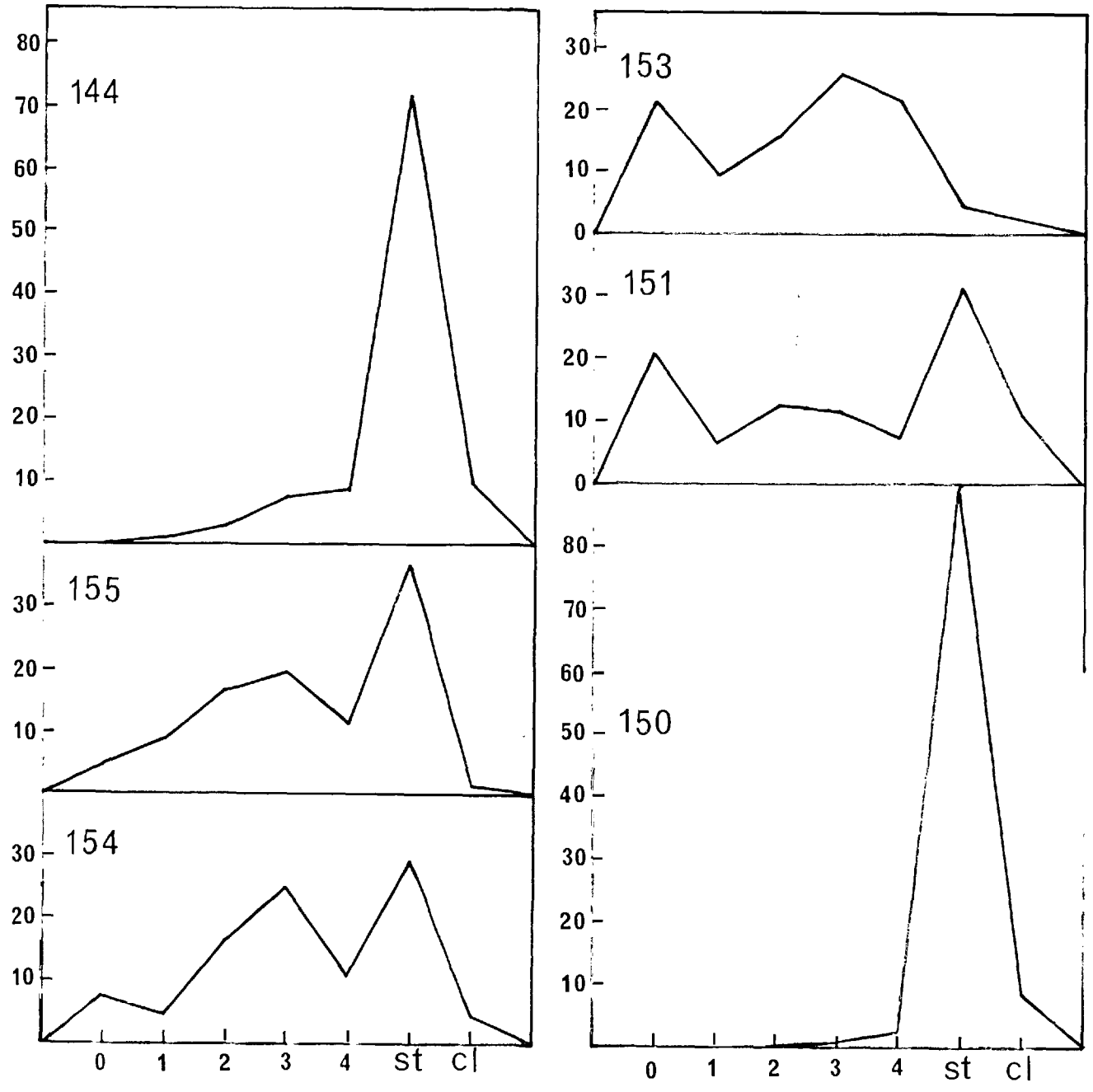
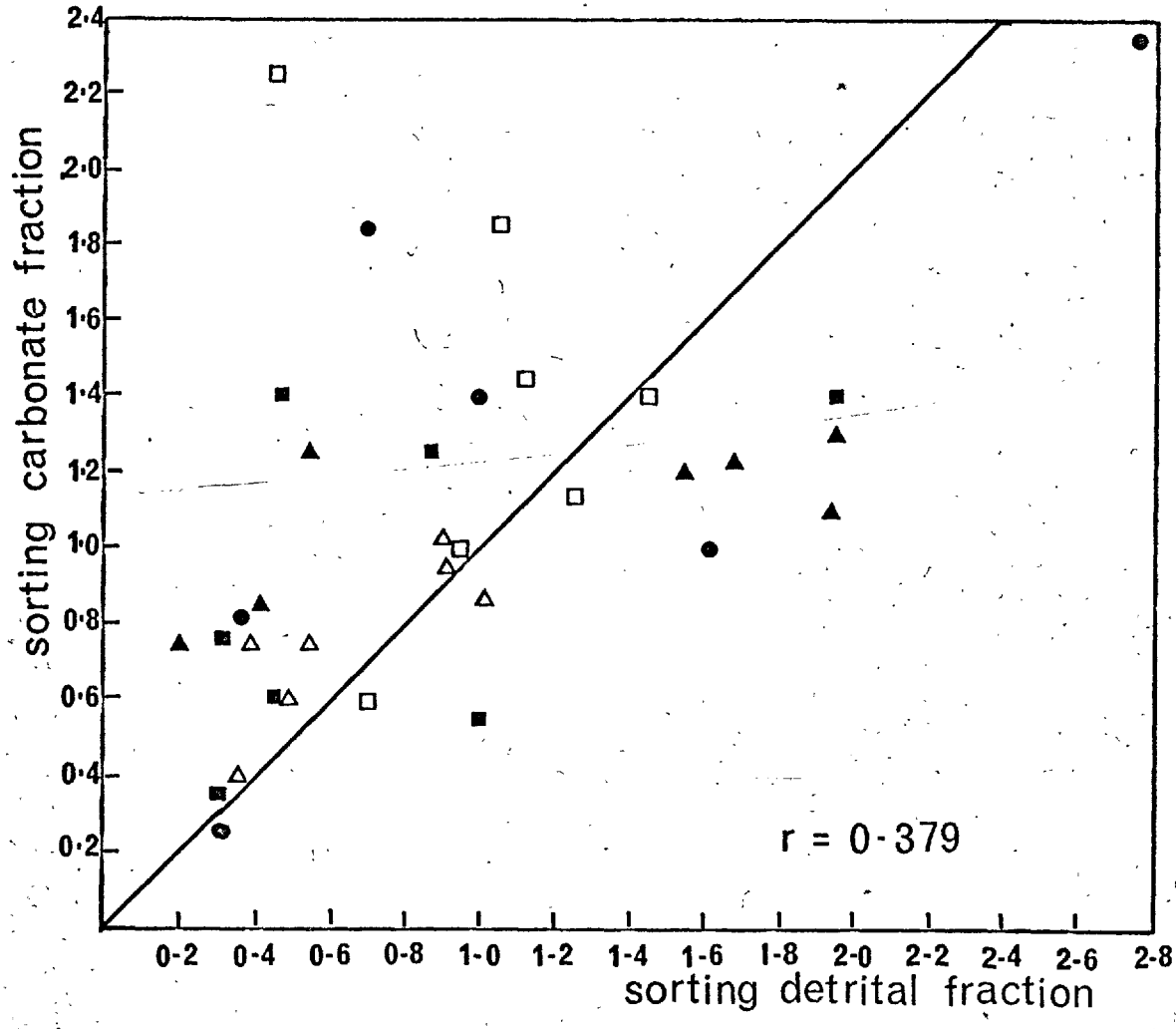


Fig.I.4.3. Granulometric characteristics of sediments from trav.5.
Vert.scale = percent.
Horiz.scale = phi units.
st = silt; cl = clay.

It is clear (Fig. 1.4.3) that continental shelf and slope silts in the Cap Sim area are unimodally distributed: by contrast, shelf and upper slope sands and silty sands are usually bimodally and sometimes polymodally distributed. The same findings were made by Nutter (1969) for sediments from the north Moroccan shelf. Even where unimodal, the size distributions of silts and sands off north and south Morocco are sufficiently broad as to result in poor sorting values (greater than 0.5 determined by Inman's method) with very few exceptions (125, 150, 1083, 1085). Evidently, from the degree of polymodality and the poor degree of sorting, the majority of samples examined here, and by Nutter (1969), are to some extent mixed grain populations out of equilibrium with the prevailing environmental conditions. In particular (cf. also Nutter, 1969) it is clear that these sediments are often mixtures of separate sand and silt populations; clay contents are everywhere low. A constraint placed on the interpretation at this stage is that the median diameter is partly a function of mixing of biogenic skeletal debris with detrital clastic mineral grains and rock fragments and the distribution of these phases must be examined before the origins of the admixed grain populations can be assessed.

Comparing the median diameters of carbonate and detrital phases in selected samples, it is clear that the detrital phase is always finer than the associated carbonate (Fig. 1.4.4a). This effect can be mainly due to either (1) mixing of fine detrital material with coarser carbonate at different times and under different hydrodynamic conditions or (2) the hydraulic equivalence effect whereby under the same environmental conditions, coarse but relatively light carbonate particles will behave in the same way as finer but denser detrital constituents. Examination of the individual frequency distributions shows that both factors have been operative to varying degrees in different Cap Sim samples (Fig. 1.4.4b)and examination of Nutter's (1969) data suggests that the same findings apply to northern Morocco. It is clear that



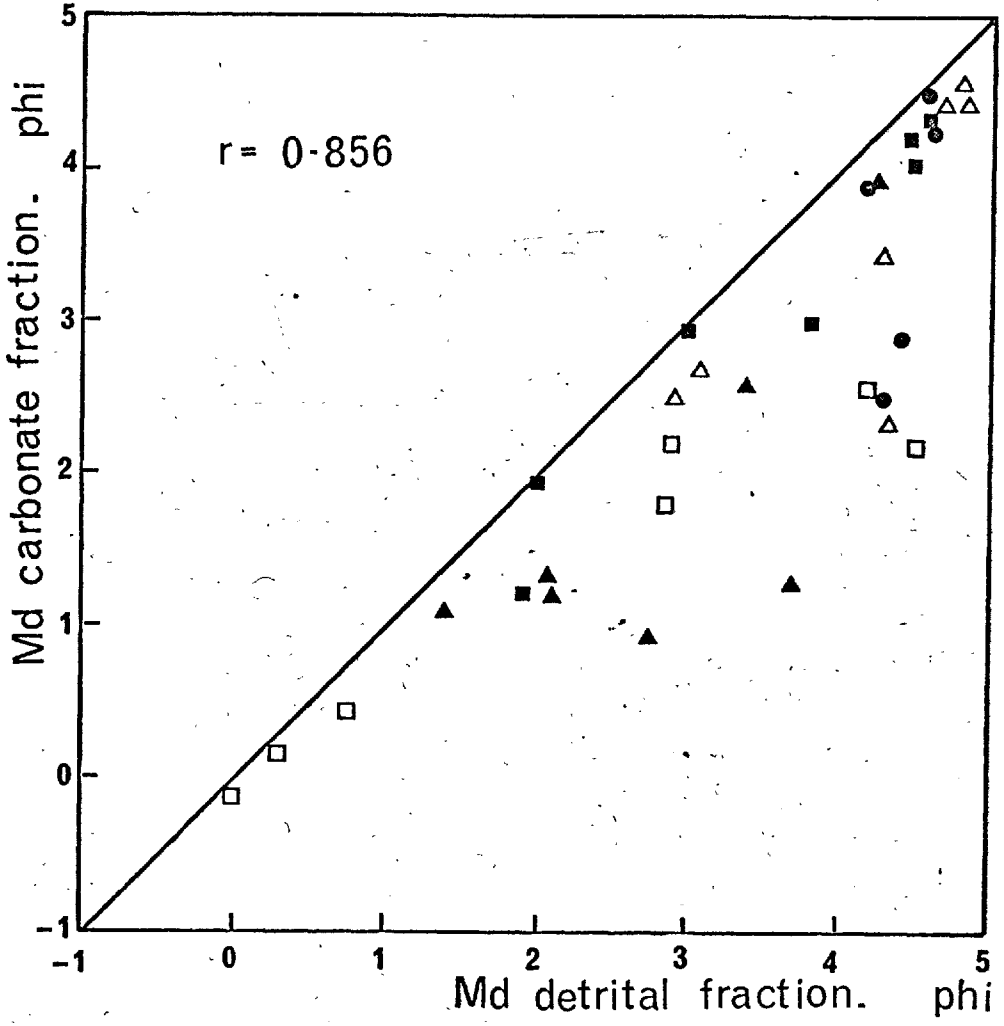


Fig.I.4.4.a. Comparison of granulometric properties of the detrital and carbonate fractions of Moroccan sediments (phi units). Correlation coefficients (r) refer to Fig.I.4.5.A. ; trav.5 = ●; trav.10. = ▲; trav.14 = □ ; trav.15 = ■ ; trav. 22 = △ .

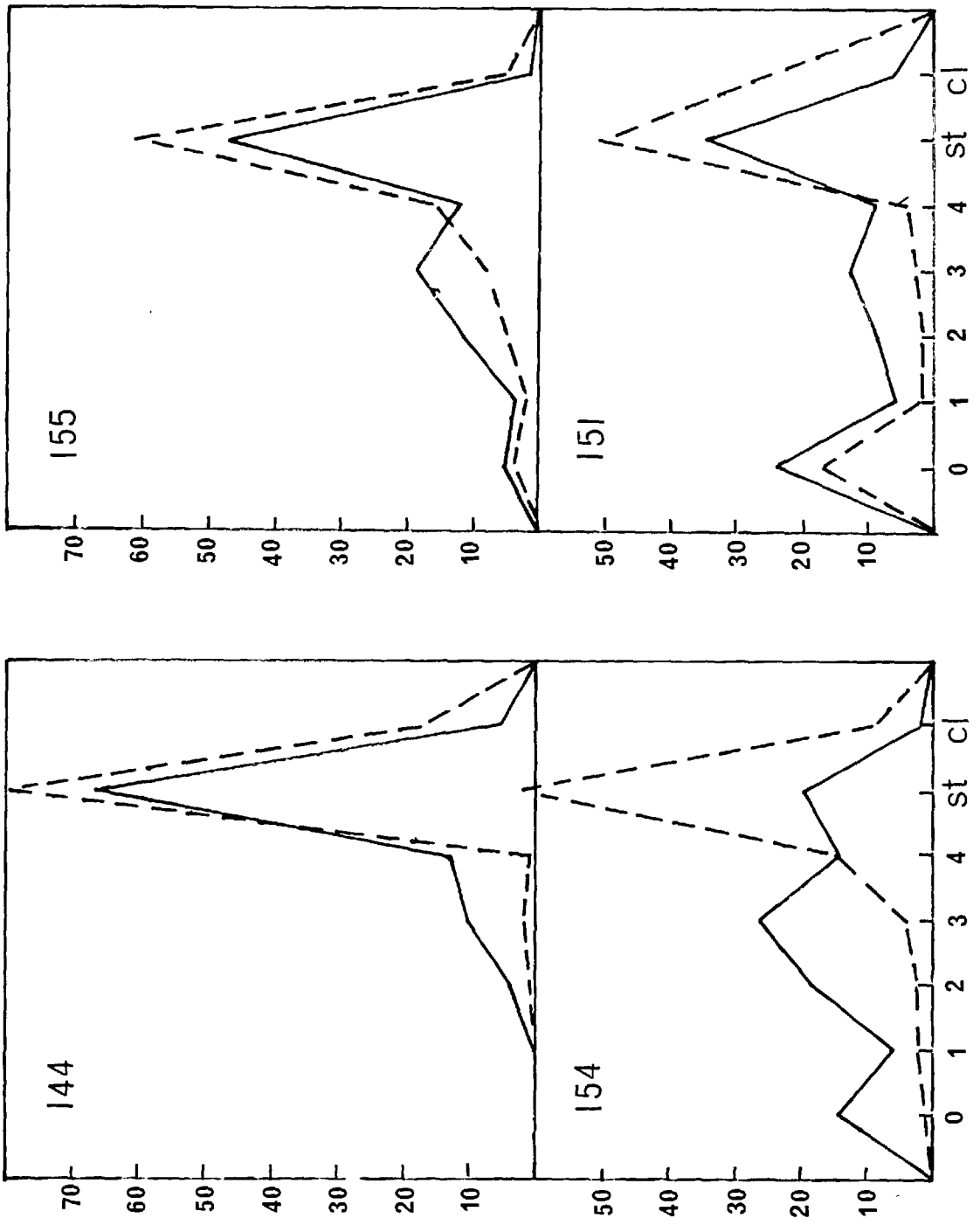


Fig.1.4.4.b. Granulometric characteristics of the detrital (dashed line) and carbonate (solid line) fractions of samples from trav.5. vertical scale = percent; horiz.scale = phi units (st=silt;cl=clay)

there is a fair degree of correspondence between the distribution of carbonate and detrital phases in each grade and the slight bias of detritals towards finer sizes suggests the operation of hydraulic equivalence and deposition under basically the same depositional conditions. In several cases however, despite broad parellelism of sand sized carbonate and detrital phases, there has been later admixture of a detrital rich silt component. In these cases the overall sediment texture may not be a true reflection of the nature of the detrital phase.

Comparing the median diameter of the total sediment with that of the detrital phase it is apparent (Fig. 1.4.5) that although the detrital phase is slightly finer there is reasonable correlation between median diameters suggesting the textural distribution map does broadly reflect the distribution of the detrital fraction. As pointed out however, in some samples the detrital and carbonate distributions diverge pro foundly. Those samples in which there is divergence from carbonate distribution are (a) inshore sands 986 and 987 in which the detritals are bimodal silty sands and which are sited on the edges of the silty sand belt in which the total sediment including the detrital fraction is usually bimodally distributed; (b) 1086 the detrital components of which are dominantly silt but which is sited among the silty sands on the edge of the silt belt; (c) among the offshore sands, 1088 has the detrital composition of a bimodal silty sand as also have sands 993 and 926 and all three are sited on the margins of the silty sand belt, or in the case of 926, along the projected extension of an outer shelf silty sand belt; (d) slope silty sands 126, 154 and 155, the detrital components of which are poorly sorted or bimodal sandy silts.

It should here be noted that several of the offshore sands have a small detrital-rich silt mode indicating a minor degree of mixing of silt with previously extant detrital sands. From the examination it is clear that the general textural classification of shelf sediments does apply to the detrital

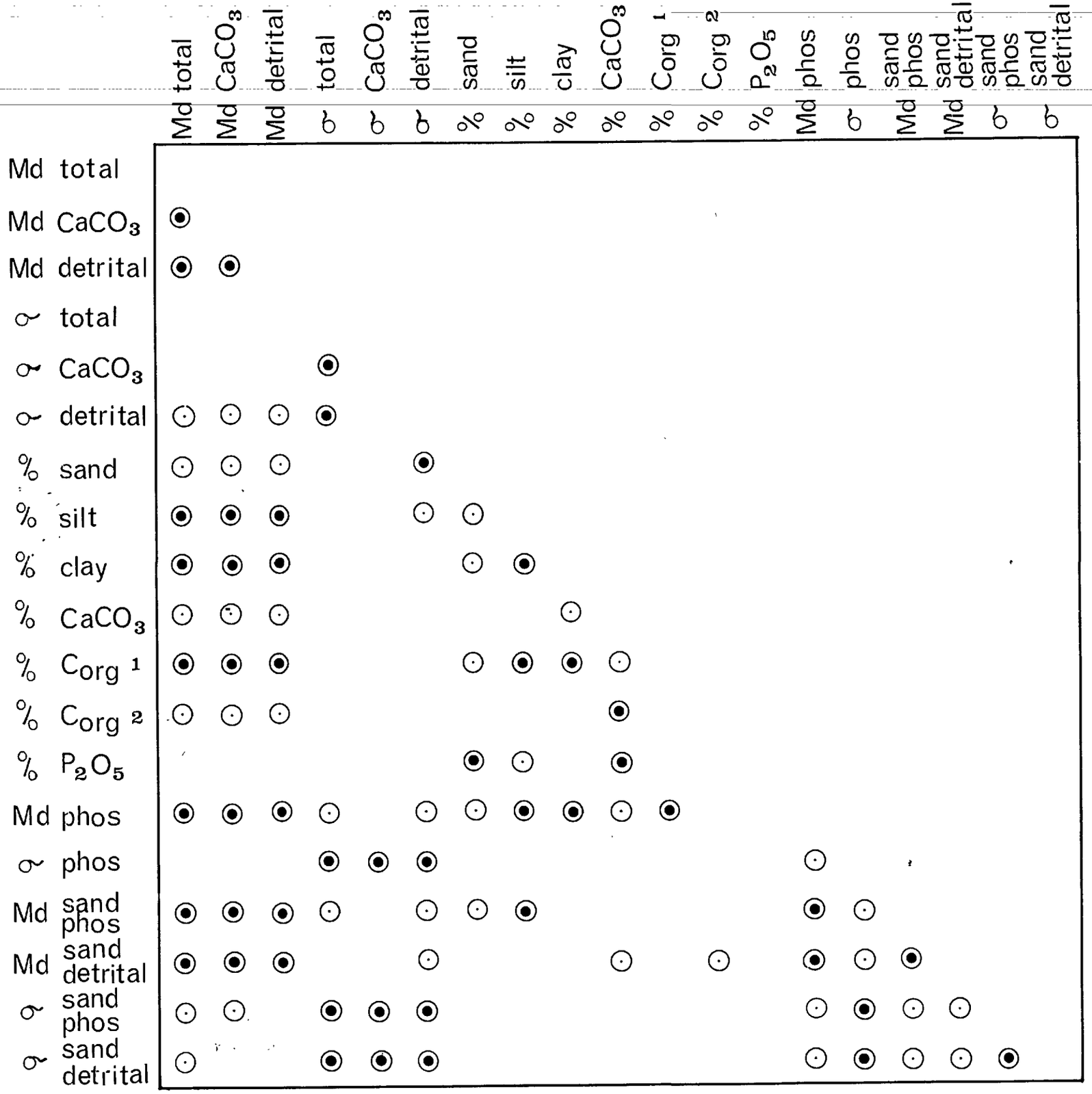


Fig.1.4.5.A. Product-moment correlation coefficient matrix showing relations between median diameter and sorting of the total sediment, the carbonate fraction and the complete and the sand only populations of the detrital and phosphate fractions, and between the silt, clay, sand, phosphate, carbonate, and organic (total = 1; carbonate-free = 2) contents. Calculated using the programme of Garrett 1967 (PhD thesis;London) ⊙= significant + corr elation, and ⊙= significant - correlation at the 99% confidence level.

fraction. Notable exceptions are that in terms of detritals the outer shelf southern silt belt may continue north at least as far as Sta 926, and the silt zone may be a little wider than mapped and may include some of the adjacent sediments at present classified as silty sands or sands. The prevalence of even a small silt mode among the outer shelf sands tends to suggest that the entire shelf may be in some small respect covered by parts of a silt and clay blanket which reaches its most extensive development in the silt belts and begins to die out in the silty sand belts either as a function of transport and supply directions or due to current patterns and turbulance on the seafloor.

1.4.c Mineral Component Analysis

Qualitative binocular microscope examinations were carried out on the sand fractions of those samples from the detailed study area which had been texturally analysed. After dissolution of the carbonate phases in 25 per cent vol. acetic acid over a two day period, the acid insoluble residues of each size fraction of these samples was also microscopically examined. Qualitative assessments of mineralogy so determined are presented in table 1.4.1.

Biogenic Remains

Specimens of the inshore sand belt were not examined in any detail but cursory visual inspection shows them to consist mainly of molluscan skeletal debris with detrital minerals and no glauconite. In the silt belt (150) molluscan remains are absent, probably because conditions are not suitable for benthic filter feeders; major biogenic components are foraminifera and sponge spicules. In mid and outer shelf samples and to a lesser extent on the upper slope molluscan remains are again abundant particularly in the coarser sand grades. The molluscan debris consists chiefly of angular abraded weathered and bored shell fragments with a rather aged appearance in contrast to the fresh appearance of fragments from shallow water near

the shore.

Foraminifera occur mainly in finer sand grades and in any one grade the ratio of foraminifera to molluscan debris increases seaward from the outer shelf onto the slope.

Miscellaneous biogenic debris comprise echinoid fragments or sponge spicules which are rare constituents of most sand grades on both shelf and slope; bryozoa and coral are even more rare. Fishbones and sharks teeth are extremly rare on the shelf but occur in small amounts in the coarse, medium and fine fractions of some, but not all, slope samples. Faecal pellets are rare constituents of almost all samples.

Inorganic Constituents

Owing to the mode of occurrence of glauconite which is found coating and replacing detrital mineral grains or rock fragments on the shelf it is difficult to assess the contribution of detrital clastics to the coarser sand grades but it appears considerable. Because of this difficulty the relative proportions of glauconite coated fragments and glauconite (table 1.4.1) do not accurately reflect the concentration of either in shelf samples where glauconite coats or replaces rock or mineral fragments. In the very coarse sand grade, rock fragments on the shelf are not infrequently coated with glauconite but can be seen to constitute up to 90 per cent of this fraction: mudstone and phosphorite fragments are commonest, limestone more rare. On the continental slope, phosphorite, mudstone, sandstone and limestone fragments occur in this grade and are infrequently glauconite coated.

In the coarse and medium grades mudstone is again commonest in shelf samples where it is often accompanied by phosphorite but in slope samples phosphorite, though present, is much less abundant; on the slope phosphorite is again accompanied by limestone and sandstone. In the finer grades phosphorites and mudstones are not at all abundant although often recognised as minor

constituents of shelf and slope samples on examination of acetic acid insoluble residues (table 1.4.1). It is important to remember that with increasing fineness of grade the recognition of mudstone and phosphorite grains becomes increasingly difficult and they may be lumped together with undifferentiated detritals.

Inner shelf sands were not examined for inorganic constituents, but the mud belt was and proved to contain no rock fragments.

Quartz is the dominant terrigenous detrital mineral phase and, like the rock fragments, is frequently subangular in shape. It is a very rare constituent of the coarse and medium grades on the slope, where it is usually only recognised in the acid insoluble residue. In the fine sand grade it is a minor component of nearly all shelf and slope sediments. In the very fine grade it is abundant in the mud belt, fairly common though never abundant in mid and outer shelf sediments where its abundance increases seawards, and common in the upper slope sands; in the remaining slope samples it is much less abundant although still more common in this grade than in any other grade.

Miscellaneous detritals include feldspar and unrecognisable accessory minerals or rare rock fragments. These tend to be most abundant where quartz is abundant but the ratio of quartz to other detritals is always very high.

Glauconite occurs coating and replacing mineral grains or rock fragments, as black subrounded grains with syneresis cracks and as the internal casts of foraminifera. Its characteristics are discussed later in this chapter.

Comparable mineralogical analyses of north Moroccan shelf and slope sediments by Nutter (1969) and Matthieu (1968) gave results substantially in accord with the present data with regard to the presence of weathered molluscan debris on the outer shelf and the abundance of quartz among detrital phases. Matthieu reports that the quartz is frequently red-stained and may be

accompanied by rare hornblende epidote and magnetite but red stained quartz was not observed in the detail study area off Cap Sim. Glauconite is found in northern Moroccan sediments where it does not exceed 5 per cent of all constituents and occurs as rounded or subrounded grains and as foraminiferal casts. Nutter also recognised subangular and subrounded grains and granules of phosphorite among the detrital mineral constituents.

The results of these textural and mineralogical investigations are in general agreement with the results of a reconnaissance carried out by McMaster and Lachance (1969) although, since their sampling lines were no closer than 100 km. and their sampling density was low, the detail resulting from this present study naturally represents a more realistic appraisal of the regional sedimentation characteristics. According to these authors, clays in the northern silt belt comprise illite and kaolinite with subsidiary chlorite while the southern belt also contains montmorillonite.

1.4.d Glauconite (table A.2.5.)

Glauconite occurs in about half the samples from the muddy sand and sand belts of the outer shelf and slope, ranging in depth from 87m. (Sta 859) to 915m. (Sta 880) in surface sediment samples. According to data given by Cloud (1955) Ehlman, Mulings and Glover (1963) and Pratt (1963) glauconite is rare above 10m. and below 2000m., and commonest in 30 - 700m. (Porrenga 1967).

Mode of Occurrence

In examined shelf samples (832, 833, 834, 836, 873, 151, 153) the glauconite occurs mainly in the 1 to 2 phi fraction as light green angular to subangular grains with a knobbly surface texture and banded or layered agglomeratic appearance as if caused by the irregular stacking of small subangular blocks of glauconite. Broken grains show the glauconite to be both coating and

replacing reddish-brown rock fragments which resemble ferruginous mudstones, the original bedding of which appears to have given rise to the layered or banded aspect of the replacing mineral. Similarly, the agglomeratic appearance may have resulted from preferential replacement along transverse joint and bedding planes. These angular glauconites dominate the coarser sand grades but are succeeded in importance in the fine sand grades by the light green internal casts of foraminifera, many with parts of the foraminifer test still adhering to or even totally covering the glauconite. Elongate, segmented grains have the appearance of being replaced faecal pellets although some, with a distinctly curved or arcuate shape are more probably foraminifer casts modified by continued growth of glauconite. In the finer fractions dark green, rounded or ellipsoidal, botryoidal grains with syneresis cracks, a more typical form of glauconite, form a subordinate proportion of grains; these may be modified faecal pellet or foraminiferal casts. In the very coarse sand fraction, pellets or grains are rare, glauconite being mainly present as thin coatings on fragments of mudstone, never on phosphorite or limestone fragments. These coatings are not present in all samples (for example 833 has uncoated pebbles). Foraminiferal casts may be pale or dark green with all gradations in between and are normally mixed with a very few cream or pale brown casts; cream and green segments may even coexist within the same foraminifer cast. X-ray diffraction analysis demonstrates that both green and brown casts are composed of glauconite.

Near the shelf edge sand belt glauconite occurs in the 3 to 4 phi fraction of sediments examined (836 and 837). Pebble coatings are absent and angular coated or replaced rock fragments constitute a far smaller percentage of glauconite grains than hitherto. Instead, glauconite is predominantly in the form of black, glazed, ellipsoidal and cracked botryoidal grains. In the finer fractions dark or light green foraminiferal casts are most abundant and are mixed with the familiar modified casts where glauconite accretion

has been greatest. Glauconite is also seen to replace some organic skeletal material and is found forming in pits in the surface of molluscan shell/ debris and in hollows in the centre of bone fragments. Again, admixture of small numbers of pale brown and cream casts is apparent.

Finally, in samples from the continental slope, glauconite occurs entirely as black ellipsoidal grains in coarser fractions or as foraminiferal casts in finer fractions. Again the transition from casts, through modified casts to pellets is evident. Black glauconite also coats pebbles in the very coarse sand grade. Casts are generally a lighter green although admixture of brown cream or yellow casts is observed. Glauconite is concentrated in the 1 phi fraction of sample 882 and 155, and in the 2 to 3 phi fraction of sample 154.

Detrital glauconite is also recognised where fragments of the glauconitic phosphorite, common to this region, are observed in coarser sand fractions.

Much smaller amounts of glauconite are found in the sediments from the north Moroccan shelf where they were first recorded by Gallilher (1935) and later studied by Matthieu (1968) and Nutter (1969) who found glauconite foraminiferal casts in the outer shelf and upper slope sediments off Casablanca, and by Bell and Goodell (1967) who report red-brown glauconite pellets from the shelf off Rabat. On the Spanish Saharan shelf glauconite is recognised as foraminiferal casts (de Llarena, 1950) and is not widely dispersed in this environment. Off Villa Cisneros, glauconite coated rock fragments occur near the shelf edge.

Size Fraction Analyses

The distribution of glauconite in separated size fractions (Fig. 1.4.6) does not follow the distribution of glauconite free components taken to represent detrital minerals, suggesting these two sediment components are unrelated. In finer fractions glauconite predominantly occurs as foraminiferal casts

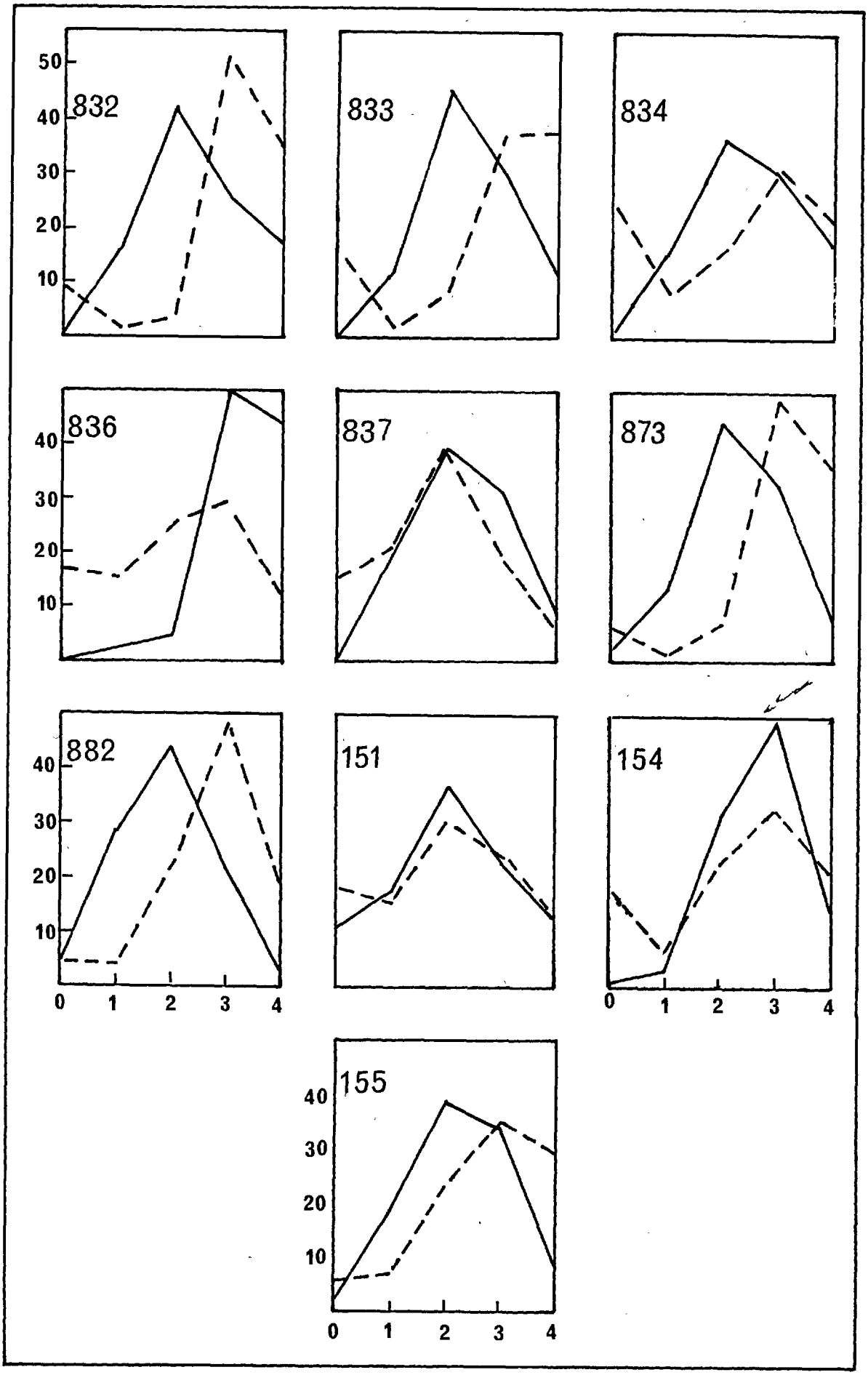


Fig.I.4.6. Granulometric distribution of glauconite and non-glauconitic detrital fractions in the sand grades of selected south central Moroccan sediments : horizontal scale = phi units ; vertical scale = percent.

which may or may not still be attached to or concealed by skeletal material. In coarser grades these discrete casts are modified by additional growth but still preserve their arcuate shape and segmented character in many specimens. Growth appears to lead to the development of syneresis cracks and the partial breaking up of grains; some specimens are seen to be formed by the coalescence of two or more casts which may be modified or unmodified by growth. Finally, it is considered possible that continuation of growth of either faecal pellets or foraminiferal casts leads to the development of the large black ellipsoidal pellets of the coarser fractions of outershelf and slope sediments.

On the shelf, glauconitisation of angular mudstone fragments appears to be the major source of glauconite in the coarser sand grades. In this case the glauconite distribution must at least in part reflect the distribution of detrital minerals or rock fragments; foraminiferal casts however still predominate in finer fractions. That some glauconite is possibly actively forming is evinced by its occurrence as rock fragment coatings in the coarsest sands. Interestingly the glauconite coatings are only developed on mudstones, never on limestone or phosphorite pebbles, suggesting a definite genetic relation. Glauconitisation of rock fragments is a well recognised phenomenon (cf. Pantin 1960) as also is glauconitisation of micas, particularly biotite (Galliher 1935, 1939) which might be expected to be concentrated in certain mudstones.

Radiometric Age Determinations

Despite evidence for some possibly Recent glauconite formation, K.Ar dating kindly carried out by Dodson and Rex, Geology Department, Leeds University, on separated size fractions from samples 155, 833, 882 (Appendix 4) show that the coarser glauconite grains are not geologically young.

These subsamples contained very few casts and consisted in the case of

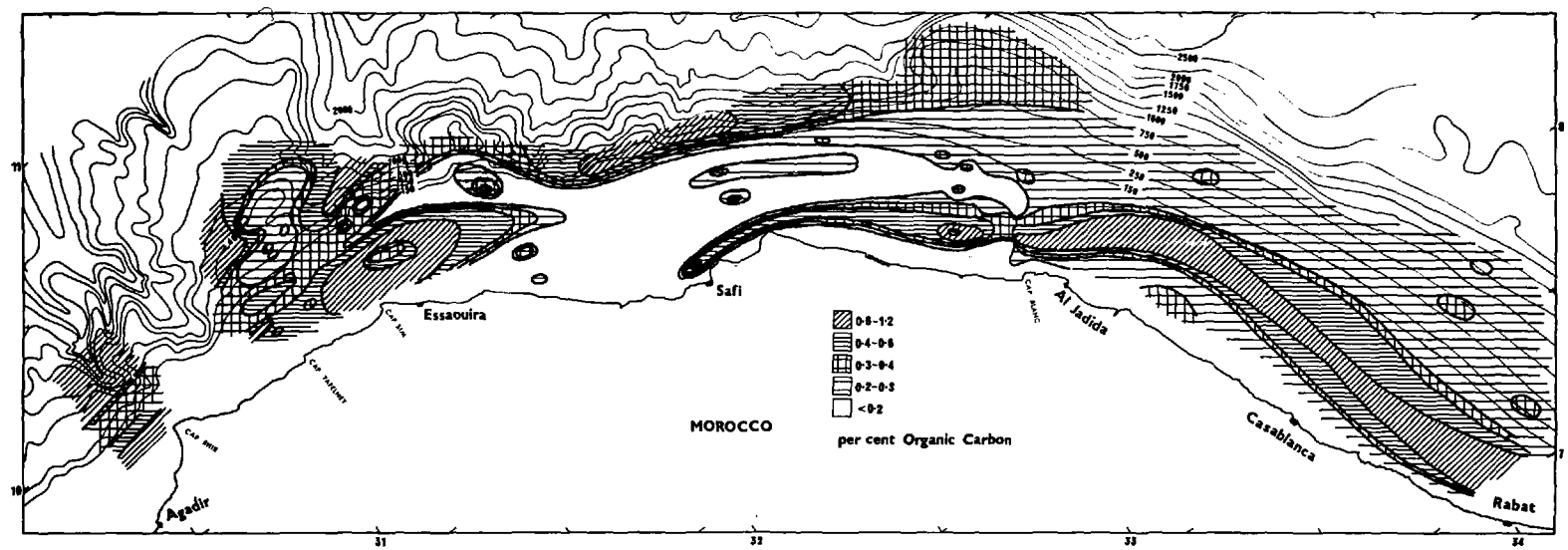
continental slope samples 155, 882 mainly of black to very dark green botryoidal grains with a distinctly authigenic appearance. Those shelf samples from site 833 consisted of rather angular to subangular "knobbly" grains some of which may be replaced rock fragments (Appendix I). No coated rock fragments were included. The possibility cannot be ignored that in the case of the shelf samples some inherited radiogenic argon may be present, if indeed these are of replacement origin. This argument does not apply to the continental slope samples.

1.4.6 Organic Content, Colour and Redox Conditions

There are strong similarities between the distribution of organic carbon (Fig. 1.4. 7)and other sediment characteristics such as texture and carbonate content. The C.org is distributed in belts parallel to the Moroccan continental margin and in these belts the C.org content does not exceed 1.0 per cent except at isolated sample sites (Sta. 806 = 1.1% C.org; Sta. 902 = 1.26% C.org). Those sediments richest in C.org (>0.4%) are the shelf silt belts and the silts of the continental slope south of Cap Blanc, whereas the sediments poor in C.org (<0.4%) are the inner, mid and outer shelf, and, off Cap Sim the upper slope, sand and silty belts. This is a generalisation which does not so readily apply to the continental slope north of Cap Blanc where both silts and sands are relatively poor in C.org.

Clearly there is a tendency for increasing fineness to correlate with increasing C.org, a relationship widely reported from Recent marine sediments (Trask, 1939). The correlation coefficient between Md total sediment and per cent C.org is 0.709 which is significant at the 99% confidence level; between C.org and per cent silt there is a correlation of 0.582 and between C.org and per cent clay the correlation is 0.701 but there is no significant correlation between per cent C.org and per cent sand (Fig.I.4.5A). Trask attributes this relationship to the similar sedimentation characteristics

Fig.I.4.7.
Distribution of organic carbon (per cent) in sediments off the Moroccan coast.



of clay and organic particles, both of which may have dimensions commonly near the colloidal range. However, in detail, the concentration of organic matter here in the finer sediments could reflect (1) river supply of finely divided organic matter accompanying silt and clay (2) settling of fine organic material of marine origin with the ultimately land derived silt and clay under similar hydrodynamic conditions (3) preferential absorption from seawater by silt and clay of uniformly distributed organic matter (4) the more rapid decomposition and dissolution and winnowing from well oxygenated and current swept sands of organic material which may be uniformallly supplied to the entire region. The carbon and carbonate distributions are more or less antipathetic (Figs. 1.4.1 and 1.4.7 and Fig.I.4.5A): as the carbonate reflects biogenic accumulation it is evident that post depositional removal of organic material may be occurring from sands rich in organic (skeletal) material. Without detailed examination of the nature of the nonskeletal organic remains throughout the sediments no decision can be made regarding the origin of these observed variations. Nevertheless since the carbonate rich sands are so impoverished in organic carbon the winnowing hypothesis is preferred as far as being the probable major influence on regional C.org distribution.

The texture - C.org relationship holds good over most of the area with the notable exception of the slope sediments north of Cap Blanc as mentioned above. Either the rate of sedimentation of organic remains is not constant along the slope or there is an increase in post-depositional removal of organic material north of the Cape. This area tends to be slightly richer than the southern area in carbonates reflecting possibly decreased supply of silt and clay and consequentally decreased supply of finely divided organic material. At present there is not sufficient evidence on the nature and distribution of seabed currents, biological productivity and the proportions of live-to-dead species in bottom sediments to allow further

conjecture as to the reasons for the observed increase in carbonate and decreases in organic carbon and silt and clay detritus.

Colour

A general visual appraisal (without the aid of a standard colour chart) was made of the colour of the stored dried samples from the detailed study area south of Safi. In general, shelf sands are pale yellowish-brown or greyish white, while muddy sands and muds are pinkish brown and very occasionally olive hued. Glauconitic sediments are black or brown speckled and brown hued except where glauconite is sufficiently abundant for them to merit the description 'black sands'. The sand coloration appears to reflect the hue of fresh and/or weathered shell material and tends to be yellowish-grey when mixed with larger amounts of quartz, like the sediments off the east coast of the U.S.A. (Stanley, 1969). In cores, there is a tendancy for samples to be pinkish brown at surface and to become pale greenish grey or olive at depth, although such transitions were not observed in all cores. Where there are sandier (and usually shellier) layers, the colour becomes more greyish. From north of Safi, Nutter (1969) reports the presence of buff shelly sands and brown fine foraminiferal sands and brown silts. However, when, quite late in the present study, soluble Fe and Mn determinations were effected on sediments from the central Moroccan shelf (cf. Chapter 3) some considerably Fe and Mn enriched samples were found in the general vicinity of Cap Blanc. Visual investigation of selected Fe-Mn rich samples showed them to contain bright orange to red-brown rock fragments and shell remains, all with a very iron-stained appearance. Examination of some of the larger shell remains showed that Fe impregnation was not always complete right through the shell although this was found to be the case with smaller fragments. Within individual shell fragments were observed some dark "twig-like" structures representing formation of some mineral in internal cavities. Leaching in cold dilute acids to remove calcareous material disclosed abundant rich orange-brown foram casts in many samples, in addition to dendritic

structures probably representing the "twig-like" structures from mollusc shells. Orange-brown rock fragments and quartz were also left after leaching.

Leaving the total,and acid leached samples to stand overnight in a 10 per cent Na-dithionite solution resulted in complete bleaching of all components (including clays and silts from the $<64\mu$ fraction). These investigations suggest that, at least among the low C_{org} sands between Safi and Al Jadida there has been extensive Recent accumulation of authigenic iron minerals - probably hydrated oxides. The extent of this accumulation is assessed and discussed in Chapter 3.

Bell and Goodell (1967) and Nutter (1969) both reported the presence of oxidised glauconites from the north Moroccan shelf. By contrast with the oxide region sands which contain $<0.2\%$ C_{org}, the glauconitic sands of the Cap Sim region characteristically contain 0.2 to 0.4% C_{org}. These variations most probably reflect variations in the redox potential of the environment; the absence of widespread greenish muds suggests that oxidising conditions are widespread. Formation of glauconite in the south attests to the presence of locally reducing conditions even if only in micro-environments.

Redox potential measurements made during the 1968 reconnaissance cruise (table 1.4.3) show surface silts on the lower slope off Cap Blanc to be considerably more oxidising than those off Rabat or off Cap Sim (with the exception off Cap Sim of sample 155 which is highly oxidising). At depth in continental slope cores in each environment redox conditions rapidly become less oxidising but, in the cores examined, there was no associated colour change; core 143 for example remained both brown and slightly oxidising over its entire length (fig.2.2.2 and I.4.8).

Among continental shelf sediments, regardless of texture, redox conditions which are highly oxidising near the shelf edge become less oxidising as the

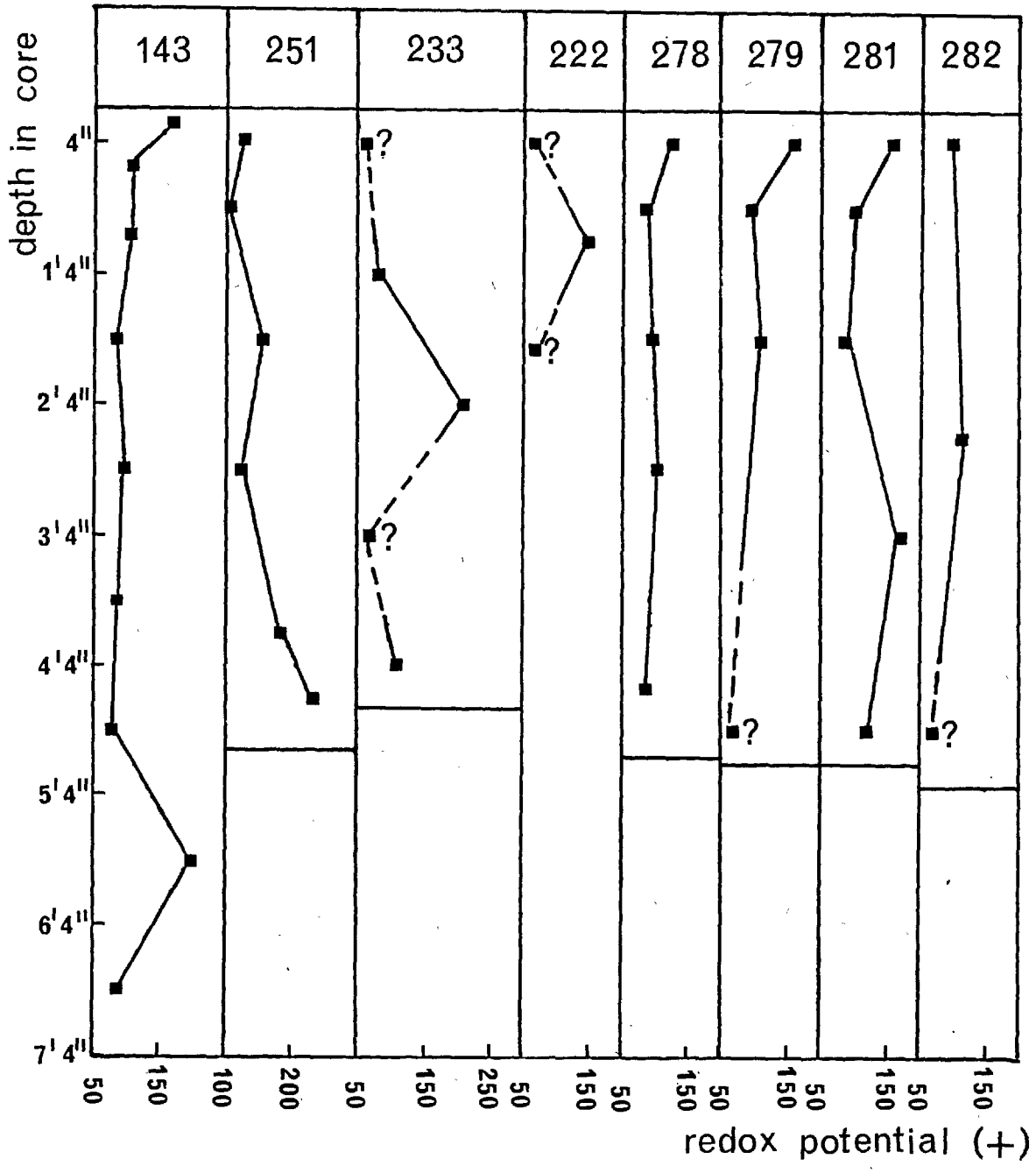


Fig.I.4.8. Changes in redox potential (mv) with depth in sediment cores; the (?) symbol represents results less than the detection limit (+67mv).

coast is approached, reaching levels less than 100mv among inner shelf silts off Cap Sim and inner shelf sands off Cap Blanc.

The Cap Sim glauconitic sediments are clearly oxidising but this need not preclude the formation of glauconite in reducing microenvironments (cf. van Andel and Postma, 1954; Emery, 1960). The prevalence of strongly oxidising conditions in the central shelf region tallies well with the concentration there of iron oxide accumulates.

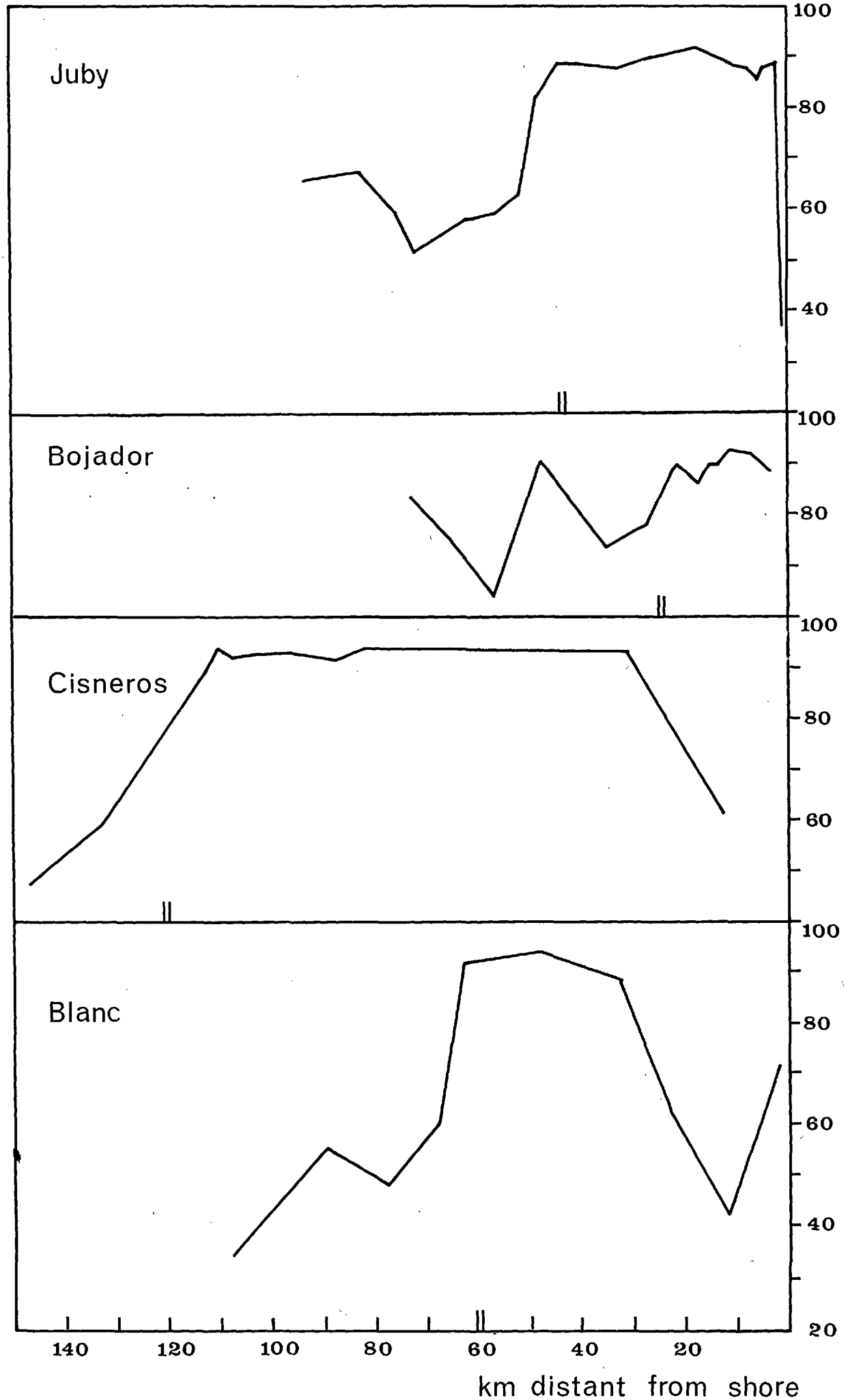
1.5 Spanish Sahara

1.5.1 Regional Sediment Characteristics:

No samples were collected from the southernmost Moroccan shelf between Agadir and Cap Juby but surveys of this area by Navarro (1947) and McMaster and Lachance (1969) show shelly sands and calcarenites to increase in prominence as detrital sands and silts decrease southward from Agadir. Between Cap Juby and Cap Bojador previous surveys by De Llarena (1950) and McMaster and Lachance (1969) show a shell regime to prevail on the shelf; this regime extends south to Cap Blanc. Among these sediments, De Llarena finds glauconite abundant as foraminiferal casts although according to McMaster and Lachance (1969) this mineral never constitutes more than about 6% of the sediments. Other mineral phases reported, apart from biogenic debris, are quartz, feldspar and zircon.

The present new reconnaissance data do not substantially change this picture, confirming that calcareous biogenic sedimentation exceeds all other over the shelf. Nevertheless, carbonate analyses show there to be a regional zonation of this component in belts of differing carbonate abundance parallel to the coast and the shelf-edge (fig. 1.5.1). Close inshore, carbonate levels are less than 90% although infrequently less than 60%. On the mid and outer shelf carbonate levels are unfailingly high, being greater than 90% on the

Fig.1.5.1. Distribution of carbonate in sediments off the Spanish Sahara : shelf edge shown by short double line.



southern part of the shelf and 85 - 95% on the northern part. Only on the slope does the rate of detrital sedimentation increase sufficiently to result in carbonate levels consistently less than 90% and frequently less than 60%. Slope sediments off the southern Saharan coast contain the largest proportion of detrital components.

Visual analyses supports a classification of slope sediments as muds or oozes whereas shelf sediments are all sands, the textures of which may differ considerably but which contain very little silt. On the upper continental slope of the northern Sahara fairly coarse sands are found, similar in all respects to adjacent outer shelf sediments.

All surface sediment samples were visually analysed for glauconite which is found to be rare, always occurring as only a minor constituent, usually as casts. It is generally more common to the shelf sediments south of Villa Cisneros than to those in the north.

Seismic profiles and P.D.R. traces discussed in Chapter 5 show the northern Saharan shelf between Caps Juby and Bojador to be extremely rugged and rocky with not much more than a thin veneer of sediment. Further south recent sediment cover thickens until, off Cap Blanc, it reaches some 17 to 35m. and results in a relatively smooth shelf profile. Presence of rock outcrops on the inner shelf suggests that recent sediment cover thins landward.

Algal stromatolites, laminated structures in which layers of calcareous sediments are cemented by films of algae (Logan, Rezak & Ginsberg, 1964), extensively coat rock outcrops at several sites off Cap Bojador (Sta. 258, 259, 260, 262, 263). These stromatolites appear to be in situ growths unlike the spheroidal algal structures (oncolites) found locally in shallow water around the Canary Islands (McMaster and Conover, 1966) although occasionally spheroidal forms are found here and off Cap Blanc in Morocco. The

Saharan stromatolites differ slightly from those off Cap Blanc in which algal layers are separated by fine laminae of detrital clastic silt. A purplish living surface layer is present in most samples. The general absence of oncolites from the northwest African shelf suggests that although the environment is ecologically suitable to algal stromatolite formation, it is not physically suited to the extensive formation of detached spheroidal forms (oncolites) such as those found elsewhere, the occurrences of most of which have been listed by McMaster and Conover (1966) with the exception of a recent record from the subtropical continental shelf off northernmost New Zealand (Summerhayes, 1969).

1.5.2 Size Fraction Analysis

Because of their anomalously high phosphate contents, four samples from the northern Saharan outer shelf and upper slope were selected for size fraction analysis and although discussed in some detail in Chapter 2, some discussion of the results is warranted here.

Binocular microscope examination was used to establish the relative proportions of different constituents (fig. 1.5.2). The coarse fractions consist chiefly of angular and broken but not always abraded molluscan debris, the remains of gastropods and some bryozoa. Some of the shell has a fresh appearance but more tends to be subangular, broken, pitted or bored, weathered and abraded. In the finer fractions, foraminifera predominate. Miscellaneous biogenic debris, never quantitatively important, chiefly consists of fish bones, echinoid fragments, algal debris.

Quartz, always in small amounts forms the major detrital constituent, and is concentrated in the fine and very fine sands. In the coarser grades are angular to subangular brown to orange rock fragments often with a dark brown glazed surface and often containing black glauconite grains. These fragments

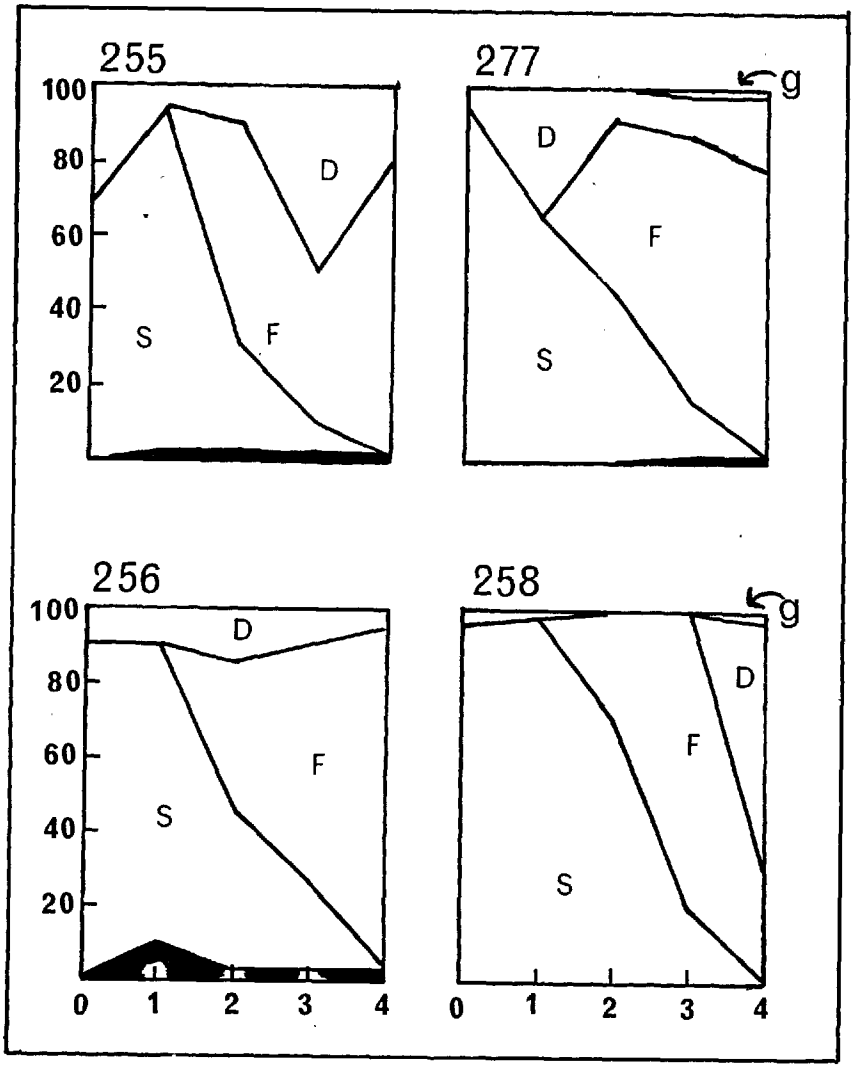


Fig.I.5.2. Results of binocular microscope coarse fraction analysis of selected Saḥaran phosphatic sands, showing percent frequency of occurrence of variables in each sand fraction (phi units).
S=shell, F=foraminifera, D=detrital rock and mineral fragments, g= glauconite, solid black area = miscellaneous skeletal debris

have all the appearances of being phosphorite or sandy to muddy limestone of detrital origin and are intimately associated with rare broken or abraded orange or yellow-brown and often glazed-surfaced biogenic skeletal remains which have the appearance of reworked fossils.

Off Cap Bojador, the proportion of brown abraded foram casts and shell fragment is highest on the outer shelf and decreases on the upper slope. Also the very fine sand grade of shelf sample 258 contains more quartz and less foraminifera than samples from the slope all of which suggests that the source of these rock and mineral fragments must be on the outer shelf. Many of the rock fragments are incorporated into the construction of agglutinated foraminiferal tests.

Some black, broken and abraded glauconitic foraminiferal casts are observed differing considerably from those pale green casts found within or partly covered by the remains of recent foraminiferal tests; both types are rare and even more rare are dark green botryoidal pellets. The recent pale green glauconites never exceed, and only rarely reach, 2% of the finest sand fractions.

Examination of the acetic acid insoluble residues of different size grades from two samples (258 from the Bojador shelf, and 277 from the Juby slope) throws more light on the nature of detrital and authigenic mineral and rock constituents. In both samples, the acid insoluble residues of coarse and medium grades contain a considerable amount of mud and very fine grade quartz thought derived from the dissolution of muddy and sandy limestone fragments noted above. Numbers of pale yellow-brown angular rock fragments resembling phosphorite, and similarly coloured or orange-brown foraminiferal casts also occur in these size grades. Because of their fine sand size the latter can only have been derived by dissolution of rock fragments, probably limestones containing foraminiferal casts. Rye (1969), has examined a

limestone dredged from the lower slope off Cap Bojador (252) and found it to be Recent but to contain numbers of abraded yellowish-brown phosphatised Lower Pliocene foraminifera possibly related to these shelly upper slope sediments. Solution of carbonate in the fine and very fine sand grades produced chiefly quartz and subsidiary feldspar with a few pale green and pale brown foraminiferal casts. The ratio of pale green to pale brown casts diminishes rapidly as the ratio of foraminifera to detritals decreases and it is assumed that most of the brown casts, though not necessarily all, were derived, as are those in the coarse fractions, by dissolution of rock fragments. The finer grades of slope sample 277 contain mainly pale green casts; pale brown casts tend mainly to occur in the coarse and very coarse grades where rock fragments are found. Obsidian and pumice fragments were obtained from the very coarse fraction of this sample.

Examination of the coarse fraction of a surface sample (280) from lower down the slope shows it to be primarily composed of foraminifera but to contain angular rock grains in which foraminifera are cemented by a pale yellow mineral; one or two pale yellow foraminifera are also observed. The acetic insoluble residue consists mainly of mud with quartz and black, shiny, irregular grains of obsidian. Small amounts of a yellow mineral which may be sedimentary apatite from the rock grains are also observed.

1.5.3 Deep Sea Photographs (Fig. 1.5.3)

Two photographic stations on the continental slope off the Spanish Sahara were successful; other stations off Morocco were unsuccessful.

Sta 253 (315 fms)

Much of the seabed is disturbed by pits and mounds reminiscent of the random burrowing actions of some organism. Ripples are locally developed and cross-rippling is notable in some of the photographs from this station.

Fig.I.5.3. Deep Sea Photographs

Plate I ; Station 253 ; depth 315 fms p.32b

a. Field of vision c.5x4 metres. Imprint of camera frame visible,top centre; generally flat bottom with minor irregularities suggestive of cross-rippling and (?) organically originated pits and mounds; edge of prominent ripple field seen, top left; note sparse weed.

b. Field of vision c.4x3 metres . Note cross rippling, sparse weed, few animal tracks, two holothurians (top centre and left centre).

Plate II ; Station 253 ; depth 315 fms p.32c

a. Field of vision c.4x3 metres . Note cross rippling, sparse weed, animal tracks, rather coarse texture of sediment between ripples.

b. Enlarged view of the holothurian seen at top centre of Plate I.b. showing well-developed cross-rippling.

Plate III ; Station 253 ; depth 315 fms p.32d

a and b . Field of vision c.4x3 metres . The slight irregularities evident on these plates suggests more widespread organic activity; small weed-like growths are apparent, and rippling is less obvious.

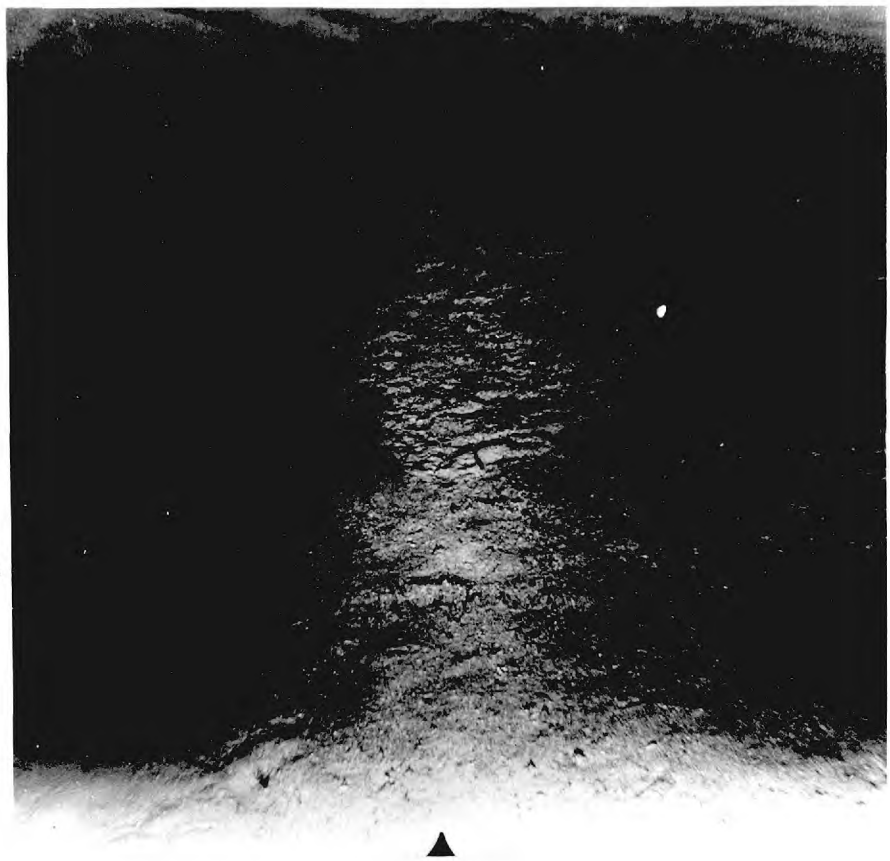
Plate IV ; Station 236 ; depth 230 fms p.32e

a and b. Field of view c.4x3 metres . Small weed-like growths are widespread; shadows suggest topographic irregularity; sediment texture seems coarse; rippling is not developed.

Plate V ; Station 236 ; depth 230 fms p.32f

Field of view c.4x3 metres. Small weed-like growths are widespread; shadows suggest marked local topographic irregularities; sediment texture seems coarse; one holothurian is seen at bottom centre.

Plate 1



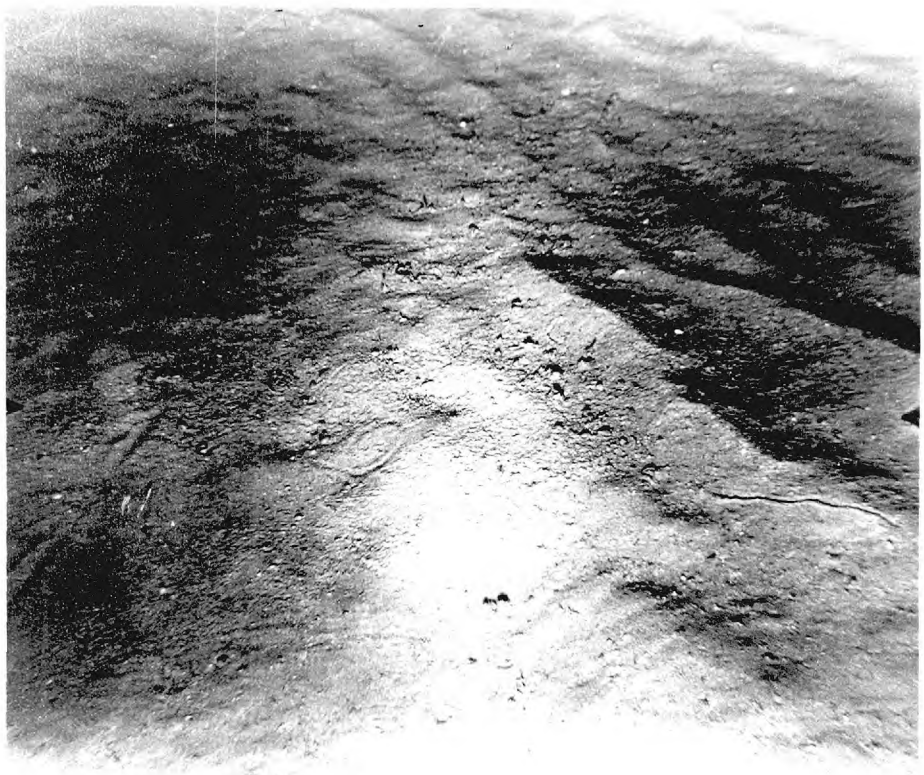
A



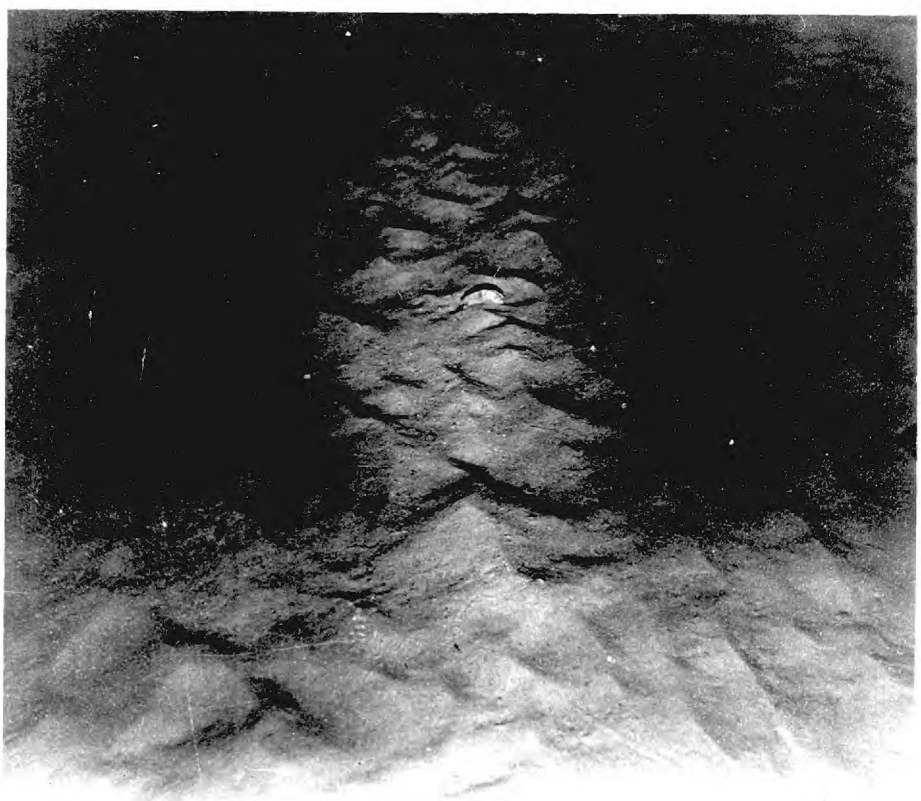
B

Pl.2

A

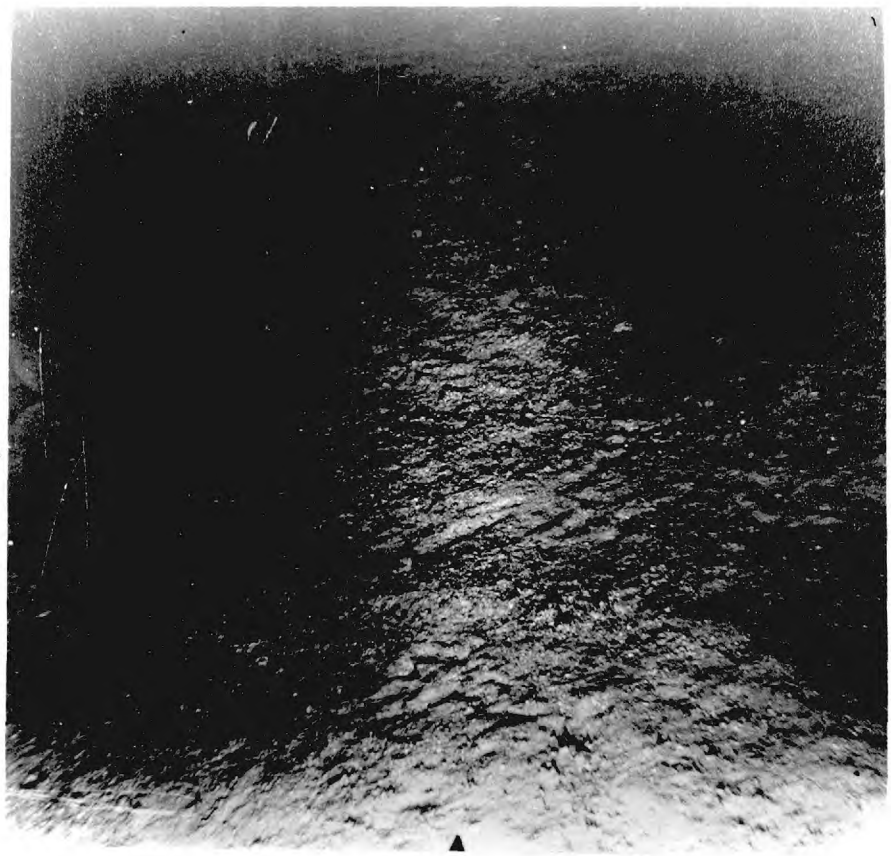


B

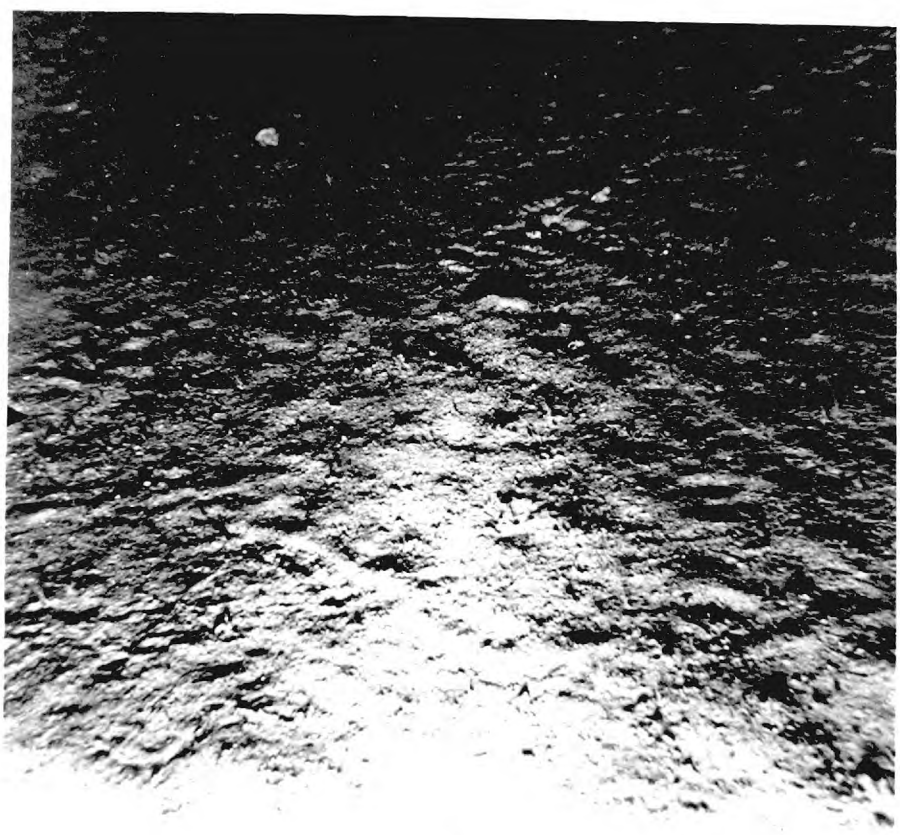


Pl. 3

A

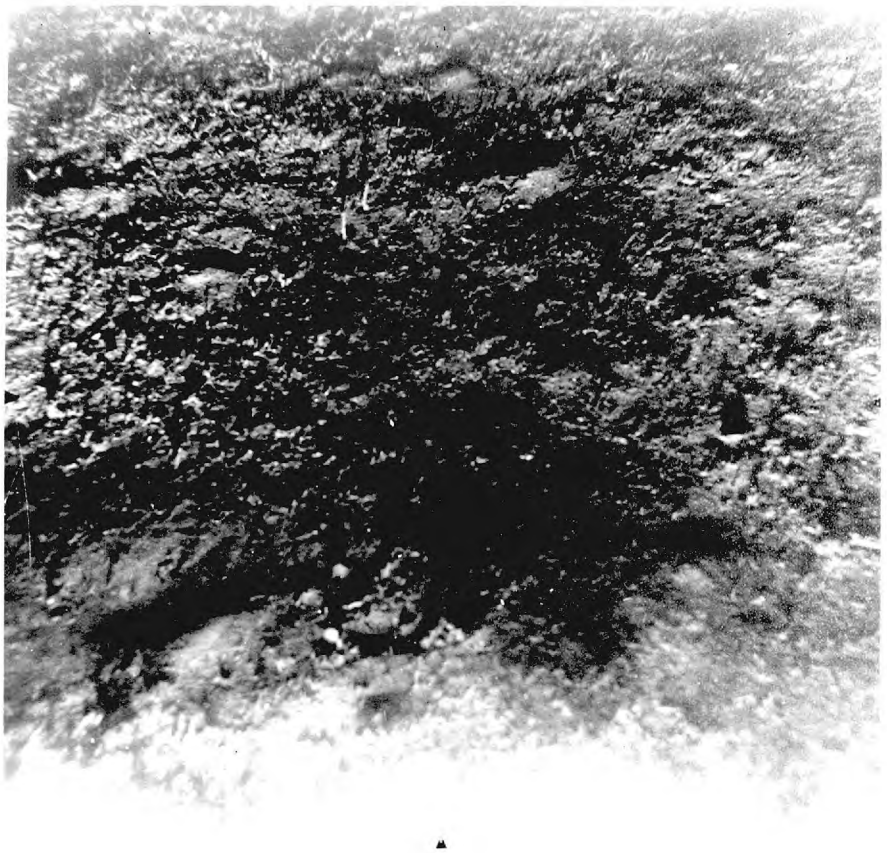


B

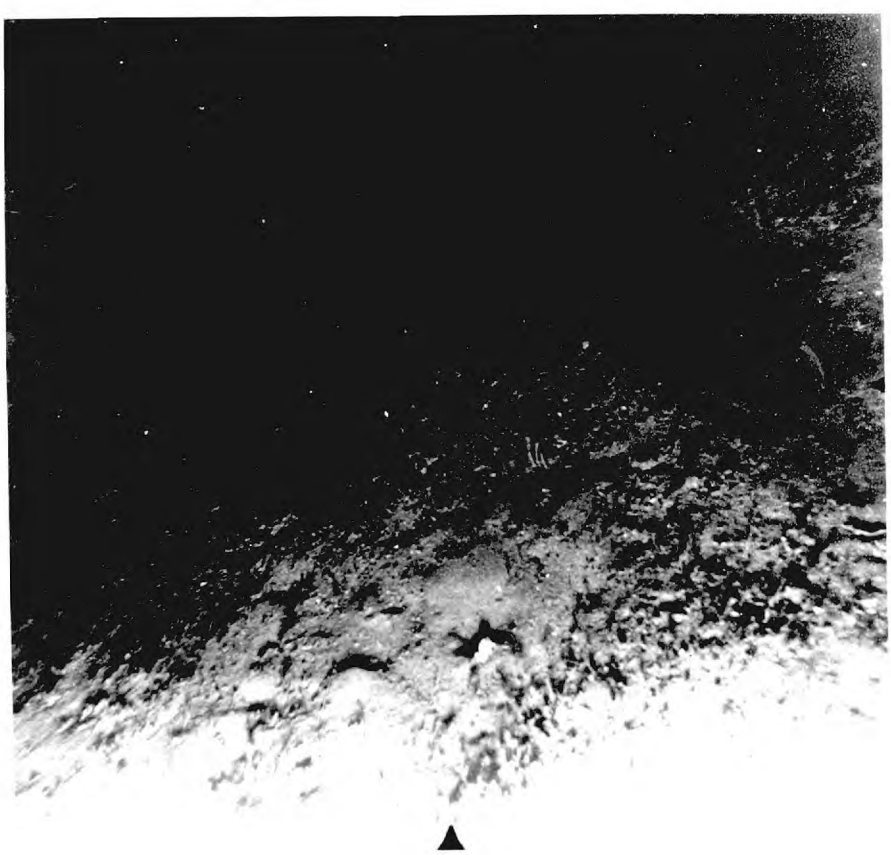


Pl.4

A



B



Pl.5



The incidence of holothurians, although low, indicates the presence of sufficient sediment for mud feeders. In part of the area covered by this station numerous small weed-like growths are observed. In other parts are seen sinuous trails representing the tracks of bottom crawling animals. The rapid change from rippled to non rippled and burrowed or weed covered seabed suggests quite sharp local variations in the velocity and or direction of bottom currents.

Sta 236 (230 fms)

The degree of irregularity of the seafloor suggests it is rather rocky as none of the observed irregularities have the appearance of biogenic origin and several of the shadows are sufficiently large to suggest the presence of steep slopes or hollows for example around boulder like objects, perhaps partly buried and veneered with sediment. Weed, in comparison with the previous station, is prolific whereas holothurians and animal tracks are not visible suggesting the absence of suitably thick sediment. Rippling is not seen which may indicate relatively slow current velocities. That the sedimentation rate must be slow, and that the rocky substrate must be near surface is independantly suggested by the steepness of the continental slope at this site and the successful dredging of rock from adjacent stations 234 and 235.

1.5.4 Redox Condition, Colour and Organic Content

Off the Saharan coast the organic carbon distribution appears somewhat more complex in that as well as there being a tendency for slope samples (most of which are silts and contain detritals in the form of silt and clay) to be richer in C_{org} than shelf samples (all of which are sands and contain predominantly sand sized calcareous skeletal debris), there is also a southward increase in the organic carbon content of both slope silts and shelf sands (fig. 1.5.4). It is clear from fig. 1.5.4 that among shelf samples

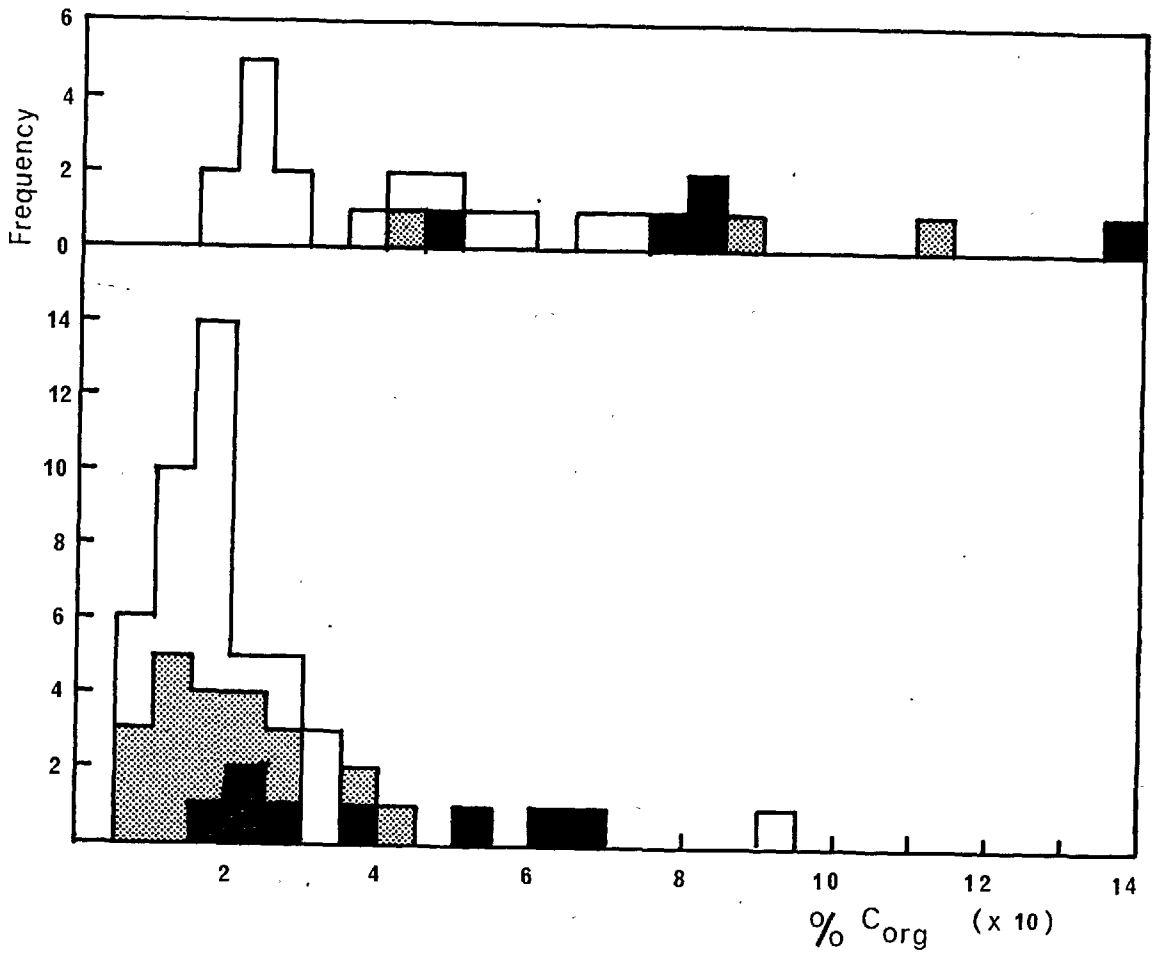


Fig.1.5.4. Organic carbon levels in Saharan sediments; black squares =Cap Blanc traverse, grey squares = Villa Cisneros traverse, others are from Cap Juby and Bojador traverses. Upper diagram = continental slope; lower diagram = continental shelf.

the Cap Blanc sediments are richest in C_{org}, the remainder showing more or less normal distribution around 0.18% C_{org}, while among slope samples, both the Villa Cisneros and Cap Blanc samples tend to be richer in organic carbon than samples further north. These changes parallel an observed change in colour and redox potential from brown and oxidising (Eh $>$ + 200mv) sediments off the northern Sahara to green and only mildly oxidising (Eh $<$ + 200mv) (cf. table 1.4.3 Fig. 1.5.5). The observed colour change most probably reflects an increase in abundance of chlorophyll derivatives such as pheophytin (cf. Pantin 1969). Significantly these changes correlate with a southward enhancement in upwelling and biological productivity (Jones and Folkard, 1968) which also appears to be reflected in the thickness of carbonate sediment accumulation on the shelf (Chapter 5).

Off the Spanish Saharan coast surface shell sand sediments generally have the same pale yellowish brown colour as those further north. Off Cap Juby, between 38 and 47m. (Sta. 267, 269, 270, 271) red brown stained calcareous sands like those between Safi and Al Jadida were dredged from among the rock outcrops of this rugged part of the shelf. This staining is typical of the iron oxide coatings observed on relict sediments of many of the world's continental shelves (cf. Emery, 1968) and Stanley (1969) suggests this is caused by their subaerial exposure during periods of lowered sea-level. Off Cap Blanc the shelf sediments sometimes have a greenish hue. All cores from the continental slope off Cap Juby and Cap Bojador are reddish brown at surface and greenish grey at depth. Further south cores off Villa Cisneros and Cap Blanc are greenish over their whole length.(Fig.2.3.2)

Within all cores (Fig. 1.4.8) there is usually a decrease in Eh below surface but at depth in cores, redox conditions fluctuate mildly such that levels are occasionally slightly more than at surface.

No well defined interrelation exists between organic carbon level and redox

potential (Fig. 1.5.5) but it is clear that at moderately oxidising redox levels (Eh $\lesssim$ + 200mv) there is a far greater range in C_{org} (0.1 - 1.2%) than at highly oxidising redox levels (Eh $>$ + 200mv; C_{org} always $<$ 0.5%).

1.6 Sedimentation History

1.6.1 Morocco

Present Day Sedimentation

Progressive seaward decrease in grain size from inshore sand to offshore silt belts as wave energy and the power of bottom currents decrease with increasing water depth most probably reflects deposition of these sediments here, as on other continental shelves, under present day conditions (cf. Curray, 1964; Shepard 1963; Emery, 1968, and many others). Supporting evidence comes from the unimodal distribution and relatively good sorting in particular of silts from both the southern and northern silt belts, suggesting good adjustment to prevailing hydrodynamic conditions. Glauconite, an authigenic mineral normally forming in areas where sedimentation is slow or negligible on the continental margins (Cloud, 1955) is not found either in the inshore sand belt or in the silt belts although it is found further offshore suggesting that sedimentation rates preclude glauconite formation at the present in the silt belt. Further, the degree of seabed smoothness and the indications of burial of bedrock topography by at least 10 metres of sediment only in the silt belts argues for more rapid and therefore probably more recent sedimentation here than elsewhere on the shelf. Moreover, assuming the Holocene rate of deposition of calcareous biogenic skeletal debris to be constant at any depth, then the observed variations between silt and sand zones most probably reflect recent or present day detrital sedimentation conditions.

As suggested by McMaster and Lachance (1969) the distribution of silt and

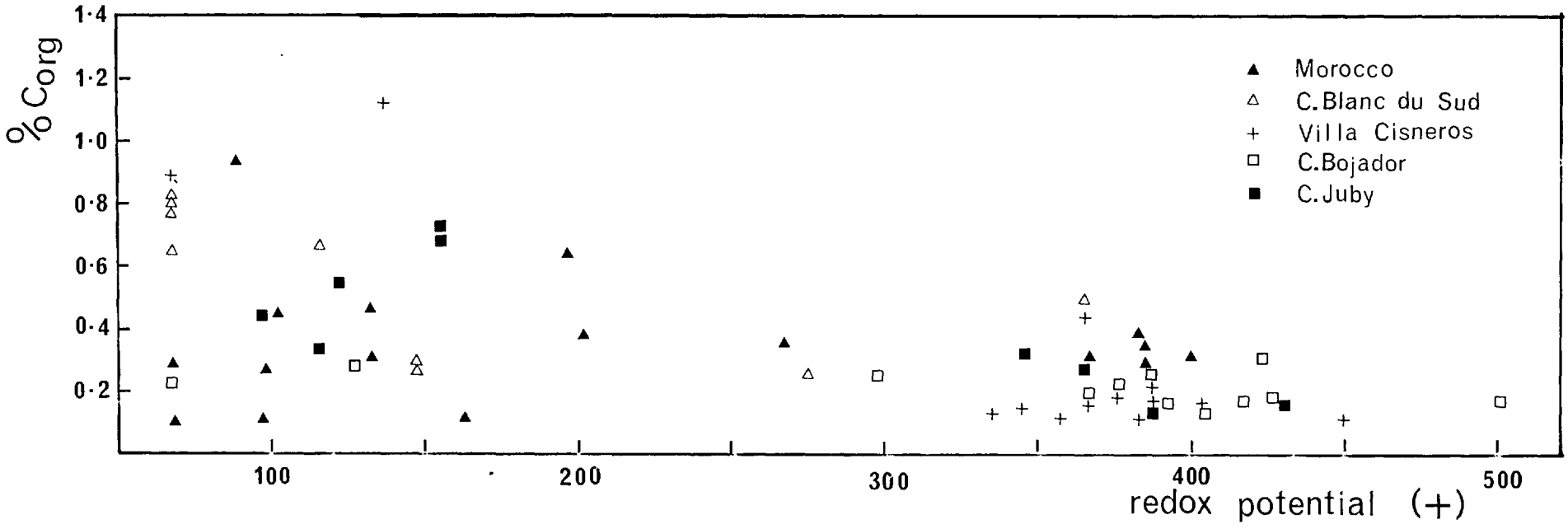


Fig.I.5.5. Variation in redox potential (mv) with organic carbon content in Moroccan and Saharan sediments.

clay on the Moroccan shelf most probably relates to present day river supply. Several small rivers reach the coast but the most notable are the Sebou near Casablanca, the Souss near Agadir, and the Tensift near Safi. The Canary Current flows slowly south in the eastern Atlantic but Sverdrup, Johnson and Fleming (1942) show that Atlantic water moves east through the Strait of Gibralter and that the greatest flow is from the south. Furthermore, Defant (1961) shows tidal currents along this part of Africa to be northwardly directed. McMaster and Lachance (1969) argue that this northwardly directed coastal system controls the dispersion of fine particulate matter on the shelf.

The manner in which the southern silt belt pinches out and becomes progressively further removed from the coast northwards suggests a southerly source, probably ultimately the Souss debouching at Agadir. The northern silt belt commences close inshore near Safi where the Tensift debouches; as it widens northwards there is a simultaneous decrease in grain size suggesting a northwardly directed transport system. These interpretations support McMaster's suggestions. That the two silt belts have different sources is suggested by mineralogical data presented by McMaster and Lachance (1969) who show the southern belt to contain montmorillonite in addition to illite, kaolinite and chlorite.

The paucity of detrital constituents in the inshore sand belt may have been induced by the drowning, during the Holocene transgression, of river channels, and the resultant formation of estuaries in which much sand sized material may be trapped or into which sand sized material may even be moving from offshore (cf. Moore, 1968; Emery, 1968; Curray, 1964).

Relict Sediments

In mid and outer shelf sediments as on most of the shelves of the world (Emery, 1968) is seen a reversal of the trend towards decreasing grain size

away from the coast. The silty sands and sands are carbonate rich and it might be argued that their grain size distributions reflect adjustment to present day depositional conditions. Several lines of evidence show that this is not the case. 1: Coarse molluscan debris characteristic of some shallower water environment are abundant here and their degree of weathering indicates deposition long since; similar outer shelf belts of weathered shallow water molluscan debris are recognised for example of the Atlantic shelf off the U.S.A. (Milliman, Pilkey and Blackwelder, 1968). 2: Granular distribution of carbonate is paralleled by the distribution of sand (although often not silt) sized detritals indicating deposition of both under the same hydrodynamic conditions. 3: The coarse detrital and biogenic constituents clearly cannot have been transported seaward over the silt belt and erosional processes on the outer shelf and upper slope are known to be inadequate to transport and abrade detrital minerals of sand grade (Sverdrup, Johnson and Fleming, 1942; Kuenen, 1950; Shepard, 1963). Therefore these shelf edge and outer shelf detrital sand concentrates are considered to reflect wave energy processes of some lowered sealevel (cf. Emery, 1968; McDougall and Brodie, 1969; Summerhayes, 1969). Comparison of textures with those of shallow water detrital sediments of sand grade shows they were probably deposited in similar nearshore high energy environments. 4: The subangular, subrounded and sometimes angular character of the detrital components and their association with pebbles and granules indicates local derivation by erosion of shelf outcrop rather than blanketing by the movement of sediment into the area from elsewhere. 5: Foraminifera on the outer shelf are infrequently abraded suggesting deposition in water less disturbed than that prevalent when the molluscan remains were broken and abraded. 6: That sedimentation on the mid and outer shelf where sands have accumulated is slow is evinced both by the presence of rugged topography and the abundance there of glauconite particularly within foraminiferal tests.

Indeed the available evidence suggests that the characteristics of mid and outer shelf sediments reflect an original depositional environment in water shoaler than that at present and subsequent preservation of these sediments by some degree of current winnowing which has prevented burial by a silt blanket. These sand sized detritals can be classified as relict in agreement with Emery's findings that about 70 per cent of worldwide shelf sediments, particularly those on the outer shelf, are relict.

Many sediments, particularly mid and outer shelf sands and silty sands, are polymodally distributed and show signs of mixing of recent silts with relict sand populations. Mixing most probably occurred during the progressive migration of the strand line across older shallow water pebble and coarse sand deposits which became reworked and mixed with finer sediments deposited in quieter water in the wake of Pleistocene transgressions. In the Gulf of Mexico, Curray (1960) and van Andel (1960) find the silt and clay dispersion pattern to be independant of sand dispersion, sands being only deposited at present close inshore whereas silt and clay derived nearshore or from the coast are dispersed on the outer shelf and slope. Curray (1960) also points out that the low rate of deposition of fines on the shelf allows time for considerable mixing with the original sands both by current action and bioturbation resulting in polymodal grain distributions in individual samples. The present findings indicate similar depositional mechanisms on the Moroccan shelf,

On the continental slope off Cap Sim are sands and silty sands which have, like the silty sands of the shelf, originated by mixing of later silt with coarser detrital sands. The silts are everywhere thought more recent by virtue of the stronger currents required to move sand grains. Sands on the ridge crest probably derived from erosion of the ridge near sealevel at some time in the past; downslope slumping has transported these coarser materials

from the shelf and from the ridge crest into deeper water where they are now mixed with silts on the ridge flanks. The ridge crest is, at 260m. water depth, not much below the lowest Pleistocene sealevel stand and, in view of the recognised tectonism of this region, it is quite likely that downwarping has been the main cause of sinking of the ridge crest. Because of the morphology of the ridge, topographically induced current activity has winnowed out fine material which accumulates elsewhere on the surrounding slope.

The localised decrease in detrital silt at the continental shelf edge is a commonly recognised phenomenon (Kuenen, 1950; Shepard, 1963, Emery, 1968) and most probably reflects the winnowing effects of shelf edge oceanographic phenomena such as the turbulence caused by the confinement of landward moving tidal currents, and the formation of internal waves at the shelf edge (Sverdrup, Johnson and Fleming 1942; Defant, 1961). It is unlikely to reflect a decrease in supply of detrital silt since silts are abundant on either side of the outer shelf sand zone and the sands of this zone frequently contain subdominant silt modes reflecting recent supply. Then too, the sand zone appears to be consistent with the geomorphology and not with the distribution of silt belts which tend to be angled across the shelf and would be expected to cross the shelf edge at some point.

Glauconite Origins

The finding of abundant oxidised glauconite off Rabat and to a lesser extent off Cap Sim (Bell and Goodell, 1967) and the K.Ar ages of separated Cap Sim glauconites suggests that much of this material represents late Tertiary deposition, probably in a similar geologic setting to the present one. Oxidation is presumed to have occurred during Pleistocene reworking and may be continuing. Bell and Goodell (1967) also assumed that the mineralogical differences between the glauconite and the associated clay signified derivation from a different source. The validity of this assumption is open to

question since there are a number of opinions on the formation and parent material of glauconite. Galliher (1935) favours biotite; Takahasi (1939) some ferro-alumino-silicate gel; Burst (1958) and Hower (1961) favour degraded illite/montmorillonite; Pantin (1966) points to rock replacement; calcareous skeletal replacement is widely recognised and found in some of the rock samples studied here (Chapter 6); moreover, Porrenga (1967) and Seed (1968) in finding no relation between marine glauconites and associated clays do not regard this as at all significant with respect to the age of glauconites in other environments.

With regard to the present formation of glauconite (rock coatings and foram fillings) a range of redox potential must be present in the environment to allow coexistence of ferric and ferrous iron, both of which are present in glauconite in significant amounts (cf. Burst, 1958) and it must be supposed that this mineral forms in locally reducing microenvironments within generally oxidising sediments (cf. Burst, 1958; Hower, 1961; Pantin, 1966). While there is no abundance of iron minerals in the associated sediments, a sufficient concentration of this element exists in continually circulating seawater to provide a source for the iron enrichment characteristic of glauconite. Ferric oxides in seawater are probably transported mainly as adsorbed hydroxide phases on organic colloids (cf. Cooper, 1948) and Pantin (1966) has suggested that where the total supply of organic material to the sediment is low, bacteria will flourish particularly in suitably protected microenvironments such as faecal pellets and foraminiferal tests, whence they would scavenge the vagrant iron bearing organic constituents of seawater. At the intermediate levels of redox potential expected in such an environment, reduction of ferric iron would occur, then, either by combining directly with dissolved potash and silica, or by reacting with detrital aluminous illite, or other suitable mineral phases, the glauconite would be formed (cf. Pantin, 1966). In view of the local paucity of clay in certain

glauconite-rich sediments Seed (1968) concludes that .....'A theory of precipitation from solution in the special environment offered by a calcareous host cannot be ignored..'

Certainly where glauconite is abundant (Cap Sim) the organic content is higher than where oxidised glauconites abound. This tends to suggest that the oxidation reflects present rather than past conditions such as subaerial Pleistocene erosion and oxidation as implied by Bell and Goodell (1967). On the basis of this survey it seems that much of the glauconite is detrital but that the present environment off Cap Sim is still suited to glauconite formation which in fact may be proceeding. The lighter green colour of casts probably reflects this situation as Ehlman, Hulings and Glover (1963) find pale green casts elsewhere to have a more expandable lattice, less K and more H_2O, and thus to be less mature than dark varieties of this mineral.

The high redox potential and generally brown colour of Moroccan sediments is taken to indicate adsorption of ferric hydroxides which only occasionally are reduced at depth in cores, giving rise to an olive hue (cf. Pantin, 1966; Stanley, 1969). Rather than being the result of subaerial exposure (cf. Stanley, 1969) the iron oxide formation on the central shelf is taken to be a Recent marine phenomenon relating to the redox conditions of the environment.

1.6.2 Spanish Sahara

Despite the sparse sampling coverage and lack of detailed examination of Spanish Saharan continental margin sediments, certain conclusions can be drawn regarding the sedimentation history of this region.

The abundance of fine sand grade quartz in outer shelf and upper slope sediments off Caps Juby and Bojador is interpreted in terms of deposition

near some low sealevel stand, since their grain size is typical of shallow water sands from high energy environments known at the present time (cf. Moore, 1968; Summerhayes, 1969) and it is difficult to see how they could be transported seaward across the rugged shelf at present. In agreement with this suggestion, weathered and abraded molluscan fragments and subrounded and subangular rock fragments with characteristics of shallow water high energy environments are also abundant on the mid and outer shelf. That the rock fragments are probably local is inferred from the fact that they are highly phosphatic whereas other shelf sediments are not (Chapter 2). Formation of a dark brown glaze on these detrital rock fragments predates coating by recent algae implying, if the glaze is phosphatic, that phosphate formation is not here a recent phenomenon. Then, too, the oxide staining of north Saharan sediments (shell and detritals) implies a substantial lapse since their deposition. These characters all argue for the relict nature of the mid and outer shelf sediments. By contrast, detrital minerals (predominantly quartz) which form a notable contribution to inner shelf sands in an environment where recent sediment movement is likely to be active, may be derived by present day coastal erosion.

Offshore from Cap Blanc is an inner shelf belt of detrital rich sediments which forms the northern extension of an extensive belt of detrital sands covering virtually the whole of the shelf off Mauritania (McMaster and Lachance, 1969). Why this should not have been obscured by the accumulation of more recent biogenic skeletal debris is not clear in view of the acknowledged southward increase in organic productivity unless windborne sand is a major contributor. Alternatively, the upwelling productive water at the continental margin may be sufficiently depleted in nutrients by the time it reaches the inner shelf that it cannot support a large enough organic population to provide much in the way of recent biogenic skeletal debris. Jones and Folkard (1968) show that nutrient rich upwelling water does not extend

right across the shelf.

On the continental slope carbonate levels are lowest in the south implying that, if organic productivity and therefore carbonate biogenic sedimentation is constant, as appears to be the case, the rate of detrital sedimentation must be increasing. This correlates with the increased incidence of dust storms which are both frequent and westwardly directed off the southern Saharan coast (Radczewski, 1939), and is being followed up by J.D. Milliman of Woods Hole Oceanographic Institution.

The local presence of glauconite (cf. Cloud, 1955) argues for very slow conditions of sedimentation and its preservation within unabraded foraminiferal tests (this section, and De Llarena, 1950) implies formation subsequent to commencement of the Holocene transgression either now or in the not too distant past.

In the absence of river supply it is argued that there are four major contributions to the non biogenic mineralogy of relict and recent sediments in this region; 1. shelf bedrock erosion and the deposition of in situ sand sized debris; 2. coastal erosion and longshore transport; 3. volcanic dust and ash from the Canaries; 4. windblown sand and dust from the Sahara. Whatever the dominant supply it is clear from visual inspection of samples that the finer detrital constituents predominate on the slope while most of the detritals on the shelf are coarse components; this is expected to become apparent in analysis for trace metals (Chapter 3).

CHAPTER 2

THE DISTRIBUTION, MODE OF OCCURRENCE AND ORIGIN OF PHOSPHATE IN SEDIMENTS

2.1 Introduction

In order to test the hypothesis, of which McKelvey is a chief protagonist (McKelvey, 1963; 1967; McKelvey and Chase, 1966), that Recent authigenic phosphates may be forming on the seafloor off the coast of northwest Africa, the distribution and mode of occurrence of phosphate in certain northwest African continental shelf and slope sediments is examined in some detail. Discovery off Morocco of a phosphatic 'nodule' reported by Murray and Chumley (1924) tended to lend a certain amount of credence to McKelvey's concept but other marine geological studies in this region (McMaster and Lachance, 1969; De Llarena, 1950; and Navarro, 1947) were concerned primarily with faunal and textural characteristics and not in detail with mineralogy and there are apparently no other reports of phosphate minerals from the sediments off Morocco or the Spanish Sahara. Apart from the possibilty that authigenic apatite may be found within the Recent sediments, previous writers do not seem to have considered that some contribution of detrital phosphate minerals may be expected from the extensive onshore Cretaco-Eocene phosphorite deposits. Furthermore the hitherto unsuspected outcrop of phosphorites on the seafloor may be considered as another source of detrital phosphate minerals at least during the Pleistocene regressions.

In this chapter the regional, textural and mineralogical controls of phosphate distribution are established and the degree of correlation between relict and recent sedimentary phosphate with potential phosphate sources including rock outcrops and upwelling is investigated. The data obtained

from the Moroccan shelf between Essaouira and Agadir during the compilation of this report are considered in combination with data obtained by Nutter (1969) during a complementary and contemporaneous study of the Moroccan shelf and slope sediments north of Essaouira. In a second section of this chapter the results of a further study on the distribution of phosphate in Spanish Saharan continental margin sediments are examined.

Analytical techniques used for phosphate determination and employed in this study are described in some detail in Appendix 2. Essentially, colorimetric analyses using the vanado-molybdate technique were carried out on total sediment samples, subsamples taken at 6cm intervals from sediment cores, different size fractions of selected surface sediment samples, and on mineralogical separates from further selected samples.

2.2 Morocco

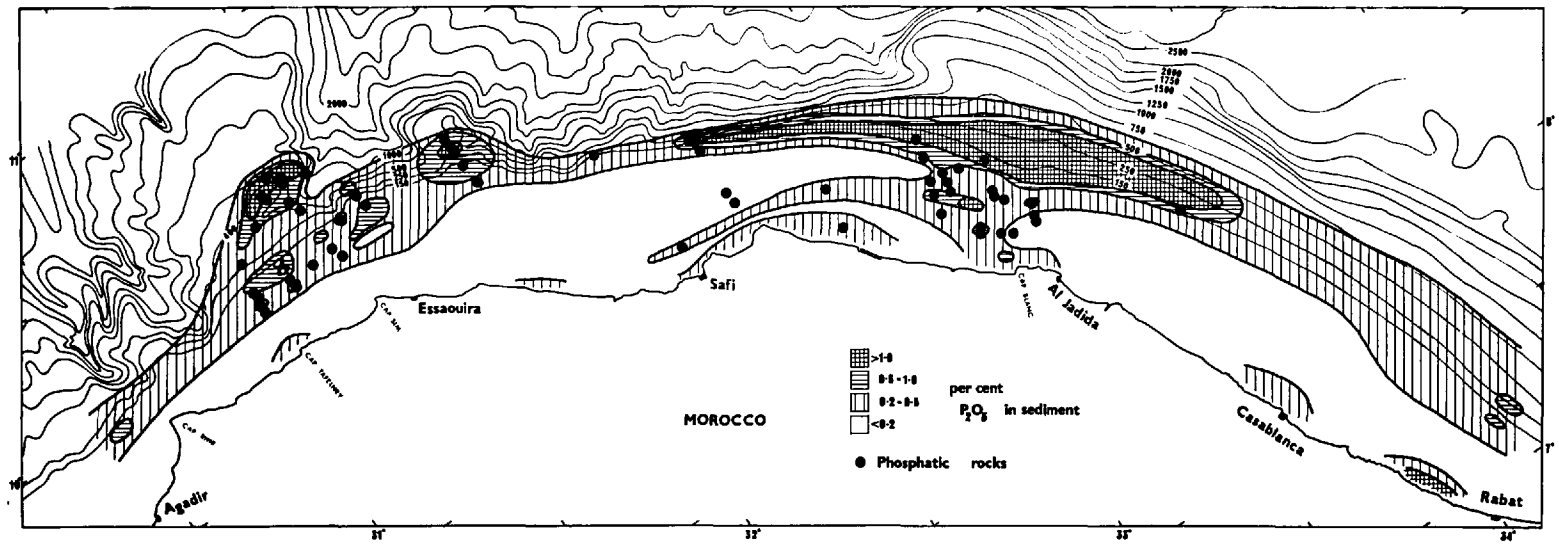
2.2.a Regional Distribution of Phosphate:

1. In Surface Sediments

Phosphate between Essaouira and Agadir is found to be concentrated in a narrow outer shelf and upper continental slope zone apparently continuous with that delimited by Nutter (1969) between Essaouira and Rabat (Fig. 2.2.I.). Phosphate contents on the inner shelf and outer slope in the present study area are mainly less than 0.2% P_2O_5, averaging 0.15% P_2O_5; lowest recorded values are about 0.09% P_2O_5. These phosphate levels are comparable with average P_2O_5 values quoted by Turekian and Wedepohl (1961) of 0.16%, 0.04%, and 0.09% for shales, sandstones and limestones respectively. The shelf edge zone of anomalous concentration appears best delimited by the 0.2% P_2O_5 isopleth. For most of its extent between Essaouira and Agadir it is confined approximately between water depths of 90 and 500m. although off Cap Tafelney the zone bulges seaward and extends further downslope, possibly as deep as

Fig.2.2.1.

Distribution of phosphate (as per cent P_2O_5) in sediments off Morocco, and the location of sites at which phosphorites or phosphatic limestones were dredged. Sediment phosphate data from north of Safi taken from Nutter (1969).



1250m. although without detailed sampling, definition is impossible. Within the phosphate zone are isolated patches where the phosphate content exceeds 0.5% P_2O_5 and in which values may exceed 1.0% P_2O_5, but never 2.0% P_2O_5 south of Essaouira. A discontinuous group of these maxima occurs on the outer shelf, and two further maxima are recorded from topographic highs on the uppermost slope. Nutter (1969) showed there to be a pronounced maximum on the outer shelf between Safi and Casablanca where phosphate levels were found to reach 7.88% of P_2O_5. In addition, Nutter (1969) demonstrated the local existence, between Al Jadida and Safi, of a mid-shelf phosphatic sediment zone which was not found by the writer south of Safi. In both studies, a discontinuous inshore zone of slight phosphate enrichment was also discovered immediately adjacent to the coast.

In relation to texture (compare Figs. 1.3.1 and 2.2.1) it is evident that the phosphatic sediments are essentially sands although not all sands are phosphatic: an extensive region of non-phosphatic sands for example occupies much of the mid-shelf region between Cap Sim and Cap Blanc. The silts are not phosphatic although some of the silty sands, particularly on the outer shelf and upper slope may be so. It has been established both in Chapter 1 for the region south of Essaouira, and by Nutter (1969) for the northern region, that the sands are essentially relict and originated during former low stands of the Pleistocene sea, whereas the mid-shelf silts appear to represent a sediment blanket relating most probably to the present hydrodynamic conditions. The absence of outer shelf and upper slope silt, and locally even of mid-shelf silt, is thought to reflect interaction of sediment dispersal patterns and local incidence of current induced turbulence which, particularly at the shelf edge may have prevented settling of fines (Chapter 1). That the outer shelf sand belt represents a region of slow or negligible Recent sedimentation implies that conditions may be ideal for the formation of authigenic phases such as apatite. As shown in the previous

section, this is in fact an environment where authigenic glauconite does appear to be forming or has recently formed within the tests of unabraded and thus probably post-Pleistocene foraminifera. Nutter (1969) and Matthieu (1968) also find evidence for the formation of glauconite in outer shelf and upper slope sediments north of Essaouira. It should be emphasised that although apatite and glauconite are often associated in authigenic deposits, this association is not ubiquitous and certainly not genetic (cf. Carozzi, 1960), and the association of glauconite with phosphate in these Moroccan shelf edge deposits may be fortuitous. Besides that thought to be presently forming, much of the glauconite appears to be detrital and not authigenically forming at present.

Within the outer shelf sands occur angular to subangular sand and pebble sized rock fragments of limestone, mudstone and some brown rock with similar lithology to adjacent outcropping phosphorite. For instance, in the Essaouira-Agadir section, glauconitic phosphorite fragments are particularly common while Nutter (1969) finds a more iron stained brown variety which apparently does not contain glauconite. These differences reflect the known differences in lithology of outcropping rocks (Chapter 6).

2. In Sediment Cores

A series of eight cores were collected from the continental slope immediately seaward of the phosphate zone and one from the seaward edge of the phosphate zone (core 811). It must be borne in mind that the topmost sample from a core may not necessarily represent the sediment - water interface since cores are often subject to some degree of surface disturbance and washing during recovery. Nevertheless the vertical variations in phosphate content observed in these cores do reflect real variations in the original environment and can be used to ascertain its depositional characteristics. The cores group into those showing virtually no variation and containing very little phosphate, and those near the phosphate zone containing, at depth,

substantial amounts of phosphate.

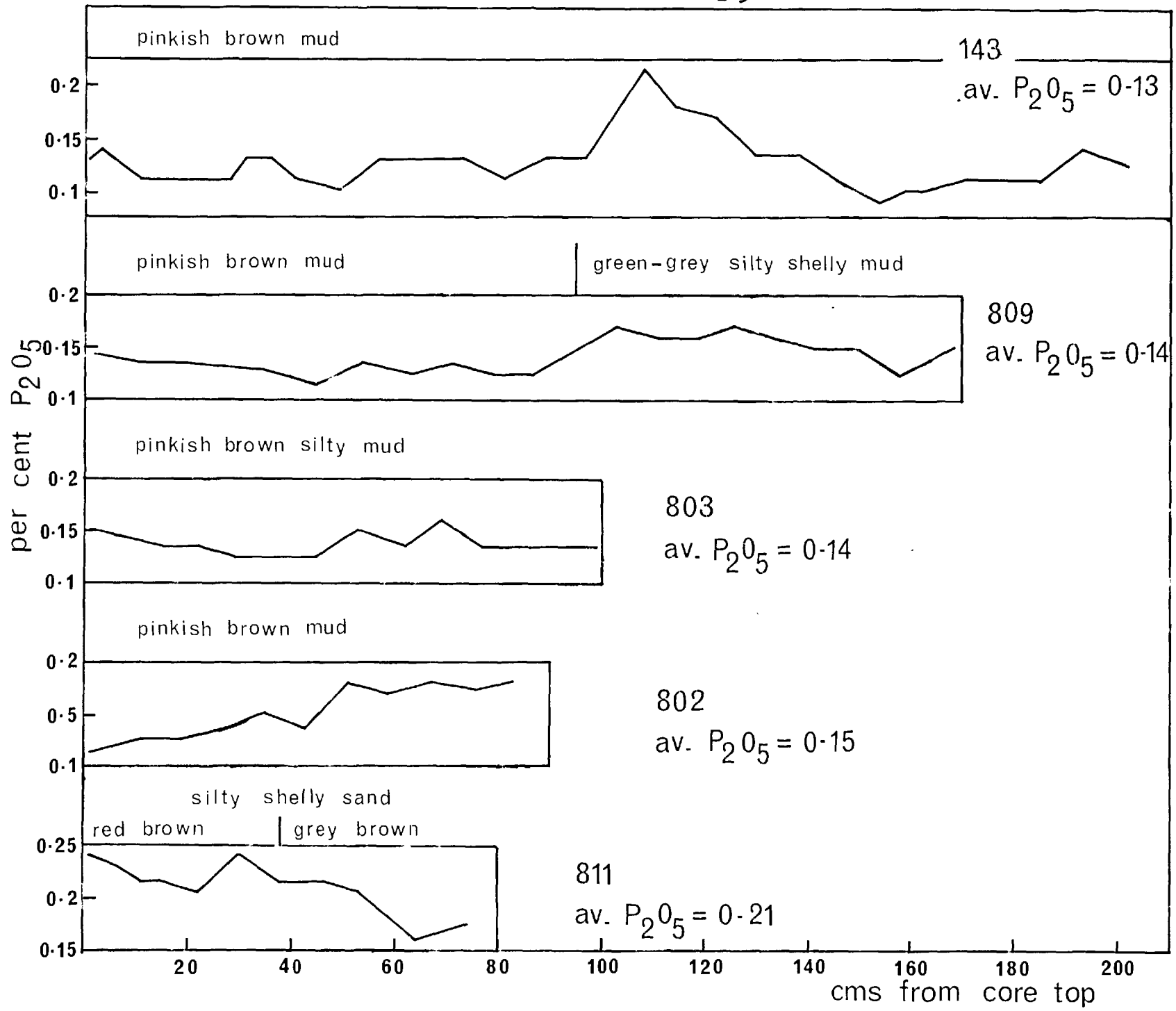
In core 811 collected from the upper slope within the phosphate zone is a decrease in phosphate with depth coincident with a decrease in the abundance of glauconite (Fig. 2.2.2). Mud cores 802, 803, 809 and 143 from the slope seaward of the phosphate zone show no tendency for systematic changes in phosphate with depth (Fig. 2.2.2). An abrupt change at depth in core 809 relates apparently to texture, phosphate increasing with increasing coarseness. No textural change was observed with the abrupt increase in phosphate at depth in core 802 nor at 130m.depth in core 143 but the possibility exists that these changes reflect minor unobserved textural and thus mineralogical changes.

The remaining cores contain much more phosphate (Fig. 2.2.3). Cores 843 and 844 from intermediate depths on the continental slope show phosphate variations which distinctly relate to textural and mineralogical changes. In core 843, phosphate increases with depth as the sediment changes from surficial sandy mud to a glauconitic sand. Over most of the length of core 844 it is a slightly glauconitic mud in which phosphate levels are uniformly low, but, below 20cm. depth phosphate increases as the mud becomes increasingly glauconitic and reaches maximum values at a glauconitic sand horizon.

Cores 868 and 879 (Fig. 2.2.3) were collected further north from an embayment separating the phosphatic zone on the outer shelf from that on the slope. In core 868 phosphate increases abruptly at depth when the texture becomes sandy and the composition glauconitic. Phosphate in the other core 879 is highest at sand or sandy mud horizons which are frequently glauconitic, and greatest where angular brown rock granules with the appearance of phosphorite are observed in subsamples.

The phosphate contents of the mud horizons in all cores do not differ much

Fig.2.2.2. Sediment characteristics and phosphate levels (%P_2O_5) in Moroccan cores.



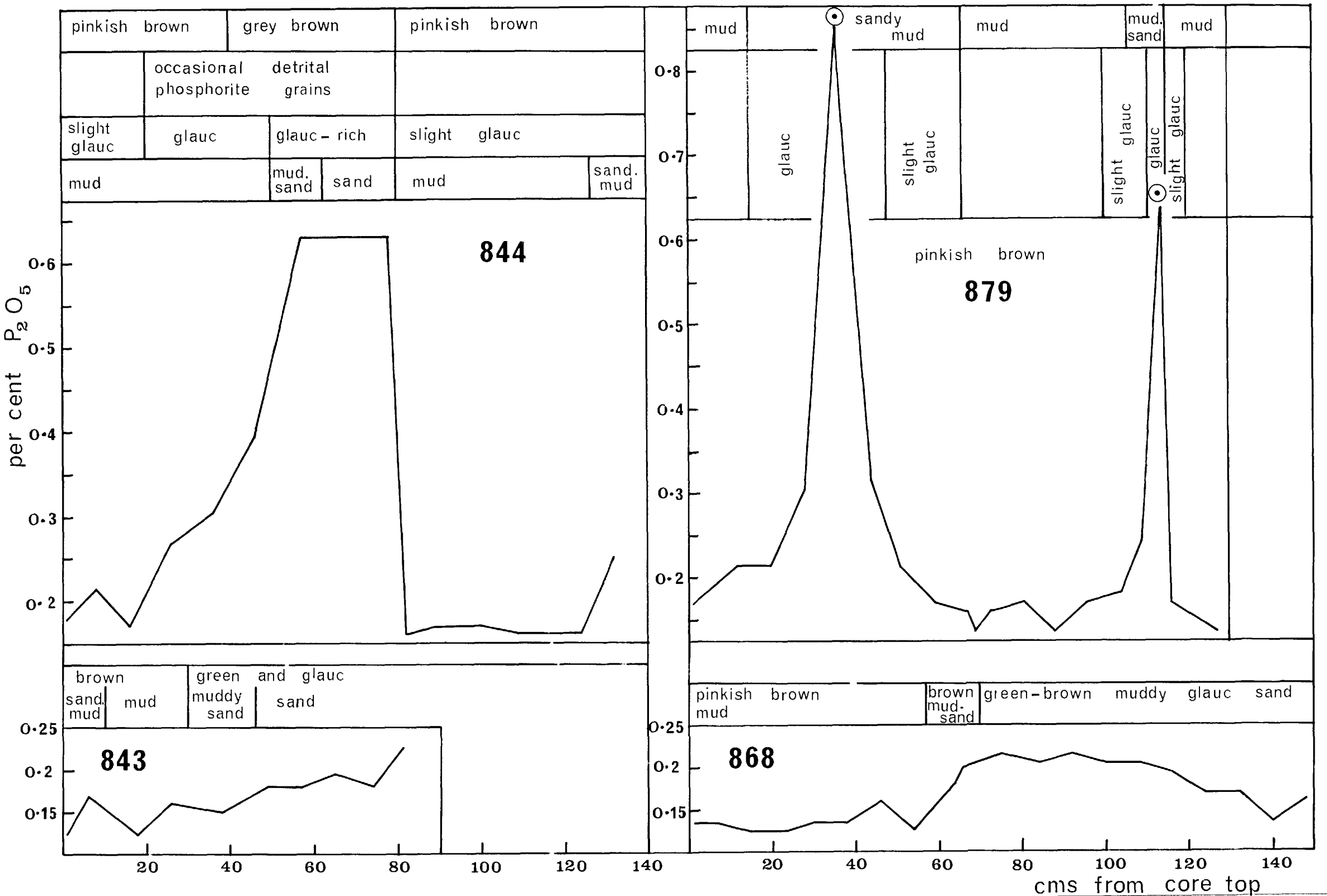


Fig.2.2.3. Sediment character and phosphate levels in cores from the south-central Moroccan area; symbols at the phosphate peaks represent occurrences of brown angular detrital granules of phosphorite.

from the worldwide average for shales, which tends to militate against any significant degree of Recent apatite formation within the sediments. Similarly, the lack of any systematic increase in phosphate with depth argues against the diagenetic formation of apatite from pore fluids within the sediment.

The glauconitic sand horizons exhibit graded bedding indicative of movement of these sediments from some relatively high energy depositional environment into a low energy environment where muds are the norm. The fact that the glauconitic horizons are phosphatic implies derivation by irregular downslope mass movement of sediment from the phosphatic-glauconitic-sandy sediment zone of the outer shelf and uppermost slope.

Similar findings to these, that there was generally no variation in phosphate content with depth in cores except as between silt and sand layers, the latter usually being seen to contain grains or granules of detrital rock fragments identified as phosphorite, were obtained by Nutter (1969) on examination of cores from the shelf and slope off north Morocco. The silt cores there, like those from south central Morocco, contain levels of phosphate not significantly different from worldwide shale averages (c.f. 1% P_2O_5).

2.2.b Intrasediment Phosphate Dispersion

In order to assess the interrelation between phosphate and other sediment components, sediments off Cap Sim from traverse 5 were subjected to size fraction analyses in which the phosphate, carbonate and non-carbonate contents of the very coarse, coarse, medium, fine and very fine sand, silt and clay fractions (Wentworth grade) were determined. Owing to the interesting results from these analyses, the sand fractions only (for reasons which will become apparent later) were analysed from a further series of samples from the south central Moroccan phosphatic sediment zone. All analyses were

performed on glauconite-free material because the glauconitic fraction is, as discussed later, a virtually non-phosphatic mixture of both detrital and authigenic material. The acid-insoluble non-carbonate phase is taken to represent, in the main, the clastic detrital mineral contribution to these sediments, and will be referred to as the 'detrital' phase.

Nutter (1969) carried out a comparable size fraction investigation of phosphate dispersion in sediments from traverses 10, 14, 15, 22, but other than making visual comparisons between frequency distribution curves for phosphatic and non-phosphatic components did not have time to consider in detail the interrelations between these sediment constituents. Accordingly Nutter's data are reappraised here together with that from south central Morocco.

For clarity and convenience, rather than presenting for consideration the individual grain size curves for each sediment sample, the data are condensed into single diagrams representing individual size fractions of all analysed samples. Firstly (Fig. 2.2.4) the concentration of phosphate in each fraction (P_2) is considered with respect to the total phosphate content of the sediment (P_1). In each of the different sand size fractions there is a clear interrelation between P_1 and P_2, which increase linearly with respect to one another. By complete contrast there is no such interrelation between P_1 and P_2 within either the silt or the clay fractions, the phosphate contents of which are more or less constant and always low.

Significantly the phosphate levels in the silt and clay fractions are usually <0.2 per cent P_2O_5 and of the same order of magnitude as the values for poorly phosphatic silts outside the phosphate zone, and for worldwide shales (0.16 per cent P_2O_5). It has already been established (Chapter 1) that the silt and clay fraction probably represents later admixture, during the Holocene transgression, of fine material with mainly relict sand. These present data imply that the fines probably have some common provenance with

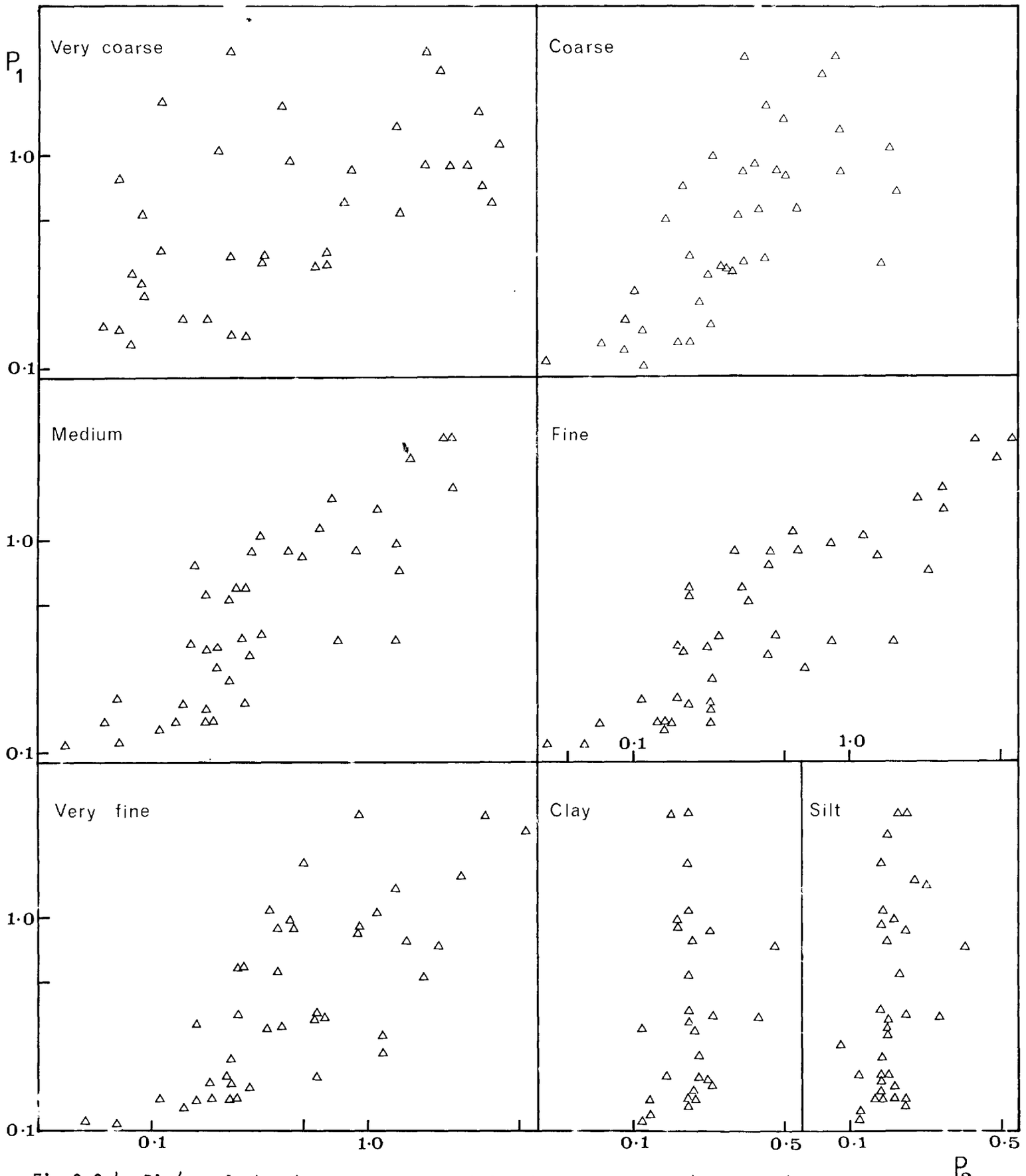


Fig.2.2.4. P1 (total phosphate, as percent P_2O_5, in the sediment) vs. P2 (, phosphate, as percent P_2O_5 in each separated sand fraction, silt and clay).

more or less uniform P_2O_5 content which is preserved regardless of depositional environment. It has also been established in this chapter that phosphatic sediments are sands or silty sands and the present data show their phosphatic components to be predominantly sand sized: variations in total phosphate are evidently caused by variations in the abundance of sand sized phosphatic constituents.

As above, instead of considering the interrelation between detrital and phosphate size fraction histograms in each sample, data for individual size fractions of all samples are presented for ease of consideration in single diagrams (Fig. 2.2.5).

The examination of single sample granulometric distribution curves (effectively summarised in Fig. 2.2.5) for phosphate and detrital constituents shows (as also pointed out by Nutter) a degree of parallelism in dispersion which suggests subjection to the same sediment dispersal conditions in the depositional environment. Despite the fact that there is a somewhat more broad scatter than for phosphate alone (cf. Fig. 2.2.4) it is clear that there is a linear relation between the phosphate/detrital ratio in each sand fraction and the total sediment phosphate. It should be emphasised that since the 'detrital' material represents the phase not dissolved in HCl, its abundance should not be influenced by the presence of apatite which is soluble in this acid. Again, as for phosphate alone, the phosphate/detrital ratio in silt and clay (Fig. 2.2.5) is more or less constant regardless of sediment type or the total phosphate content. These data can only be interpreted meaningfully in terms of the previously observed subparallelism between phosphatic and detrital grain size distributions. They imply that, in general terms, where detritals increase so too does phosphate; that there is a general linear interrelation implies subjection of these two phases of the sediment to similar dispersal mechanisms in the depositional

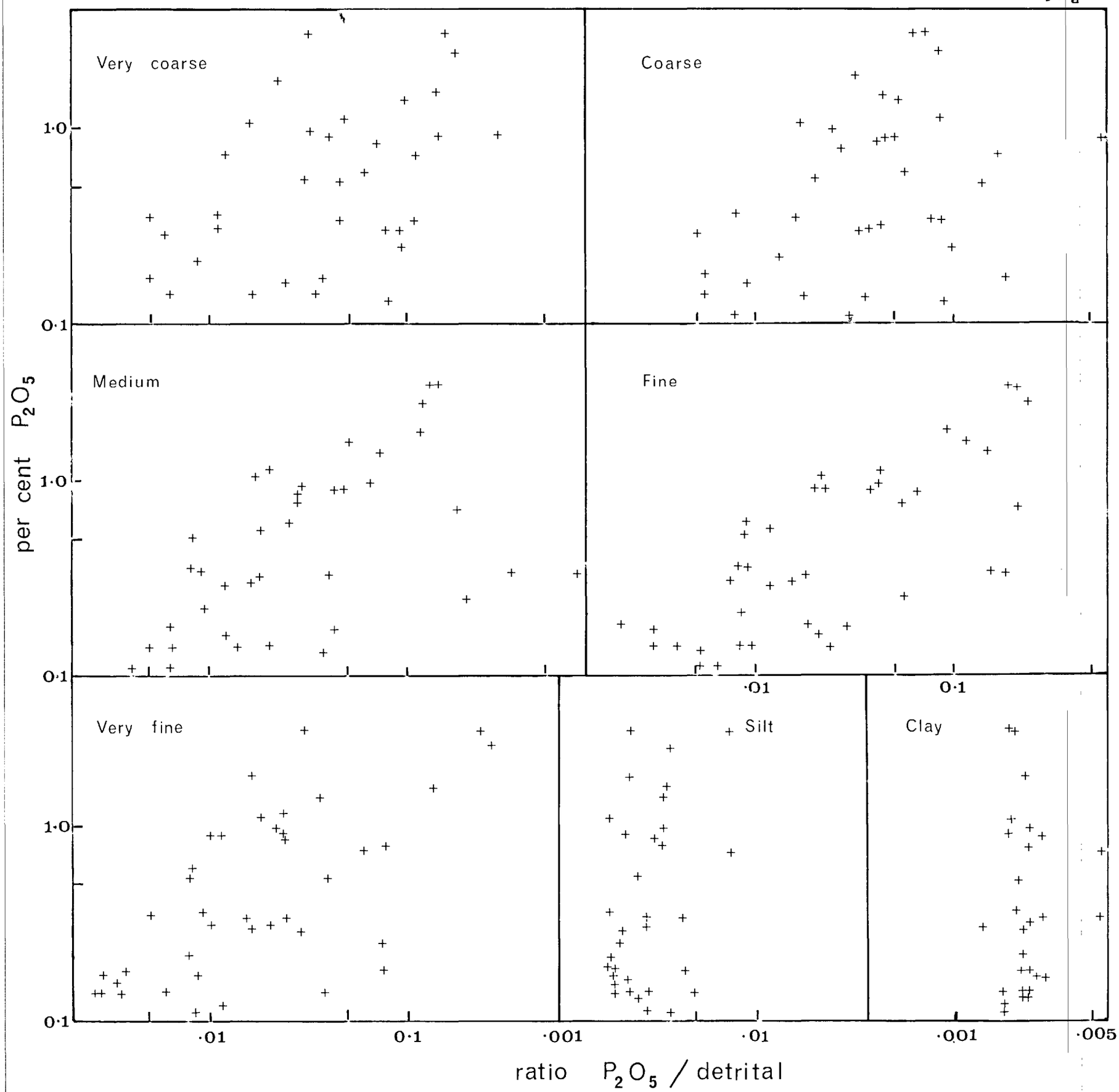


Fig.2.2.5.Percent P_2O_5 in total sediment (P1) vs P_2O_5 #detrital ratio in each sand fraction, silt and clay.

environment. The fact that the ratio does not remain constant, as it does for silt and clay, suggests the influence of provenance and perhaps also sedimentation characteristics such as density sorting etc.

The constancy of the ratio in silt and clay implies a common detrital source regardless of sediment type and not influenced in any notable way by local sources of phosphate in the continental margin. So far these interpretations are in accordance with the textural observations made in the preceeding chapter.

The possibility that the rather broad scatter may reflect authigenic or biogenic addition of sediment phosphate cannot be ignored but it must be emphasised that the results derive from the ratios of two chemical determinations (for carbonate and phosphate) and that analytical error may account for some of the spread. Alternatively the dilution of phosphatic detrital sediment by detrital material from some different source and possibly with a different phosphate/detrital ratio may be a contributory factor. Then again, the total phosphate represents analyses performed on mixtures of the apparently detrital phosphate with diluting biogenic carbonate. On the whole it is considered that either the linear or constant phosphate/detrital ratios in this assemblage of Moroccan shelf and slope sediments signifies that the majority of the phosphate is detrital in origin. In this respect it is worthy of note that (Fig. 2.2.6) the phosphate/detrital ratio decreases with sorting; this could well reflect the admixture at different times of different sediment masses characterised by different phosphate/detrital ratios which may have given rise to the observed scatter.

As far as increases in the phosphate/detrital ratio are concerned, these might indicate proximity to phosphatic sources; but, in that sediment masses may be bodily transported away from source, such an assumption would be unwarranted although the ratio may still be a function of source characteristics.

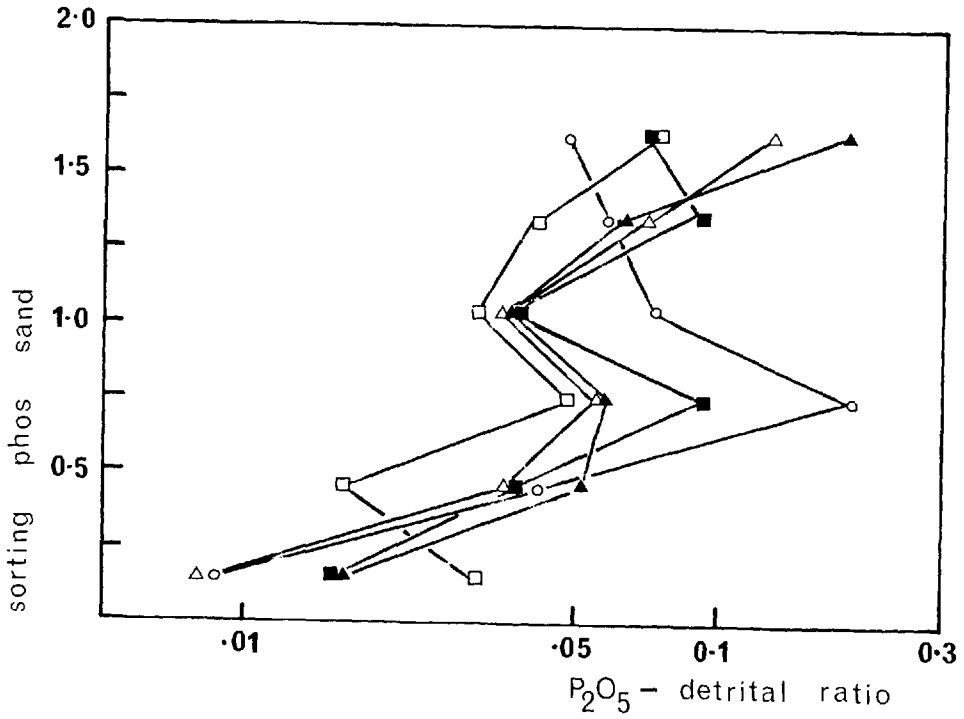


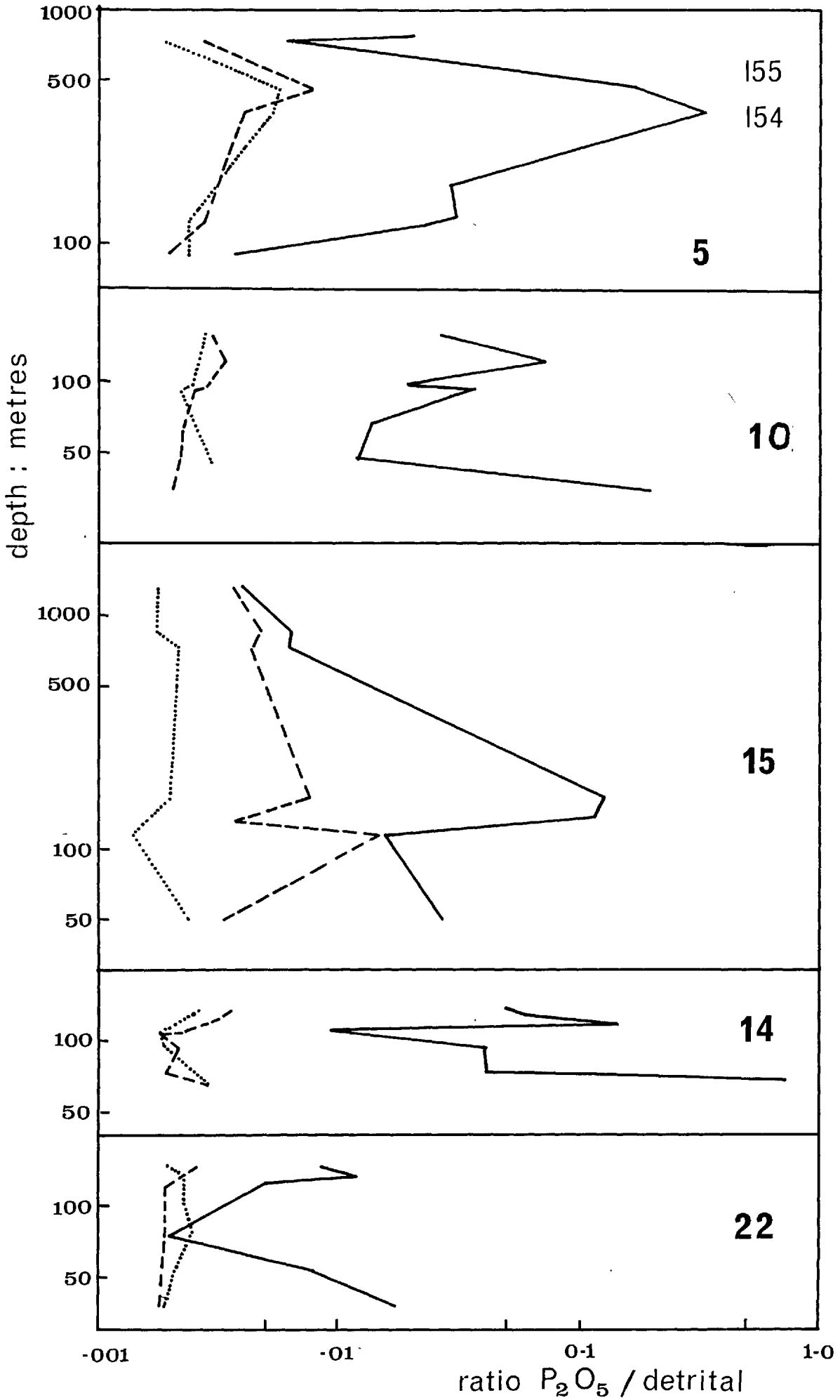
Fig.2.2.6. Average P_2O_5/detrital ratios for different sand grades, compared with the average sorting of the sediment at different sorting levels.

v.coarse sand = open triangles; coarse sand = closed triangles; medium sand = open circles; fine sand = closed squares; v.fine sand = open squares.

On individual traverses (Fig. 2.2.7) the phosphate/detrital ratio in sands (represented here by med. sand) fluctuates randomly as apparently it does in silt and clay. There is a very slight correspondence between sand fluctuations and those in silt suggesting that some small proportion of silt phosphate may derive locally from the same source as the sand phosphate. This is not true for clay. Significantly also the bulk data show there to be a regional gradient within the silt, which tends to increase in phosphate/detrital ratio seaward (with depth) but this is not true for the clay fraction. This may reflect derivation of silt on the slope in some small part by Recent winnowing at the shelf edge of rather phosphatic deposits of fine material formed during Pleistocene regressions and transgressions. That this does not apply to the clay suggests that all the clay is far derived. However, off Cap Sim there is a significant parallelism between sand, silt and clay fractions of the sediments from the upper slope depression. This is believed to be an area of very localised topographically enhanced current winnowing and it is not inconceivable that a local supply of clay and silt sized material is being contributed by the subsea erosion of soft, fine outcropping sediment deposited near former low stands of sealevel. Mineralogical investigations (see later) tend to argue against the possibility that the high silt and clay phosphate of these samples is due to authigenic additions. Were the regional silt pattern caused by Recent authigenic additions of phosphate some corresponding changes in the clay might also be expected: that this is not the case tends to argue against Recent authigenic precipitation of phosphate.

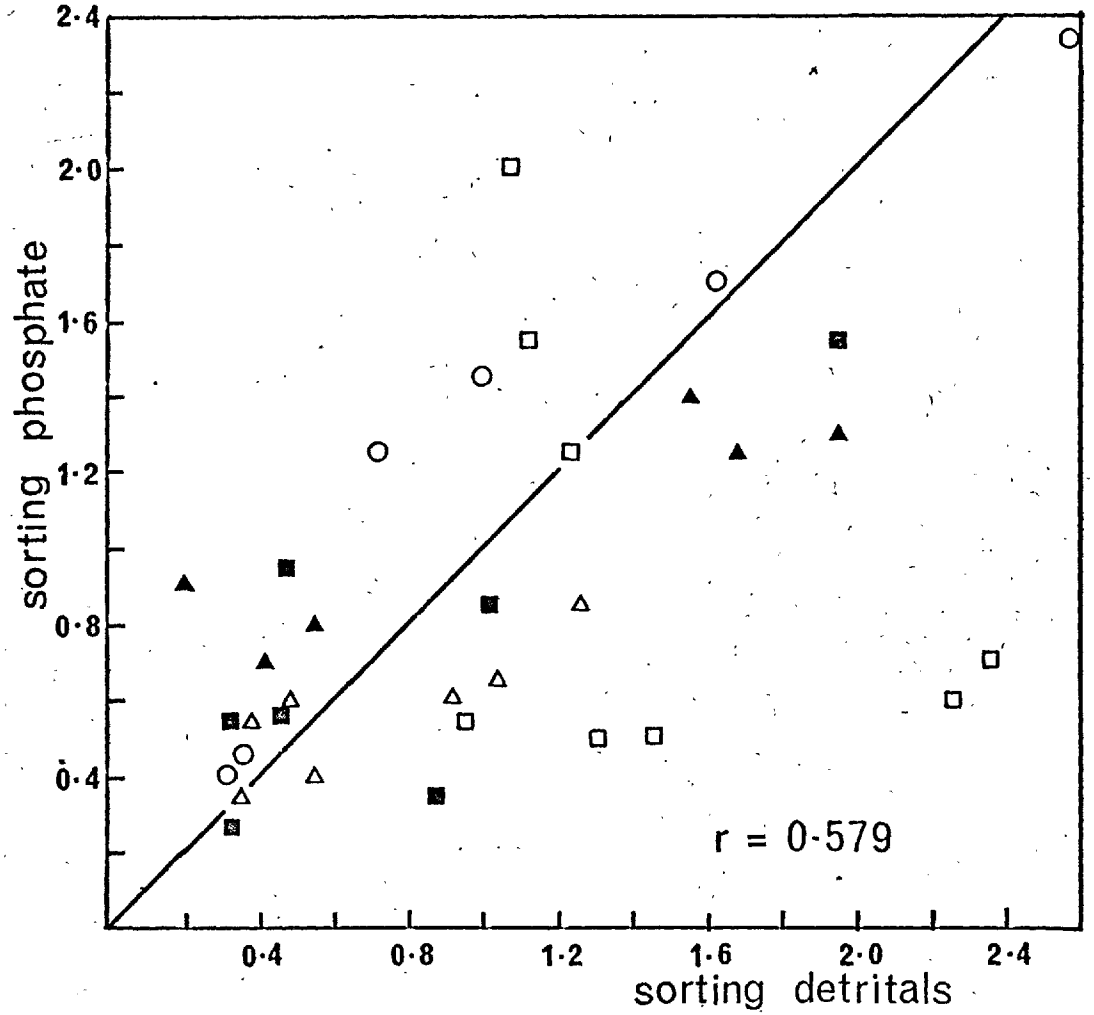
The granulometric characters of the phosphate fraction have been compared, using a correlation matrix (Fig.I.4.5A), with the characters of the detrital and carbonate fractions of the sediments. Although there is a strong correlation ($r = 0.823$) between the median diameters of the phosphate and detrital fractions the concentration of phosphate in the sand fractions results in a bias of the median diameter of the detrital phase towards the fine side

Fig.2.2.7.
Variation in carbonate-free phosphate in silt --- , clay .... and medium sand ___ fractions, with depth on different numbered traverses



(Fig. 2.2.8). Correlation between the median diameters of the phosphate and carbonate fractions is slightly better (r = 0.900) reflecting the tendency of both phases to be enriched in the sand fractions. Both $CaCO_3$ and P_2O_5 correlate positively with per cent sand and negatively with per cent fines (Fig.I.4.5A). In terms of sorting there is also a closer relation between phosphate and carbonate sorting than of either with detrital sorting; this again reflects the similar distribution of carbonate and phosphate constituents in the sand fraction of the sediment and the addition to the detrital phase of a carbonate and phosphate poor silt. Despite the relation between phosphate and carbonate sorting and median diameters there is no regional or mineralogical evidence to suggest that the relationship is genetic; the interrelation between phosphate and detrital constituents, however, warrants further examination.

Because the late admixture of relatively non-phosphatic silt and clay with sand sized phosphate obscures the original interrelation between sand sized detrital and phosphatic constituents, all analyses were recalculated on a clay and silt-free basis. The detrital and phosphate fractions are now seen to have closely similar median diameters (r = 0.902; Fig.I.4.5A; Fig.2.2.9); with very few exceptions these fractions are also similarly sorted (r = 0.852; Fig. I.4.5A; Fig. 2.2.9). Considering the very well sorted inner and mid shelf sediments (sorting values <0.66 for both components - a value chosen to allow inclusion of at least one sample from each of the five traverses considered) there is a more or less 1:1 relationship in Id values; this group includes nearly all traverse (22) samples plus samples 137, 140, 936, 927, 987, 992, 150. The sole exception to the 1:1 relationship for this very well sorted group is sample 1088. All other samples are more poorly sorted (>0.66) and show some degree of divergence from a 1:1 relation in Id between phosphate and detritals. The sole exception is sample 991.



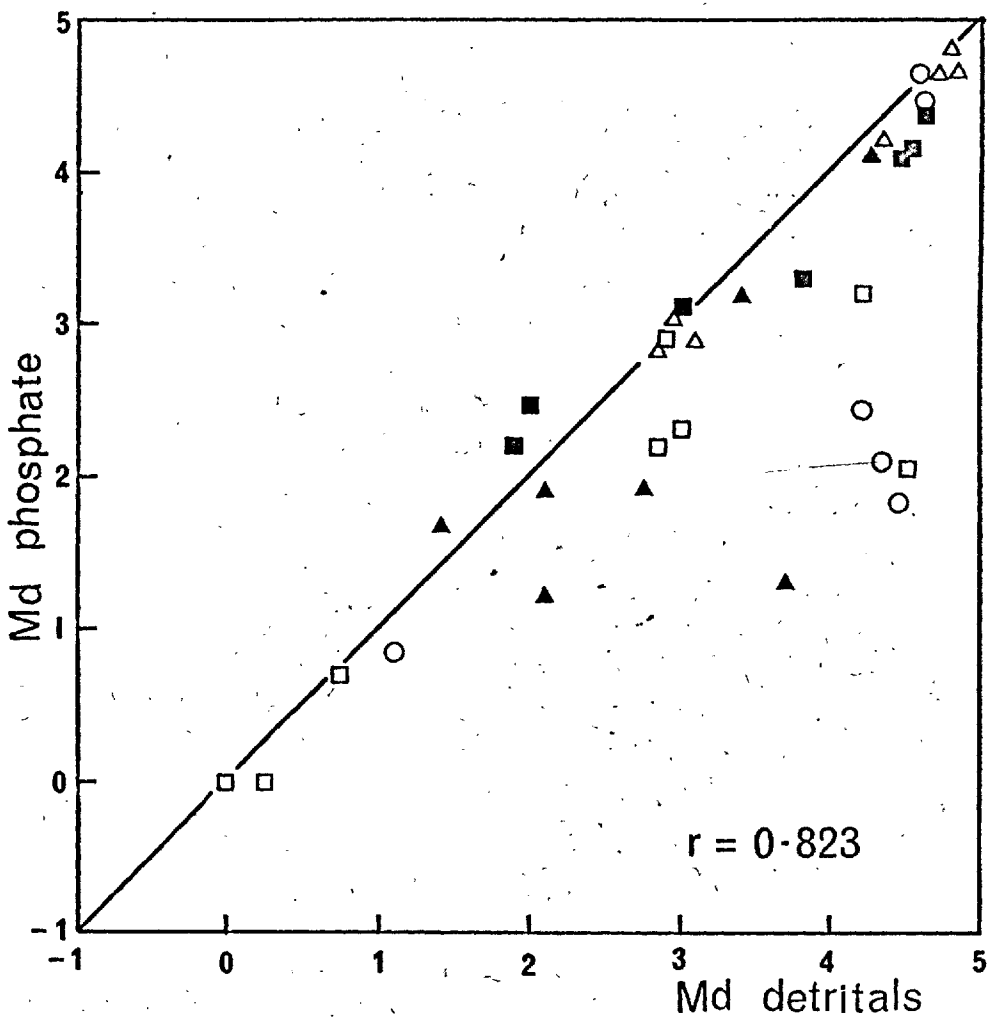


Fig.2.2.8. Comparison of granulometric properties of the detrital and phosphatic fractions of Moroccan sediments (phi units). Correlation coefficients refer to Fig.1.4.5.A. ; trav.5 = ○; trav.10 = ▲ ; trav.14 = □ ;trav.15 = ■ ; trav.22 = △ .

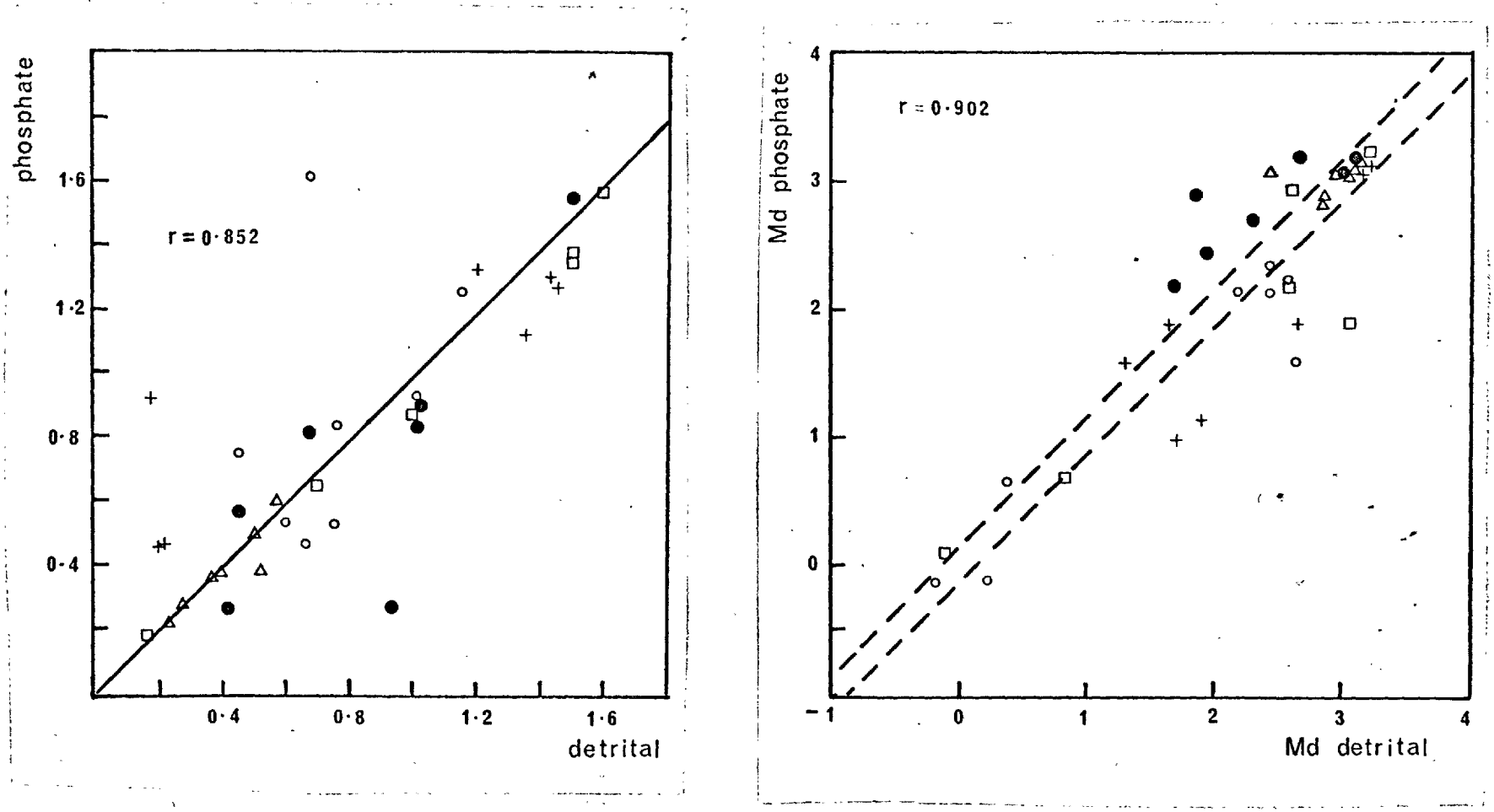


Fig.2.2.9.a. Comparison of granulometric properties of the phosphatic sand and detrital sand fractions of Moroccan sediments (left = sorting; right = median diameter; phi units). Correlation coefficients (r) refer to Fig.1.4.5.A. Dashed lines in right-hand diagram define an approximate 1:1 ratio (see text).
Trav.5 = □; trav.10 = +; trav.14 = O ; trav.15 = ● ; trav.22 = Δ .

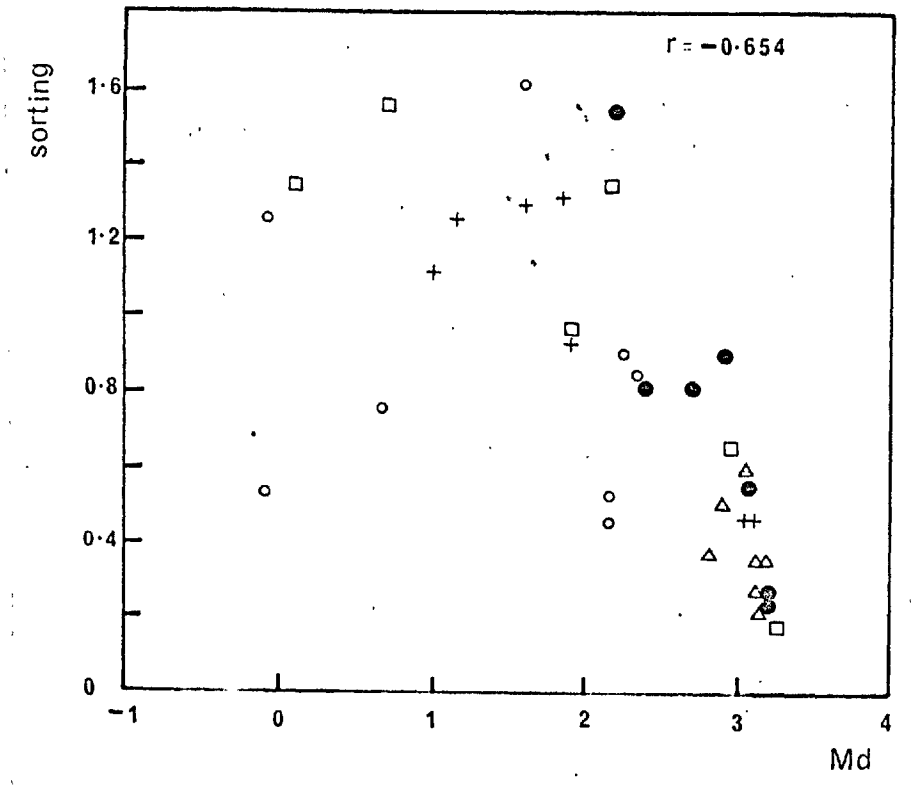


Fig.2.2.9.b. Variation in sorting of phosphatic sand fraction with change in Md phosphatic sand fraction (phi units). Symbols as in Fig.2.2.9.a.

Interestingly, many of the samples with finer phosphate than detrital components form a geographically related group comprising most continental slope samples (125, 126, 127) and outermost shelf samples (1088, 133, 134, 922, 923) from north of Safi; in addition are lower slope sample 144 and mid-shelf sample 151 from the Cap Sim region, plus innermost shelf sample 986 from near Cap Blanc. All samples exhibiting a coarser phosphate than detrital median diameter are from the inner and mid-shelf regions between Safi and Al Jadida and the mid and outer shelf and uppermost slope regions off Cap Sim.

The similarities in size (Md) and dispersion (sorting) indicate similar adjustment to the depositional environment and imply similar histories of transport, deposition and reworking for sand sized detrital and phosphatic constituents. Such correspondance would not be expected if the phosphate had other than a detrital origin.

Since the mean specific gravity of phosphorite pellets from the Baja, California, continental shelf is 2.75 - 2.80 (d'Anglejan, 1967) and not much different from quartz, it might be expected that in very well sorted sediments which have experienced considerable degrees of transport and abrasion there would be a more or less 1:1 median diameter relationship not unduly influenced by density differences between phosphorite grains and quartz. This relation is observed here in very well sorted sediments as it is in other regions. For example Visse (1953) reports that in onshore pelletal phosphorite deposits quartz and phosphorite pellets are of the same size. Examination of phosphatic continental shelf sediments off Baja, California (d'Anglejan, 1967) and the eastern seaboard of the U.S.A. (Lutenaur and Pilkey, 1967; Pevear and Pilkey, 1966) have similarly shown phosphorite in the sand fractions to be similarly sized and sorted to associated detritals which are, in the main, quartz, indicating similar histories of transportation and deposition or reworking. These deposits too are detrital and,

off the eastern seaboard of the U.S.A. found to be frequently related to continental shelf phosphorite outcrops (cf. Milliman, Pilkey and Blackwelder, 1968; Goodell, 1967; Lutenaur and Pilkey, 1966).

In these other shelf deposits and in pelletal land deposits there is a similar cut-off in phosphate below the very fine sand fraction (cf. Visse and McKelvey) which, although it could be an original feature of the grain population is more likely to reflect the energy of the depositional environment since associated quartz usually exhibits the same granulometric character.

In that group of samples from the outer shelf and slope displaying a finer phosphate diameter than that of associated detritals the possibility that this is caused by density sorting cannot be excluded. But, all these sediments are relatively poorly sorted (sorting greater than 0.66) compared with those in which the median diameter ratio is more or less 1:1. It thus seems more likely that along the outermost shelf and slope there has been influx of relatively fine phosphate into an area where coarse detritals had already been deposited. The reverse is unlikely in view of the relative current strengths required. If this is correct it implies that in this zone on the outermost shelf off northernmost Morocco there may be, or has been, a greater degree of phosphatic sediment movement than elsewhere which agrees with Nutter's interpretation of the linear shelf edge phosphate sediment zone as resulting from longshore dispersion away from the midshelf source during time of lowered sealevel.

By contrast, where the phosphatic components are coarser than associated detritals it is assumed that these sediments are a colluvial type placer little removed from source. The relative coarseness of phosphate grains may reflect (a) the hardness of outcropping phosphorite compared with associated lithologies such as mudstone and limestone and/or (b) admixture of locally

derived coarse phosphatic sands with later finer quartz sands. That the more poorly sorted sediments (sorting ≥ 0.66) usually have the coarsest median diameters (Fig. 2.2.9) supports the contention that they have been subjected to greater degrees of admixture with materials of different size, probably from different sources and possibly having different phosphate-detrital relationships from the supposed placers.

2.2.c Intra-sediment Phosphate Dispersion in Relation to Mineralogy

With the object of ascertaining in which phases of the sediments the phosphate was concentrated, a series of mineralogical separations and analyses were effected. Selected samples were first split into respective Wentworth sand grades then, using a Franz magnetic separator, into magnetic and non-magnetic fractions, the former consisting predominantly of glauconite, the latter of biogenic skeletal debris and detrital mineral grains. After several recyclings through the magnetic separator, more or less pure glauconite concentrates were obtained from several different size fractions of several different samples. Phosphate levels in these separates proved (table 2.2.2) to contain consistently less than 0.22% P_2O_5, averaging 0.17% P_2O_5 similar to the average value for shales (0.16% P_2O_5; Turekian and Wedepohl, 1961), strongly suggesting that glauconite, although abundant, does not contribute significantly to the observed phosphate levels in these samples.

From the admixtures of the non-magnetic biogenic skeletal debris with detrital minerals, detritals were removed by micropanning, together with glauconitic foraminiferal casts to which shell fragments still adhered, and analyses of the resulting biogenic concentrates (table 2.2.2) show that in the finer sand fractions the biogenic constituents, which are chiefly foraminiferal tests, contain on average between 0.11 and 0.13% P_2O_5. Coarse shell and coral fragments handpicked from the very coarse sand fraction contain 0.08%

P_2O_5. Although Nutter (1969) did not carry out any mineral separations on north Moroccan shelf samples, his analyses of those very coarse and coarse sand fractions in which there were no detrital or authigenic silicate constituents (table 2.2.4) provide comparable data showing the phosphate content of the coarse skeletal debris comprising these grades to average 0.09% P_2O_5. Compared with the average phosphate level for limestones (0.09% P_2O_5; Turekian and Wedepohl, 1961) it is clear that while there is no evidence for phosphatisation of coarse skeletal debris, despite its normally relict character and therefore long sojourn on the seafloor, the foraminiferal concentrates contain slightly more phosphate than expected.

Many of the foraminifera contain clay and others contain glauconite casts and, as discussed later, since these other components contain phosphate at levels greater than that of the biogenic fraction, the phosphate content of the foraminifera must be less than the 0.12% P_2O_5 average and may not be much different from the levels recorded for associated molluscan debris. In view of the low phosphate levels of the biogenic and glauconitic fractions all further tests were restricted to the detrital mineral phases.

From the very coarse fractions of selected sediments, small pebbles and granules of rock, selected because of a close lithological resemblance to nearby outcropping phosphorite, were found to be highly phosphatic (table 2.2.2). Grains with similar appearance were commonly dispersed throughout the sand fraction as mentioned in Chapter 1.

Detrital concentrates were obtained by leaching the non-magnetic fractions of selected sand size grades from different samples in 25% vol acetic acid; this removed skeletal debris and the few calcareous rock fragments present. After leaching, the fine (chiefly silt and clay sized) part of the insoluble residue was shaken into suspension in water and decanted into a separate container. The fines derive mainly from the interstices of foraminifera.

Using a Franz magnetic separator and Cook micropanner, glauconitic foraminiferal casts were separated from the detrital mineral grains in the coarse (non- decanted) part of the insoluble residue (chiefly sand sized material) and subsplits of these mineral phases were retained for chemical and mineralogical analyses.

Considerable concentrations of phosphate were measured in the sand sized detrital separates (table 2.2.3), which consisted of detrital clastic mineral grains (mainly quartz with subsidiary feldspar), rock fragments and rare sharks teeth, fish bones and sponge spicules. The majority of the rock fragments were dark brown to orange-brown angular grains lithologically resembling locally dredged phosphorite; in particular fragments of the common glauconitic phosphorite were often observed in coarser separates.

By contrast the decanted fine phases do by no means display the degree of phosphate enrichment observed in their coarser counterparts (table 2.2.3). Visual inspection shows this fine fraction to consist mainly of clay with admixed quartz and broken glauconitic foraminiferal casts and X-Ray diffraction analysis independently supports this mineralogical classification: apatite is not found in measurable quantities by X-Ray diffractometry in this fraction of the sample. The phosphate levels in the fines (table 2.2.3) are in nearly every case slightly less than those of the unleached silt and clay fractions (table 2.2.2) suggesting that physico-chemical conditions are not suitable to the concentration of phosphate within the interstices of foraminifera. That the observed levels are slightly lower than the untreated silt and clay fractions may obtain due to the admixture in the decanted fines of quartz and glauconite although these never reach substantial concentrations. It is significant that these phosphate levels, which it must be remembered are obtained on the material from the interstices of foraminifera, are about twofold higher than the biogenic separates (table 2.2.2). Thus

the observed levels of phosphate in the biogenic separates from medium, fine and very fine sand fractions are really composite, formed by the biogenic and the included clay components, and the average phosphate level of 0.11 to 0.13 quoted for biogenic debris probably does not indicate phosphatisation of skeletal material.

Magnetic separates consisting mainly of glauconitic foraminiferal casts from the leached residues proved to contain much less phosphate than the detrital separates (table 2.2.3). That these glauconite separates contain more phosphate than that separated from the unleached samples (table 2.2.2) is attributed to the analytical approach; not finding any evidence to support an interrelation between glauconites and phosphate less care was taken to purify the glauconite and, inevitably, detrital minerals became incorporated into the magnetic fraction with glauconite. The difficulty experienced in separating glauconite from associated phosphorite particles can also be attributed to the fact that local phosphorites are all relatively iron rich and many contain glauconite making any magnetic separation difficult. Binocular microscope examinations were made to ascertain the presence of phosphorite in these leached glauconite concentrates and to confirm its absence in the unleached glauconite concentrates.

Pale brown or cream foraminiferal casts recur quite frequently in the finer sand grades. Sufficient of these were separated from sample 882 (table 2.2.2) to allow chemical analysis which showed them to contain very little phosphate. X-Ray diffraction analysis of brown casts from samples 833, 834, 837, 873 and 882 showed them to consist essentially of clay minerals and glauconite and not to contain any apatite. In view of this the admixture of small quantities of these brown casts with the magnetic and non magnetic separates of the insoluble residues of these and the other samples is not considered to have contributed in any way to the high phosphate levels of

these separates. Apatite is only recognised in the diffraction patterns of samples in which angular detrital grains resembling phosphorite were recognised under the binocular microscope.

Phosphatic teeth and bones are always quantitatively unimportant constituents of the sediments and cannot give rise to the observed regional and textural variation phosphate.

Nutter's (1969) binocular microscope investigations showed that the phosphatic samples from north of Essaouira also contained abundant brown detrital fragments identified as phosphorite by analogy with the lithology of local outcrops. It is therefore concluded from these data that the main form in which phosphatic components occur in offshore Moroccan sediments is as detrital sand sized grains of locally derived phosphorite.

2.2.d Relation of Phosphatic Sediment to Phosphatic Bedrock Outcrops

Comparing total sediment phosphate with the distribution of dredge hauls in which locally derived phosphorite or phosphatic limestone pebbles or bedrock fragments were obtained (Fig. 2.2.1) it is clear that there is a very close relationship between phosphatic rock and phosphatic sediment distribution. With the exception of the phosphatic sediments at the extremes of the zone and in the nearshore region the phosphatic sediments almost everywhere overlie phosphatic rock outcrops. Within the Essaouira-Agadir region, stratigraphic studies (Chapter 5) show the phosphatic rock to crop out on the shelf and uppermost slope from beneath a pronounced unconformity; within this region the maximal concentrations of phosphate are found to be restricted to those areas where phosphatic rocks outcrop from beneath the unconformity (Fig. 2.2.1 and 5.3.4).

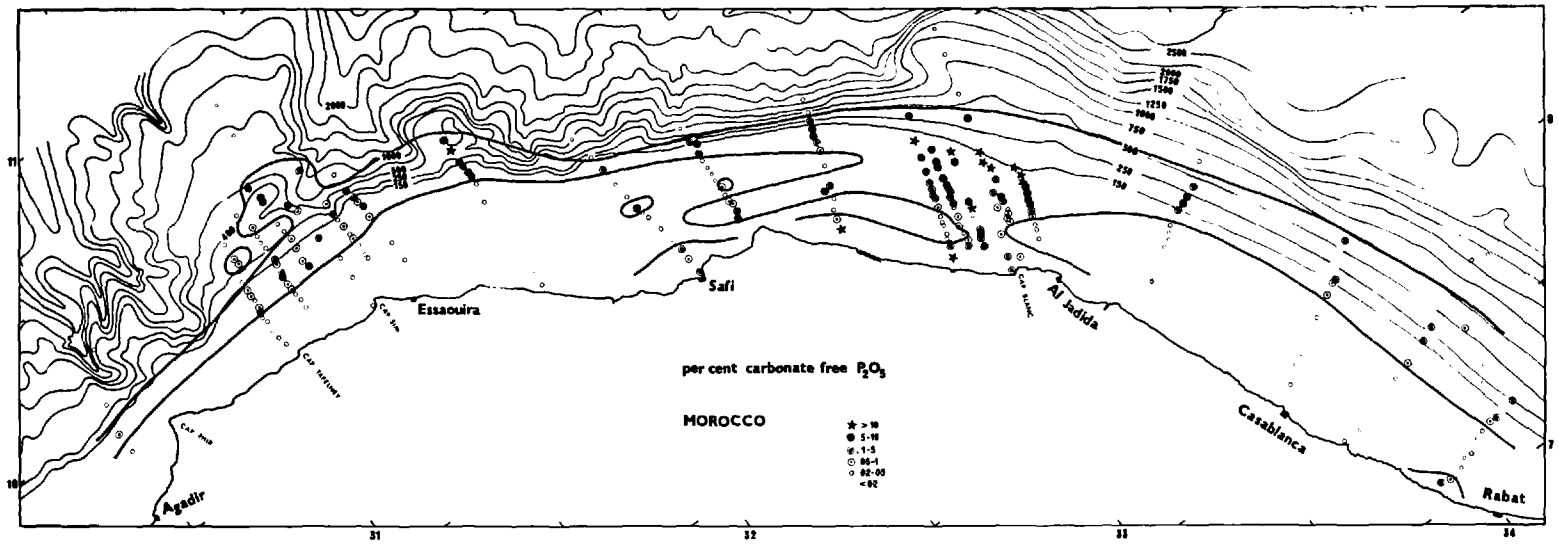
In that the foregoing preliminary examination strongly tends to imply that the majority of phosphatic constituents are detrital, the diluting effects

of biogenic carbonate accumulation are removed by recalculating phosphate contents on a carbonate free basis and the distribution of phosphate expressed as a percentage of the detrital (non-carbonate) phase is considered (Fig. 2.2.10). Essentially the same zonal arrangement of phosphate obtains as for uncorrected phosphate values, there being a continuous well defined narrow belt of phosphatic sediment along the shelf edge, a discontinuous inshore zone which is particularly rich off Cap Blanc, and a mid-shelf zone between Al Jadida and Safi. The mid-shelf phosphate-poor sands between Essaouira and Cap Blanc generally contain less than 0.5% P_2O_5. Within the silt belts of the slope and shelf phosphate is also depleted, usually not exceeding 0.2% P_2O_5 in the northern silt belt, and 0.5% P_2O_5 in the southern silt belt. In view of the previous findings that the silts represent Recent supplies of detrital material possibly derived from some distant provenance and are compositionally unrelated to the relict sands, it was decided to use the 0.5% P_2O_5 isopleth to define zones of phosphate enrichment. The fact that non-phosphatic sands and some of the silts contain slightly more phosphate than the average for shales (0.16% P_2O_5) most probably results both from the fact that these present results are expressed on a carbonate free basis and reflects the abundance of phosphorites among the provenance rocks onshore.

Again it is clear that the zones of carbonate free sedimentary phosphate enrichment relate closely to phosphatic rock outcrops and are not absolutely dependent on geomorphic criteria as might be expected were they causatively related to oceanographic phenomena such as upwelling. The degree of phosphate enrichment off Cap Blanc is quite considerable, frequently in excess of 10% P_2O_5. That this enrichment is greatest where the largest expanse of phosphate rock would have been exposed to erosion during Pleistocene regressions again reveals the probable detrital character of the surficial deposits; such an association would not be expected to result from phenomena associated

Fig.2.2.10

Distribution of carbonate-free phosphate (as P_2O_5) in sediments off Morocco: information for sediments north of Safi calculated by the writer from data given by Nutter (1969).



with upwelling.

In view of the granulometric relation between phosphate and detritals, extension of the phosphatic sediment zone beyond the area of outcrops is taken, in agreement with Nutter (1969) to indicate (1) off Cap Blanc, seaward transport of phosphatic components at times of lowered sealevel and (2) longshore current dispersion over the entire region, again at times of lowered sealevel.

2.2.c Moroccan Shelf Phosphatic Sediments: Summary and Conclusions

In spite of the apparent suitability of the Moroccan continental margin as a site for the contemporaneous formation of authigenic marine phosphate minerals, the data presented here militate against this hypothesis and marshal in favour of multiple detrital sources related to onshore and offshore outcrops of early Tertiary phosphorite deposits common to this region. In this respect the Moroccan shelf deposits differ in no way from the phosphatic sediments of the Atlantic continental shelf of the U.S.A. This conclusion is based on (1) the existence of sand sized phosphorite grains which can only have been derived from local outcrop and are particularly common in relict sediments from the outer shelf where they occur among or immediately seaward of phosphorite outcrops;

(2) linear covariation of phosphatic and detrital components with respect to phosphate sources and covariance of their granulometric properties indicative of shared sedimentation histories;

(3) textural and other evidence for the regional deposition of a phosphate-poor silt and clay blanket, unrelated in the main to local sources, and the consistency of whose phosphate-detrital ratio implies absence of phosphate adsorption and, on the contrary, an inherited provenance characteristic;

(4) the fact that phosphate is not replacing biogenic skeletal debris even where it has been exposed for sufficient length of time to allow formation

of glauconite within foraminiferal tests;

(5) the absence of any notable degree of accumulation of phosphate within foraminiferal tests despite the common occurrence in these tests of glauconite, and indications that this is an environment suitable to authigenic mineral formation.

The sedimentation history of the Moroccan shelf phosphate deposits apparently relates to fluctuations in Pleistocene sealevel. In the immediate vicinity of outcrop are poorly sorted coarsely phosphatic sands; seaward are finer phosphatic sands implying that at least between Safi and Al Jadida, seaward transport has occurred from the midshelf source region to the outer shelf and has resulted in formation of a 'transported anomaly' not directly overlying source rocks. The tremendous dispersion of phosphate between Safi and Rabat in this shelf edge zone may result, since phosphorite outcrops are not widespread over the entire region, from current dispersal in a Pleistocene nearshore zone, probably as Nutter (1969) suggested, by longshore drift. Off southern Morocco, by contrast phosphorite outcrops beneath the outer shelf on which phosphatic sand is concentrated and all examined samples showed signs typical of a 'residual' as opposed to a 'transported' anomaly. Some degree of dispersion must have operated alongshore in this zone but, because of proximity to source, effects of transport are masked. Nevertheless it is suggested, since geological evidence presented in Chapter 5 shows the Eocene phosphorite outcrops to be restricted to the Cap Sim region and not to extend as far south as Agadir, that the phosphatic maximum on the outer shelf off Agadir may result from the same longshore drift dispersal as caused the formation of the northern Moroccan anomaly. Since there is but one traverse in the vicinity of Agadir and none between that and the Cap Sim phosphatic sediment zone, the present survey is not adequate to allow further conjecture.

Some contribution from rivers to the outer shelf during low sealevel stands

must also be anticipated in view of the existence of large inland phosphorite deposits and of the discontinuous inshore belt of phosphatic maxima. These inshore sediments are believed to be river derived because their nearshore setting is far removed from known offshore phosphorite outcrop and also because the phosphate-detrital ratio in the sand fraction of these sediments decreases radically seaward in the 'non-phosphatic' mid shelf sediments before increasing again as the mid and outer shelf phosphatic sediment zones are approached. Such fluctuation would certainly not be expected as a function of sand transport shoreward from the phosphatic zone. Nutter (1969) has also demonstrated the existence of a restricted linear mid shelf zone, between the outer shelf and the coastal zones, which appears to be related to mid shelf phosphorite outcrops and the phosphate dispersal in which is thought to result from longshore drift during low sealevel stands.

Preservation of these relict Pleistocene phosphatic sand deposits formed at low sealevel stands is thought to be the direct result of the paucity of Recent sediment accumulation in these regions. Nevertheless it appears that there is everywhere, with the exception of the Cap Bim depression, a silt and clay blanket of Recent origin, which has become mixed with the outer shelf sediments. This blanket is best developed in the inner shelf zone but locally, off north Morocco extends well out onto the mid shelf. For a variety of reasons the source of this silt and clay is thought to be in the main terrestrial and unrelated to the sand components of the majority of shelf and slope sediments.

2.3 Spanish Sahara

2.3.a Distribution of Phosphate in Surface Sediments

Traverse separation is too great to justify intertraverse interpolation of phosphate isopleths and accordingly profiles of phosphate concentration for

each traverse are presented individually (Fig. 2.3.1a). In order to assess the effects of diluting biogenic carbonate, the uncorrected and carbonate free phosphate values are presented. Phosphate distribution is extremely irregular, yet considering for a moment only the uncorrected levels, it is abundantly clear that the northern two traverse are relatively phosphate-rich compared with the southern two. Off Villa Cisneros for example, phosphate levels higher than 0.17% P_2O_5 were not encountered. There is along this traverse a very clear but gradual seaward increase in phosphate toward a maximum at Sta. 234, at which phosphatic limestone bedrock was dredged. Although higher than uncorrected P_2O_5 levels, the carbonate-free phosphate level does not exceed 1.0% P_2O_5 and is usually much less than this. Off Cap Blanc, with the exception of a phosphate low at Sta. 228, there is by contrast with the previous traverse, a general shoreward increase in phosphate which averages 0.17% P_2O_5 and reaches a maximum of about 0.3% P_2O_5. Again, the carbonate free phosphate is always less than 1.0% P_2O_5; although it does not quite so clearly follow the pattern of total phosphate there is clearly no tendency for marked local concentration such as seen off the northern coast. Discovery samples collected between these two traverses generally contain less than 0.15% P_2O_5; an exception is Sta. 6590 where 0.31% P_2O_5 was recorded (Fig. 2.3.1b).

Phosphate is considerably enriched in the outer shelf and uppermost slope sands off Caps Juby and Bojador and moderately enriched in a narrow zone some 10km. off Cap Juby. Outside the confines of these zones, phosphate levels are generally below 0.2% P_2O_5 (uncorrected; or below 1.0% P_2O_5 on a carbonate-free basis). Maximal recorded total phosphate levels are 5.2% P_2O_5 on the uppermost slope off Cap Juby (Sta. 277), and, on the uppermost slope and outermost shelf off Cap Bojador, 4.2% (Sta. 258), 5.4% (Sta. 255), and 8.3% P_2O_5 (Sta. 256). The average level outside the zones of enrichment is approximately 0.16% P_2O_5.

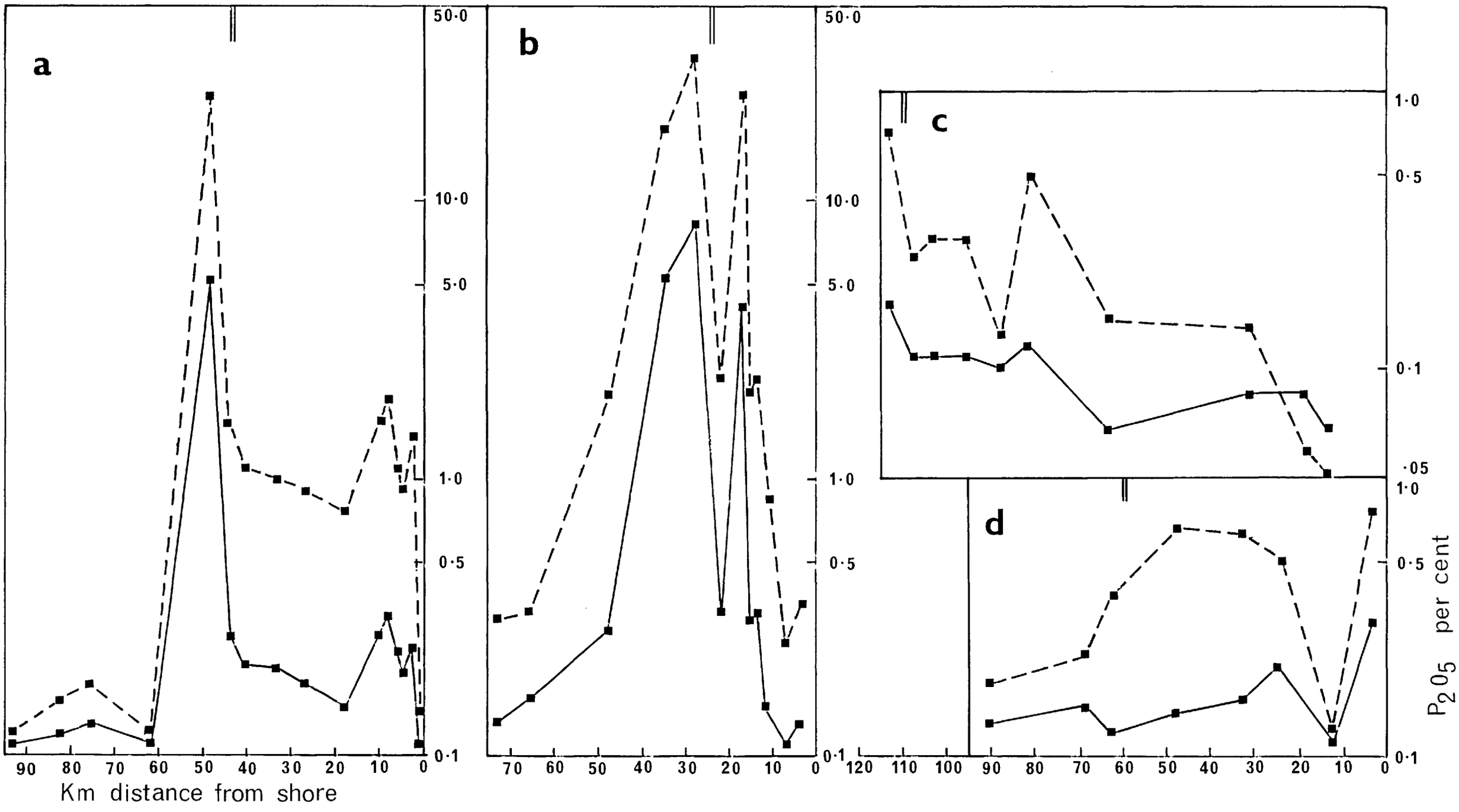
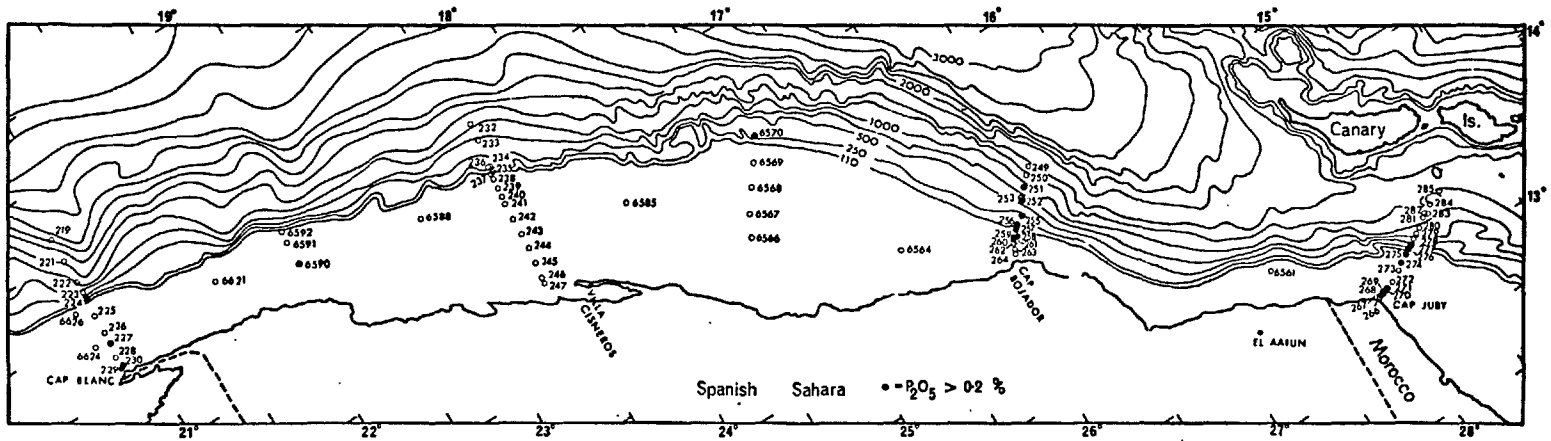


Fig.2.3.1.a. Distribution of total percent P_2O_5 (solid line) and percent carbonate free P_2O_5 (dashed line) in Saharan continental margin sediments. Trav.a is Cap Juby; b is Cap Bojador; c is Villa Cisneros; d is Cap Blanc. Shelf edge is marked by a double line symbol at the top of each diagram.

Fig.2.3.1.b.

Regional distribution of phosphatic and non-phosphatic sediments off the Spanish Sahara.
All samples were analysed except 236,253,261.



Size fraction analyses carried out on samples 255, 256, 258 and 277 (Chapter 1) show them to contain abundant angular lithic fragments of a yellow-brown rock together with limestone fragments containing orange-brown internal casts of foraminifera. These yellow - to orange-brown fragments and foraminiferal casts are the most abundant constituents of the acetic acid insoluble residue. From their resistance to acid attack, their external appearance and the elevated phosphate content of these samples (reaching 20 - 30% P_2O_5 on a carbonate free basis) it is deduced that they are phosphorites or phosphatic limestones. All available evidence (Chapter 1) suggests that these coarse sediments are dominantly relict and represent detritus from some local outcrop subjected to erosion during some lowered stand of the Pleistocene sea. It should be emphasised that whereas Recent unabraded unphosphatised foraminifera predominate in the very fine sand fraction, the phosphatic casts predominate in the coarser fractions whence they can only have been derived by the dissolution of rock fragments. According to Rye (pers.comm.) these samples all contain derived phosphatised Lower Pliocene foraminiferal remains, here taken to indicate the age of the outcropping strata from which they were eroded.

Between Cap Bojador and Villa Cisneros, shelf samples 6564 to 6585, collected from R.R.S. Discovery by R.H. Belderson of N.I.O., are low in phosphate, which averages 0.08% P_2O_5. But, just below the shelf edge, sample 6570 contains 0.45% P_2O_5 and may represent a southerly extension of the phosphatic zone discussed above. Since some slight enrichment was also observed in this position off Villa Cisneros, the possibility cannot be excluded that the shelf edge and upper slope phosphate zone is continuous from Cap Juby at least to Villa Cisneros.

2.3.b Distribution of Phosphate in Cores

The series of muddy foraminiferal ooze or calcareous mud cores collected

from the Saharan continental slope (Fig. 2.3.2) did not yield any subsamples containing more than 0.2% P_2O_5 excepting in core 251 where the sediments average 0.2% P_2O_5. Changes from a more muddy surface to a lower siltier deposit, or vice versa, are recognised in three cores (233; 278; 279); in each case the phosphate levels in the siltier parts of the core are higher than where mud prevails. Gradual increases of phosphate with depth in the core are not recognised except in the deeper cores off Cap Juby (281 and 282). The significance of this gradual change has yet to be established since there has not been time within the framework of the project to undertake detailed textural analyses to complement the chemical data. However, it is worth pointing out that all the recorded phosphate levels are not more than two-fold different from average shales and the observed variations could very easily represent changes in the carbonate-detrital ratio. Since higher levels are not noted, there are no sure grounds for suggesting that Recent formation of sedimentary apatites is the cause of the gradual increases. With regard to the observed textural association in other cores, further investigation is warranted.

2.3.c Discussion of Saharan Data

The belt of phosphatic sediment on the outer shelf and upper slope off the north Saharan coast appears, as does that off Morocco, to be a relict detrital placer formed by the erosion of nearby outer shelf exposures of phosphatic rock during the Pleistocene. That this belt is not continuous southward may be due to burial by enhanced biogenic sedimentation (Chapter 1) resulting from the increased productivity of southern as opposed to northern Saharan waters (cf. Jones and Folkard, 1968). Whereas this southward upwelling enhancement might be expected to create an environment favourable to authigenic apatite formation, the observed concentrations of phosphate in sediments outside the main northern phosphatic zone show no geographical variation which might support an interrelation between sediment phosphate

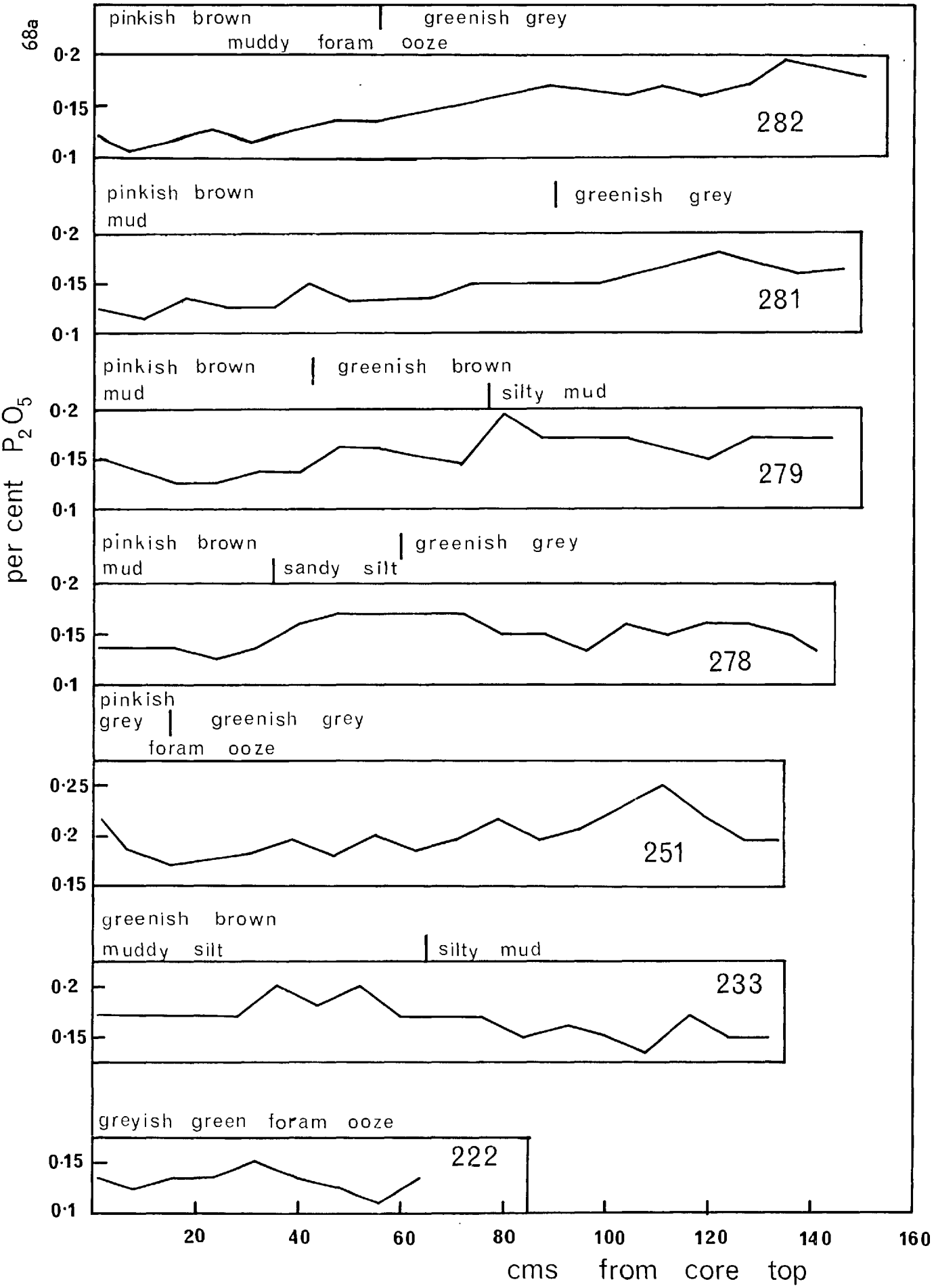


Fig.2.3.2. Sediment characteristics and phosphate levels ($\%P_2O_5$) in Spanish Saharan cores.

and upwelling. There is no evidence to suggest that calcareous skeletal material is being replaced, and the compatibility of regional phosphate levels outside the phosphate zones, and at depth in sediment cores, with shale and limestone values argues against any local concentration relating to upwelling. This despite the evident slowness of Recent sedimentation on the Saharan shelf (Chapter 1) and the fact that upwelling off the southern Saharan coast is more intense than elsewhere in the region (cf. Jones and Folkard 1968). Consequently it must be assumed that the present physico-chemical conditions of this environment do not favour authigenic apatite formation. There are however strong grounds for suspecting that authigenic apatite did form in the Pliocene along the shelf edge under similar conditions to those prevailing at present and it is suspected that whatever the environmental change required to produce apatite formation on a notable scale, it is but slight.

2.4 General Conclusions

Although the northwest African continental margin is an environment of active upwelling of phosphate-rich water where biological productivity is high and the sedimentation rate very low, Recent formation of authigenic phosphate deposits does not appear to be occurring contrary to the general predictions of McKelvey and others. There is no evidence for phosphatisation of carbonate skeletal debris, adsorption of phosphate onto clay or silt, or the formation of apatite precipitates either from seawater or interstitial water. Instead, as far as present data are concerned, phosphate is present in the main as a detrital constituent derived by the erosion of continental shelf and nearby land phosphorites. Its dispersion patterns are interpreted in terms of formation of mid and outer shelf deposits during low sealevel stands of the Pleistocene, during which it was distributed over the region by current activity and, in particular, by longshore

drift. These conclusions substantiate the earlier tentative conclusions of the writer, based on 1968 shipboard phosphate determinations carried out during the first reconnaissance cruise (Tooms and Summerhayes, 1968). Accordingly, the hypothesis that in zones of active divergent upwelling of phosphate-rich water off the western, arid coasts of continents in regions such as that examined here, conditions are more or less ideal for the Recent formation of marine apatite deposits (cf. McKelvey, 1963, 1967) must be regarded as questionable, if not totally without foundation, in relation to the present oceanographic milieu. The validity of the upwelling hypothesis is further critically examined in Chapter 8 .

CHAPTER 3

REGIONAL SEDIMENTARY GEOCHEMISTRY

3.1 Introduction

Previous studies on the geochemistry of shallowwater marine sediments have established to varying degrees the fundamental control of sediment geochemistry by its mineralogy (among others cf. Goldberg and Arrhenius, 1958; Hirst, 1962 a and b; Moore, 1968; Hazelhoff-Roelfzema, 1968). Following from this has developed the use of multielement geochemical mapping and statistical techniques in assessment of the provenance and dispersal of modern marine sediments (Moore, 1968; Rumeau and Vanney, 1969; Till, 1970, White, 1970). The use of multielement soil and stream sediment geochemical mapping and statistical analysis in simulation of mineralogical studies to differentiate source bedrock types whose mineralogy differs in significant degree is long established (Webb, Nichol and Thornton, 1966; Armour-Browne and Nichol, 1970). Multielement geochemical analysis offers a more rapid reconnaissance method of estimating sediment mineralogy than do detailed mineralogical studies. In this context the U.S.G.S. has recently commenced a large scale regional sediment geochemical reconnaissance of the submerged eastern part of the U.S.A. to rapidly detect and evaluate offshore mineral reserves (Holmes, 1969). As the differences between coarse and fine sediments are usually mineralogical as well as textural, this analytical approach may also offer a rapid means of estimating broad sediment textural characters. In this chapter the validity of this hypothesis in regard to northwest African shelf and slope sediments is investigated. An attempt is made to establish the mineralogical dispersion of the non-biogenic phases and to assess their relationship to the apparently detrital phosphatic constituents. By means of single element dispersion studies, interelement correlation

assessment and factor analysis, the non-biogenic phases of these sediments are classified into different facies from which further understanding may be obtained of shelf sedimentation processes in general and the characteristics of the phosphate deposits in particular.

3.2 Analytical Methods (See Appendix 2 for Details)

To assess sedimentation patterns from sediment geochemical studies it is first necessary to attempt a separation of the mechanically derived (detrital) products from biogenic debris, sorbed material and authigenic phases. In this study the widespread presence of authigenic and detrital glauconite and of an authigenic iron-oxide phase makes such a clear division impossible. It was decided to remove only biogenic remains and loosely sorbed elements, by using a cold 25% vol. acetic acid leach (after Hirst and Nicholls, 1958). After leaching it was found that this had partly dissolved the iron oxide phase (cf. Chester and Hughes, 1967) but not sufficiently to obscure the authigenic mineralisation pattern. This approach also neglects the influence of lithic fragments of calcareous rocks which occur in some samples; however, the majority of the sediments are fairly mature and contain only a little such material. Contaminants, in the form of ship's clinker, were recognised in a number of samples but were usually sufficiently coarse to be easily sighted and removed. The resultant compositions therefore should be fairly representative of the detrital and authigenic mineralogy of these sediments.

The insoluble residues of material collected during the 1968 reconnaissance cruise to Morocco and the Spanish Sahara were analysed by a then available Direct Reading Emission Spectrograph (table 3.3.1.a). These samples form population subset 1. Apart from colorimetric phosphate analyses, which were carried out on all samples, this subset was analysed for Al, Ca, Fe,

Mg, K, Si, Ba, Be, Bi, Cd, Co, Cu, Cr, Ga, Pb, Mn, Mo, Ni, Ag, Sc, Sr, Sn, Ti, V, Zn, Zr. Because the analytical technique has been found unreliable for Be, Bi, Cd, Sc, Sn, Mo, Ag and Zr (Young, 1970, A.G.E.G. Internal Report) and as these usually occurred either in very small or trace amounts, they were not further considered. The following discussions of population subset 1 are therefore concerned with 19 variables (including phosphate).

All Moroccan samples collected in 1969 were analysed, and the 1968 Moroccan samples were re-analysed, using an optical emission spectrograph (the direct reading instrument not being available) for the following fourteen elements:- Ba, Co, Cr, Cu, Ga, Mn, Mo, Ni, Pb, Sr, Ti, V, Zn and Fe_2O_3 (table 3.3.1.b). Values determined by this method do not differ greatly from those determined by direct reading emission spectrography (Appendix 3) and comparisons of interpretations reached from the two sets of data are considered valid. The Moroccan samples form population subset 2.

Population subset 3 comprises all those samples for which granulometric analyses were available.

Acetic acid extractable Fe and Mn determinations were carried out using an atomic absorption spectrophotometer (table 3.3.1.b); for the purposes of statistical analysis those samples containing measurable Fe and Mn form population subset 4. To remove the diluting effects of biogenic debris and to facilitate comparison with the detrital phase these results have been calculated on a carbonate free basis.

3.3 Single Element Dispersion in Relation to Mineralogy

3.3.1 Size Fraction Analysis

To test the assumption that total sample geochemical analyses can be used to estimate mineralogical and therefore also textural characteristics, the silt

and clay fractions were separated from selected samples of traverses 5 and 15 and, after removal of biogenic and loosely sorbed material by weak acetic leach, were analysed by direct reading emission spectrography. An approximation to the composition of the sand fraction is obtained from analyses of total sediment samples containing $>70\%$ sand: off Cap Sim these are 153 and 155; off Cap Blanc, these are 133, 134 and 137 (table 3.3.1.a).

As, on each traverse, there is little compositional difference between separate silts and clays from adjacent sample sites the mean clay and silt compositions were calculated for each traverse (table 3.3.1). Clays are found enriched relative to silts in Al, Mg, K, Fe, Cr, Cu, Zn, Pb, Ga, V, Ni, silts being enriched relative to clays in Ti, Si, Ca, P_2O_5, Ba, Sr, Mn and Co. Relative to silt and clay, sands are enriched in Ca, P_2O_5, Fe, Mg, Pb, and, in addition, off Cap Sim-K and Cr and off Cap Blanc Mn and Sr. These data are taken to indicate concentrations of clays and heavy minerals in the silts and clays and concentrations of apatite (Ca, P_2O_5), dolomite (Mg), glauconite (Fe, K), and possibly Fe oxides (Fe, Mn, Pb) in the sand fractions. The dolomite, glauconite and Fe oxides all exist as integral constituents of phosphatic rocks from this region (Chapter 6) but glauconite and Fe oxides may also form discrete mineral phases in the sand fraction (Chapter 1). These analyses imply that, because of mineralogical controls, fine grained sediments will be enriched in the bulk of analysed elements except Ca, P_2O_5, Fe, Mg, K, Cr and Pb, which would apparently be concentrated where sands predominate. Within silty sediments, enhancements in Al, Cu, Zn, Ga, V and Ni would probably signify an increase in clay sized relative to silt-sized components.

Further examination shows that there are regional compositional differences between each fraction: with respect to the corresponding Cap Blanc sediments, Cap Sim clays are enriched $>5\%$ in Ca, P_2O_5, Sr, Ba, Cu; Cap Sim silts are

enriched >5% in K, Si, Ni, Ba. Within the sands only Fe, K and Ba are consistently enriched >5% off Cap Sim. Off Cap Blanc, clays are enriched >5% in Mn, Fe, Ni, Cr, Co, V; silts are enriched >5% in Al, Mg, Fe, Ca, V, Co, Mn, Sr, Zn and sands in Al, Ti, Mn, Co, Pb, Ga, Ca. The differences between the clays are exactly the same when element/Al ratios are considered as when total abundances are considered (table 3.3.1). Since this ratio is thought to reflect clay mineral provenance (cf. Hirst, 1962 b; Porrenga, 1967 b) a provenance difference may be indicated for the sediments of the two silt belts. The differences between the sands are not entirely real in that these are not sand separates but very sandy samples in which some silt and clay are mixed. Nevertheless, although this may explain the element enrichments in Cap Blanc samples it does not account for the Fe, K, Ba enrichment in the glauconitic Cap Sim samples. Accordingly it appears that as well as showing relative grain size differences (based on mineralogy) this technique will disclose mineralogical differences within samples of similar texture.

3.3.2 Histogram Analysis: Population Subset 1

The validity of these findings, as far as a regional survey was concerned, was tested first by considering the frequency distributions for individual elements in total sediments from population subset 1 (Fig. 3.3.1). Within this population are several well defined subsets representing regional differences between similarly textured samples or local differences between differently textured samples. (In the following discussion the term silt is used to signify a fine grained sediment dominantly composed of silt-sized material.) The major elements P_2O_5, Al, Ca, Fe, K, Mg, and Si display texturally induced variations off both Morocco and the Sahara. The minor elements Ba, Co, Cu, Ga, Pb, Mn, Ni, Sr, Ti are texturally influenced off the Saharan coast but off Morocco only Cu, Ga, Pb, Ni, Sr, and Ti show this type of influence clearly. Sands tend consistently to be enriched in P_2O_5,

Mg

Ca

P_2O_5

Fe

Al

K

Sr

Ba

Co

Cr

Cu

Ga

Mn

Ni

Pb

Si

V

Ti

Zn

Fig. 3.3.1 Frequency distribution of individual elements in acid insoluble residues of samples from population subset 1.

■ = south Saharan sands; □ = north Saharan sands; ▩ = north Saharan silts; ■ = glauconitic Moroccan sands and silty sands; ▲ = nonglauconitic Moroccan sands and silty sands; △ = Moroccan silts

Ca, Sr, Fe, Mg, Pb and locally Mn and Sr, whereas silts tend consistently to be enriched in Al, K, Ga, Cu, Ba, Co, Ni, Ti and to a lesser extent Si and Mn. These variations mirror those disclosed by size fraction analysis of selected Moroccan samples and imply that apart from quartz, the major sand minerals of the northwest African shelf are apatite and dolomite from phosphate rocks (Ca, P_2O_5, Sr, Mg) in company with iron minerals (Fe, Mn, Pb probably represent glauconite and/or iron oxides). Despite the existence of regional variations in either sands or silts the textural groupings remain very distinct.

Regional differences may signify provenance differences if the constituents of any one size fraction in all samples have had very similar transportational and depositional histories. Accepting this assumption then there are provenance differences between north Saharan sands (enriched relative to south Saharan sands in Ca, P_2O_5, Fe, V, Ba, Co, Mn, Sr, Zn) and south Saharan sands (enriched in Si and Ti). This supports visual observations which show the southern sands to be more quartzose and the northern sands to be more phosphatic and often iron-oxide coated (cf. Chapter 1). That Moroccan silts are enriched (relative to Saharan silts) in Al, K, Mg and Si but depleted in Cu, Pb, Ba, Co, Cr, Ni and Ti may also signify a provenance difference. Comparing phosphatic and non-glauconitic north Saharan with Moroccan sands, differences are seen which may be texturally rather than provenance induced. The enrichment of Moroccan (relative to north Saharan) sands in Al, K, Mg, Mn, and Sr is most probably governed by the preferential admixture of silt and clay with Moroccan as opposed to Saharan sands (cf. Chapter 1). The differences between north and south Moroccan sands is taken to reflect concentration of glauconite in the latter and iron oxides in the former possibly as a result of authigenic rather than detrital provenance influences; this will be investigated in some detail later in this chapter. As between north and south Saharan sediments there is a general phosphate

decrease southward, among shelf sands, which probably reflects the lesser degree of exposure, southward on the shelf of phosphatic source rocks.

In summary, mineralogically controlled geochemical differences relating to source or sediment type allow division of the sediments into distinct geochemical groups on a regional and textural basis.

With regard to the absolute abundances of these elements, compared with average shales, the Saharan and Moroccan sediments contain similar amounts of most elements except Pb, Cr and V which tend to be slightly enriched off northwest Africa, probably due to local provenance characters. Consideration of the maximum determined values for individual elements suggests that no metal deposits of economic interest have been revealed by the reconnaissance. Maximum elemental values (in ppm) are as follows:- Ni:170; Pb:130; Co:24; V:700; Cr:450; Ba:500; Ga:20; Cu:300; Sr:1000; Mn:c1000; Ti:c1000; Zn:300.

3.3.3 Single Element Distribution in Relation to Sediment Type off Morocco

The degree to which individual element distribution maps may reflect mineralogy and texture on a regional basis was tested on Moroccan sediments using data from population subset 2 together with analyses of soluble Fe and Mn. To facilitate comparison of elemental and textural distribution, elemental abundances are represented by five or six symbols representing specific concentration ranges and giving the maximum features of the areal distribution: these are superimposed on a base map displaying the main textural features of the Moroccan shelf and slope (Fig. 3.3.2). In that the textures are those of total sediment whereas the elemental abundances are those of the detrital phase, an exact correlation is not expected; but as in Chapter 1 it was shown that the detrital and total sediment textures closely correspond, this means of assessing the geochemical-textural relation is regarded as valid.

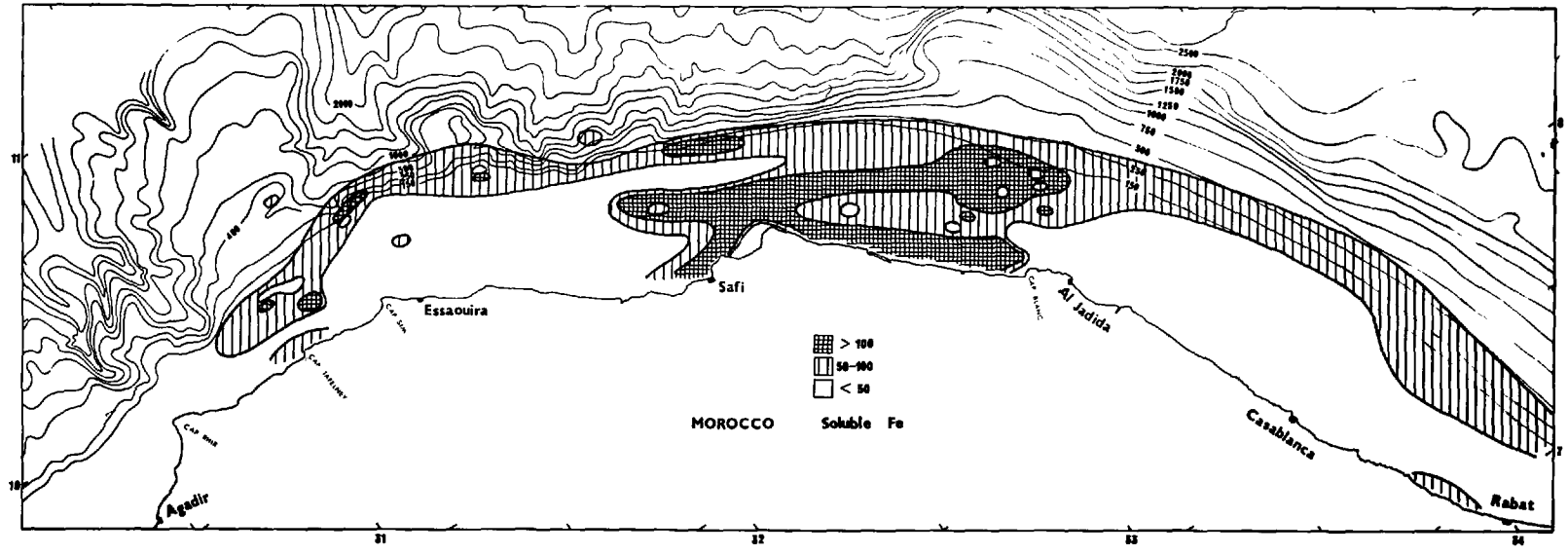


Fig.3.3.2.(I) Distribution of acetic acid soluble Fe (ppm on a carbonate-free basis) in sediments .

Fig.3.3.2.(2) Distribution of acetic acid soluble Mn (ppm on a carbonate-free basis) in sediments.

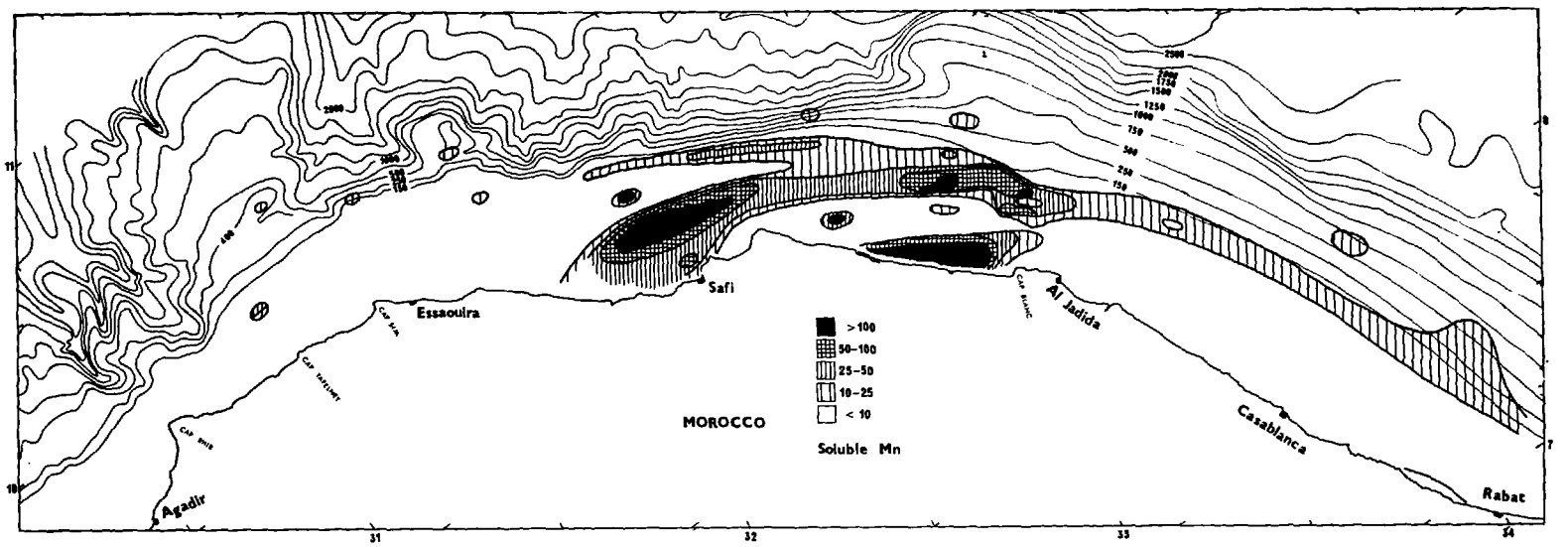


Fig.3.3.2.(3) Distribution of Ba in acetic acid insoluble residues of sediments off Morocco.
Contours represent outlines of the main sediment zones shown in Fig.I.3.I.

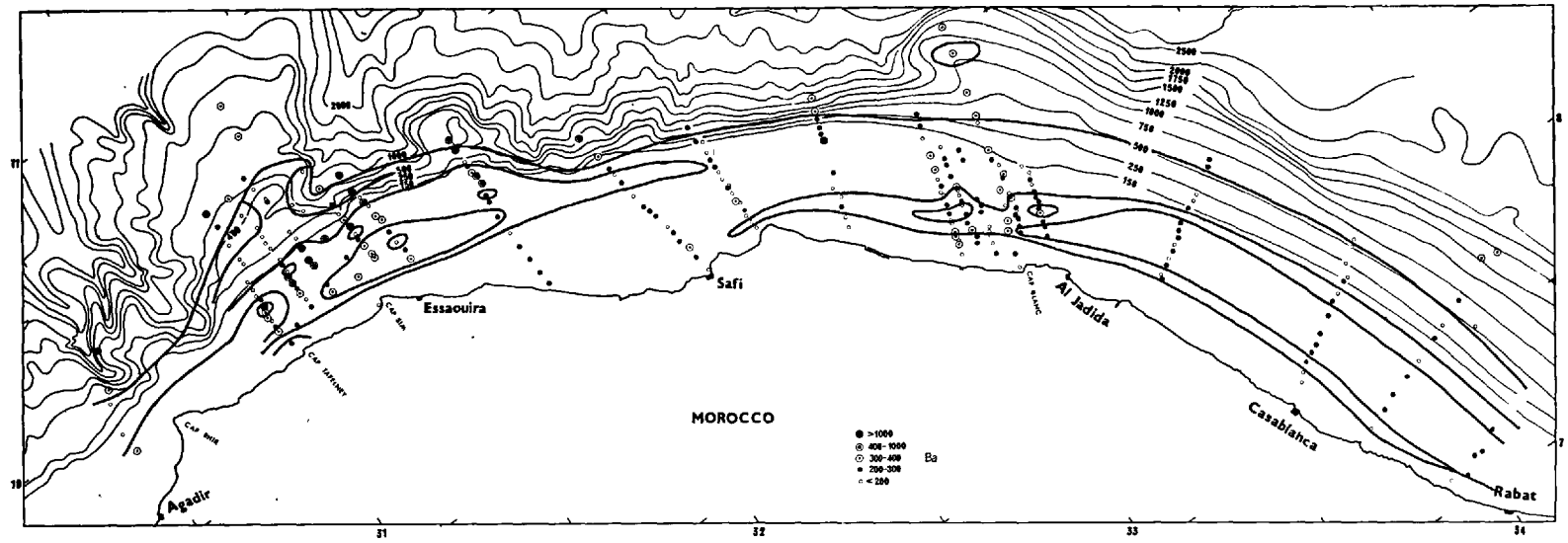


Fig.3.3.2.(4) Distribution of Co in acetic acid insoluble residues of sediments off Morocco.
Contours represent outlines of main sediment zones shown in Fig.1.3.1.

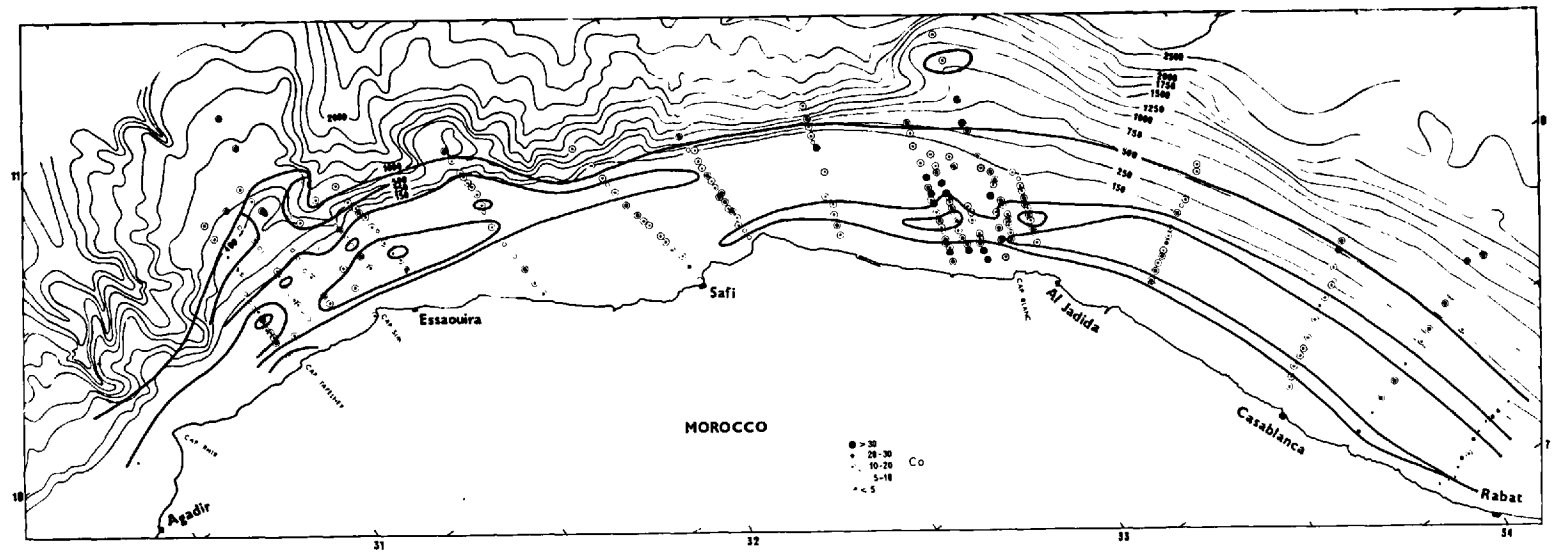


Fig.3.3.2.(5) Distribution of Cr in acetic acid insoluble residues of sediments off Morocco. Contours represent outlines of the main sediment zones shown in Fig.1.3.1.

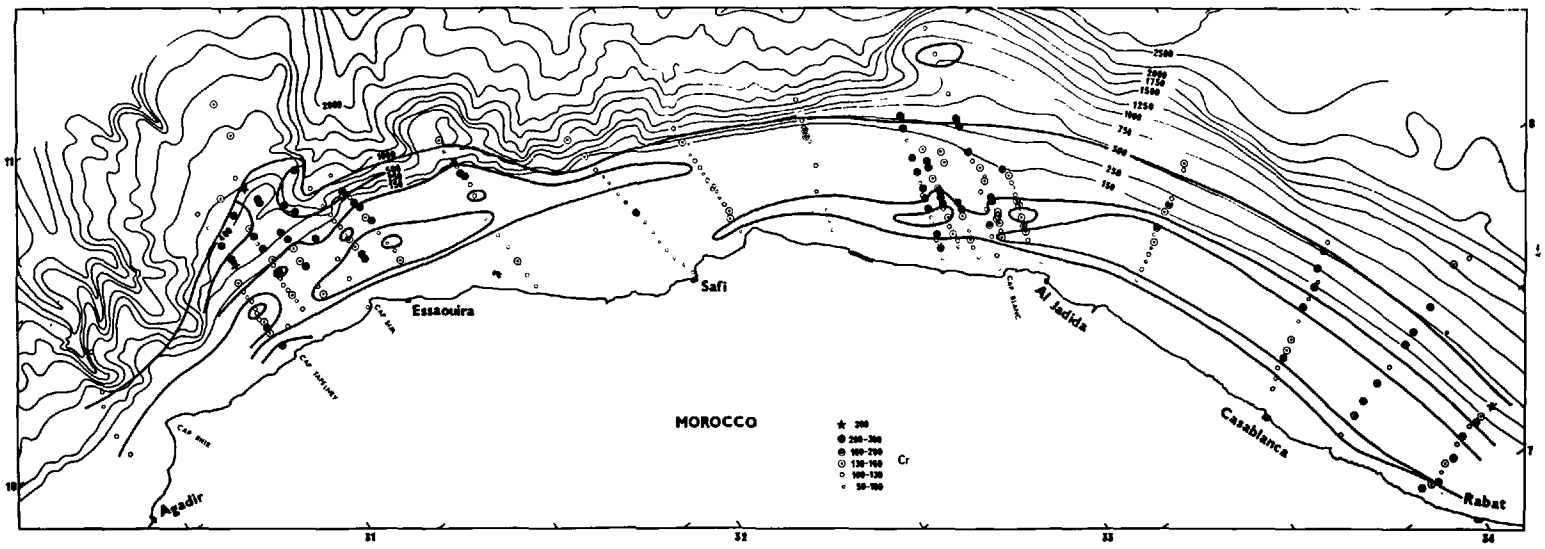


Fig.3.3.2.(6) Distribution of Cu in acetic acid insoluble residues of sediments off Morocco. Contours represent outlines of the main sediment zones shown in Fig.1.3.1.

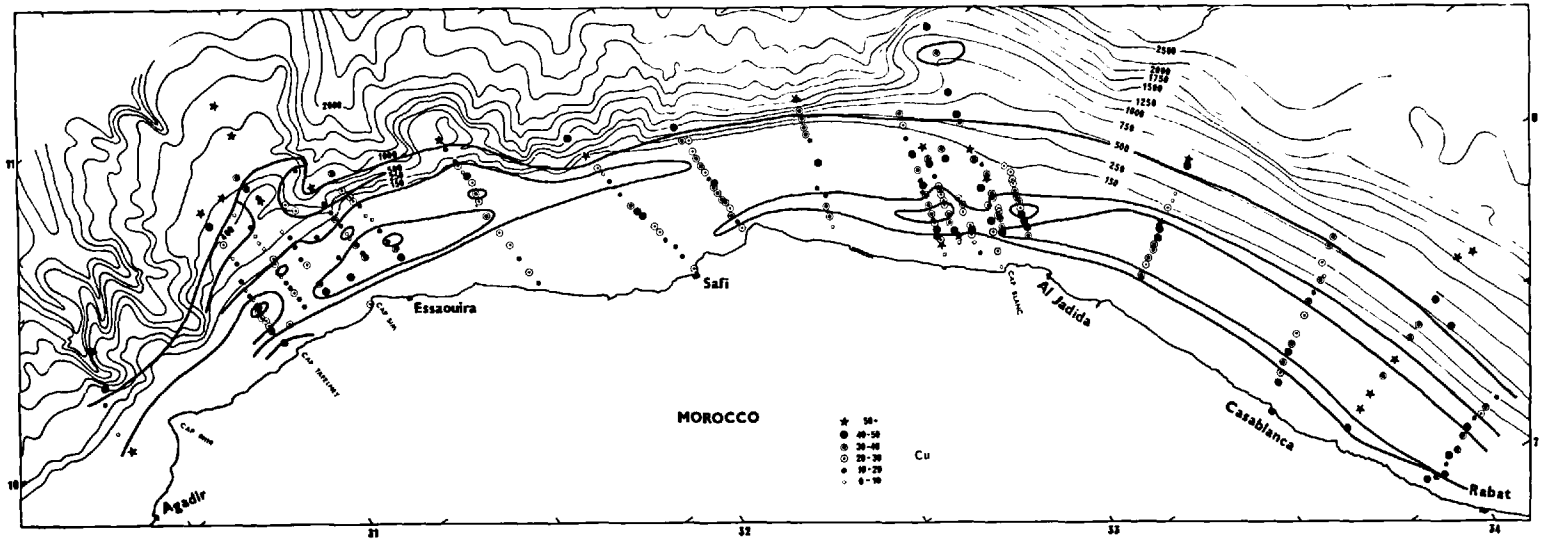


Fig.3.3.2.(7) Distribution of Ga in acetic acid insoluble residues of sediments off Morocco. Contours represent outlines of the main sediment zones shown in Fig. I.3.I.

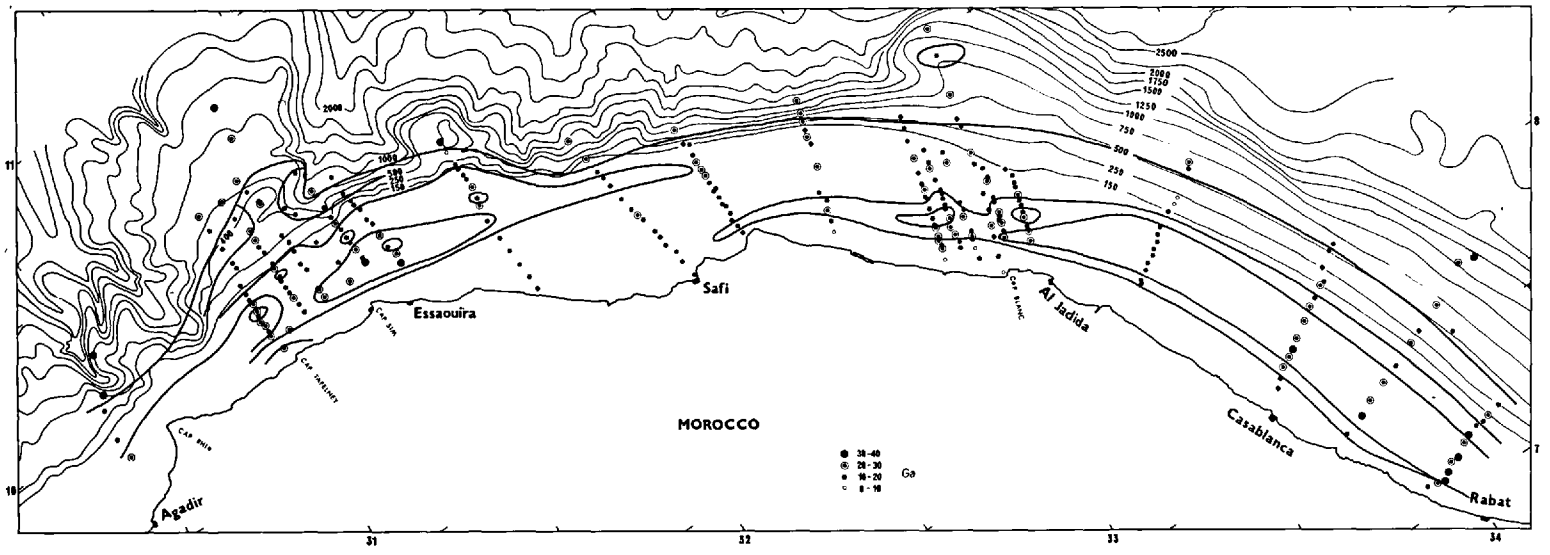


Fig.3.3.2.(8) Distribution of Mn in acetic acid insoluble residues of sediments off Morocco. Contours represent outlines of the main sediment zones shown in Fig.1.3.1.

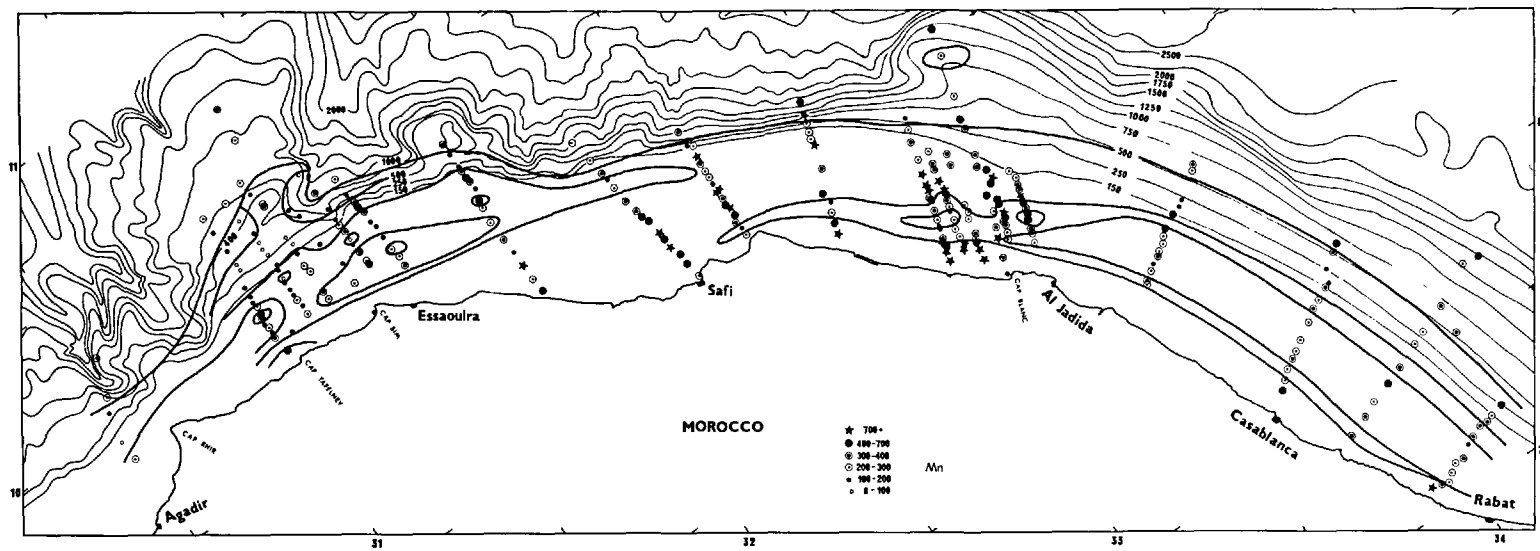


Fig.3.3.2.(9) Distribution of Mo in acetic acid insoluble residues of sediments off Morocco. Contours represent outlines of the main sediment zones shown in Fig.I.3.I.

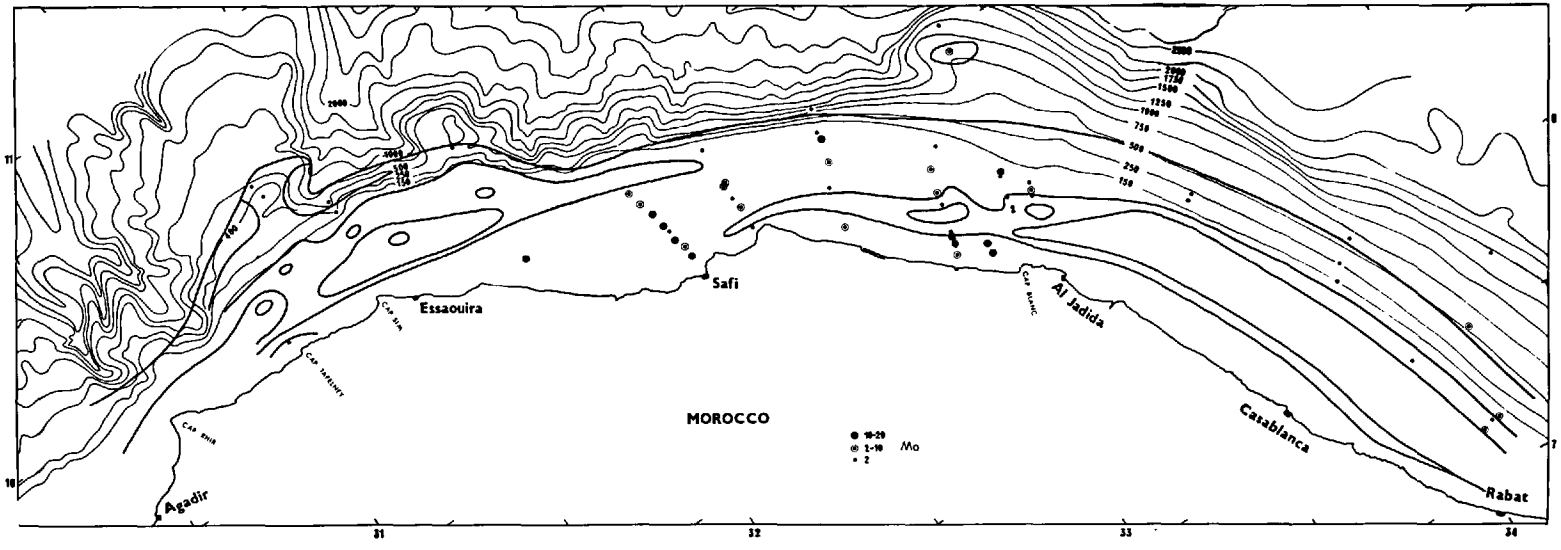


Fig.3.3.2.(10) Distribution of Ni in acetic acid insoluble residues of sediments off Morocco. Contours represent outlines of the main sediment zones shown in Fig.1.3.1.

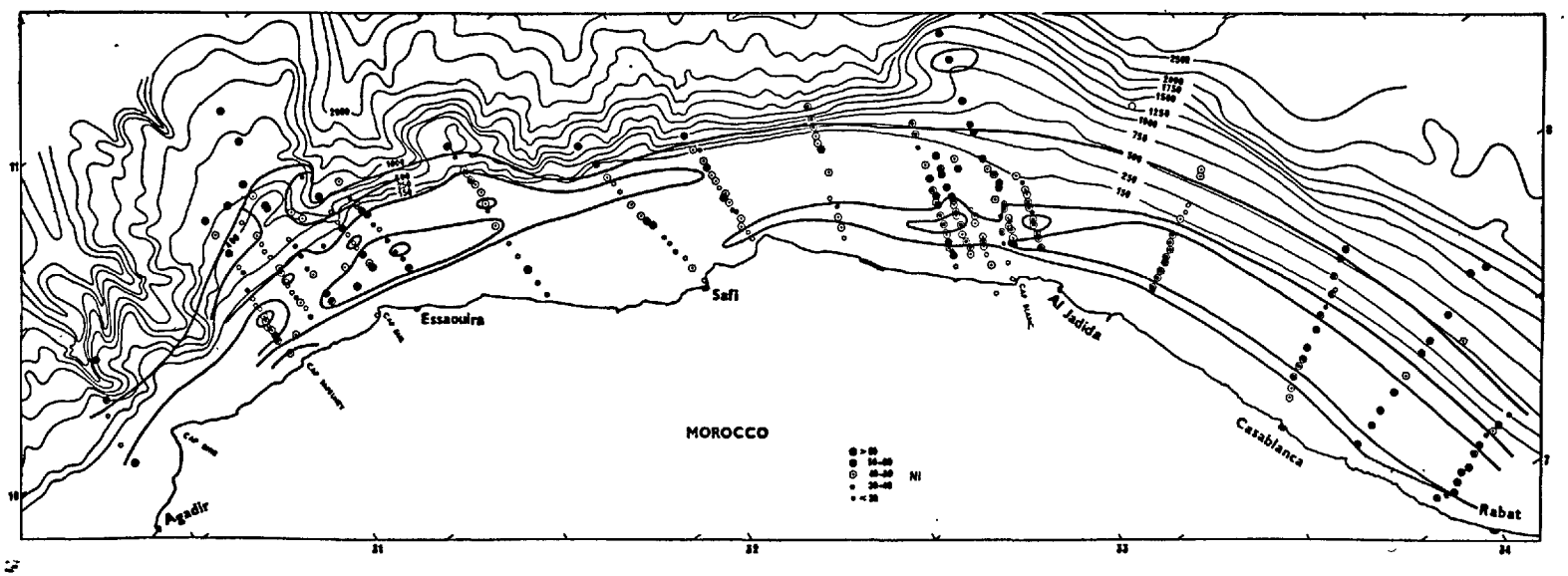


Fig.3.3.2.(II) Distribution of Pb in acetic acid insoluble residues of sediments off Morocco. Contours represent outlines of the main sediment zones shown in Fig.I.3.I.

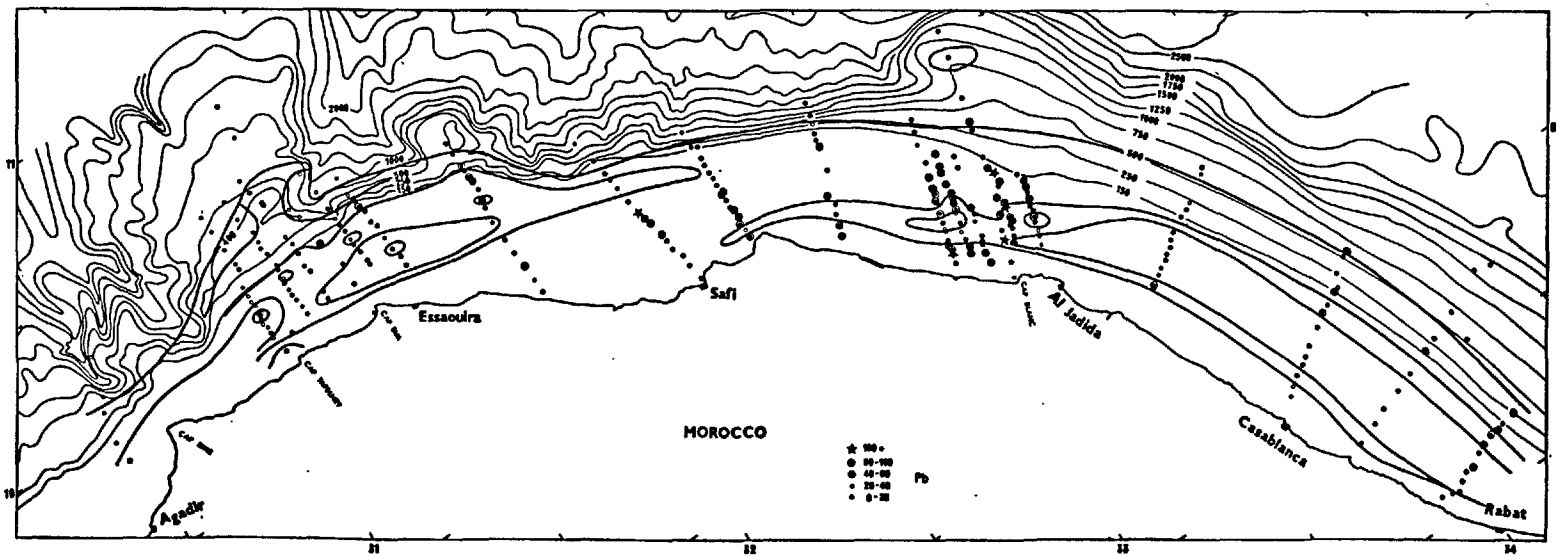


Fig.3.3.2.(12) Distribution of Sr in acetic acid insoluble residues of sediments off Morocco. Contours represent outlines of the main sediment zones shown in Fig.1.3.1.

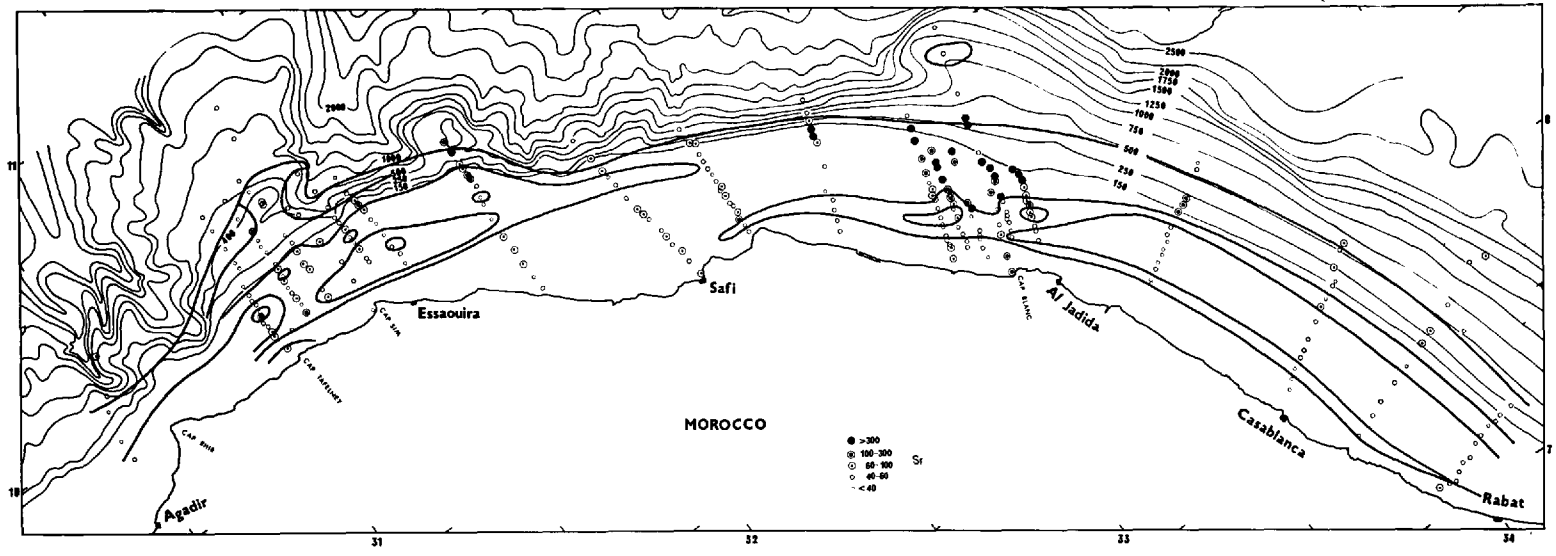


Fig.3.3.2.(13) Distribution of Ti in acetic acid insoluble residues of sediments off Morocco. Contours represent outlines of the main sediment zones shown in Fig.1.3.1.

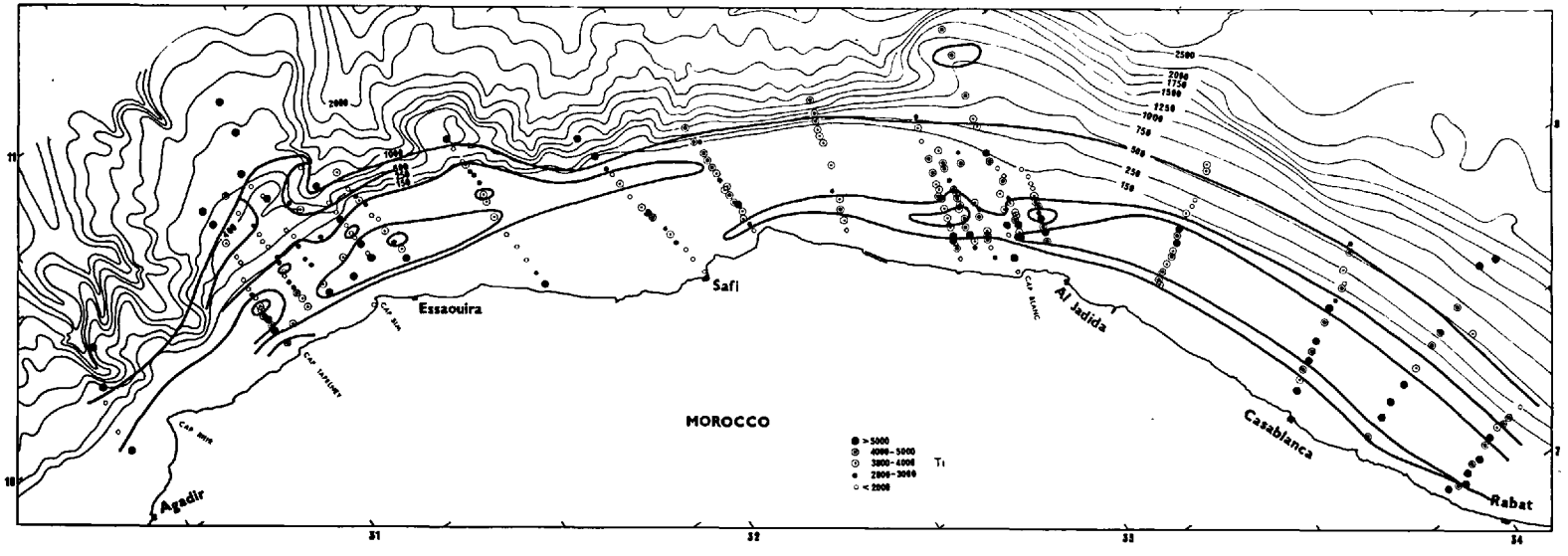


Fig.3.3.2.(14) Distribution of V in acetic acid insoluble residues of sediments off Morocco. Contours represent outlines of the main sediment zones shown in Fig.1.3.1.

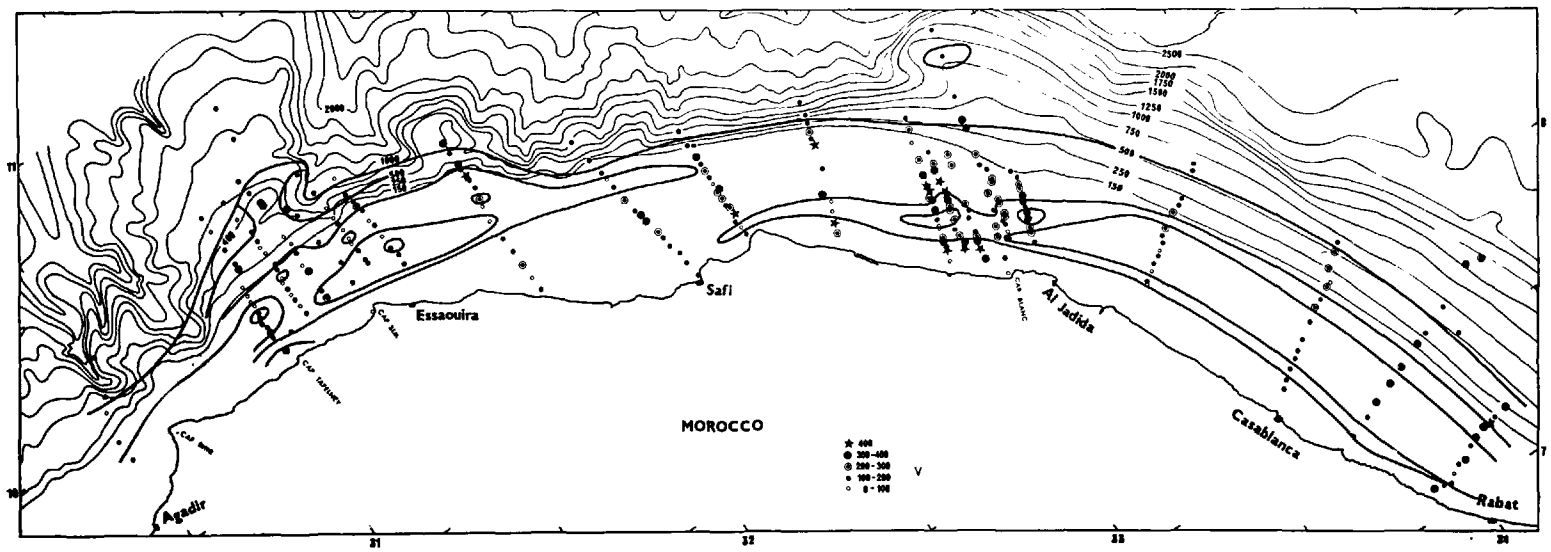


Fig.3.3.2.(15) Distribution of Zn in acetic acid insoluble residues of sediments off Morocco. Contours represent outlines of the main sediment zones shown on Fig.1.3.1.

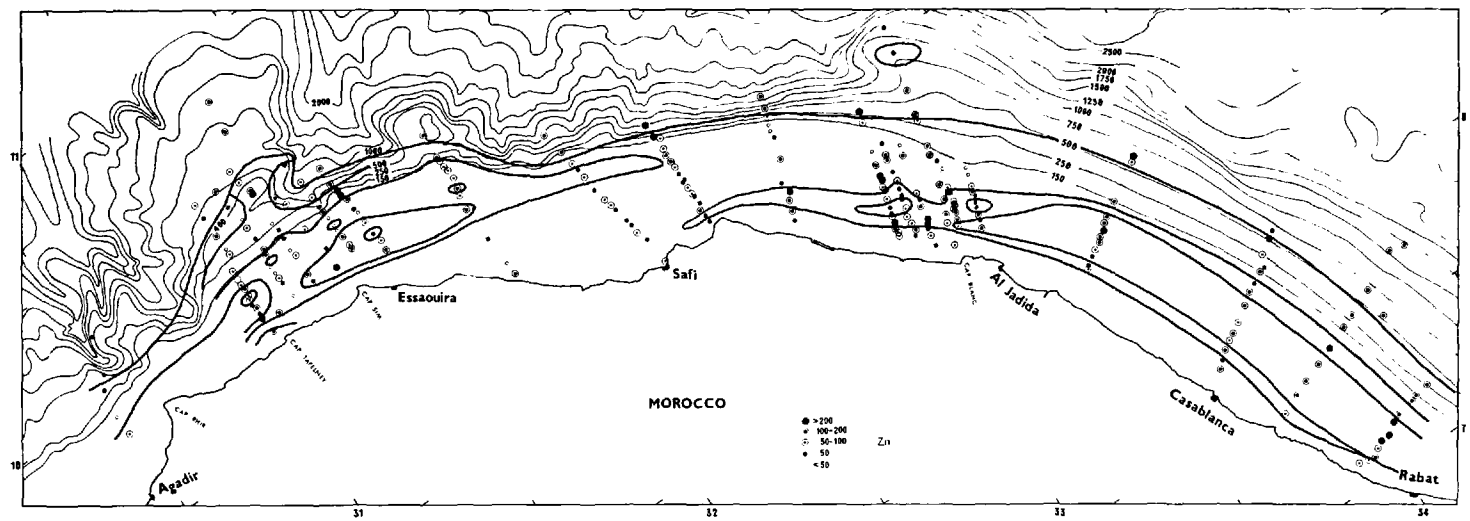
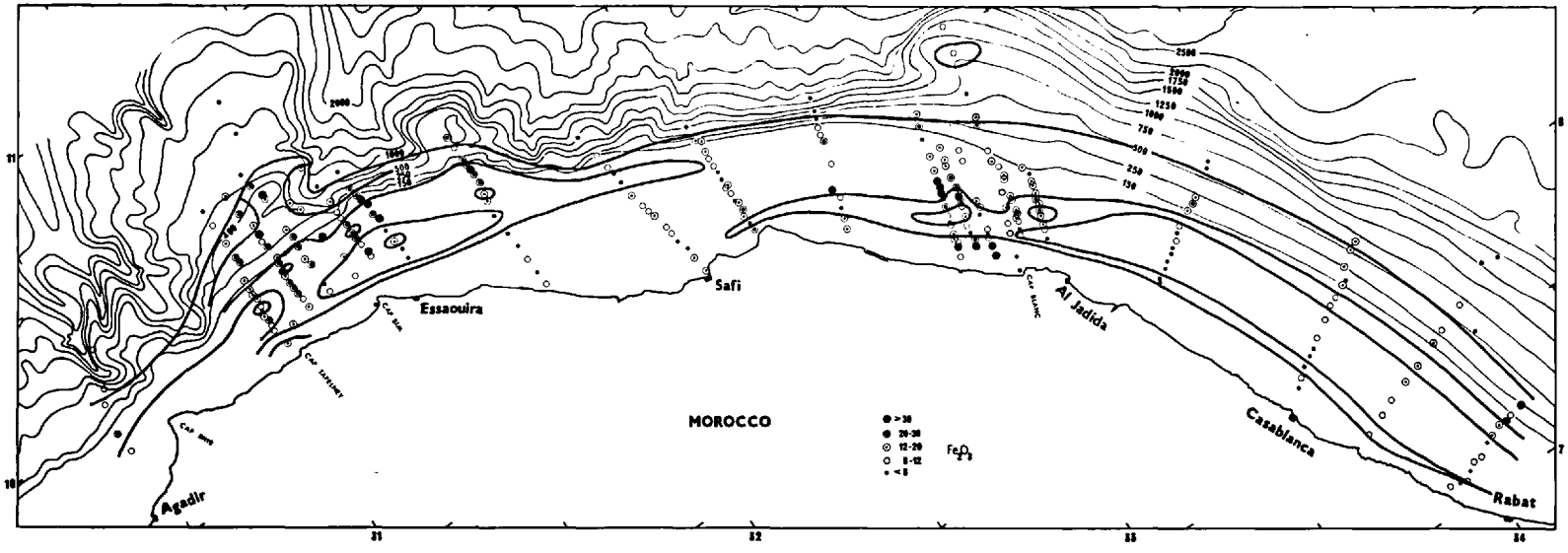


Fig.3.3.2.(16) Distribution of iron as Fe_2O_3 in the acetic acid insoluble residues of sediments off Morocco.

Contours represent outlines of the main sediment zones shown in Fig.1.3.1.



In accordance with previous findings, certain elements show a clear distributional relation to texture, but often the patterns are made more complex than previous analyses suggested, primarily because of mineralogical variation in the sand fraction. In general Ba, Cu, Ni, Ti and Zn are enriched in silts while Sr, and Fe_2O_3 are enriched in sands (Fig. 3.3.2) as too is P_2O_5 (Fig. 2.2.10). In the central shelf sands between Essaouira and Al Jadida, certain elements (notably Fe, Mn, V, Pb, Co) which are depleted relative to adjacent silts off Essaouira, become progressively concentrated north toward Cap Blanc where they are enriched relative to adjacent silts. It is in these metal rich sediments that most of the detectable Mo is found. Of these elements, Pb, V and Co in southern sands are almost everywhere depleted relative to southern silts but their relation to northern silts is obscured by the central shelf sand maxima. Another element influenced strongly by sand mineralogy is Cr which is enriched relative to silts in the southern glauconitic sands. The opposite is true for the northern sediments.

The Ga dispersion is unusual in that instead of, as anticipated, being concentrated among the fine sediments, it is more or less evenly distributed throughout the area in amounts between 10 - 20ppm. Even the use of different class intervals of 0 - 15 and 15 - 20ppm did not significantly change this picture. This even distribution is thought due to the bonding of Ga in feldspars in the sands and within clays in the fine sediments. That some of the silts have notably enhanced Ga content is taken to reflect local increases in clay content, for instance in the northern part of the northern silt belt (this is supported by Nutter's textural analyses, cf. Nutter, 1969), and among certain slope sediments. The northward Ga increase in northern shelf silts is paralleled by Cr but not notably by other elements. Differences are apparent between the northern and southern slope silts which may reflect provenance although without detailed investigations this remains

conjectural: northern silts tend to contain more Cr and Co while southern silts tend to contain more Ba. These intra-silt differences do not mask the fundamental differences between silts and sands.

Soluble Mn is notably concentrated in the mid, inner and outer shelf sands north of lat. 32°N, but is always very low among southern shelf sediments (cf. Figs. 3.3.2. and 1.3.1). Silts are everywhere low in soluble Mn compared with sands. In general the sediments richest in soluble Mn are much the poorest in organic carbon (compare Figs. 3.3.2 and 1.4.7). Soluble Fe distribution (Fig. 3.3.2) more or less parallels that of soluble Mn on the northern shelf. A signal difference in the regional pattern, in comparison with soluble Mn, is that a tongue of sands and silty sands rich in soluble Fe extends right along the edge of the southern shelf; on the outer shelf off Agadir is the highest recorded soluble Fe level of traverse 1 (45ppm at Sta 805) and it can be assumed that this zone is continuous.

These patterns are attributed to part solution (1) of sand sized glauconite, which is notably concentrated among southern outer shelf sediments, and (2) of iron-manganese oxides known to stain central and northern, but not southern, shelf sands (cf. Chapter 1). That the iron-manganese phase mainly occurs in well-oxidised sands very poor in organic carbon, but not in the glauconitic and rather more carbonaceous southern shelf sands and silty sands, supports the suggestion that its formation is Recent (cf. Chapter 1).

The metal enrichment in the central shelf sands seems well correlated with the supposed secondary ferromanganese concentrations. One reason why several elements do not clearly show the boundaries of the northern silt belt is suggested by the occurrence, among outer shelf sediments, of presently recognised secondary oxides and (cf. Nutter, 1969; Matthieu, 1968) of glauconite.

3.3.4 Summary

In summary it is clear that single element data alone cannot be used to indicate mineralogical and textural features although silts and sands can be differentiated into natural groups on the basis of their total geochemical character. Salient points emerging from these analyses are that (1) different and geochemically distinct subpopulations appear to represent natural mineralogically controlled groupings; (2) The principal mineral controls appear to be, in sands, apatite, quartz, glauconite and iron manganese oxides, and in silts, heavy minerals and clays, in accordance with what is known of the sediment mineralogy (cf. Chapter 1); (3) regional geochemical mapping techniques can assist in determining the boundaries of mineralogical and textural groups. Particular problems emerging from this study are that (1) there is information repetition due to geochemical affinities between certain elements (2) the degree to which certain mineral phases control specific elements cannot be quantified and (3) province boundaries are obscured where one or more elements occur in two or more minerals. To resolve certain of these problems a statistical analysis of the data was undertaken.

3.4. Correlation Coefficient Analysis

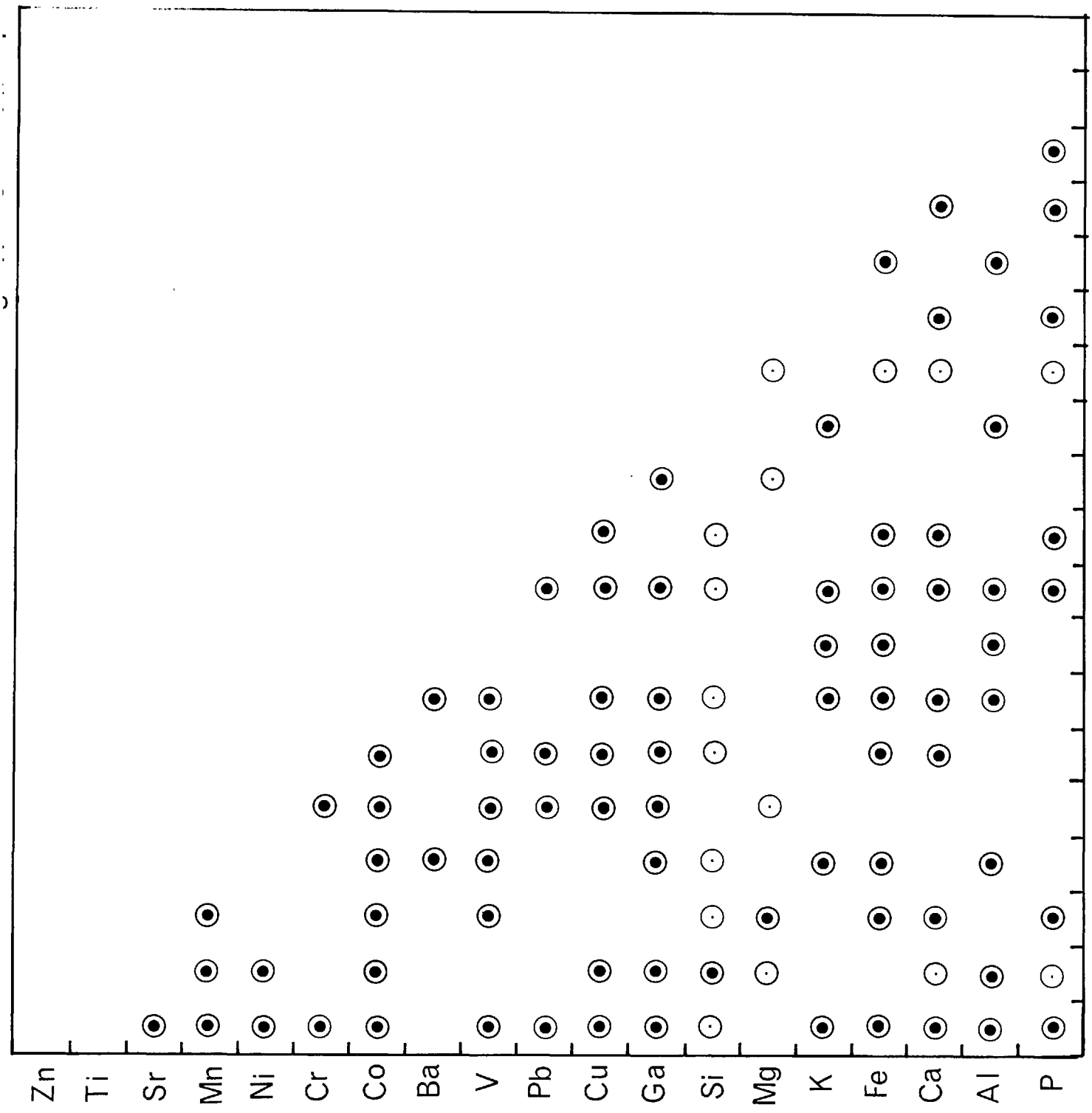
The product-moment coefficient of linear correlation (r) was computed between all pairs of variables using the method of Garrett (1967); results are presented diagramatically in the form of a correlation coefficient matrix (Figs. 3.4.1.). The prime object is to establish the degree to which the elemental data are causally related; i.e. the degree to which they are significant mineralogical indicators.

Limitations in the interpretation of inter-element correlation coefficients are (1) the requirement that variables be normally distributed before a

Fig.3.4.1.a. Population subset I. logtransform data. Product moment correlation coefficient matrix.

⊙]= significant [+ correlation at 99% confidence level

⊙ = significant - correlation at 99% confidence level



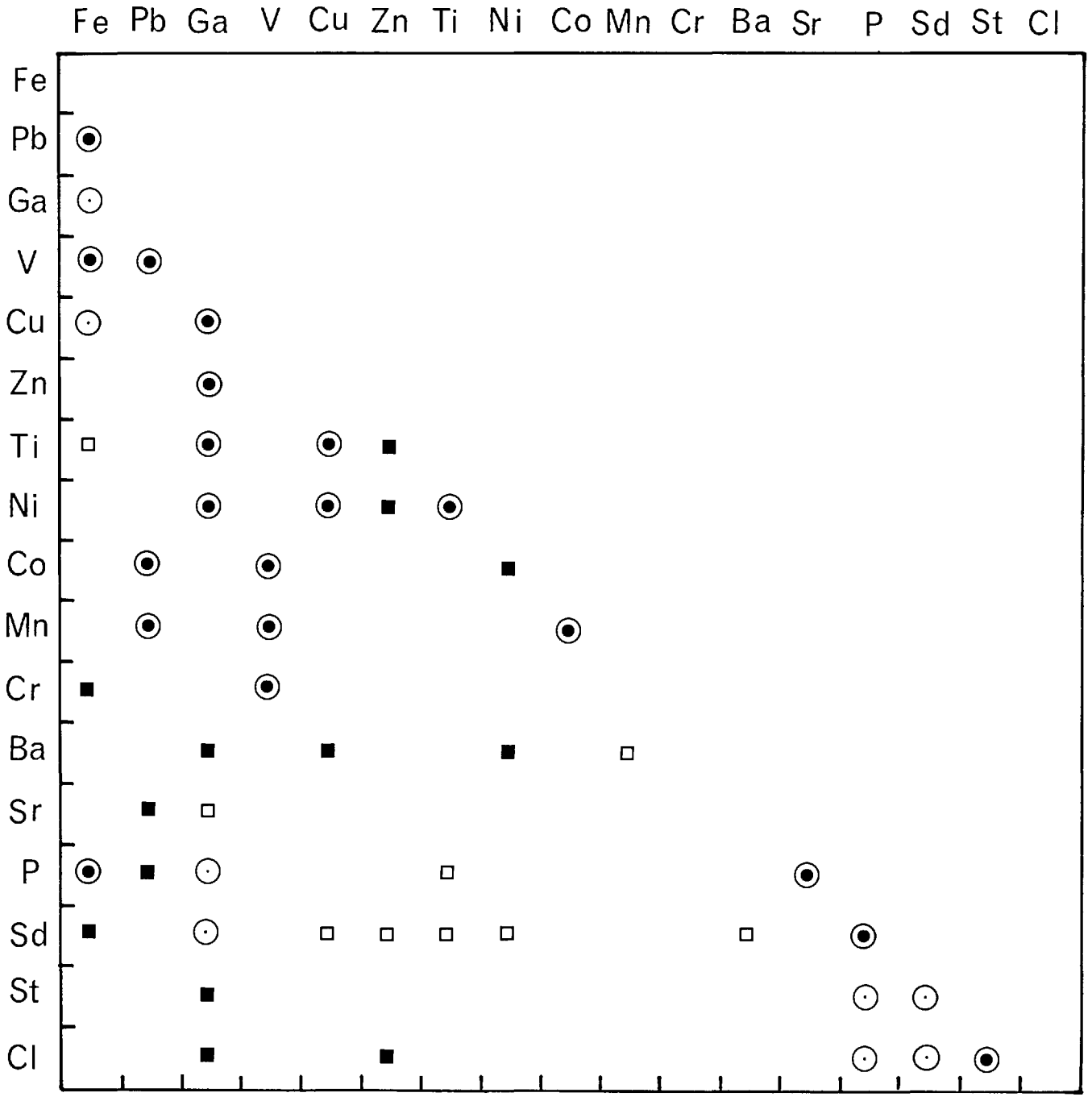


Fig.3.4.1.b. Population subset 3.Logtransform data. Product-moment correlation coefficient matrix.

⊙ = signif.+ correlation 99% confidence level

■ = signif.+ correlation 95% confidence level

⊙ = signif.- correlation 99% confidence level

□ ==signif.- correlation 95% confidence level.

Sd = Sand percent

St = Silt percent

Cl = Clay percent

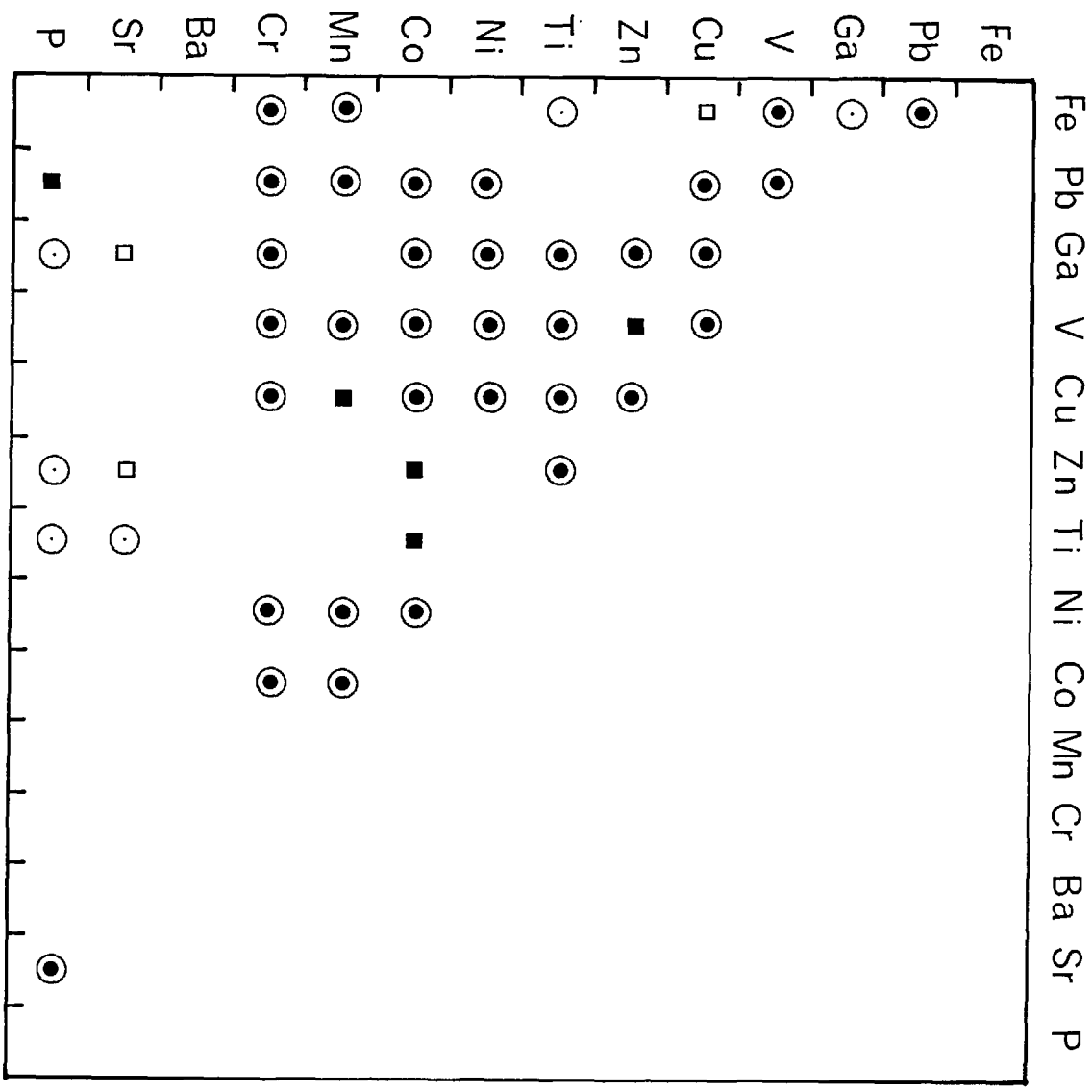


Fig.3.4.1.c. Population subset 2. Arithmetic data: product -moment correlation coefficient matrix (for comparison with Fig.3.4.1.d.).

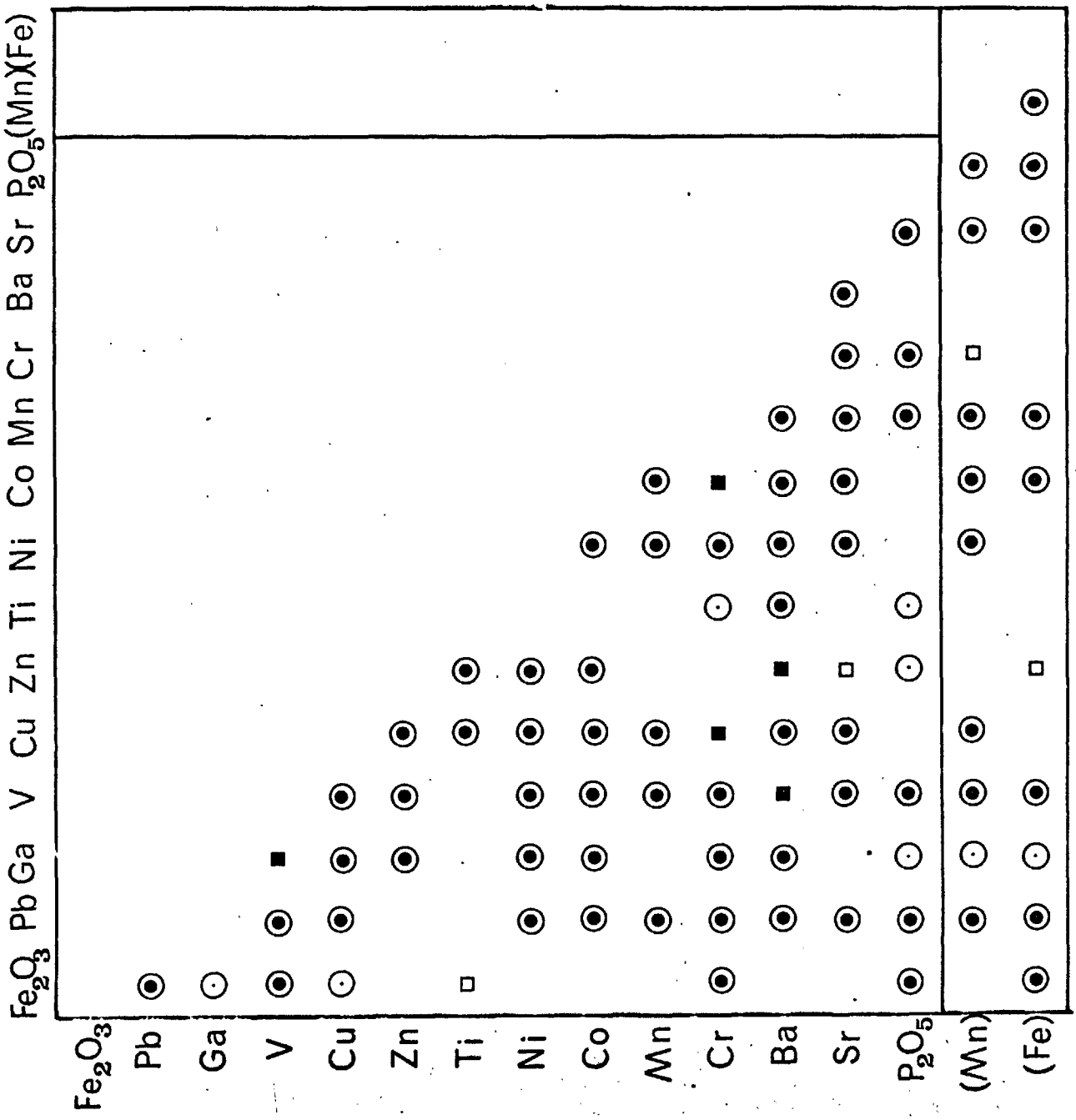
⊙ = significant + correlation; 99% confidence level.

■ = significant + correlation; 95% confidence level.

⊗ = significant - correlation; 99% confidence level.

□ = significant - correlation; 95% confidence level.

Fig.3.4.1.d Population subset 2 ; logtransform data : product-moment correlation coefficient matrix. Also shown is part of the correlation coefficient matrix for population subset 4 (Sol.Mn and Fe); essentially the same correlations exist between all elements in the insoluble resid -ues in both population subsets, although in subset 4 there is significant - correlation between Ga and Sr, and no significant correlation between Cu and Ti, or Zn and Ba.
The symbols used are the same as in Fig.3.4.1.c



correlation coefficient matrix can be established, and (2) the existence of associations induced by sample matrix effects or line interferences in the spectrographic method. Examination of elemental distributions in histogram form showed that most elements approach normality in distribution although they frequently displayed positive skew (table 3.4.1). It was found that logtransformation of the data substantially reduced the degree of skew (table 3.4.1) and such a transformation was applied in the derivation of all correlation coefficients. The second problem, concerning in effect the validity of the original data is assessed in Appendix 3 and essentially appears non significant.

The assumption is made throughout that where elemental abundances exceed 1000ppm they reflect occurrence of a specific mineral phase (e.g. Ti = rutile; Mn = ferromanganese oxides) but otherwise they are probably only trace constituents of specific minerals and will tend to follow the major elements indicative of these minerals. The sole exception is that, where Al analyses were not carried out, Ga is taken to represent this element (with which it has very strong geochemical affinities; cf. Goldschmitt, 1954) and hence the alumino-silicate minerals (chiefly feldspars and clays).

3.4.1 Population subset 3 (Fig. 3.4.1)

This subset comprises the limited number of Moroccan samples for which granulometric and geochemical data were simultaneously available. Insufficient data prevent the processing of Mo in this and other subsets.

The correlations strongly confirm previous findings regarding control of element dispersion by mineralogy and hence texture. Taking P_2O_5, Fe_2O_3, Mn, Ga and Ti to represent the major mineral controls, a number of causal relations are recognised. The correlation of P_2O_5 and Sr is taken to be causally related to apatite; their correlation with sand confirms the findings of Chapter 2 and their correlation with Fe_2O_3 reflects both the

recognised concentration of iron minerals in the sand fraction (cf. Chapter 1) and in phosphate rock (cf. Chapter 6). The correlation of Pb and V with both the Fe_2O_3, Cr and sand phase, and with Mn, Co, may signify a dual control by an iron rich sand component and a manganese-rich mineral which is independant of texture.

Whereas off Morocco Ga was found to be enhanced in clayey sediments it was also seen to be a poor indicator of accepted silt - sand boundaries which were rather better defined by other metals (Ti, Cu, Ni, Zn, Ba). Despite this, the present analysis shows a strong Ga-silt-clay correlation and a strong correlation of Ga with these same metals. This suggests that although Ga dispersion alone cannot be used to define the silt boundaries, a Ga-metal association can be so used.

3.4.2 Population Subset 2 (Fig. 3.4.1)

This subset comprises all analyses of the acid insoluble fraction of Moroccan sediments. Both arithmetic and logtransformed data were used for comparison; logtransformation reduced skew (table 3.4.1) but the transformation caused certain differences in association to arise. On the whole, these differences are slight and, as the skew is reduced by transformation, the transformed data are preferred.

Despite the absence in this subset of the 'mineralogical' variables sand, silt and clay, essentially the same elemental associations emerge as from the previous subset. This strongly bears out the suggestion that these geochemical groupings are causally related and mineralogically controlled by a limited number of phases. Differences between the two subsets are that although in subset 3 Ti and Ga are antipathetic to elemental associations reflecting the sand fraction (P_2O_5 and Fe_2O_3), they are not themselves strongly correlated. This may be due to the previously noted concentration of Ti in the silt and Ga in the clay fractions. Some control of Co and Cr

by clays is also suggested by the addition of these elements to the group previously found correlated with Ca. Mn is now found to correlate weakly with P_2O_5 which may reflect a general regional tendency for authigenic manganese-rich mineral phases to form in sands. The further association of Mn with Cu, Ni and Ba may be causally related to the characteristics of the oxide phase although since these elements have hitherto been found mainly associated as a hydrolysate group, the present Mn association may reflect a dual occurrence of Mn both in clays and as oxides.

3.4.3 Population Subset 4 (Fig. 3.4.1)

This subset comprises all Moroccan samples for which soluble Fe and Mn values were available: only the correlations of other elements with these two variables are presented for discussion because correlations between the other variables were the same as those determined in the previous subset. The very strong correlation between soluble Fe and soluble Mn and the previously recognised insoluble Mn, Pb, V, Co group bears out the suggestion that this represents causal control by a partly soluble ferro-manganese mineral phase. The very weak correlation between soluble and insoluble iron supports other mineralogical observations (Chapter 1) which show there to be two main iron minerals - oxide and glauconite; the latter is a relatively insoluble mineral poor in Mn and this has tended to obscure the Fe-Mn association in previous subsets. The correlation of soluble Fe and Mn with P_2O_5 and Sr, as suggested above, may be a function of either shared provenance or preferential formation of authigenic oxides in relict sands, many of which are phosphatic.

3.4.4. Population Subset 1 (Fig. 3.4.1)

This subset represents a mixture of Moroccan and Saharan sediments; that most of the associations are similar to those for Moroccan samples alone signifies a fundamental similarity of mineralogy in these two areas.

The correlation of Ca with Sr represents a well established geochemical association (cf. Goldschmitt, 1954); their correlation with P_2O_5 is causal and relates to the presence of apatite. The correlation of Fe, V and Pb with apatite (and possibly also Zn - although this was not previously associated with Fe in other subsets) again most probably reflects the occurrence of iron minerals in the sand fractions where apatite is concentrated. Antipathy of this group to Si and Ti is taken to represent provenance differences resulting in regional groupings of phosphatic sands and quartzose sands containing ilmenite or rutile. Al is taken to represent the hydrolysate fraction as these sediments contain very little feldspar. The correlation of Al with K is thought causal; in illitic clays K is sited in interlayer positions. The remaining elements which are correlated with Al, with the exception of Ba which usually follows K, have ionic radii similar to Al and are often contained within the hydrolysate fraction of sediments (cf. Goldschmitt, 1954). Correlations with Ga are essentially the same as for Al, except that Ba is no longer present and there is addition of Cu, Ni and Cr all of which have ionic radii similar to Al and occur quite commonly in hydrolysates (Goldschmitt, 1954). The slight difference between the Al associations and the Ga associations may be attributed to the presence of different clay minerals or to regional provenance differences among the same mineral species. The correlation of Fe with K and Ba implies the existence of an iron-potassium mineral, probably glauconite. The correlation of Fe with Ca, P_2O_5, Sr has been explained above. Its correlation with Mn, V, Zn, Cr, Pb, Co may result from the admixture of iron oxides with glauconite. Although in previous Moroccan subsets, Mn was not correlated with the hydrolysate group, this appears to be its main control in subset 1; the substitution of Mn for Al in the hydrolysate fraction is widely recognised (Goldschmitt, 1954). Presumably the presence of large numbers of Saharan samples, in which Fe-Mn oxides are not widely developed, has

obscured the presence of a discrete Fe-Mn mineral phase. The textural control of Mn in Saharan sediments was demonstrated earlier in this chapter. Finally, Ti is found to correlate with both the hydrolysate fraction (Ga-Al) and Si (representing quartz) reflecting a dual dispersion between silts and sands.

3.4.5 Summary

Product-moment correlation coefficient analysis confirms that the geochemical assemblage can be described in terms of a limited number of distinct associations representing specific mineral controls. The main mineral phases and the elemental associations to which they give rise are as follows:-

Apatite: Ca, P_2O_5, Sr

Glauconite: Fe, K, Cr (possibly also Pb and V but these also follow Mn)

Fe-Mn oxide: Soluble Fe and Mn; insoluble Mn, Co, Pb, V (and probably Fe)

Hydrolysates (clays): Al, K, Ga, Cu, Ni, Zn, (and often, but not always, Ba, Co, Ti, In, V, Cr).

Whereas the sands are characterised (where not quartzose) by various combinations of apatite, glauconite, and Fe-Mn oxide assemblages, the fines are represented solely by the hydrolysate assemblage.

A disadvantage of this form of statistical analysis is that because of similar sedimentological characteristics, several of the variables may be correlated with one another and this obscures the real associations; for example iron minerals are mixed with apatite. Furthermore the occurrence of elements such as Fe with two different mineral controls makes difficult the accurate identification of the associations specific to each control; the same applies locally to Ti, which may occur in sands or silts, and possibly also to Ga which although it generally correlates well with the

fine fraction may occur in different clay minerals with different metal associations. A technique is required which can (1) distinguish the specific elemental associations related to each control (eg. can separate the associations specific to each of the Fe phases); (2) identify the different controls existing in each sample and (3) establish quantitatively the regional variation in each control by assessing its relative importance at each sample site. R-Mode Factor Analysis and the calculation of R-Scores provide the means of data reduction allowing such a simultaneous assessment of the areal variation of all elements in terms of their main controls, provided the associations revealed by the analysis are geochemically meaningful and not just mathematical abstractions.

3.5. Factor Analysis

3.5.1 Introduction

Multivariate statistical analyses of the type known as vector or factor or principal components analysis appear to have been first applied to the study of marine sediments by Imbrie and Purdy (1962) and Imbrie and Van Andel (1964). Subsequently Cronan (1967) and Glasby (1970) have applied the technique, with varying degrees of success, to geochemical analyses of manganese nodules. Turekian and Imbrie (1966) and Cronan (1969) applied the same technique to geochemical analyses of pelagic sediments; Rumeau and Vanney (1969) and White (1970) used it to indicate mineralogical controls of the geochemistry of shallow water sediments. The technique has been widely used in the analysis of stream sediment geochemical data (Garrett, 1967, Khaleelee, 1969; Armour-Brown and Nichol, 1970).

3.5.2 Description of Method

Essentially, Factor Analysis groups the variables (elements) of a sample population into associations (factors) on the basis of their degree of

intercorrelation; as different minerals are characterised by distinctive element associations these may be found to be represented by specific factors. The factors are statistically the most dominant features controlling the data variation. In this study they were determined using the programme of Garrett (1967); the method is described in some detail by Garrett (1967), Khaleelee (1969), Cole and King (1968), among others.

The first step is the establishment of a correlation coefficient matrix: as explained earlier, the dataare first logtransformed to produce statistically more meaningful correlations. The factors are determined from the correlation matrix by constructing axes through clusters in 'N' dimensions of the most highly correlated variables. The first axis is placed to account for the maximum amount of data variation; each subsequent axis, constructed orthogonal to the preceeding axis, and through a second cluster of variables, accounts for decreasing amounts of data variance and the axes can thus be ranked. The ranking, or amount of variability explained by any one axis, is expressed by eigen values, and where these are less than 1.0, factors are not considered significant. The amount of correlation of any one variable with any one factor is expressed as the factor loading and loadings are high where correlation coefficients are high. After initial construction of the axes, the orthogonal axial complex is rotated (Varimax Orthogonal Rotation) to maximise the loadings on each factor; this clarifies the factors and assists interpretation (cf. Khaleelee, 1969; Armour-Brown and Nichol, 1970). Khaleelee (1969) and Armour-Brown and Nichol (1970) have suggested that variables with factor loadings $> \pm 0.300$ represent significant associations and this significance level is used in the present study.

A series of different factor models containing 2, 3, 4 etc. factors can be generated by this method. The model containing the most meaningful number of associations (factors) in terms of the expected geological associations

is subjectively chosen. The proportion of the data variance which is explained by the model is known. Finally, having selected a suitable model the weighting at any one site of each factor in the chosen model is determined; the weightings are designated R-scores.

3.5.3. Factor Analysis Results

An 8 factor model (table 3.5.1), accounting for 91.8% of total sample variance, was generated from geochemical and granulometric data from population subset 3. Above factor model 5, fragmentation of the associations commences and geochemically non meaningful factors which contain only one or sometimes two variables with factor loadings $\geq \pm 0.300$ are generated. As the factors of model 5 represent characteristically strong associations which appear geochemically meaningful, this model is taken as the optimum representation of the system. The associations of each of the factors in this model persist more or less unchanged through the remaining models; this suggests that they represent specific mineral controls.

The presence of separate P_2O_5 sand and Fe_2O_3 sand associations suggests the occurrence of different sand mineral controls for these constituents. Both associations are antipathetic to either clay and silt and/or hydrolysate elements known to be concentrated in fine sediments. The association of Cu, Ni, Ti, Ga, Zn, Ba, Co, is taken as more or less typical of clay and silt (fine sediment) control. The associations of the remaining factors appear to represent the main controls of sand phase geochemistry. Whereas the correlation matrix showed P_2O_5 and Fe_2O_3 to be correlated but did not point to the Fe_2O_3 - Mn correlation anticipated from the raw data, the present analysis tends to confirm the existence of three distinct sand mineral phases or controls. The strong Fe, Cr, V, Pb probably represents glauconite control; Pb is only weakly loaded in this factor and is not part of this association in factor models 7 and 8 so may not be significant. A

strong Mn, Fe, Co, V, Pb association is interpreted as due to ferromanganese oxide control. Thirdly, a strong Sr, P_2O_5 association is taken as indicative of apatite control. That the agglomeration of these three associations in factor model 2 is antipathetic to silt is taken to suggest their fundamental control by sand phase minerals. The significance of the association of Ba with Sr, P_2C_5, and the antipathy of Ba to the Mn, Co, V, Pb, Fe association, and of Ti to the Sr, P_2C_5, Ba association is not fully understood and may be due to the small sample population used in this analysis.

More or less the same factors and associations emerge on analysis of population subset 2 (table 3.5.2). A 6 factor model explaining 86.3% of total sample variance is chosen as representative because (1) in this model P_2O_5 is no longer associated with Fe_2O_3, or Ba and (2) the associations of each factor are geologically meaningful. Fragmentation of associations in factor models 7 and 8 produces some impersistent and meaningless associations.

Again, there is clear antipathy between the hydrolysate association representing clay and silt control (Ga, Cu, Ni, Cr, Co, Zn) and P_2O_5 which represents sand control. Apatite control is represented by the Sr, P_2O_5 association. Separation of this from the Fe_2O_3, Cr, V association, representing glauconite control, is a subtlety anticipated in the raw data but not clearly shown by the correlation analysis. The Mn, Co, Pb, V, Ni, Cu association is taken to represent iron-manganese oxide control: loss of Fe_2O_3 from this association suggests that there is greater spread in data variability in the glauconitic sediments and this obscures the known Mn-Fe correlation in oxidate sediments. Independence of the Mn association from P_2O_5, although these were found to be correlated, suggests independent genesis for apatite and secondary oxides.

The two subsidiary factors Ti, Zn (explaining only 10.9% of total sample variance) and Ba (explaining 7.8% of total sample variance) are less geochemically meaningful and not fully understood at this stage.

A closely similar factor analysis result is obtained for population subset 4 (table 3.5.2) in which soluble Mn and Fe are included. Again, a 6 factor model, explaining 85.3% of total sample variance) best explains the data in geochemically meaningful terms. The hydrolysate factor is no longer found to be specifically antipathetic to P_2O_5 and also differs slightly from the analysis result of population subset 2 in the addition of V. The apatite (Sr, P_2O_5) association is now distinguished by the addition of soluble Fe, which is not surprising in view of the common association within the local phosphorites, of apatite and iron minerals. As anticipated from single element and correlation analyses the Mn factor (representing ferro-manganese oxide control) is distinguished by the addition of soluble Fe and Mn to the Mn, Pb, V, Co, Ni association previously recognised. Incorporation of P_2O_5 into this association reflects the common association or relict apatite-rich sands with Recent authigenic oxides. The apparently glauconite controlled Fe_2O_3, Cr, V association is not altered, suggesting, as was previously intimated, that glauconite is far less soluble than the ferromanganese oxide.

The same unexplained Ti, Zn and Ba factors are found as in the analysis of population subset 2.

In the analysis of population subset 1 (data from mixed Moroccan and Saharan sediments) a 7 factor model explaining 88.7% of total sample variance seems to provide the most meaningful results (table 3.5.3); in this model two separate iron factors are developed. The association of Ca, P_2O_5, Sr and Mg with Fe and Co, and the antipathy of this association to Si and Ti most probably reflects the known regional division into quartz

sands and apatite-rich sands in which apatite and dolomite and iron oxides occur together in phosphorite grains and may also be associated with later authigenic iron oxides. The presence of two iron factors resolves the complex correlations noted for this subset and suggests control (1) by glauconite (Fe, Cr, Zn, K, V) and (2) by iron oxides (Fe, Pb, V, Ca); incorporation of Ca in the latter association probably reflects the association of apatite and iron oxides in Saharan sands in particular. Unlike the analyses of other subsets, two hydrolysate factors are developed here; one, comprising an association of Ni, Cu, Cr, Pb, Ga, Ti, Zn, V, Co is similar to that obtained on analysis of Moroccan samples alone while the other has not previously been recognised. Conceivably these two hydrolysate associations reflect regional differences in clay mineralogy. The absence of Mn from the 'oxide' association, and its strong association with a hydrolysate group may reflect (a) the abundance of relatively manganiferous Saharan clays (see earlier) or (b) the absence of many oxidate Moroccan sediments from the analysed subset.

As for Moroccan samples alone, a separate Ba factor is generated but in this subset it is found to be strongly associated with K. The association is a natural geochemical association (cf. Goldschmitt, 1954) and may represent feldspars and clays such as illite.

In most respects there are sufficiently strong similarities between the analyses of all four subsets to support the suggestion that basically the same minerals control Saharan as control Moroccan sediment composition and that the gross mineralogy is relatively simple.

3.5.4 R - Scores:

R - Scores are generated for the factors of the selected models of population subsets 1 and 2 to quantify the influence of each factor at individual sample sites. Proof that the associations of the two subsets are related

is obtained by plotting against one another the R-Scores for apparently similarly controlled factors in those samples common to both subsets (Fig. 3.5.1). There is no equivalent for the subset 2 Ti factor in the factors from subset 1. Otherwise the associations and factors are extremely reproducible between these different subsets despite regional differences. This facilitates interpretation of the associations from subset 2 for which major element analyses were not available.

Population Subset 1 (table 3.5.4)

Evaluating the significance of the scores in terms of their relation to samples of known mineralogy, it is clear that high R-scores for the apatite factor are only found for those sand samples known to be rich in phosphorite grains (cf. Chapter 2). The glauconite factor has highest R-scores on Moroccan glauconitic samples but moderately high R-scores are also often found for Saharan shelf sands. Glauconite is acknowledged to be a common accessory mineral in Saharan shelf sediments (Navarro, 1947; McMaster and Lachance, 1969). Samples from close inshore and on the southernmost Saharan shelf (Cap Blanc), which are known to be very highly quartzose and contain little glauconite do not have positive glauconite factor scores. The iron-manganese oxide factor has high scores on the north Saharan shelf, particularly off Cap Juby in samples which were notably brown stained (267-272 inclusive). Negative scores for the south Saharan shelf support previous findings regarding the absence there of secondary oxides. The hydrolysate Al factor scores highly only for those samples designated silts, both off Morocco and the Sah ra. By contrast, the hydrolysate Ga factor, which is known to correlate with silt and clay fractions of Moroccan sediments (see earlier) has far higher scores on Saharan than on Moroccan sediments regardless of sediment type. This is thought to signify some fundamental difference between the regions in the nature of the clay minerals of the fine fraction. Finally, the Ba, K factor shows no significant change either

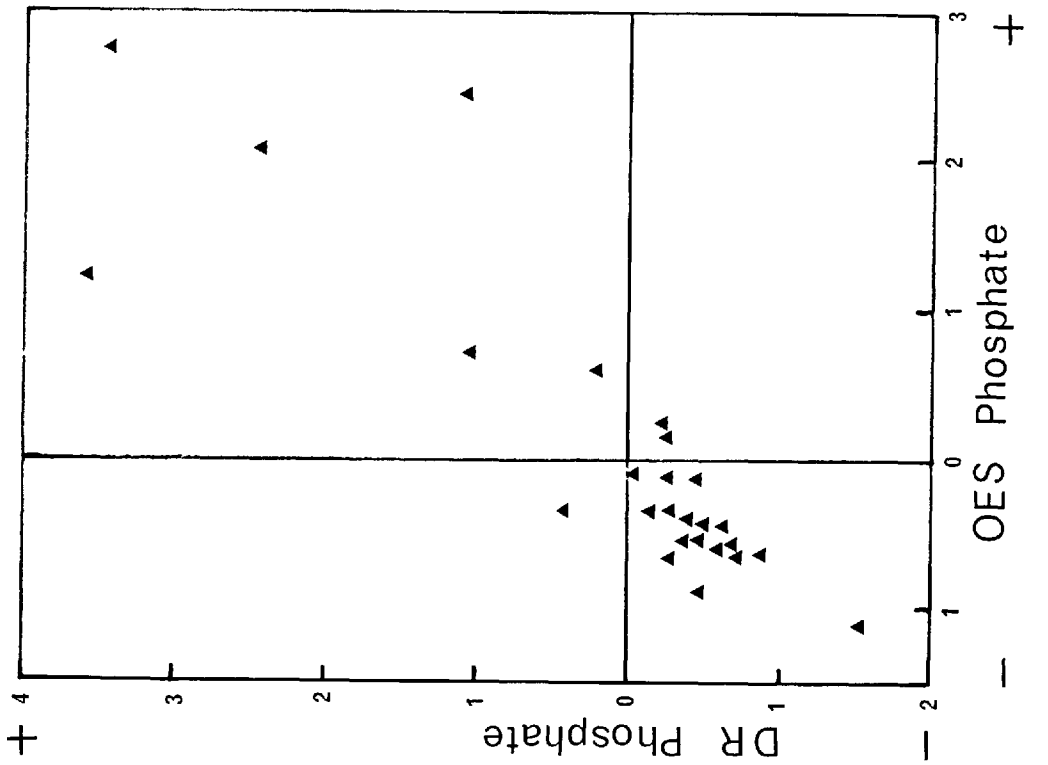
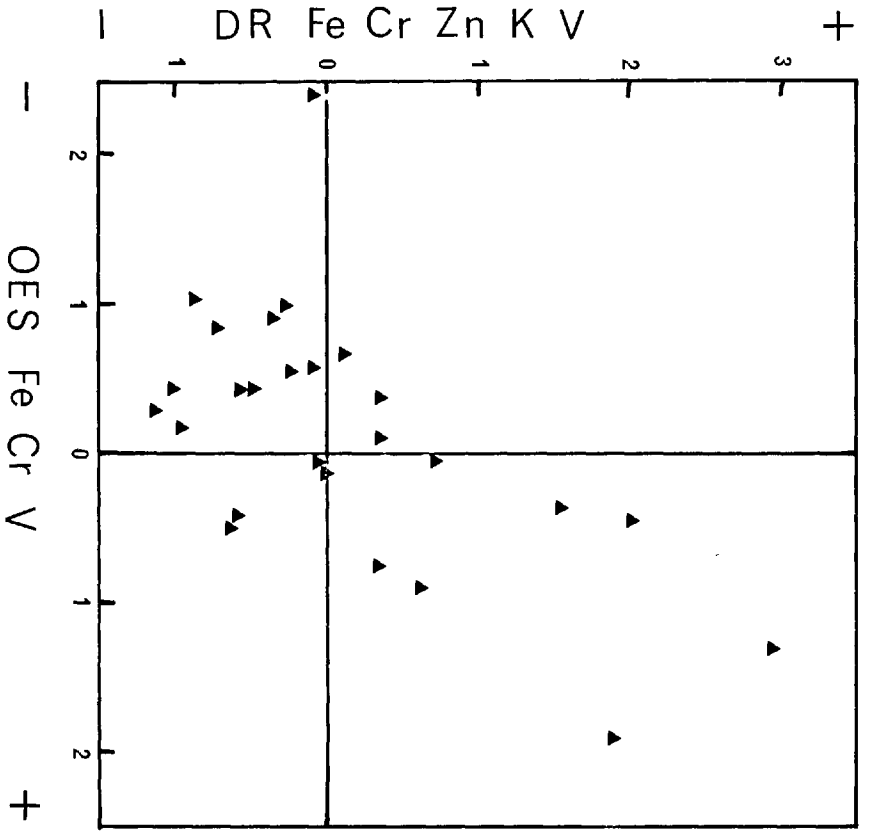


Fig.3.5.1. Comparison of R-mode factor scores from population subsets 1 (represented by DR) and 2 (represented by OES). The factors are givenin tables 3.5.1. and 3.5.3. and the diagrams are more fully explained in text. Different factors are compared on the following pages (92b, 92c and 92d).

Fig.3.5.1.(continued)



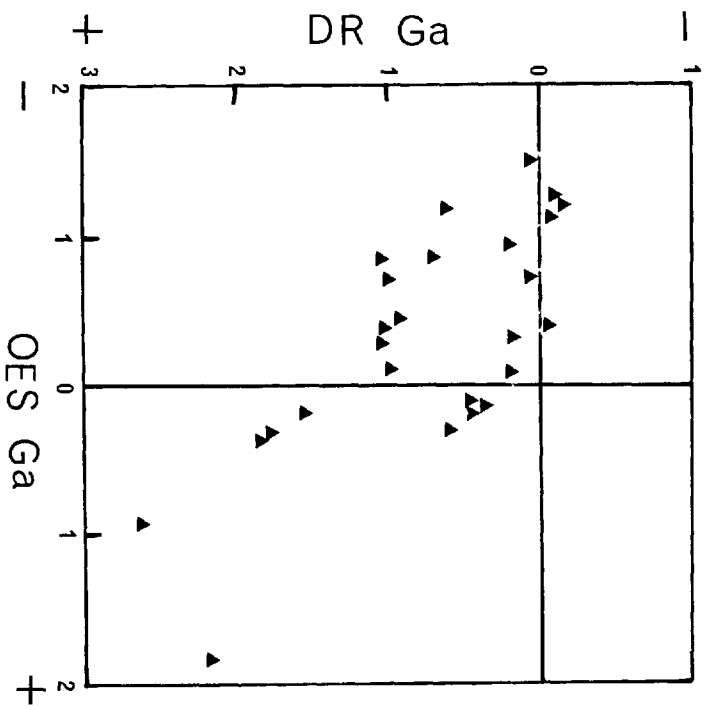
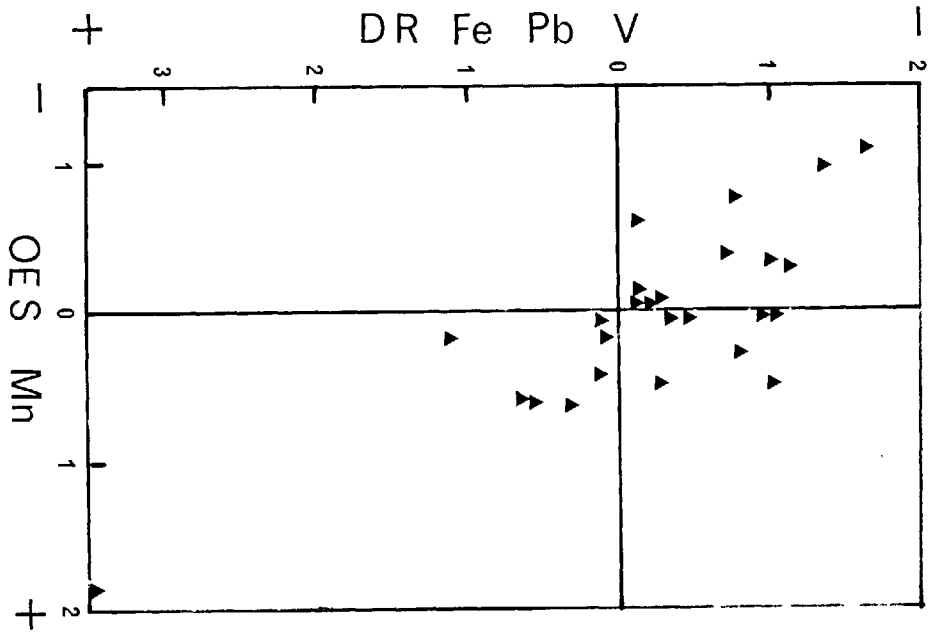


Fig.3.5.1.(continued)



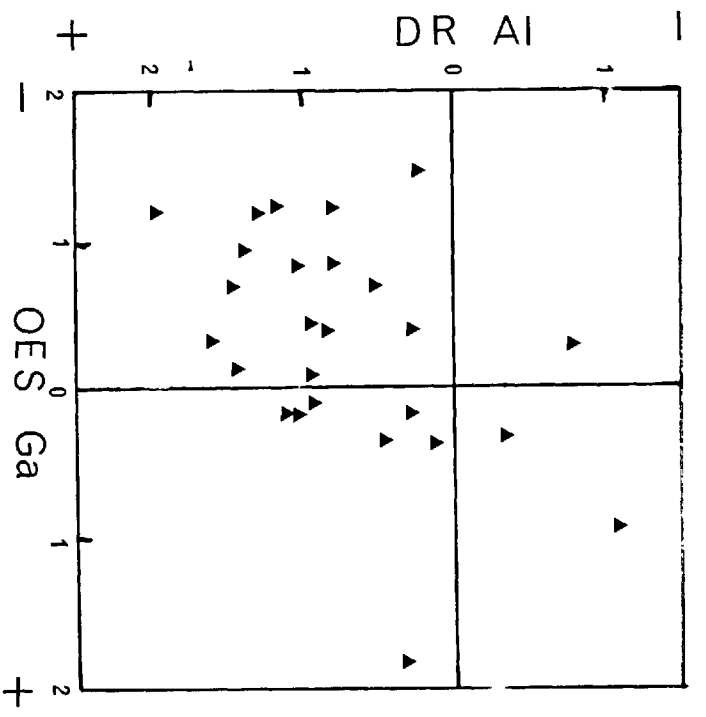
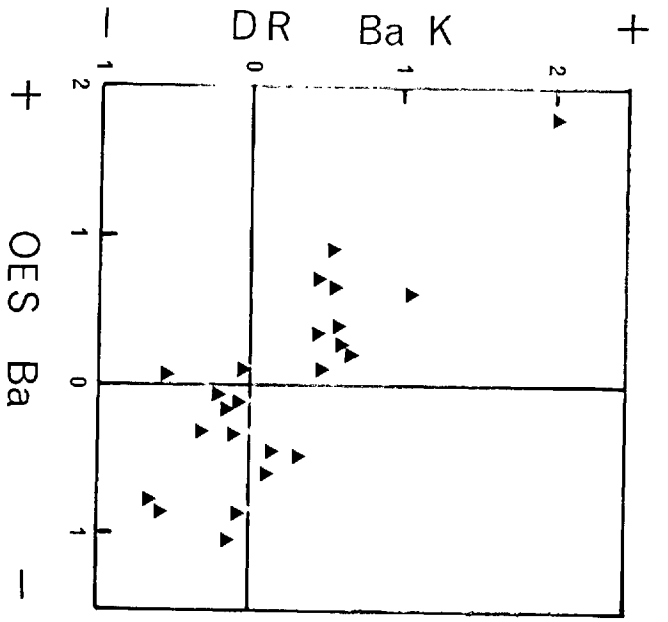
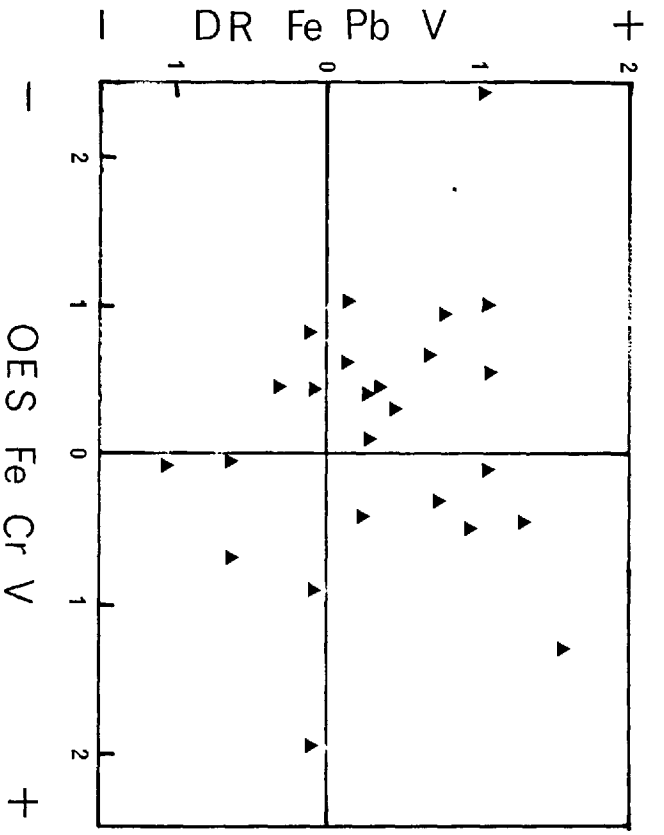


Fig.3.5.1.(continued).





with geography or texture, supporting the suggestion that it represents the geochemical affinity of Ba for K and does not represent a specific mineral phase control.

Population Subset 2

Having found a clear relationship between certain factors and certain mineral controls and found that the R-Scores on these factors reflect the concentration of the control minerals, the regional pattern of R-Scores for each factor is expected to reveal the regional distribution of its mineral control. Morocco is chosen to test this assumption, since this area is relatively densely sampled.

The distribution of positive Ga factor scores (Fig. 3.5.2) closely reflects the pattern of silt distribution ascertained from total inspection (cf. Chapter 1). It has already been shown that this factor represents an association of elements whose distribution is controlled by silt and clay. The pattern suggests a hitherto unrecognised belt of silt exists among the outer shelf coarse sands between Safi and Al Jadida. The highest scoring samples (> -1.0) on the shelf are from the northern part of the northern silt belt where samples are relatively clay-rich (cf. Nutter, 1969). That the Ga factor scores are also high on the slope to north and south of the Cap Blanc region suggests a relative offshore increase in clay content.

Positive phosphate factor scores (Fig. 3.5.2) are restricted to sandy sediments (cf. Fig. 1.3.1), as expected, and, in distribution, relate very closely to that of carbonate free phosphate (cf. Fig. 2.2.10). The positive scoring samples usually do not contain less than 1.0% P_2O_5 possibly because below this level some other mineral phase or phases have more influence on sample geochemistry than apatite. As a result, the phosphate factor score pattern is not quite as widely distributed as poorly phosphatic sediments are known to be. Certain exceptions to the relation between phosphate

Fig.3.5.2.(I)

The distribution of R-mode factor scores in Moroccan continental margin sediments :Phosphate factor

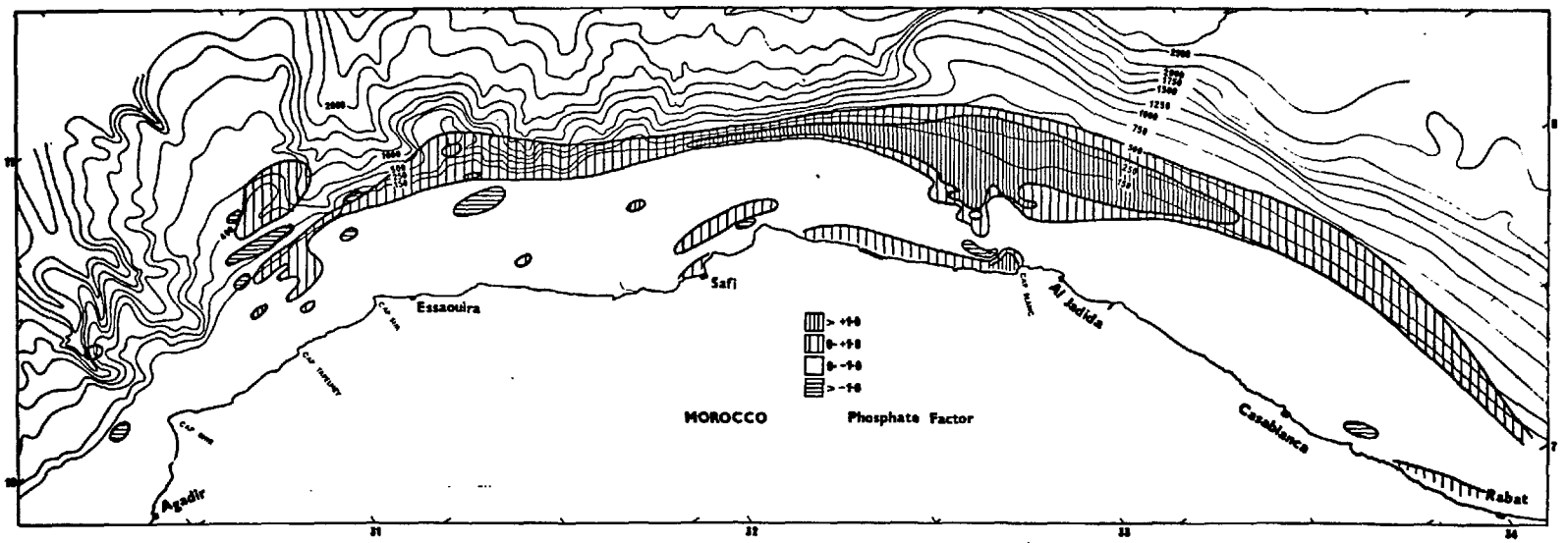


Fig.3.5.2.(2)
The distribution of R-mode factor scores in Moroccan continental margin sediments: Fe factor

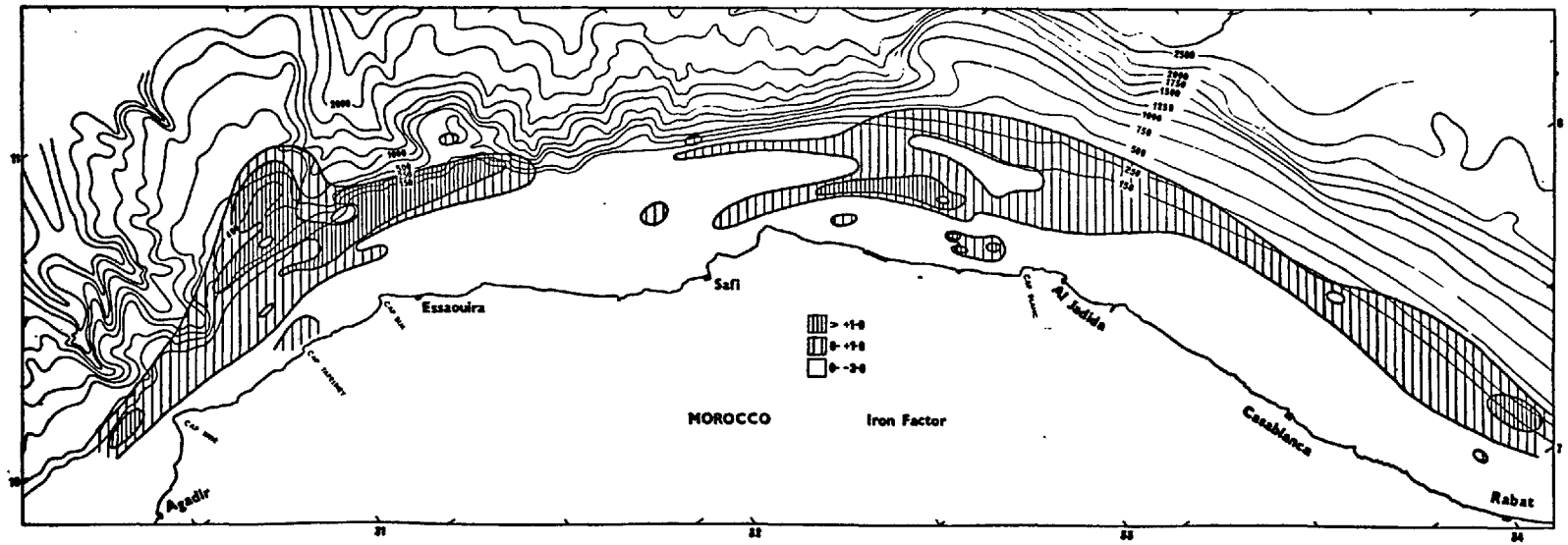


Fig.3.5.2.(3)

The distribution of R-mode factor scores in Moroccan continental margin sediments: Ga factor

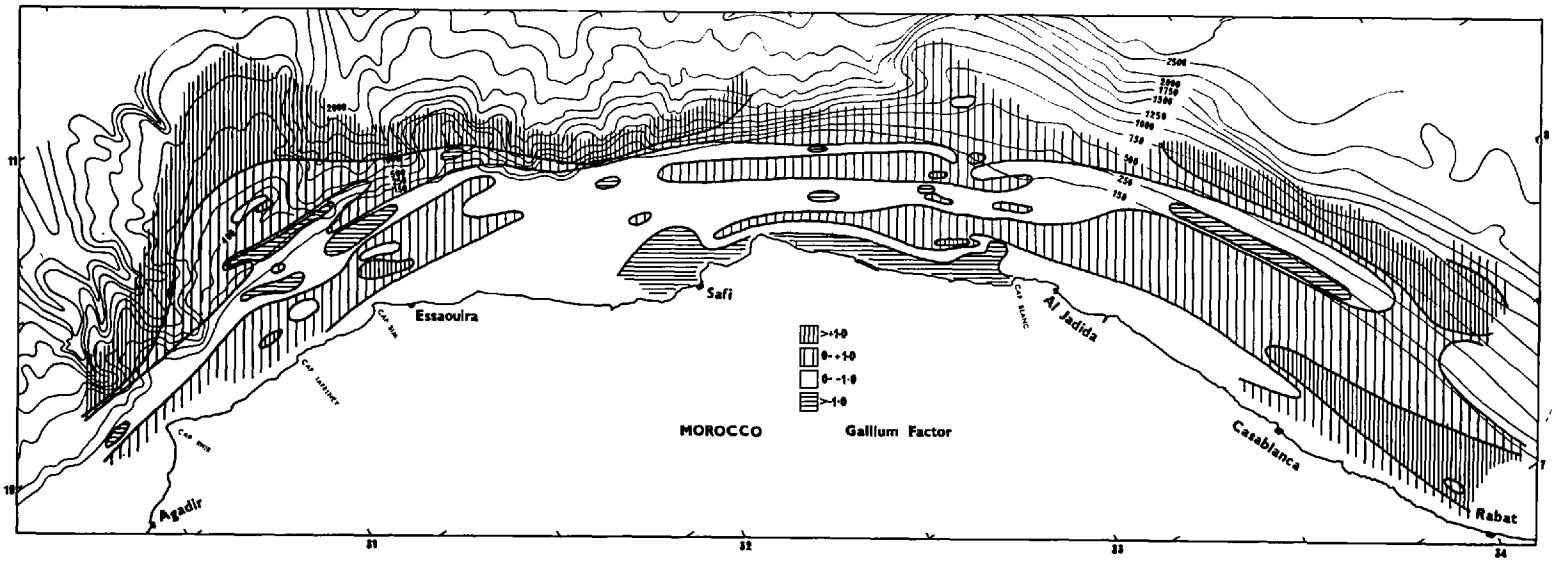


Fig.3.5.2.(4)

The distribution of R-mode factor scores in Moroccan continental margin sediments: Mn factor

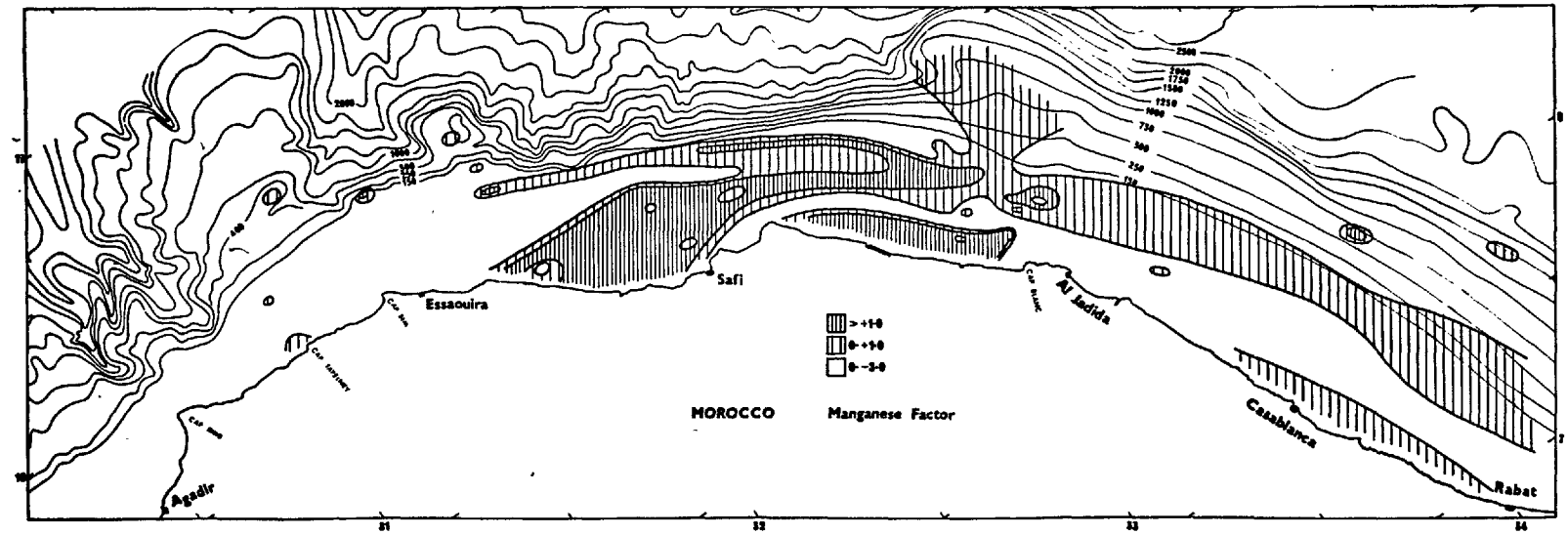


Fig.3.5.2.(5)

The distribution of R-mode factor scores in Moroccan continental margin sediments:Ti factor

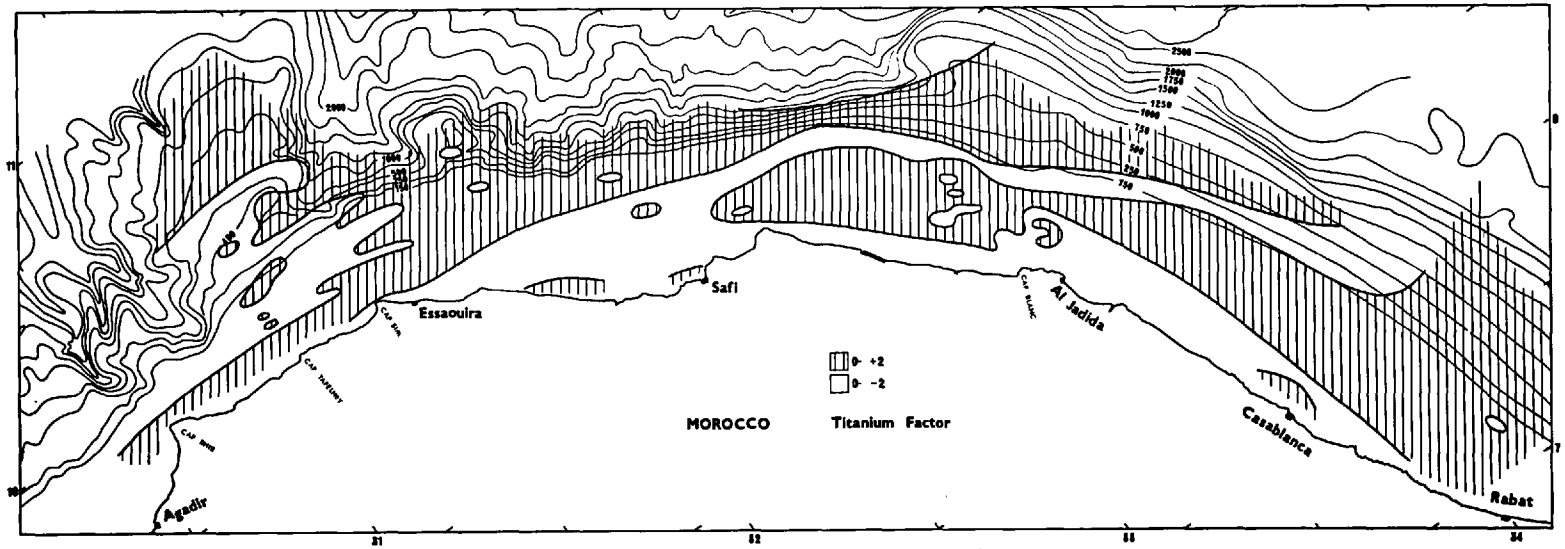
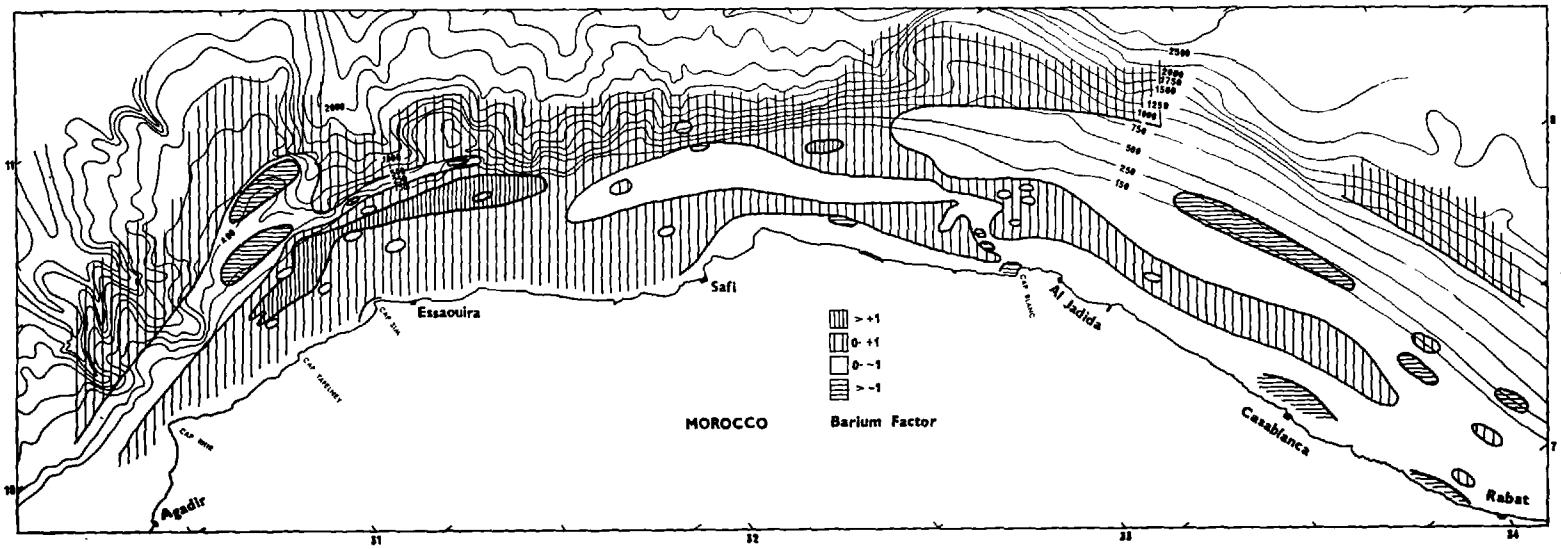


Fig.3.5.2.(6)

The distribution of R-mode factor scores in Moroccan continental margin sediments: Ba factor



content and phosphate factor scores are found in the inner shelf off Cap Blanc where negative scores are sometimes obtained for moderately phosphatic sediments. Again, this probably reflects the more profound influence on sample geochemistry of some other mineral phase or phases.

The glauconite factor scores (Fig. 3.5.2) are positive mainly among outer shelf and upper slope sands and silty sands with a few exceptions on the mid and inner shelf between Safi and Al Jadida. Scores are consistently highest among the upperslope outer shelf sands and silty sands off Cap Sim in which glauconite is common, sometimes resulting in the formation of 'black sands'. The presence of this mineral among northern shelf sediments was recognised by Matthieu (1968), Nutter (1969) and Bell and Goodell (1967) but it was not previously appreciated that it might be, as present data suggest, distributed in a well developed shelf edge zone. The relatively low scores for northern shelf samples supports previous findings that glauconite among these sediments is never a prominent mineral phase. The geochemical mapping of glauconitic facies of Recent shelf sediments has also been achieved elsewhere (western U.S.A.) by White (1970) using Q-mode factor analysis in which samples are grouped according to gross geochemical similarities.

The origin of the Fe, Cr, V, (Zn), K association characterising these glauconitic sands is somewhat obscure. K and Fe are normally found to be associated in this mineral which is an iron-potassium alumino-silicate (cf. Hower, 1961). The Cr, V and Zn associations with Fe may be due to preferential sorption of these metals during growth: all are capable of substituting isomorphically for Fe (cf. Goldschmitt, 1954). The abundance of Cr may indicate formation under reducing conditions, this element being preferentially concentrated in reduzate sediments (cf. Krauskopf, 1956; Goldschmitt, 1954).

In terms of detrital mineralogy, those sands outside the influence of the glauconite factor are presumed, where not phosphatic, to consist primarily of quartz, in support of visual observations to the effect that phosphorite, glauconite and quartz are the three main species of sand mineral (cf. Chapter 1).

The Ba factor scores (Fig. 3.5.2) do not bear any marked relation to texture (cf. Fig. 1.3.1) although high positive scores are found in parts of the southern silt belt which might signify a slight difference in clay mineralogy from the northern belt. Negative scores tend to follow positive glauconite factor scores probably because the Ba-K relation in detrital minerals is rather different from that in glauconites which formed in the marine environment. Similarly, the Ti factor scores (Fig. 3.5.2) show little relation to texture (cf. Fig. 1.3.1) although they tend to be positive among silts rather than sands or silty sands. As neither of these factors assist in determining the gross mineralogy of the sediments they are not further considered.

Those sediments rich in soluble Mn (Fig. 3.3.2) have positive Mn factor scores (Fig. 3.5.2) although the latter are slightly more widely distributed. In the main, sediments with positive Mn factor scores, are often found to be brown stained and are sands or silty sands, and on the outer shelf, silts. The main associations from this iron-manganese oxide factor are - soluble Fe and Mn, insoluble Fe, Mn, Co, Pb, V, Ni, Cu, and Mo. These associations, and the concentration of these elements in the oxidate phase, are most probably due to the scavenging (sorptive) properties of the ferro-manganese oxides (cf. Krauskopf, 1956). Some or all of these elements have been found enriched, for example, in marine limonite concretions (Hirst, 1962 b), marine manganese nodules (Cronan, 1967; Glasby, 1970), lacustrine ferro-manganese concretions (Gorham and Swaine, 1965),

and alluvial manganese deposits (Nichol, Horsnail and Webb, 1967). Similar factors and associations have often been reported from other sediments. Using R-score analysis of stream sediment data Khaleelee (1969) found an oxide zone weathering factor comprising Mn, Co, Ni, Fe; he also found, in sediments derived from a deep borehole, a Mn, Mo, Ni, Co, Fe factor interpreted as a primary depositional feature. Similar associations thought to represent the influence of manganese micronodules, and reported from deep sea sediments, are Mn, Ni, Co (Turekian and Imbrie, 1966), and Ni, Mo, Mn and Fe, Co, Pb, Mn (Cronan, 1969). Furthermore, using factor analysis on continental shelf sediments off the French coast, Rumeau and Vanney (1969) found there to be a strong Fe, V, Cr, P_2C_5, Pb, Mo factor attributed to oxidation of relict sediments.

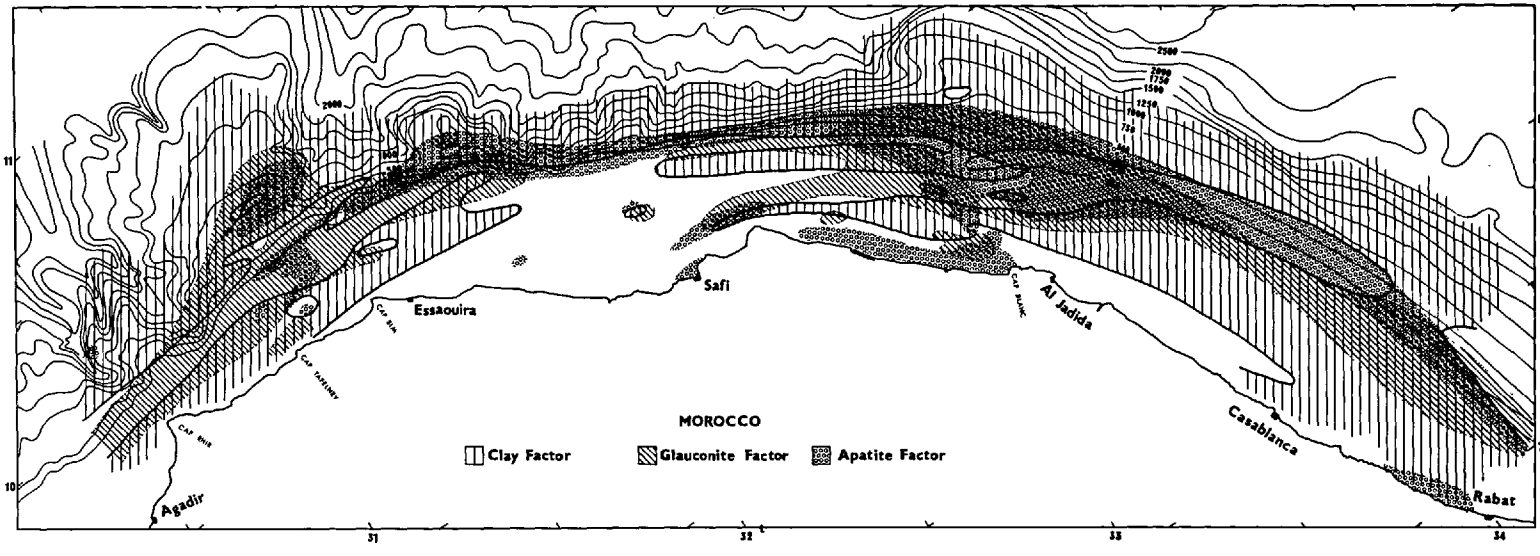
The oxide and glauconite factors tend to follow one another quite closely on the outer shelf north of Safi (Fig. 3.5.2): Nutter (1969) and Bell and Goodell (1967) report that glauconite from this region is often oxidised whereas as shown here, that from the south is not. The presence of this oxide factor is taken to indicate the relict character of the original sediment. Extension of oxide mineralisation across the entire width of the shelf suggests the hitherto unsuspected conclusion that most of the sand fraction of all but the sediments from very close inshore must be relict.

Facies

Combination of the relevant R-score maps (Fig. 3.5.3) results in maximal simplification of the data in terms of geochemical facies representing gross sediment mineralogy and hence also texture. In that only the nature of the original sediment body is required, the oxide factor is not considered in the combination; nor, since they do not appear to add to the understanding of mineral dispersion, are the minor Ba and Ti, Zn factors considered. The apatite, glauconite and hydrolysate factor scores are

Fig.3.5.3.

Geochemical facies map compiled by combining representative clay, glauconite, and phosphate R-mode factor scores from Fig.3.5.2.



combined; where none of these factors score positively it is assumed (see earlier) that the sediment is quartzose, quartz being the main mineral phase not explained by the present analyses. Five main facies can be defined:- (1) phosphatic sands and silty sands; (2) phosphatic-glauconitic sands and silty sands; (3) glauconitic sands and silty sand; (4) silts; (5) probable quartzose sands. This geochemically derived facies distribution correlates well, as anticipated from the foregoing analyses, with the recognised distribution of different textures. The origins of the phosphatic sediments and of the textural patterns have already been discussed (Chapters 1 and 2) but one or two further points for consideration emerge from the facies map.

The prominence of (probable) quartz sands away from the shelf edge glauconitic facies and the regions of probable phosphate rock outcrop suggests widespread mineralogical maturity for most mid and inner shelf sediments.

The dominant geochemical influences on outer shelf and upper slope sediments are apatite and glauconite. As previously shown, the apatite dispersion relates closely to the incidence of phosphorite outcrops (Chapter 2). This is not true for glauconite although some glauconitic sands are associated with glauconitic rocks. Glauconite distribution may be geomorphically related because its formation is restricted to certain depth limits by bottom water temperature (cf. Porrenga, 1967). Whatever the cause, these data suggest that during the past,more or less uniform environmental conditions prevailed along the shelf edge allowing widespread glauconite formation. That conditions are no longer uniform is shown by the soluble Mn and C_{org} distributions remarked on earlier. A further point emerging from the non-ubiquitous association of apatite and glauconite is that these deposits are not cogenetic.

The newly defined outermost shelf belt of silt between Cap Blanc and Safi appears separated from the remaining silt belts and probably represents a relict feature of Pleistocene sealevel fluctuations. The seaward change from silt to glauconitic silt in the northern and southern shelf silt belts shows that most of the outer shelf is a region of virtual non-deposition.

3.5.5. Summary

The hypothesis that multielement geochemical data can be used in lieu of mineralogical and granulometric analyses to determine broadly the distribution of detrital and authigenic mineral species, and to delimit facies characteristics in Recent unconsolidated seafloor sediments, has been tested and proven satisfactorily using R-mode factor analysis and R-scores.

Both correlation and factor matrices produced similar geologically interpretable elemental associations from different population subsets. Correlation matrices and single element data indicate that more than one control may influence the dispersion of certain elements: factor analysis defines the responsible factors, resolves subtleties and ambiguities in the original and correlation data, and allows the influence of each factor at different sites to be assessed. Essentially the distribution of primary sediments on the northwest African shelf can be explained in terms of four main mineral factors or controls:- apatite accounts for the association Ca, Sr, P_2O_5; glauconite accounts for the association Fe, Cr, V, K, (Zn); quartz accounts for Si (and is usually antipathetic to apatite and glauconite); silt and clay are accounted for by a Gallium-metal association (Ga, Ni, Cu, Cr, Co, Zn) which correlates further with an Al, K, association fundamental to clays. In terms of this last factor there are profound regional differences between the Saharan and Moroccan fine sediments; probably this is a provenance difference. Combinations of these main factors results in

production of a meaningful facies map. Furthermore the definition and delimitation of a hitherto unrecognised secondary iron-manganese oxide zone provides new information of value in clarifying shelf history.

CHAPTER 4

SUMMARY OF MAIN CONCLUSIONS, AND RECOMMENDATIONS FOR FUTURE RESEARCH: SEDIMENTS

4.1 Summary of Main Conclusions

1. The unconsolidated Pleistocene and Recent sediment cover is normally very thin, not exceeding about 10m over most of the shelf, although locally reaching about 30m in the Souss Trough and off the Southern Spanish Sahara.

2. Apart from the innermost shelf where some Recent sand movement may be occurring, and parts of the Moroccan mid shelf where a Recent silt blanket occurs, shelf sediments are mainly relict sands.

3. The location of Recent mid shelf silt belts off Morocco, and the absence of silt from the Saharan shelf, is mainly a function of climate and drainage; topographically enhanced current activity prevents the settling of fines at the shelf edge and results in preservation off Morocco of a shelf edge sand belt.

4. Geochemical and probably mineralogical provenance differences exist between the fine sediments of the Sahara, north and south Morocco.

5. Most relict sands are iron-stained except where the organic carbon content is relatively high off south central Morocco and the southern Spanish Sahara. Off south central Morocco the organic detritus is not carbonate - associated and therefore is probably river derived whereas off the southern Sahara it is associated with extremes of carbonate sedimentation and relates to upwelling; increases in organic content result in decreases in redox potential, thus preventing iron oxide formation.

6. Relict sands can be either calcareous or detrital, and consist mainly of biogenic (mainly molluscan) debris, detrital quartz and phosphorite, and detrital and authigenic glauconite.

7. The Moroccan outer shelf and uppermost slope environment is now and appears to have been during the later Tertiary, an ideal environment for glauconite formation; apparently Recent glauconite coatings on rock fragments and glauconite foram casts are mixed with older pellets and detrital grains, all of which are most abundant off south central Morocco possibly because of the effects there of topographically induced current winnowing of fines over a wide region.

8. Moroccan phosphatic sediments form three main belts: a. a continuous shelf edge belt; b. a restricted mid shelf belt, and c. a discontinuous innermost shelf belt. Phosphatic sediments also form a prominent shelf edge belt off the northern Spanish Sahara.

9. The phosphatic and detrital sand fractions appear to have had similar transportational and depositional histories.

10. Phosphatic sand components are subangular clastic fragments of phosphorite lithologically similar to adjacent outcropping phosphorite.

11. Phosphatic sands are richest among or near to phosphorite outcrops.

12. There is no evidence at present for phosphatisation of carbonates, or local phosphate precipitation, nor any relation between phosphate abundance and upwelling concentration.

13. The data are consistent with these phosphatic sediments being placers formed at or near lowered Pleistocene sealevels, the detritus being derived from local outcrops.

14. Longshore drift probably contributed extensively to shelf edge dispersal of phosphate beyond the outcrop region.

The main advance represented by this work is that the validity of the upwelling theory of phosphorite formation, as applied to northwest Africa, must now be regarded with grave suspicion. The project has led to the determination of the character, facies, distribution and origin of a large but hitherto unrecognised detrital sedimentary phosphate deposit, and to an understanding of the nature and origin of northwest African shelf sediments in general. Furthermore the application of multielement regional geochemical and statistical analyses to the mapping of subsea sediments has been demonstrated for the first time.

4.2 Recommendations for Future Research

1. The inshore phosphatic sand belt should be studied to determine its nature, origin, and economic potential as it represents the most potentially workable of these deposits.

2. The extensions of the shelf edge phosphatic sand belt north of Rabat and south of Agadir should be examined to test further, away from the region of phosphorite rock outcrop, the possibility that recently formed phosphate minerals may occur off northwest Africa.

3. Using vibro-coring and sono-probe techniques, the stratigraphy of the phosphatic sands should be assessed in detail to indicate their degree of homogeneity and economic potential, and to throw further light on their origins.

4. The regional distribution of different grain size modes should be established to ascertain sediment dispersal paths.

5. Drainage sediment samples should be collected to allow assessment of phosphate supply, in solid and dissolved form, by continental runoff.

6. The petrography of phosphorite grains should be examined in detail to establish their relation to potential source rocks.

7. The possibility of phosphatisation of calcareous skeletal debris with time should be examined by studying skeletal debris from selected cores.

8. The interstitial water of cores should be examined to determine levels of dissolved phosphate so that calculations can be made to explain the apparent absence of phosphatisation or phosphate precipitation.

9. The nature, age and origin of local authigenic iron minerals should be ascertained to allow more detailed understanding of present environmental chemistry in this region.

10. Side-scan sonar records should be obtained to clarify the presently deduced sediment dispersal patterns and to establish the horizontal extent of sand bodies of potential economic interest.

SECTION II

PHOSPHATIC ROCKS OF THE NORTHWEST AFRICAN CONTINENTAL SHELF AND SLOPE

CHAPTER 5

GEOLOGY AND STRUCTURE OF THE NORTHWEST AFRICAN CONTINENTAL MARGIN

5.1 Introduction

A series of continuous seismic reflection profiles and precision depth records were obtained across the continental shelf and slope off the coasts of Morocco and the Spanish Sahara from R.R.S. John Murray in January and February 1968 and 1969. In principal these were obtained to define the shallow geological structure of the northwest African continental margin, to aid in the interpretation of its development, and to allow estimation of the stratigraphic setting, and horizontal and vertical extent of phosphatic rock deposits. Reconnaissance profiles were made at widely spaced intervals off the Saharan coast (Fig. 5.1.1) and at closer intervals off the Moroccan coast (Fig. 5.1.2) between Agadir and Rabat.

Additional information was available from profiling surveys (McMaster and Lachance, 1968; Dillon, 1969; Rona, 1970) and unpublished side-scan sonar records (R.H. Belderson, Nat. Inst. Oceanogr: pers.comm.). Palaeontological data have been kindly provided by D. Carter and S. Rye of the Micropalaeontology Section, Geol. Dept., Imperial College, and by Dr. H. Bhat of the Societe Nationale des Petroles d'Aquitaine, Pau, France.

In this chapter, all Saharan profiles and profiles 1 - 8 inclusive from south Morocco are considered in detail; the north Moroccan profiles have been discussed in detail by Nutter (1969). However, in that age determinations were made subsequent to the completion of Nutter's dissertation, some further discussion of the geology of the north Moroccan region is also given in the following pages.

Fig.5.1.1.

Situation of continuous seismic reflection profile lines off the Spanish Sahara; distance markings are at 10 km intervals. Dated dredge samples are upper miocene (um), lower miocene (lm), lower pliocene (lp) and probably pliocene (?p). Profiles 1,3,4 and 5 respectively represent reconnaissance sampling and geophysical traverses D,E,F and G shown in Fig.1; profile 2 was not sampled.

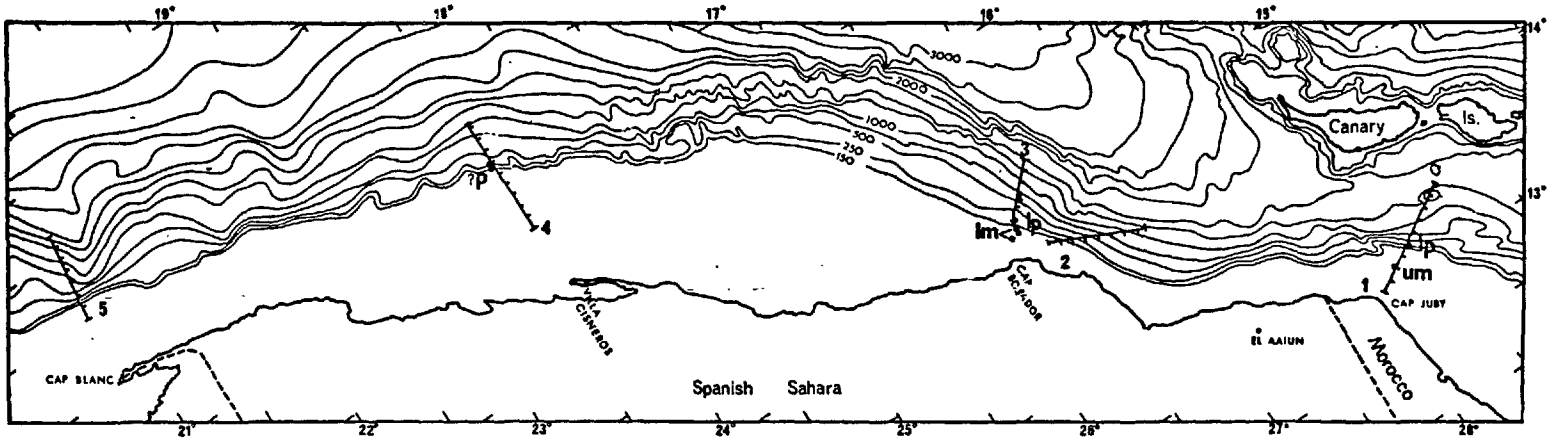
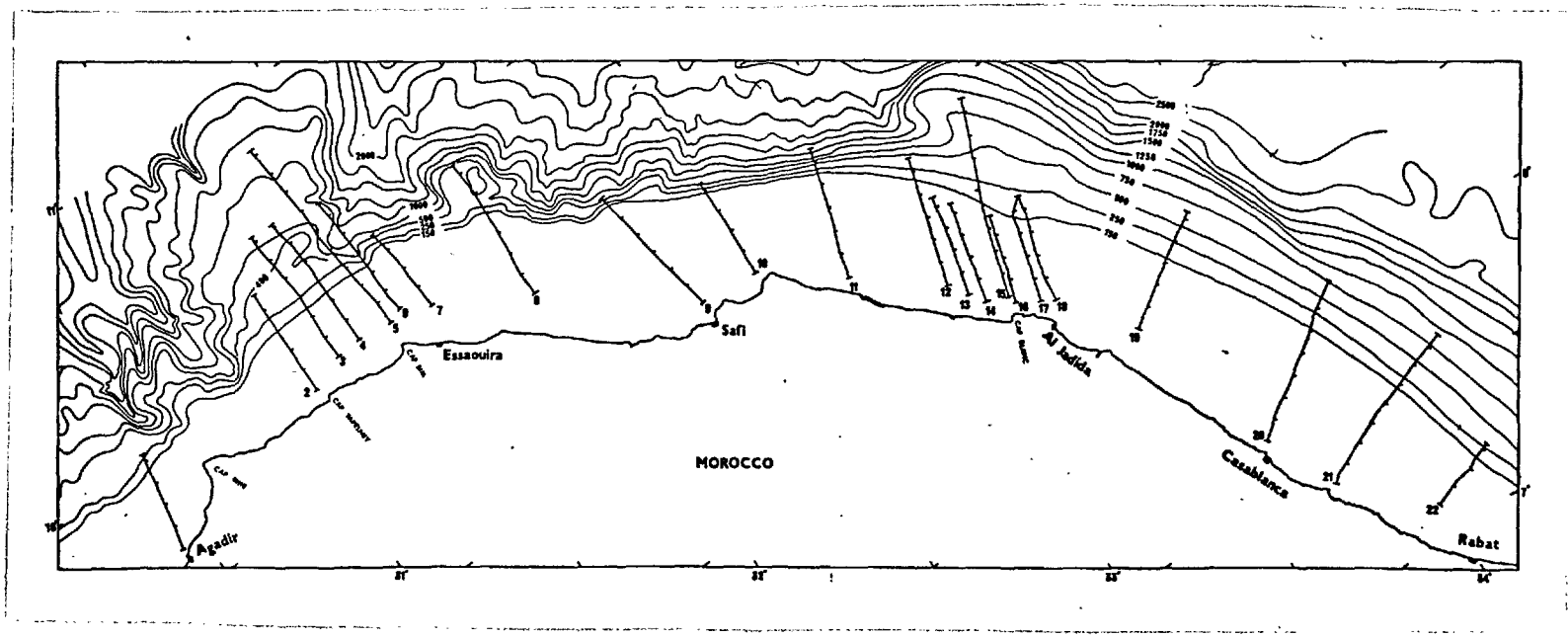


Fig.5.1.2.

Situation of continuous seismic reflection profile lines off Morocco; distance markings are at 10 km intervals. Profiles 21,15 and 5 respectively represent 1968 reconnaissance profiles A,B and C shown in Fig.1. Profiles 1 to 8 inclusive are the subject of the present report; remaining profiles have been described and discussed by Nutter (1969).



5.2 Profiling Operations and Record Interpretation

Continuous seismic reflection profiling was carried out using a conventional E.G. & G. sparker unit, amplifier and recorder, operated in 1968 by Dr. E. Bosshard of Imperial College, and in 1969 by Mr. S. Jones of the N.E.R.C. Technical Staff. Both spark source and hydrophone array were towed astern of the ship at depths of 3 to 6 feet; the spark source, or firing array, was generally 50 feet behind the ship, the hydrophone array was a further 150 feet distant although the separation of these two units was varied with sea depth to improve results.

On the 1968 reconnaissance cruise, a 100 foot hydrophone with 6 active elements was used; during the 1969 cruise the hydrophone length was reduced to 50 feet, still with 6 active sections. To obtain vertical reflections in very shallow water of 20 - 40 metres depth, the length of the towing cable was reduced and only one active element was used.

Maximum power output possible on the R.R.S. John Murray was 8000 joules although it was found that best results were obtained using 1000 - 1200 joules in water depths of 10 to 200 metres, 3000 joules in depths of 200 - 750 metres, and 5000 - 8000 joules beyond that. On profiles taken north of Safi, Morocco, in 1969, a power output of 500 joules was used in water depths of less than 50 metres. Satisfactory results were obtained at cruising speeds of 6 to 7 knots, above which the signal to noise ratio decreased to levels at which the quality of the record considerably deteriorated. The triggering rate was dependant on the power output. Returning energy was filtered at between 80 - 200 cycles per second to remove sea and ship's noise, and amplified and recorded on 28cm electrosensitive paper at a rate integrated with the triggering rate.

Penetration was obscured by multiples of the seabed reflection in water

shoaler than about 100m so records are generally poor across the inner continental shelf where penetration averages 50 - 150 milliseconds. By contrast, penetration beneath the continental slope reached maximum values of 400 - 900 milliseconds. In the interpretation of these data an average value of 2km/sec has been assumed for the velocity of sound in sedimentary rock (cf. McMaster and Lachance, 1968; Stride et al 1969) and, as penetration is recorded as two-way travel time from source to reflector and back, 100 milliseconds corresponds to 100 metres penetration.

For the sake of clarity, the data are presented as line drawings of recognisable reflectors representing sediment interfaces. Owing to the length of the spark pulse, resolution is normally not less than 30 metres.

Ships tracks have been adjusted to each other where they intersect, and on rare occasions when substantial discrepancies were observed, to the regional bathymetry as defined by previous surveys. Geological specimens were collected by sampling the profiled lines on a reverse course.

Corrections for the draught of the vessel and Matthews corrections for variation of the velocity of sound through seawater were applied to all bathymetric data, and all depths were converted to metres.

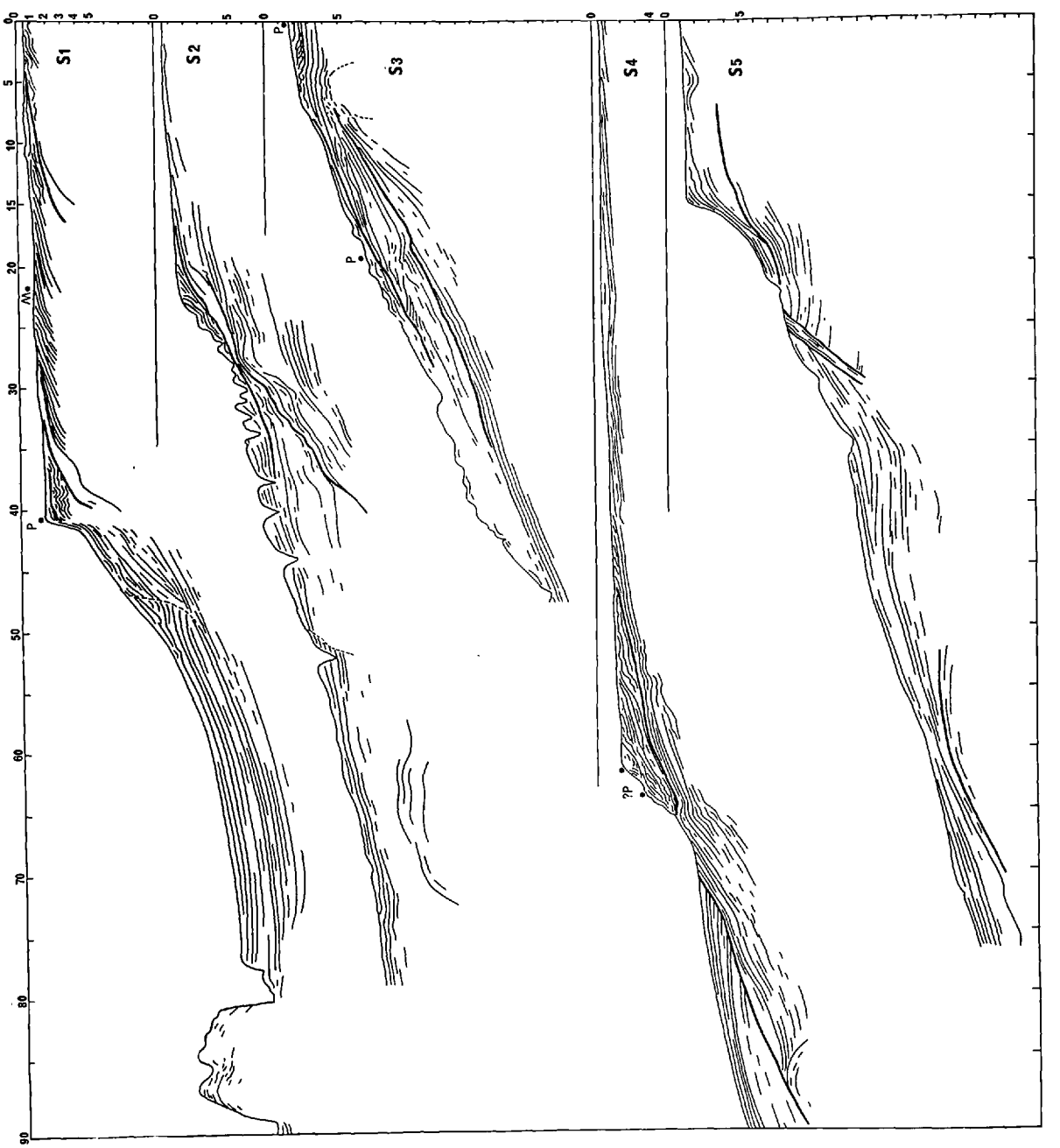
5.3 Continental Margin Geology and Structure.

5.3.1 Spanish Sahara (Fig. 5.3.1)

Echo-sounding and side-scan sonar records show that the northern Saharan shelf is extremely rugged and rocky with no sign of terracing and little sediment accumulation although below 70m the outer shelf off Cap Juby (profile S.1) has a very smooth aspect reflecting sediment accumulation. By contrast off Villa Cisneros and Cap Blanc (profiles S.4 and S.5) the almost flat southern shelf has a smooth aspect only locally disturbed by

Fig.5.3.1.
Continuous seismic reflection profiles (cf.Fig.5.1.1.) from the Spanish Saharan region.
Horizontal scale in km; vertical scale in units of 100 ms two-way travel time. M = upper Miocene dredge haul; P = derived lower Pliocene phosphorite fragments in sediments; (?P) = outcrop of probable Pliocene phosphatic limestone. Heavy lines represent unconformities.

Fig 5.3.1



terracing. The average depth to the shelf break is 111m which compares favourably with values of about 115m previously noted in this area by McMaster and Lachance (1968). The continental slope is usually steepest near the shelf edge; canyons are not widely developed according to presently available data.

Sidescan sonar records show the regional strike to be subparallel to the continental margin and confirm that a much greater degree of rock exposure differentiates the northern from the southern shelf area (Belderson, pers. comm.).

Several subsurface phenomena are common to all profiles (Fig. 5.3.1). Beneath the shelf, strata are well bedded, only locally slightly folded, and dip gently seaward. Their inclination is but slightly greater than the present shelf surface and increases gradually toward the shelf edge until subparallel with the present surface of the continental slope. Sparker and P.D.R. records do not show any flat lying sediment on the shelf except beneath the outer shelf off Cap Juby (profile S.1) and it is inferred that despite the smoothness of the southern Saharan shelf the thickness of recently deposited sediment must be less than the 30m resolution of sparker records. These data are supported by the observations of McMaster and Lachance (1968) who, using a low-powered sparker system with better resolution of shallow subsurface structures, found there to be some 17 - 35m of flat lying sediment over much of the southern Saharan shelf while only a thin sediment veneer was reported further north.

Within the slope, structures show progressive increase in deformation southward and are disrupted by an unconformity whose magnitude suggests development during the Oligocene, the major local fold period (cf. Querol, 1966; Martinis and Visintin, 1966). Outcropping on the shelf above the unconformity are upper Miocene, lower Miocene and lower Pliocene rocks (Figs. 5.3.1

and 5.I.I); no lower Pliocene outcrop was dredged but Rye (pers. comm.) palaeontologically identified rock fragments of this age in shelf edge and upper slope sediments presumably just seaward of or overlying outcrops. Derived lower Pliocene foraminifera are also found in Quaternary limestones dredged well down the slope off Cap Bojador (Rye, 1969). Phosphatic limestones assumed to be of the same age also outcrop at the shelf edge off Villa Cisneros (S.4) but do not contain sufficient biogenic remains for dating purposes. Since these last samples are thickly encrusted with glauconite they cannot be Recent and since the phosphatic Eocene known on land is encountered deep beneath the shelf in boreholes these outcrops are most likely to be Pliocene. Thus there appears to be a continuous Pliocene phosphatic limestone deposit along the shelf edge off the northern Sahara (cf. Fig. 5.I.D). In that the major unconformity is overlain by these Miocene and Pliocene strata and, not far north of Cap Juby is underlain by Eocene rocks on the outer shelf (Dillon, 1969) its Oligocene age seems reasonably confirmed. The major unconformity off Villa Cisneros and Cap Blanc is also identified by Rona (1970) who regards it as the buried margin of the continental terrace. Although Rona does not make any conjecture as to the actual age of the buried slope he states that it appears to be of erosional origin and is now mantled by a constructional wedge of slope sediments. The erosion is here assumed to be Oligocene for reasons outlined above.

Rotational slump structures (cf. Rona, 1969; Stride et al 1969) are seen within the slope off Caps Juby and Bojador (profiles S1, S2, S3) and off the latter there are also well developed surficial slumps giving rise to hilly topography. Small canyons also cut the Bojador slope where their degree of penetration shows that they are geologically relatively young (late Tertiary or Quaternary). The contorted attitude of shelf edge sediments off Villa Cisneros (profile S4) implies shelf edge dumping of sediment

in the past, possibly prior to the formation of outcropping Pliocene phosphatic limestones.

Other local unconformities are recognised off Cap Juby where, beneath the shelf edge, is a more or less horizontal disconformity relating to the present shelf surface and therefore probably Quaternary. Below this is a further angular unconformity which may, in view of local geological history, be Plio-Quaternary (cf. Querol, 1966). Its outcrop near the apparent outcrop area of Pliocene phosphatic limestones tends to support this contention.

A geologically young unconformity is also recognised off Cap Bojador (profiles S2 and S3) although since it is best developed at shallow depth beneath the uppermost slope where it underlies evident slump structures, it may be a plane of decollement. Similar slumping on the steeper uppermost slopes off the southern Sahara may have contributed to the exposure there of pre-Oligocene sediments from beneath the major unconformity (cf. Rona, 1970).

Further structures of interest are, off Cap Juby (profile S1), the presence of a steep sided topographic high apparently that named "Shadow Sea-knoll" and associated with magnetic anomalies implying a volcanic origin (Dillon, 1969), and, beneath the upper slope off Cap Bojador (profile S3), an intrusive body lacking any pronounced reflecting surface or internal structure which may be diapiric similar to other subcircular uplifts thought to be salt domes noted locally both offshore and onshore (King, in Querol, 1966, p. 39).

5.3.2 Morocco

5.3.2.a Surface Characteristics

Topographic characteristics of the shelf have been established from examination of P.D.R. records which are not presented here since the seismic

records (Fig. 5.3.3) give a general indication of shelf topography.

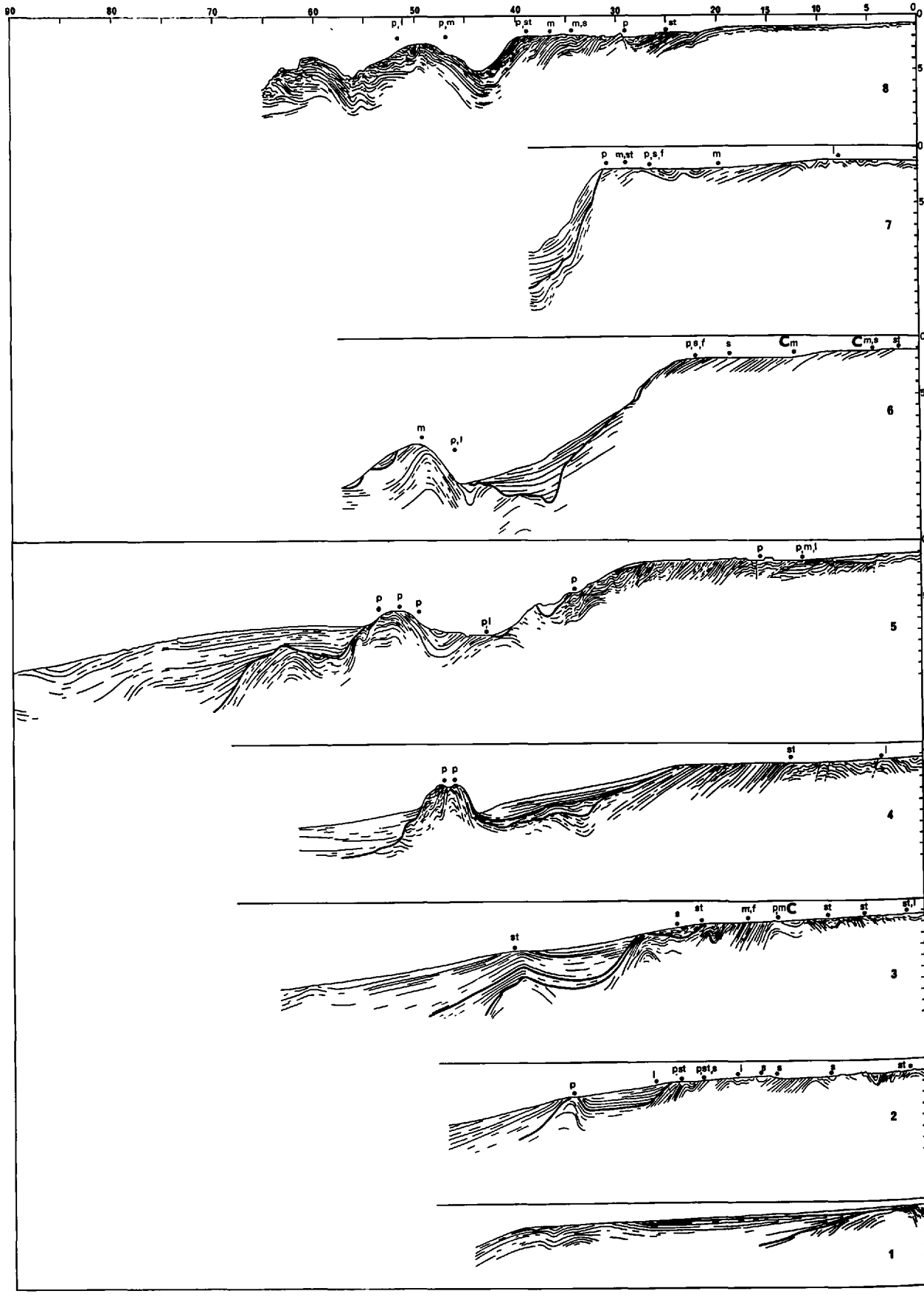
Off Agadir the shelf surface is smooth but between Cap Tafelney and Safi it is often rocky with rugged densely reflecting rock outcrops some 10 - 30 metres in height displaying shoreward facing scarps and protruding through less densely reflecting smoother patches interpreted as ponded sediment. Nutter (1969) shows that the ruggedness decreases northwards until the shelf is again smooth north of Al Jadida.

Sub-bottom reflectors parallel to the seafloor were locally seen on P.D.R. records and show sediment accumulation to reach about 14m at mid shelf depths off Cap Sim and 11m off Casablanca (Nutter 1969). Such reflectors were not picked up by the sparker suggesting that the maximum thickness of Recent sedimentation on the shelf is less than the 30m resolution of that equipment. Independent support is given by McMaster and Lachance (1968) who find sediment is only present as a thin veneer over much of the area but in patches reaches thicknesses of 17 - 34m. The buried surface follows the same pattern (cf. Nutter, 1969) suggesting that the localisation of ruggedness is due to the situation of profiles 2 - 8 (inc.) where the Atlas Mountains reach the sea; the absence of major rivers in this Atlas region may be a contributory factor.

An average shelf edge depth of 150m, calculated from all Moroccan profiles, is in substantial agreement with the data of McMaster and Lachance (1968). Accordingly a 150m isobath has been added to the bathymetric charts to approximately define the shelf edge (cf. Fig. 5.I .2). The observed depth range is from 135m (profiles 8 and 9) to between 150 and 160m (profiles 19 - 22 cf. Nutter 1969). All traverses display some degree of terracing but in the absence of a far more detailed survey conjecture as to the number and extent of terraces is not warranted.

Fig.5.3.3.
Continuous seismic reflection profiles (cf.Fig.5.1.2.) from the Moroccan region.
Horizontal scale in km; vertical scale in units of 100 ms two-way travel time. Black dots indicate dredged rock samples: p = phosphatic rocks (Eocene and/or Miocene), m = mudstone, st = siltstone, s = sandstone, l = limestone, f = flint. Soft Cretaceous mudstones = C. Further information regarding ages is given in Fig.5.3.5.: heavy lines represent major unconformities.

Fig 5.3.3



The continental slope off Morocco (Fig. 5.1.2) has already been described in broad detail by Gougenheim (1959) and Guilcher (1963). Well developed canyons slice into the slope off south central Morocco where their heads often indent the shelf edge. Elsewhere the slope is rather smooth and gently sloping, interrupted locally by slight irregularities with only a few metres relief except off Cap Sim where large topographic elevations interrupt the regular slope surface. A 40km long north trending ridge crests in some 260m on the upper slope off Cap Sim. Its elevation increases north from a vertical relief of about 180m on profile 4 to 256m on profile 5, but decreases rapidly further north. It has moderately steep flanks usually displaying some minor topographic irregularities, and a slightly rounded top in which there is locally a median depression 30m deep margined by inward facing scarp-like slopes (Fig. 5.3.3). North on the slope between Essaouira and Safi is a flat-topped rugged and rocky elevation with about 180m relief cresting in 198m and separated from the shelf by a broad depression (Figs. 5.1.2 and 5.3.3).

5.3.2.b Subsurface Characteristics (Fig. 5.3.3)

Beneath the outer shelf are usually well-bedded strata with moderately steep seaward inclination similar to or greater than the present continental slope, despite local contortions. Landward changes in dip result in the occurrence beneath the mid and inner shelf or near horizontal or landward dipping strata, often more contorted than those beneath the outer shelf. These two groups of strata may be separated by a slight unconformity (cf. profile 4). Off Agadir, a zone of broad shelf edge folds separates slope strata from a gently folded shelf syncline. Truncation of these substructures has occurred on all profiles. Off Agadir this has been followed by the deposition of some 30m of sediment which has also been folded and eroded near the shelf edge. That post-erosional deposition may have been widespread is shown by the faulted inlier of younger strata off

Cap Sim (profile 5). Faults affecting the erosion surface are also clear on profile 8. By contrast, Nutter (1969) has shown that north of the present study area, Moroccan shelf strata invariably dip gently seaward and are little, if at all, folded or faulted.

The outershelf strata continue beneath the continental slope where they have been quite strongly folded into broad folds and later truncated at a prominent erosion surface which outcrops near the shelf edge. This unconformity has itself been broadly folded about approximately the same fold axes recognised in the truncated strata beneath. Locally, strata at the cores of the major anticlines are more steeply folded than those on the flanks suggesting that intrusion may play a part in fold evolution. By interpolation between profiles, the axes of the two major folds in the major unconformity can be determined and are plotted together with contours representing the burial depth of the unconformity in Fig. 5.3.4. Where the crests of these folds intercept the seafloor older strata outcrop and the folds are manifest as long ridges, the best developed of which is that furthest seaward. Unfortunately, profile 7 ends on the upper slope but P.D.R. records along the seaward continuation of this line show no signs of any topographic high and it is concluded that the anticline is closed at both ends, as also it appears is the inner and weaker of the two folds. Interpolation between profiles of the outcrop of the unconformity allows definition of the region over which older strata outcrop. It appears that in the vicinity of the main redge crest are some 50sq. km. of the older strata which also outcrops over most of the continental shelf.

Bathymetric data suggest that there is no connection between the folds of profiles 2 - 6 (inc.) and those of profile 8. The topography of the continental slope high on profile 8 gives the appearance of being a dome-like structure. Finally, off Agadir, shelf strata wedge out landward and onlap

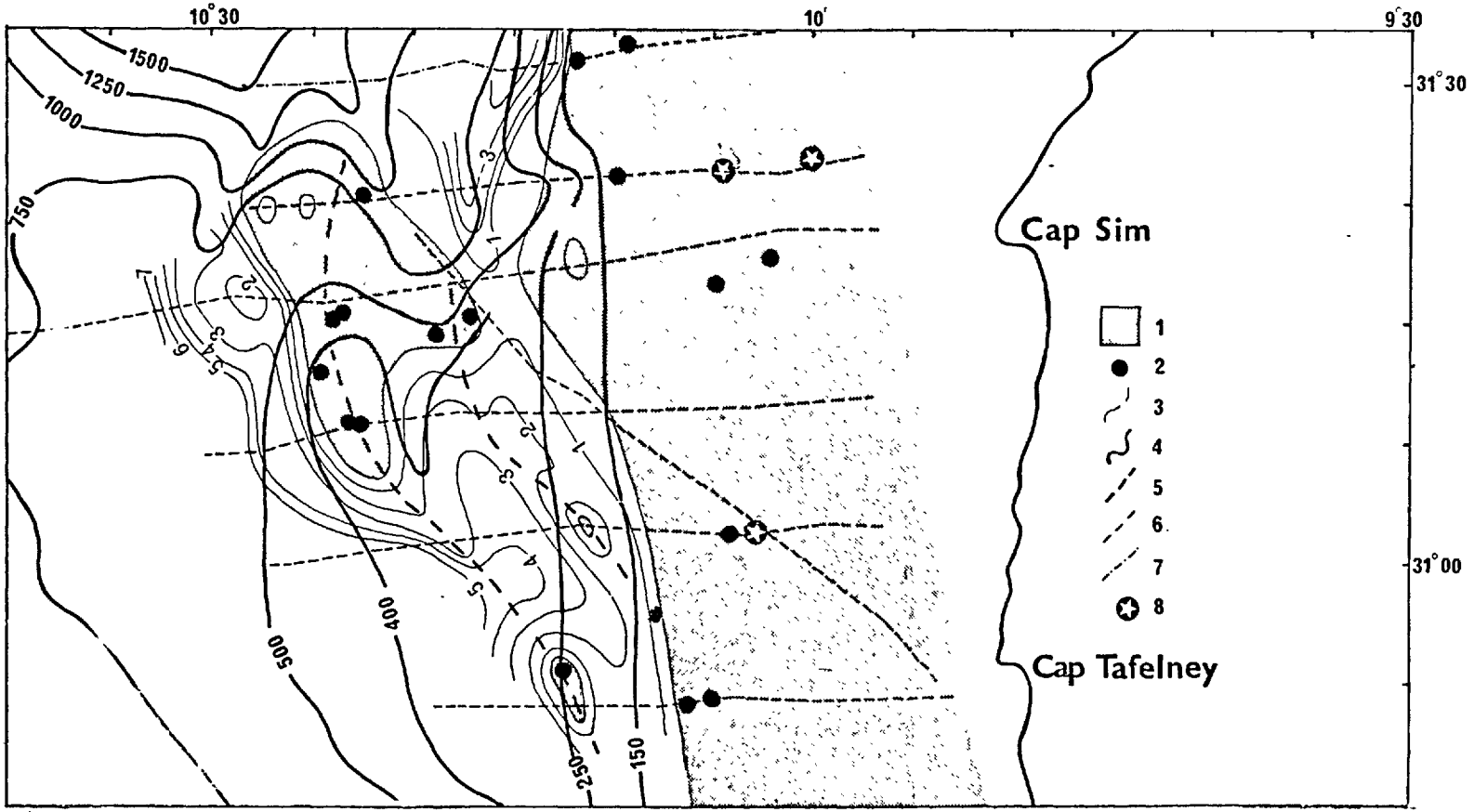


Fig.5.3.4.

Isopachs on the buried Oligocene unconformity off Cap Sim, showing (1) area over which pre-Oligocene rocks have been dredged;(2) location of Eocene and/or Miocene phosphatic samples;(3) burial depth of unconformity (contoured in units of 100 ms two-way travel time) ;(4)depths in metres; (5) major anticlinal axes; (6) sparker profile lines; (7) P.D.R. profile line; (8) location of dredged soft Cretaceous mudstone.

a well developed buried erosion surface which approaches the seabed near the coast. The thick series of sediments overlying the major unconformity beneath the slope, and in some cases the outer shelf, generally dip seaward more or less parallel to the present slope surface, thicken seaward, onlap the unconformity landward, and are often slightly folded and truncated at the seafloor. They are absent from the steeper parts of the slope on profiles 5, 6 and 8, where the slope is covered by but a thin veneer of Recent sediment. On these profiles the slope is notably steeper than to the north (cf. Nutter, 1969) or south, implying that tectonic oversteepening has caused continued slumping and maintained older strata at surface. Both younger and older stratal groups often display internal contortions indicative of slumping.

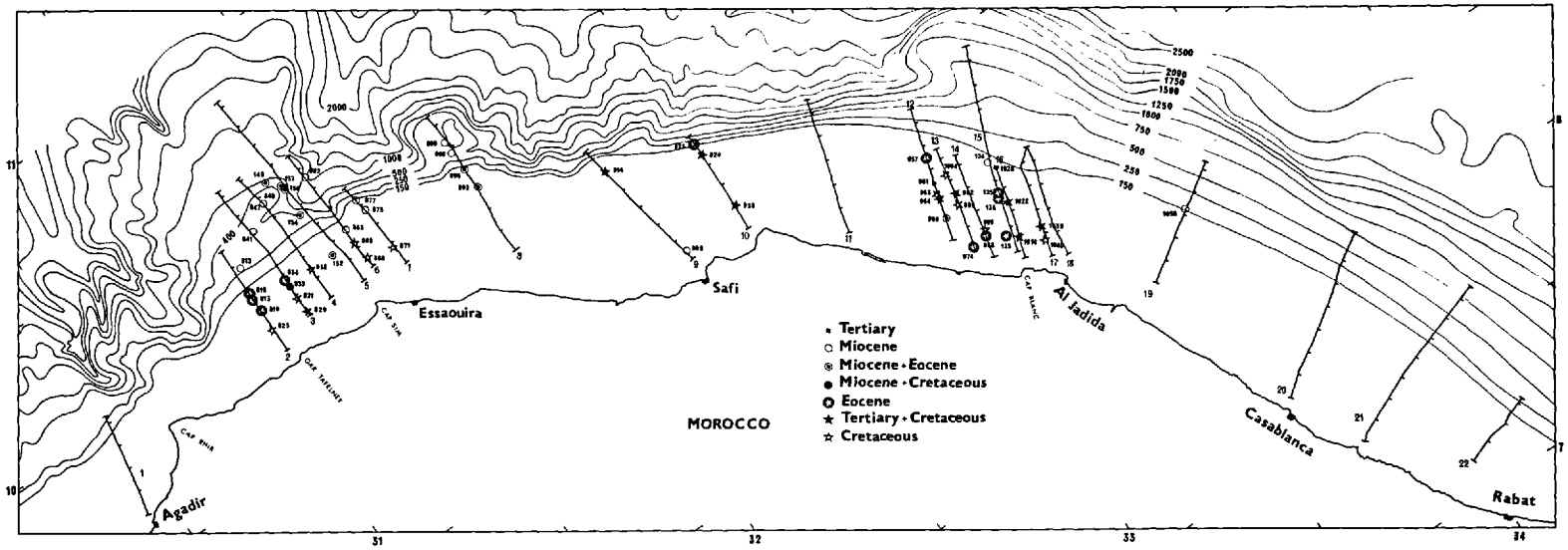
5.3.2.c Geology (Figs. 5.3.3 and 5.3.5) (table 5.1 and 5.2)

Eocene samples, many of them phosphorites, were dredged at several sites on the outer shelf and from the outcrops of these same strata at the crest of the main slope anticline. From the more contorted inner and mid shelf region, Cretaceous samples were obtained in keeping with the fact that nearly all coastal outcrops (except Plio-Pleistocene sands) are Cretaceous (Fig. 5.3.6). That the Cretaceous samples are dredged from more contorted strata than Eocene samples accords with the report of Choubert and Faure-Muret (1962) that upper Cretaceous folding and regression occurred in nearby south central Morocco.

As discussed in detail in the following chapter, the most common form of phosphatic rock to this southern region is a glauconitic conglomerate of Miocene age which incorporates Eocene pebbles. This rock has the characteristics of a basal conglomerate and must have formed after the Oligocene onset of Atlas folding reported from this region (Choubert and Faure-Muret, 1962). It crops out on the seafloor only within the area of outcrop of older strata from beneath the major unconformity (Fig. 5.3.4). It is here

Fig.5.3.5.

_Locations and ages of palaeontologically or radiometrically dated rock samples, showing their relation to seismic reflection profiles off Morocco.



assumed that the unconformity is Oligocene and that a Miocene basal conglomerate was laid down on this unconformity prior to folding and part burial by younger sediment. The widespread outcrop of Miocene conglomerate on the outer shelf implies that the present shelf surface is in the main an early Tertiary (? Oligocene) erosional feature.

As the major unconformity off Agadir (5.3.3) rises toward a coast cut into Cretaceous strata (Fig. 5.3.6) it is assumed that the unconformity is early Tertiary, probably Oligocene. Dillon (1969) recognises the same unconformity in other parts of the Souss Trough off Agadir, but designates it upper Eocene, this being the period of regression prior to Oligocene folding; Oligocene is preferred in the present account.

Some comment on the geology north of Safi is warranted by the newly available palaeontological data (Appendix 4) which supplement Nutter's (1969) geophysical study. The northern shelf is far less folded and there is but incipient development of an unconformity near the shelf edge (Nutter, 1969): shoreward of this, Eocene and Cretaceous samples were widely collected (Fig. 5.3.5). Many of the Cretaceous specimens have the appearance of being transported pebbles and they usually occur as exotics in samples composed mainly of phosphorite much of which appears Eocene and very locally derived or in situ. The Cretaceous pebbles were possibly derived during Quaternary erosion of the nearby coast. As on the southern shelf, there are occasional Miocene samples which, from their occurrence on both the inner and outer shelf are taken to represent a transgression over an Oligocene erosion surface cut into Cretaceous and Eocene strata. Subsequent Pleistocene erosion appears to have removed much of what little Miocene and Pliocene sediment accumulated on the shelf.

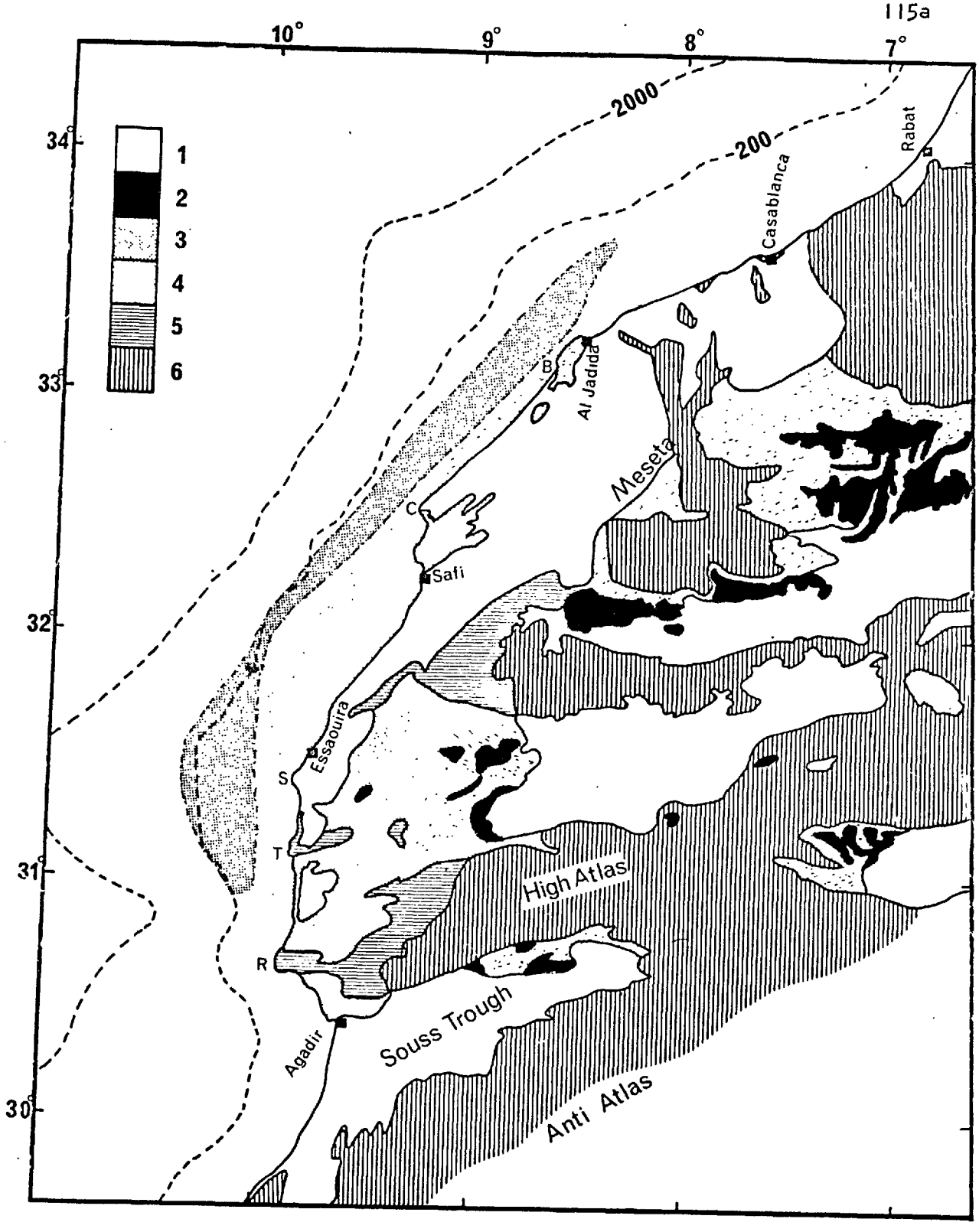


Fig.5.3.6.

Moroccan geology and the probable extent of offshore Eocene and Cretaceous exposures in the continental margin.(1)Plio-Pleistocene;(2) onshore Eocene (mainly phosphatic);(3) offshore Eocene (phosphatic);(4) onshore and offshore Cretaceous;(5) Jurassic; (7) pre-Jurassic.

B=Cap Blanc; C=Cap Cantin; S=Cap Sim; T=Cap Tafelney; R=Cap Rhir.

5.4 Discussion: Continental Margin Development

Although the present data are limited to the mid and outer shelf and the upper continental slope and omit both the inner shelf and continental rise, they allow at least a general interpretation of the structure and evolution of the northwest African continental margin. On most traverses, despite deformation and erosional interludes, the seaward dip of gently inclined strata beneath the shelf is seen to increase beneath the outer shelf and shelf edge until approximately parallel with the present continental slope surface. Further, the thickness of individual strata, particularly observed beneath the slope where penetration is greatest, generally increases seaward such that the dip of deeper layers becomes progressively less concordant with the present seafloor. Individual strata are seen to wedge out landward and to onlap other strata and unconformities in that direction. These data suggest development of the continental margin by prograding deposition in which upbuilding of the shelf and outbuilding of the slope occurs on a subsiding basement, a model proposed for the continental margins of the United States by Moore and Curray (1963), Uchupi and Emery (1968) and Rona (1969), for Europe by Stride et al (1969) and previously for this region, although only on the basis of shelf profiles, by McMaster and Lachance (1968).

5.4.1 Morphology

The shelf surface is a marine erosion plane whose formation apparently commenced in the Oligocene and which has been modified slightly by the maximum Cenozoic regressions in the Pleistocene. In some regions, particularly off north Sahara and between Agadir and Safi, differential erosion of moderately steeply dipping and folded strata has given rise to a series of scarps and the shelf is quite rugged. Off much of south central Morocco the shelf appears to be a rocky platform thinly and patchily covered by

Recent sediments which are ponded between rock outcrops. Recent sedimentation off northwest Africa has not been constant and there are greater accumulations off the southern Sahara, on the outer shelf off Cap Juby, off Agadir and at mid shelf depths off Cap Sim.

The difference between Moroccan shelf edge depths (150m) and Saharan shelf edge depths (110m) has been attributed by McMaster and Lachance (1968) to downwarping of the Moroccan shelf in compensation for the marked coastal uplift of the later phases of the Atlas orogeny. Moreover, the average value of 110m for the Spanish Sahara is rather shallow compared with Shepard's average worldwide datum of 130m (72 fms), and some degree of regional upwarping may be indicated.

The large south central Moroccan canyons (Fig. 5.1.2) tend to be sited where present rivers would outfall during the maximum Pleistocene regressions. It could be assumed that these canyons were cut by dense sediment laden water debouching from these rivers when near the shelf edge, a widely accepted hypothesis recently reiterated in explanation of the origin of other Atlantic canyons by Stride et al (1969) and Il'yin and Lisitsyn (1968). Although an attractive hypothesis there are grounds for questioning its validity when applied to the northwest African coast. While there is an abundance of canyons off south central Morocco, such features are absent north of latitude 33° (Gougenheim, 1959) despite the presence of well developed river systems on the adjacent landmass.

Perhaps significantly the northern region, with the exception of the Rif Mountain Chain, is underlain by the stable Meseta where the level of tectonism is and has been throughout the Tertiary considerably less than off south central Morocco where the Atlas mountains reach the sea. Conceivably the enhanced tectonism and earthquake activity of this southern region, epitomised recently by the Agadir earthquake, has been of more significance

in canyon genesis than the supposed Pleistocene rivers. In contrast Shepard and Dill (1966) note that canyons are as common off unstable and mountainous coasts as off stable and lowland coasts. They also cite Chamberlain's (1964) findings that most of the sudden deepenings reflecting sediment movement in Scripps canyon were significantly related to periods of large waves following the storm season and not to local earthquake activity.

5.4.2 Spanish Sahara

The Mesozoic and Tertiary Aaiun Basin in the western Sahara (Fig. 5.4.1) is occupied by a thick series of gently westwardly dipping sediments. A greater degree of late Tertiary subsidence occurred in the northernmost part of the basin where Miocene strata are preserved onshore; elsewhere the Tertiary is represented by Palaeocene and Eocene unconformably overlying Cretaceous strata (cf. Querol, 1966; Martinis and Visintin, 1966). Subsea data confirm that the northern Aaiun Basin was the locus of deposition of Miocene sediments; they further suggest that Lower Pliocene deposition was widespread there and more Recent sediments appear to have accumulated on the outer shelf off Cap Juby suggesting subsidence continued into the Quaternary. In comparison with the 1000m of Eocene sediments found in a borehole near Cap Bojador, the 1000 feet or so of apparently post-Oligocene sediments indicates very reduced late Tertiary subsidence. That sedimentation in the northern part of the basin was very slow during the Pliocene is suggested by the formation then of widespread phosphorite. A major unconformity tentatively dated as Oligocene appears fairly deeply buried beneath the north Saharan shelf but crops out on the outer south Saharan shelf implying a much lesser degree of post Oligocene subsidence than in the northern region.

The configuration of the upper slope off the southern Spanish Sahara is

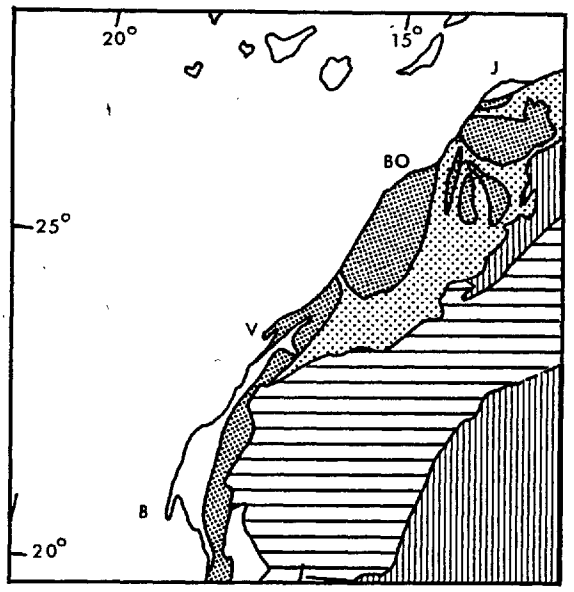


Fig.5.4.1. Regional geology of the Spanish Sahara; Mesozoic and Tertiary sediments along the coast were all deposited in the Aaiun Basin.

Blank = Plio-Pleistocene; heavy stipple = Tertiary ; light stipple = Cretaceous; vertical shading = Jurassic; horizontal shading = Palaeozoic.

J=Cap Juby ; BO=Cap Bojador ; V=Villa Cisneros ; B=Cap Blanc.

thought to result from tectonic oversteepening of the buried (?)Oligocene slope. As later shelf deposits have built out across the (?)Oligocene shelf edge, they have become unstable and periodic slumping has caused the present shelf edge to migrate shorewards a few kilometres from the buried shelf edge (cf. Ron , 1970). The slumped material has accumulated on the less steep lower portion of the slope, which has thus been built up. The profiles suggest that the shelf is in more or less the same position as during the Oligocene.

Further slight unconformities which may represent known Pliocene and Pleistocene fold periods are noted beneath the outer shelf or upper slope off the northern Sahara. The widespread nature of the Oligocene unconformity, which is also found off Morocco, may reflect the epeirogenic response of northwest Africa to the mid-Tertiary slowing of seafloor spreading reported for the Atlantic by Le Pichon (1968).

Downwarping appears to have been a slow and steady process as slump structures are restricted. Nevertheless the present slope surface almost everywhere truncates very slightly folded strata and its attitude must reflect interplay between deposition and erosion.

Off Cap Bojador a salt diapir like those from the Senegal shelf (cf. Aymé, 1966) appears to have been located. In its immediate vicinity slope sediments are rather more distorted than usual.

5.4.3 Morocco

During the Cretaceous and Eocene, three main east-west oriented gulfs are thought to have crossed western Morocco from the coast at Agadir (Souss Trough), at Essaouira, and between Safi and Al Jadida (Choubert and Faure-Muret, 1962): it is within these gulfs that the widespread Maestrichtian-Eocene phosphorites were deposited (cf. Fig. 5.3.6). The concentrations

of phosphatic samples on the shelf off Cap Blanc and Cap Sim might suggest that these gulfs continued onto the continental margin; differences of lithology between the Eocene phosphorites of these two regions (Chapter 6) argue for different depositional conditions, which tends to support the idea of offshore gulf prolongations. Furthermore, between these two regions dredged phosphorites were restricted to the outermost shelf suggesting non deposition on the inner and mid shelf off Safi. Dillon's (1969) work clearly shows that the Souss Trough did continue across the continental margin as far as the shelf edge where it was terminated at a basement high.

Available data suggest that during the first (Oligocene) Atlas fold period (possibly related to Atlantic seafloor spreading) a major unconformity developed in the vicinity of the Atlas mountains between Agadir and Safi; the unconformity dies away rapidly northward (Nutter, 1969). Oligocene tectonism apparently produced a 'proto-slope' approximately on the site of the present slope and subsequent Oligo-Miocene erosion gave rise to the present shelf in more or less its present form. Later, the proto-slope was buried and onlapped landward by sediments except where tectonic over-steepening and topographically induced current activity prevented this. The shelf and upper slope were the sites of limited accumulation of Miocene phosphatic sediments which are still preserved in patches on the northern shelf and are widespread on the southern outer shelf and upper slope; whether or not these accumulated in gulfs is conjectural. That subsidence has continued in the Souss Trough more or less until the present is suggested by profile 1 and by Dillon (1969); elsewhere the main locus of post-Oligocene sedimentation has been the continental slope-rise complex.

An approximately E-W trending Palaeozoic block interrupts the coast between Cap Rhir and Cap Tafelney (Fig. 5.3.6 and 5.4.2) and it is on the offshore extension of this block that the main Moroccan canyons are incised. Further-

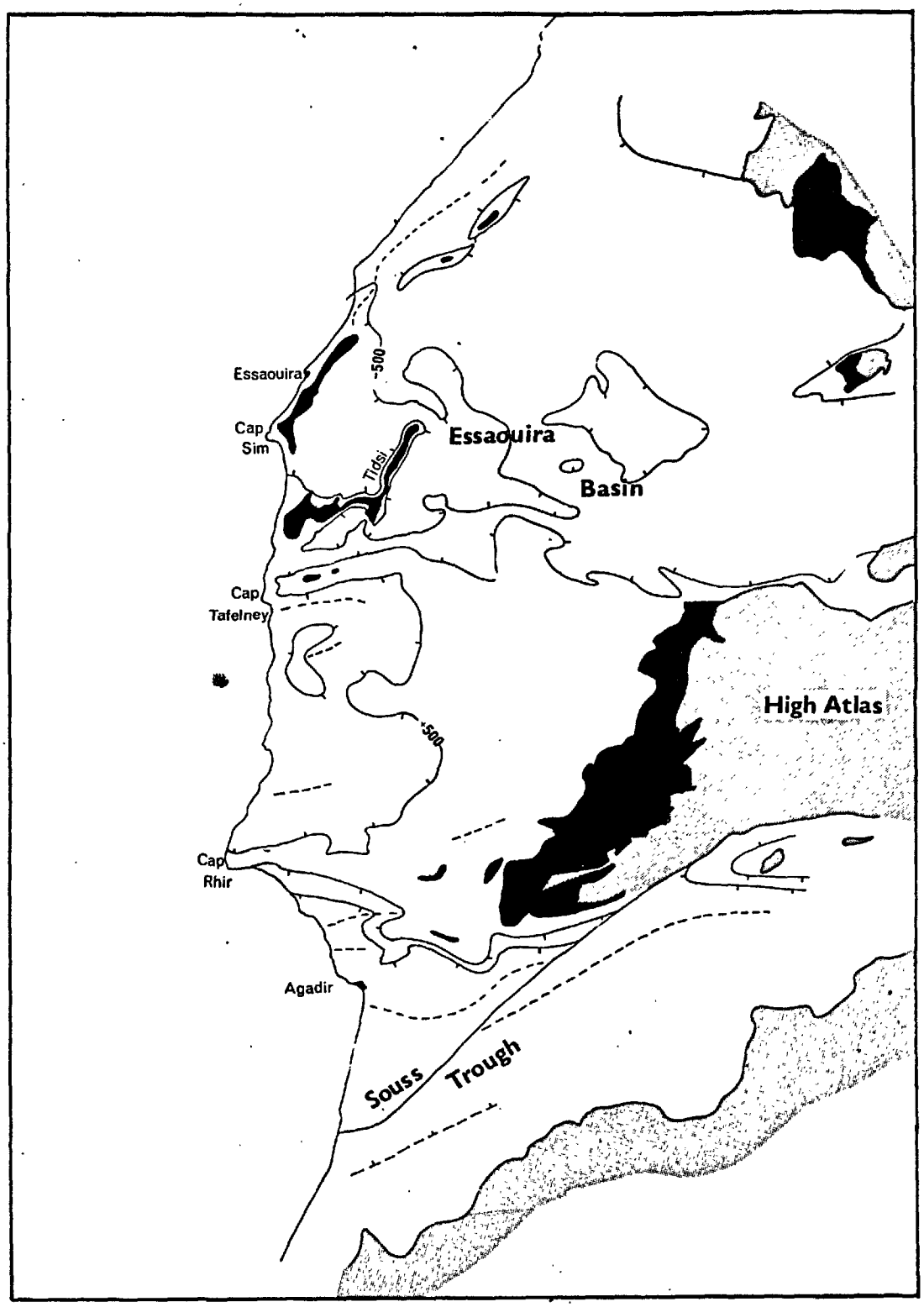


Fig.5.4.2.
Atlas structures and salt domes in south central Morocco, showing location of basins between Paleozoic blocks. Shaded area = Palaeozoic; black area = Trias. Isopachs represent elevation or depression (in metres) of the top of the Jurassic; dashed lines represent synclinal axes; major, elongate salt intrusions with Trias cores trend NW near Essaouira and E-W at Caps Tafelney and Rhir. Based on Soc.Cherif.des Petroles (1966).

more against the projected northern margin of this block is terminated a well developed NE trending fold on the continental slope (cf. Figs. 5.3.4 and 5.4.2); from this it is constructed that Atlas structures do locally affect the continental margin although in general there is little sign of this. The post-Oligocene slope folds are subparallel to and of the same size as elongate salt piercement structures found onshore just north of the Palaeozoic basement block (cf. Figs. 5.3.4. and 5.4.2). As the offshore folds are also closed structures in which the greatest deformation is often at the cores, they may similarly be salt controlled. Movement along their axes appears to have continued throughout the later Tertiary, possibly up to the present.

5.4.4 Summary of Conclusions

1. The continental margin was built up beneath the shelf and out beneath the slope by seawardly prograding sedimentation on a subsiding basement.

2. Seaward thickening of strata shows the zone of greatest sediment accumulation to be the continental slope-rise complex.

3. Off Morocco Eocene phosphorite deposition appears to have occurred in basins or 'gulfs' oriented across the continental margin; only one of these, the Souss Trough, continued to subside after the Oligocene.

4. An Oligocene epeirogenic and orogenic event related to an interruption in sea-floor spreading and to the Atlas orogeny, resulted in formation of a proto-slope almost on the site of the present slope off northwest Africa.

5. Subsequent Oligo-Miocene erosion appears to have governed basic shelf morphology: the shelf was the site of reduced deposition of Miocene and Pliocene sediments probably largely removed by Pleistocene erosion.

6. Post-Oligocene subsidence and sediment accumulation on the shelf has

been greatest in the northern Aaiun Basin and the Souss Trough; elsewhere gulfs and basins seem to have disappeared.

7. Continental margin deformation has been greatest on the offshore extension of the High Atlas Chain.

8. Salt tectonics have had important local influence on offshore structure.

9. Recent sedimentation has not greatly influenced shelf morphology.

CHAPTER 6

PETROGRAPHY OF OFFSHORE MOROCCAN PHOSPHATIC ROCKS

6.1 Introduction

To determine their regional characteristics, 53 selected samples of offshore Moroccan phosphorites and phosphatic rocks and, for comparitive purposes, 20 randomly selected limestones were petrographically analysed using a total of 130 thin sections. This type of study is not entirely ideal in that the predominance in cryptocrystalline states of carbonate apatite minerals and their common intimate admixture with finely divided argillaceous, carbonaceous and ferruginous impurities makes petrographic analysis of only general value in mineral identification (cf. McConnell, 1950; Carozzi, 1960). In this work the 'basket' - term collophane has been used throughout for isotropic or virtually isotropic cryptocrystalline varieties of finely divided carbonate apatite while crystalline varieties have all been identified as francolite, a form of carbonate apatite acknowledged to be of major importance in sedimentary phosphate rocks (cf. McConnell, 1950).

Chief among the objects of this present study are the establishment of the provenance, dispersal, depositional and diagenetic controls of offshore phosphate rock formation to allow comparison of the continental margin phosphorites with those of the same age known onshore and to aid in understanding continental margin development in general and the origin of the offshore phosphorites in particular. A secondary objective is to provide geologic data to aid in the interpretation of detailed geochemical studies being carried out on these rocks by J. McArthur (PhD thesis, University of London, in preparation).

Petrographic examinations show there to be three main phosphatic rock types. South of Safi glauconitic conglomeratic types predominate; north of Safi are pelletal types, and a third type common to both regions comprises phosphatic limestones (cf. table 5.1 and Fig. 5.3.5). Conglomeratic varieties of the first two types are extremely common and normally contain pebbles of the third type.

Bushinsky (1969) defines as phosphorite rocks containing >18% P_2O_5, approximating to 50% apatite. Using this criterion, analysed pelletal samples (135, 136, 139) and 'phosphatic limestone' (148) are all phosphorites though none contain more than about 25% P_2O_5. By contrast, analysed glauconitic samples 152 and 154, and ferruginous phosphatic rocks 156 and 157 proved to contain <18% P_2O_5 and are classified as phosphatic limestones of different types.

6.2 Glauconitic and Pelletal Phosphatic Rocks

Glauconitic Phosphatic Limestone-Conglomerates (Fig. 6 a,b,c).

These occur entirely as conglomerates and comprise angular and subangular pebbles mainly of various types of limestone phosphatised to various degrees, some massive collophane (probably representing completely phosphatised limestone), and occasional glauconitic phosphorite, all set in a poorly-sorted, unevenly-bedded matrix of partially-phosphatised, indurated lime mud containing varying amounts of sand-size glauconite, silt-sized quartz, foraminifera and amorphous iron oxides, argillaceous material and carbonaceous debris. This conglomeratic variety only occurs south of Safi but glauconitic phosphorites were also found at two sample sites moderately distant from the southern glauconitic conglomerate province. At Sta. 903, near Safi, glauconitic phosphorite fills borings into a coarse unphosphatised foraminiferal sand containing occasional pebbles of phosphatised

limestone. At Sta. 1056, the northernmost phosphatic rock sample dredged from the outer shelf near Casablanca, irregularly bedded glauconitic silty foraminiferal mud fills all available interstices within a limestone composed essentially of large unphosphatised corals. The faunal remains from between the blades of the corals indicate moderately shallow conditions; the sediment external to the coral fragments mainly contains planktonic faunal remains indicative of open sea (?) deeper conditions. The former sediment is less muddy than the latter.

Pelletal Phosphorites (Fig. 6d,e,f).

The pelletal phosphorites, only found north of Safi, are very often conglomeratic although less notably so than the southern glauconitic phosphorites. They are essentially poorly-sorted, unevenly-bedded, partially-phosphatised, indurated lime muds containing varying amounts of sand sized phosphorite pellets, silt sized quartz, foraminifera, amorphous iron oxides, argillaceous material and carbonaceous debris. Although pebbles of different lithologies are often found, the commonest are varieties of the same lithology as the matrix but often more highly phosphatised. In this respect these rocks appear more like intraformational conglomerates than do the glauconitic variety.

6.2.a Glauconite :(Fig. 6 a,b,c).

The glauconite occurs always as sand sized grains, most of which are subrounded to subangular with an abraded appearance. Very few grains are lobate or exhibit cracks and the lobate grains usually look worn or partly fragmented as though they have been partly dismembered. In several cases the grains have been completely oxidised while in others, only marginal oxidation has occurred. That this occurred prior to transportation is shown by the presence of grains which have subsequently been broken and now display incomplete oxidation rims which terminate abruptly at sharp boundaries. The sharp outline of most grains again suggests a derived rather

than in situ origin although glauconite seen filling the cavities of some foraminiferal tests may be post-depositional. It should be emphasised that in the main not more than 30 per cent of grains ever show signs of oxidation and in some samples this phenomenon was not observed

In another form glauconite is often found to impregnate the crustal millimetre or two of certain pebbles of the conglomerate. A detrital origin is excluded for this variety by virtue of its patchy and irregular character among areas of unreplaced host rock. Within the margins of some of these pebbles (Fig. 6 $_b$) is observed glauconitisation of foraminiferal tests; the process commences with formation of a thin skin of glauconite on the inner and outer walls of the test whence replacement of the test itself occurs, followed by glauconitisation of test infillings and subsequently outward growth from the now completely glauconitised foraminifera. Similar replacement is seen of large platy molluscan and echinoid fragments. Conceivably the presence of minute concentrations of organic matter and pyrite - often seen coating the inner and outer walls of foram tests - encourages nucleation of glauconite. The difference between this glauconite and that of the matrix lies in the diffuse outlines of the former and its patchy impregnation of the surrounding pebble matrix. There is as yet no evidence to suggest that matrix glauconite grains are other than allochthonous except in sample 813 where some glauconitisation of the matrix is apparent.

That the glauconite is probably local in origin is suggested by the lack of uniformity of grain shape, poor sorting, occasional part fragmentation of lobate grains, and incorporation of regular glauconite grains into the margins of certain pebbles which were evidently not indurated before being incorporated into the conglomerate.

6.2.b Pellets

The term pellet is commonly applied to individual grains of sandy phosphatic sediments; it is not used here in any genetic sense. The pellets, which are generally structureless, occur in a number of different forms varying from regular ovoids to irregular subangular or even angular grains; oolitic varieties are found but rarely constitute as much as 20 per cent of the pellet population (Figs. 6 e,f).

Usually the pellets are of medium to very fine sand size although in some rare cases only coarse silt size particles are present. They most often comprise pale brown, turbid, virtually isotropic, optically amorphous or crystocrystalline collophane usually containing abundant disseminted segregations of impurities such as iron or organic material. Different pellets within the same sample usually exhibit differing degrees of turbidity and, while some grains may be rather dark brown, others are completely clear pale yellow. Usually, regardless of shape, pellets have a marginal rim free of imputities. In most cases this appears to be a result of migration of impurities away from the pellet margin: similar phenomena have been widely reported elsewhere (cf. Cayeux, 1941; Emigh, 1958; Carozzi, 1960; d'Anglejan, 1967). The inner margin of the clear rim zone is always fuzzy while the contact between grain and matrix is almost always, sharp. In those pellets where two or more zones occur the term oolite may be applied but, since there are no clear crystal growths oriented radically to the nucleus these are more commonly referred to as pseudoolites (cf. Salvan, 1952). The concentricity is defined by rather indistinct narrow zones of segregations, apparently of organic material or iron minerals such as those at the grain centre. It appears to have originated by internal mobilisation of impurities during apatite crystallisation (cf. Carozzi, 1960; d'Anglejan, 1967). In some instances more than one growth period may have occurred and the nucleus may be composite

and include an earlier oolite and parts of its surrounding matrix

In some instances, oolitic concentricity results from the alternative of bands of isotropic collophane and slightly anisotropic francolite - a type noted elsewhere (cf. Carozzi, 1960).

Pellet nucleii, rarely central, are not common. Most often seen (Fig. 6 e,f) are silt-sized quartz, calcite, and, less often dolomite rhombohedra; foraminiferal nucleii are rather uncommon except in rare instances (Fig. 6 d) where they predominate almost to the exclusion of other material (samples 134, 966). The presence, within pellets, of dolomite rhombs and of calcite replacement rims around quartz nucleii tends to suggest that pellets originated by diagenetic intrasediment growth around nucleation centres although probably not, in most cases, within the sediment in which they are presently found. However, the majority of the pellets have no discrete granular nucleus, consisting for the most part apparently of limestone fragments phosphatised to varying degrees; relict foraminifera are often seen in these limestone fragments as are abundant microcrystalline rhombohedra indicative of local calcite supersaturation during phosphatisation.

The foraminiferal samples (134 and 966) consist almost entirely of unreplaced collophane and glauconite-filled foraminifera, encased in a perfectly moulded skin of collophane, and set in a foraminiferal sand matrix containing unbroken specimens not associated with collophane (Fig. 6 d). Some of the pellets are composite, comprising two or more foraminifera joined by a phosphatised lime mud matrix. In those cases where parts of the foraminifera project beyond the attached relict matrix it is evident that the clear collophane skin is not unique to the foraminifera but represents the pellet or grain margin and must have therefore developed

not while the foraminifera was within its previous fine grained sediment, but after it had been fragmented, since the clear rim does not extend all the way round that part of the foram still in contact with the relict matrix but extends all the way round the rock fragment as a whole. Within the pellet the matrix is seen to be penetrated by a network structure seen to be continuous with a very narrow incipient rim around that part of the foraminifera in contact with matrix.

6.2.c Quartz and Foraminifera

Quartz forms by far the most common inorganic detrital clastic mineral phase. It tends to be more common in the glauconitic samples. In samples 813, 833, 865 and 877 the conglomerate matrix comprises a phosphatic, glauconitic, calcareous siltstone; a phosphatic, glauconitic silty limestone matrix occurs in samples 152, 154, 883, 896, 898 and 899, but in other glauconitic and most pelletal samples silt-sized quartz is a very subordinate constituent. Individual grains are very rarely as coarse as very fine sand grade and most often occur as subangular silt sized particles. Usually their margins are somewhat corroded and display calcitic overgrowths indicating post-depositional instability. As for coarser components, these silt grains are poorly sorted and often patchily concentrated suggesting rather irregular current velocities in the depositional environment. The large disparity in size between quartz and glauconite or pellets suggests profound differences in their provenance and transportation histories.

By far the most abundant organic skeletal remains consist of broken and unbroken foraminiferal tests whose abundance varies considerably from sample to sample. Among glauconitic rocks foraminifera are abundant in samples 841, 847, 883, 896, 898, and 899 from the outer shelf and upper slope seaward of relatively poorly or non-foraminiferal samples. In the glauconitic samples foraminifera abundance is generally inverse to that of quartz

although in some samples neither are abundant and the conglomerate matrix comprises glauconite grains suspended in a 'lime-mud'. Foraminifera are uncommon in the pelletal samples except in rare instances (134, 966); in all except these samples they usually occur only in fragments.

In pelletal samples (except 134, 966) faunal remains are locally completely phosphatised. Although neither whole or broken foraminifera are phosphatised in the glauconitic samples, they may contain infillings of collophane but more often contain macro or micro crystalline calcite, and sometimes glauconite or some oxidised iron mineral and sometimes pyrite. In certain instances it appears that collophane is in the process of replacing calcitic infillings. Frequently, foraminiferal tests, calcite infillings and locally abundant silt-sized calcite grains (probably skeletal fragments) have been recrystalised to a microcrystalline calcite mosaic the irregular boundaries of which are ragged and irregular indicating sorption by the phosphatic matrix.

6.2.d Matrix

The matrix is usually turbid, the cloudiness reflecting the degree of admixture of finely divided argillaceous, organic and iron materials. Normally, under plane polarised light it is a pale yellow brown and under crossed nicols is seen to consist essentially of almost isotropic cryptocrystalline or optically amorphous collophane admixed to varying degrees with microcrystalline calcite, sometimes irregular and of different grain size, but often in the form of minute rhombohedra. The irregular calcite fragments are corroded and display various intermediate stages towards phosphatisation; the rhombohedra in this type of rock, according to Carozzi (1960), are usually secondary phenomena generated by local oversaturation during diagenesis. The degree of phosphatisation is very variable from sample to sample and also within individual thin sections (Fig. 6 f).

Locally, particularly where the texture is very sandy, later thin rims of radially disposed crystalline francolite (anisotropic) have formed around pellets, grains of glauconite, quartz and sometimes foraminifera and calcite but not at points where they are in contact (Fig. 6c,e,f. Around intergranular spaces these francolite growths take on the appearance of marginal geode fillings; the interstices are filled with later more or less clear collophane. Bushinsky (1935) has described similar occurrences from Russian pelletal phosphorite. In patches, later diagenetic calcite and sometimes pyrite or haematite has replaced interstitial collophane particularly where the textures are more sandy, but this is not common and the predominant diagenetic mineral is collophane.

In general (Fig. 6 e,f) the pellet phosphorite matrix is less well phosphatised than that in the glauconitic samples. It is also rather more turbid, suggesting a greater degree of admixture of finely divided impurities. In many cases the pelletal phosphorite matrix is traversed by a well developed 'network' structure comprising pale yellow clear and colourless collophane veinlets separating darker turbid patches of collophane rich in impurities. Such structures have been previously reported in phosphatised limestones (Bushinsky, 1935) and within phosphate pellets (d'Anglejan, 1967). Development of network structures coincides with increasing development of matrix phosphatisation. In some instances instead of patches of turbid collophane within the 'net' there are discrete foraminifera, calcite, dolomite, quartz crystals, or detrital phosphate pellets and oolites.

In most pelletal samples (except 134, 966) irregular erosional horizons separate irregular thin beds whose texture may be that of well-sorted to poorly-sorted sand, muddy sand or mud, and not infrequently shows some crude grading(Fig.6.e,f).The degree of phosphatisation of these different layers is often markedly different and, within any one horizon the

degree of phosphatisation increases markedly towards the erosion horizon which is also often impregnated with iron oxides. This phosphatisation bears no relation to the incidence or character of pellets, zoned examples of which are often truncated at erosion surfaces, and between which, where close-packed, intergrain contacts are restricted to the outer margins of oolites or marginal zones of structureless collophane grains. Within the glauconitic samples the matrix is also poorly sorted and within one thin section, texture may change from a well-packed, well-sorted sand in which there is contact between most grains, to a poorly sorted sandy 'lime-mud' comprising sparse sand-sized glauconite grains and, rare quartz silt grains and odd foraminifera suspended in a phosphatic lime-mud matrix (Fig. 6 a,b,c). Irregular erosion surfaces, often intensely iron oxide stained, separating regions of different texture and different degrees of phosphatisation are locally identified in the glauconitic samples. Although less common than in the pelletal phosphorites the matrix beneath these horizons often shows enhancement of phosphatisation.

6.2.e Pebbles in Glauconitic Conglomerates

A variety of lithologies, chiefly of limestones, comprise the pebble assemblage of the glauconitic phosphatic rocks. It should be emphasised that the degree of phosphatisation of the following varieties is variable and both phosphatised and unphosphatised varieties of the same lithology can be seen in the same thin section. Then too, the degree of phosphatisation ranges from complete, through partial to marginal, and in some cases, none at all. The most common varieties appear to be:-

(1) Calcareous siltstone: grading to silty limestone; usually unfossiliferous or with a very poor fauna; sometimes laminated.

(2) Foraminiferal limestone: with all gradations from foraminiferal sand through to foraminiferal ooze, each with different amounts of foraminifera and with different amounts of silt sized quartz detritus.

(3) Aphanitic limestone: unfossiliferous in the main; composed almost entirely of microcrystalline calcite.

(4) Sandy glauconitic silty foraminiferal phosphatised limestone: apparently of the same lithology as the surrounding matrix but in pebble form often with very irregular margins suggesting a lack of induration prior to sedimentation; often part oxidised.

(5) Phosphorite: ferruginous and non-ferruginous varieties which are now completely chemogenic but in which traces of original limestones are usually observable, and some of which may be dolomitic.

(6) Composite pebbles: for example pebbles of phosphorite within an unphosphatised aphanitic limestone pebble, and phosphatised limestone pebble within pebbles of type (4).

(7) Coarse shell limestones: unphosphatised. Rarer types are quartzite (833), and flint (observed in hand specimen but not in thin section).

The degree of phosphatisation of pebbles is highly variable (Fig. 6 b,c,g) in some instances limestones are completely unphosphatised even at their margins; others display a narrow or a wide rim where phosphatisation may or may not have proceeded to completion with or without accompanying glauconitisation or, in some cases oxidation of iron minerals; others have patchily phosphatised nucleii whereas a further type may be homogenously phosphatised, completely or partially, throughout. The main stages in phosphatisation appear to involve first, recrystallisation of macrocrystalline calcite plates (shell remains or foram infillings) to irregular microcrystalline mosaics; followed by corrosion of grain margins, leaving eventually a crypto-crystalline collophane matrix studded with varying amounts of minute fragments of unreplaced shell remains and, in particular, calcite rhombohedra formed due to supersaturation. Large shell and echinoid fragments may be replaced before the matrix but the normal progression appears to be (1) matrix, (2) calcitic shell fragments - usually present

as platy calcite grains, (3) foraminiferal infillings, (4) foraminiferal tests. On occasion the foraminiferal infillings and tests may remain unreplaced resulting in a mass of collophane studded with round blobs of calcite representing foram chambers (Fig. 6 *g*). Where replacement of calcitic infillings is occurring, the phosphatisation usually proceeds most rapidly at the junction between test and infilling.

It is worth emphasising that the degree of phosphatisation of pebbles seems totally unrelated to the degree of phosphatisation of the matrix (cf. Fig. 6 c) and also that the glauconitisation of pebble margins apparently occurred under differing conditions from those governing matrix sedimentation since the matrix is never glauconitised although compositionally very similar to the enclosed pebbles. Furthermore some pebbles in which marginal glauconitisation and phosphatisation have occurred have subsequently been broken prior to sedimentation (865). Yet other pebbles have burrows filled with phosphatised foraminiferal limestone of completely different character to the later matrix of the conglomerate (Fig. 6 *g*). Two or more periods of phosphatisation are suggested by these data.

In several samples the irregular shape of glauconitic pebble outlines suggests that they were soft during sedimentation; in support, glauconite grains are commonly found to be arranged around pebble margins as though adhering to the muddy pebbles.

Iron is a common constituent; several of the limestones are pyritic although in these cases an oxidised rim usually intervenes between the pebble core and its glauconitised (or non-glauconitised) margin. Yet others are richly ferruginous, containing abundant limonite or goethite often completely dispersed throughout the sample and imparting to it a dark orange red colour but at other times occurring in segregated patches within which colloform growth structures are sometimes seen. Not infrequently

these samples appear dolomitic; where they are moderately phosphatic, silt-sized rhombs possibly of dolomite, appear suspended in a micro-crystalline calcitic matrix. Pyrite is also seen in some samples to coat burrow margins. By contrast with the pebbles, pyrite is uncommon in the surrounding matrix which, indeed, is characterised by a pale brown colour due apparently to finely disseminated iron oxides.

Very narrow collophane coatings are sometimes observed around pebbles and appear to have formed prior to cementation by the present matrix. In one case later colloform francolite growths extend apophyses out into the matrix indicating that post depositional 'nucleation' has occurred (sample 847).

In rare instances, silt-sized detrital collophane forms an accessory mineral in a calcareous siltstone pebble (sample 154) indicating more than one period of phosphorite formation.

Pebbles (2) in Pelletal Phosphorites

A lesser variety of pebbles is found in the pelletal compared with the glauconitic conglomerates. Most common are pebbles with very irregular margins suggesting that at time of deposition they were but poorly indurated: this variety is of the same basic composition as the matrix although usually texturally different from their surroundings. The pebble margins do not tend to display any accretionary rims but have margins which are usually more phosphatic than either the interior of the pebble or the surrounding matrix. Within this usually clear collophane margin are frequent colloform structures and apophyses may extend from the margin far into the centre of the pebbles where they may enclose foraminifera and foreign particles (quartz, calcite) or irregular patches of matrix in which a greater degree of segregation of impurities has occurred. That this process might lead, on disaggregation, to pellet formation, cannot be ignored.

Of other pebbles, the most common type is a fine-grained foraminiferal limestone which may be moderately to highly phosphatised and may or may not have phosphatised margins. Numbers of these pebbles are characterised by abundant pyritic foram infillings. Some of them may also contain sparse accessory silt sized detrital unzoned collophane grains, indicating a complex history of phosphorite formation.

Another less common variety of pebbles consists entirely of massive cryptocrystalline to optically amorphous collophane studded with well developed rhombohedra of dolomite or calcite and probably representing an extreme stage in the phosphatisation (say) of originally aphanitic limestones. Pebbles of silty limestone are rare, although common to the glauconitic province; usually they are unphosphatised except along pebble boundaries.

As in the glauconitic conglomerates some of the pebbles are burrowed: burrows are usually filled with phosphorite which is sometimes layered and does not always contain pellets although pelletal varieties are most common. Burrow walls are usually highly phosphatised and pyritic, whereas the bored rock may be phosphate-free as may be the burrow fill (e.g. sample 1016 where a burrow is filled by aphanitic limestone, (Fig. 6 *g*).

6.3 Non-Conglomeratic, Non-Glauconitic and Non-Pelletal Phosphorites And Phosphatic Limestones

These samples fall essentially into two main categories; first, phosphatic limestones containing grains of massive, usually unzoned, detrital collophane as an accessory mineral (less than 5%) in pebbly, sandy, or silty limestones (875, 903, 923, 924, 931, 933, 950, 954, 982, 1022, 1038); second, massive limestones showing varying degrees of matrix phosphatisation (819, 855, 148, 156, 157, 136). Lastly there are those few samples containing accessory silt to fine sand sized detrital unzoned collophane in a

partially phosphatised matrix (820, 135, 1016). Several of these samples have been bored and had their borings filled with later glauconitic phosphorite (903) or pelletal phosphorite (982, 136, 1016) indicating at least three periods of phosphate mineralisation. It should be emphasised that massive and non-conglomeratic phosphorite from sites 817, 818, 832, 151, 155, 915, 973, 1035 and 1037 were not petrographically examined, and that further petrographic examination of the many calcareous and apparently non-phosphatic rock samples might reveal more examples of limestones containing detrital collophane contributions.

The phosphatisation, where moderate (136, 819, 148, 820, 1016) tends to be uniformly distributed throughout each examined specimen, and not concentrated about specific nucleation centres except in very rare instances. For example in sample 148 [illegible] irregular collophane rims around silt sized quartz grains grade imperceptibly into and are interfingered with the surrounding matrix, sometimes even to the extent of joining adjacent grains. In other samples there appears to be a gradual increase in the degree of phosphatisation of the matrix until a stage is reached in which the matrix appears entirely composed of massive collophane through which are randomly scattered minute segregations of impurities such as iron, clay or organic matter, together with minute calcite rhombohedra (and ? dolomite) which apparently originated during the phosphatisation process.

Samples 156 and 157 (Fig, 6 h) comprise bedded phosphatised ferruginous limestone in which are layers of moderately well phosphatised limestone containing abundant microcrystalline calcite or calcite rhombohedra, and round 'blobs' representing unreplaced calcite foraminiferal infillings. Faunal remains are generally not too common however. Towards the surface of each layer phosphatisation increases but the gradual nature of the change and the preservation throughout of relict foraminifera suggests

there was no original difference between the upper and lower parts of any one such layer. The bed surface is usually more densely impregnated with iron oxide than the remainder of the sample suggesting contemporaneity of phosphatisation and oxidation as is the case in the pelletal phosphorites and glauconitic phosphatic limestones discussed above. Pebbles of this same material occur in nearby conglomerates showing that phosphatisation and iron staining are not by any means Recent phenomena. Sample 157 is much less well phosphatised than 156; it is the presence of moderately abundant large rhombohedra within the dominantly microcrystalline calcite matrix of sample 157 that suggests they are dolomitic samples (this is borne out by chemical analyses - Chapter 7).

A few samples are very irregularly phosphatised and phosphatisation appears to be concentrated in patches within their matrix (855, 135). In these instances phosphate mineralisation is more likely to be less immediately post depositional than in other samples. Evidence from the thinly bedded samples 157 and 157 strongly implies that phosphatisation immediately followed deposition and confirmation of this is given by the occurrence of lithologicallysimilar pebbles in adjacent conglomerate samples in which the degree of pebble phosphatisation shows no relation to the matrix.

6.4 Dating

Several soft mudstone samples and a random selection of indurated limestones were selected for dating purposes. Unfortunately many of these proved to contain very poor faunas and dating was only possible on a few samples. All the phosphatic samples containing moderately abundant faunas were examined. Because of the difficulty in making accurate thin section identifications many samples proved literally undateable but sufficient information became available (Appendix 4) to allow some of the stratigraphic

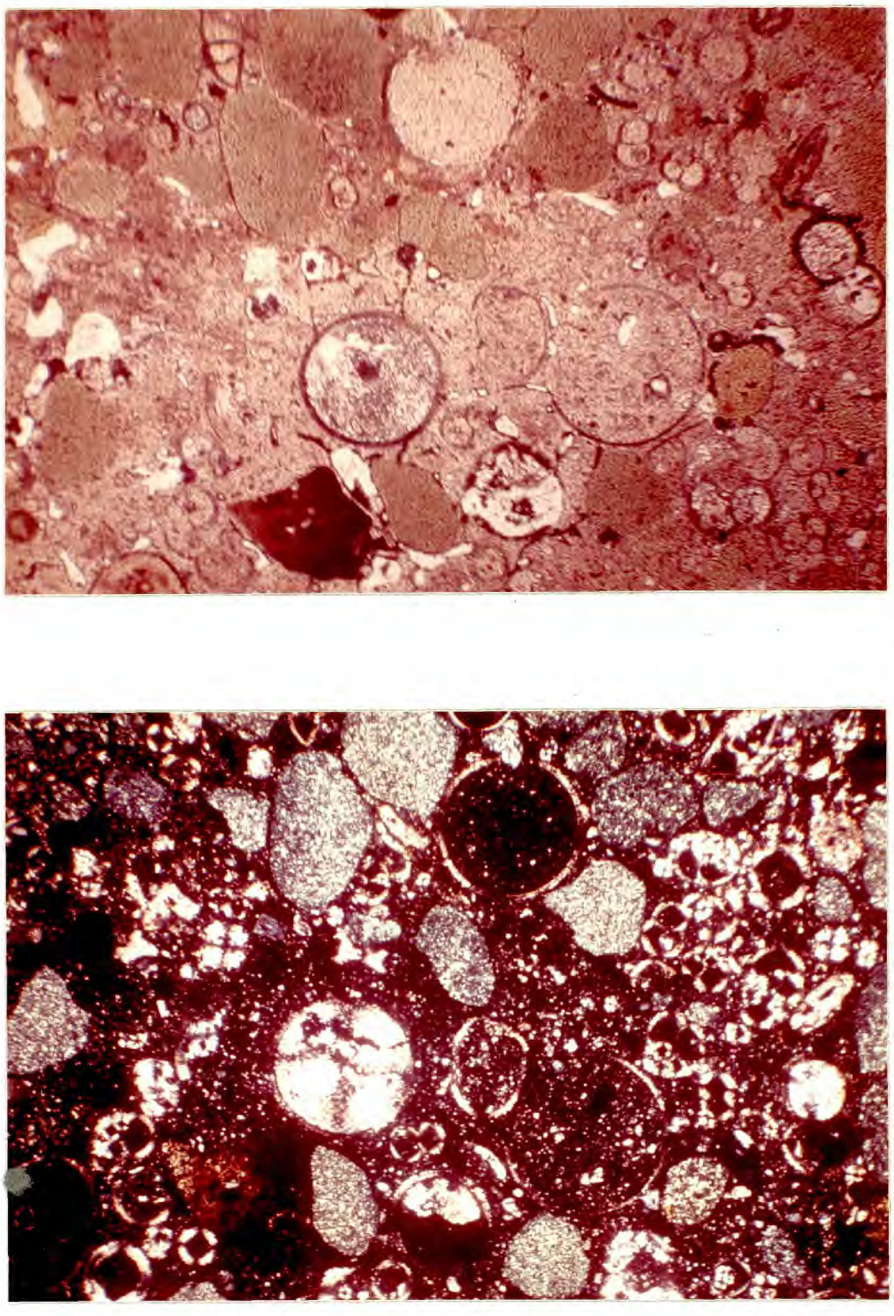
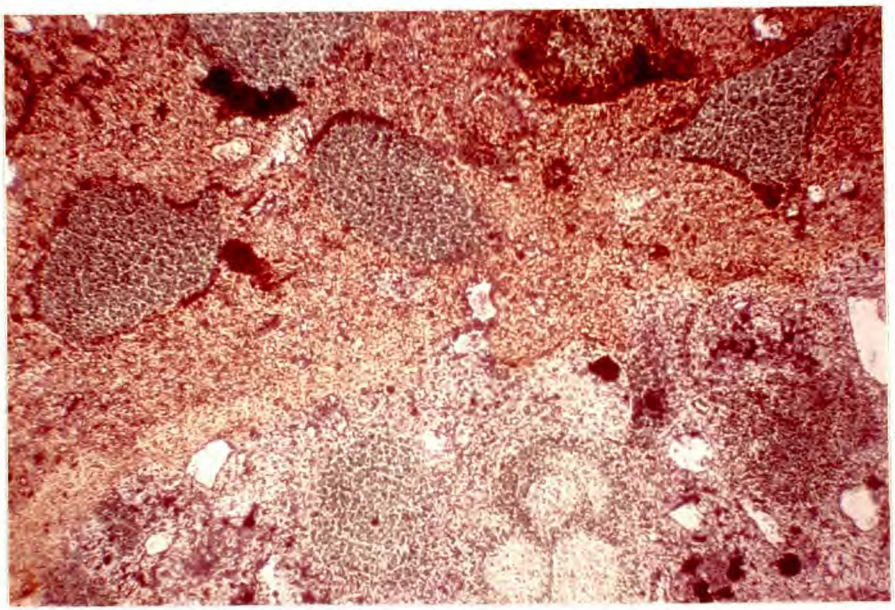


Fig.6.a. Photomicrograph of matrix of glauconitic phosphatic conglomerate 883 (upper diagram = plane polarised light; lower = crossed nicols). Glauconite grains (one oxidised - left,bottom) and unreplaced foraminifera with calcite or collophane fill, are clearly recognisable. Matrix comprises collophane and micritic calcite and rare, silt-sized quartz.



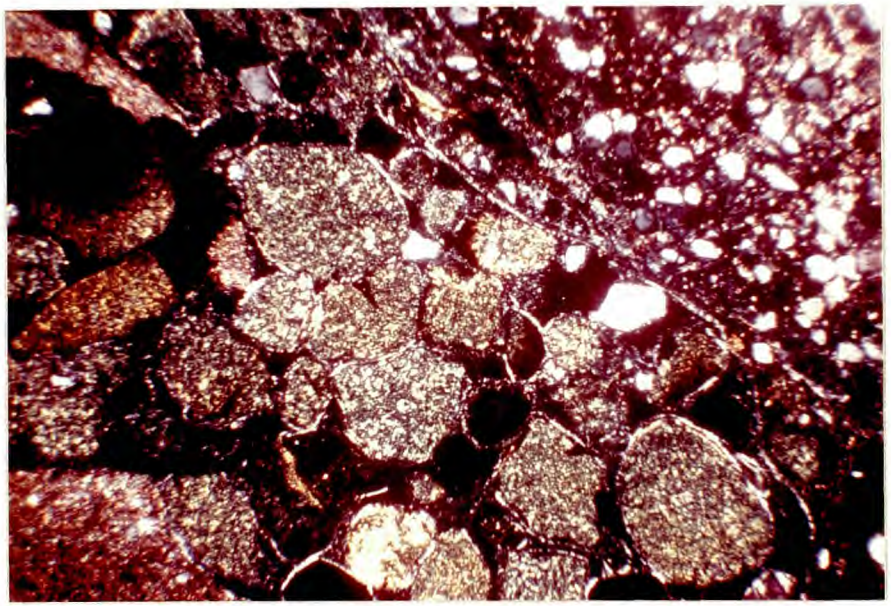


Fig.6.b. Photomicrograph of glauconitic phosphatic conglomerate 154 (plane polarised light) :Left diagram. Showing contact between unphosphatised silty foraminiferal limestone pebble and muddy sand - textured glauc -onitic phosphatic matrix. Glauconite grains have oxidised margins and are suspended in a finely divided mixture of collophane, calcite, iron oxide, (?) clay and (?) organic matter; these last three impart the dirty, red-brown colour. Within the pebble margin are glauconitised foraminiferal remains.
Fig.6.c.(Right diagram). Photomicrograph of glauconitic phosphatic conglomerate 152 (crossed nicols). Showing contact between glauconitic phosphatic sand matrix and (bottom left) unphosphatised aphanitic lime- stone pebble and (top right) phosphatised silty limestone pebble in which the degree of phosphatisation increases towards the margin. Post-depositional francolite rims have formed around glauconite grains, some of which are partially oxidised.

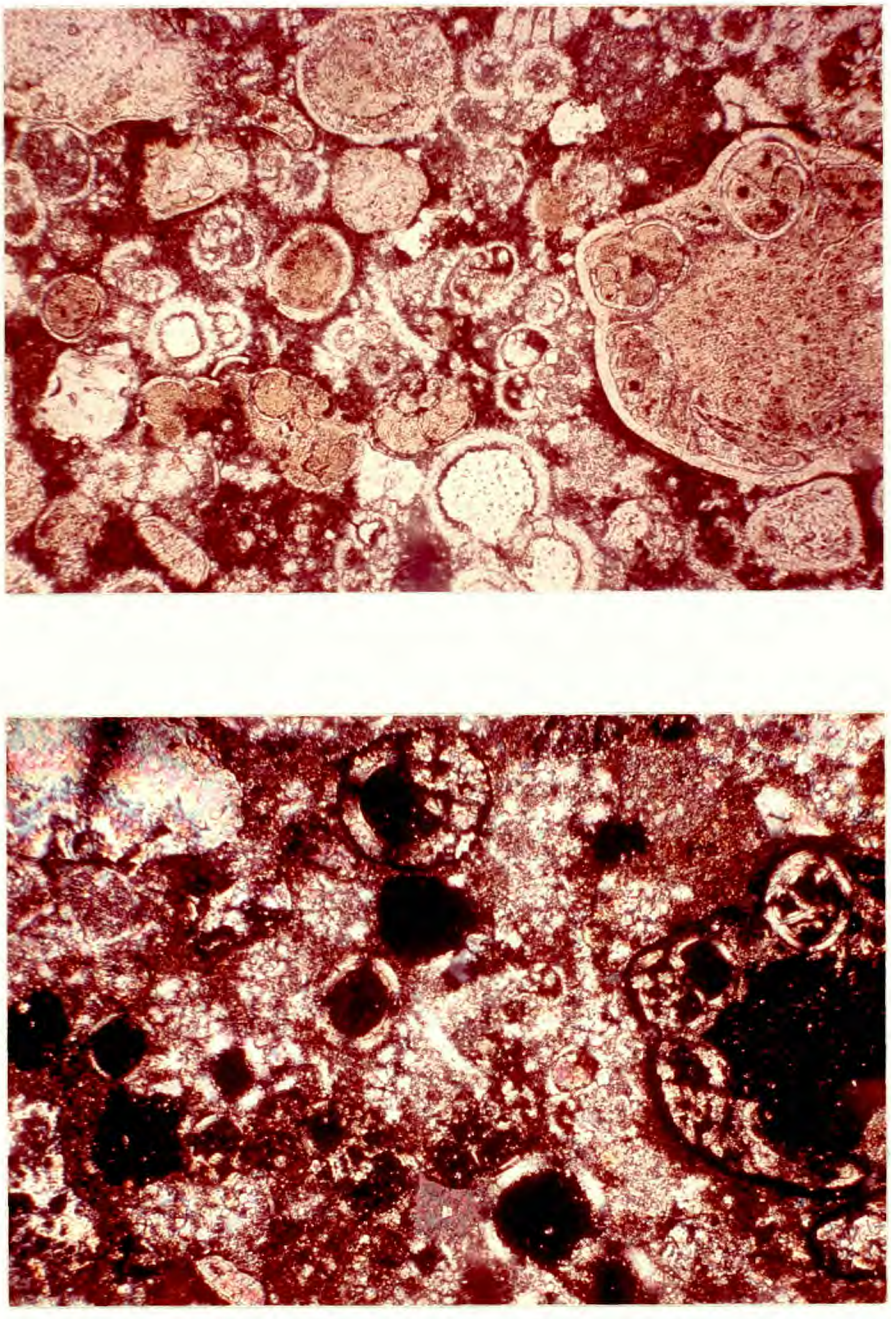


Fig.6.d. Photomicrograph of matrix of pelletal foraminiferal phosphatic limestone 134 (upper photo = plane polarised light; lower = crossed nicols). Pellets are either fragments of phosphatised muddy foraminiferal limestone, or are entire or broken foraminifera , and often have a clear collophane skin . Foraminifera outside the pellets have a calcite- fill and are set in an iron oxide-rich micritic calcite matrix.

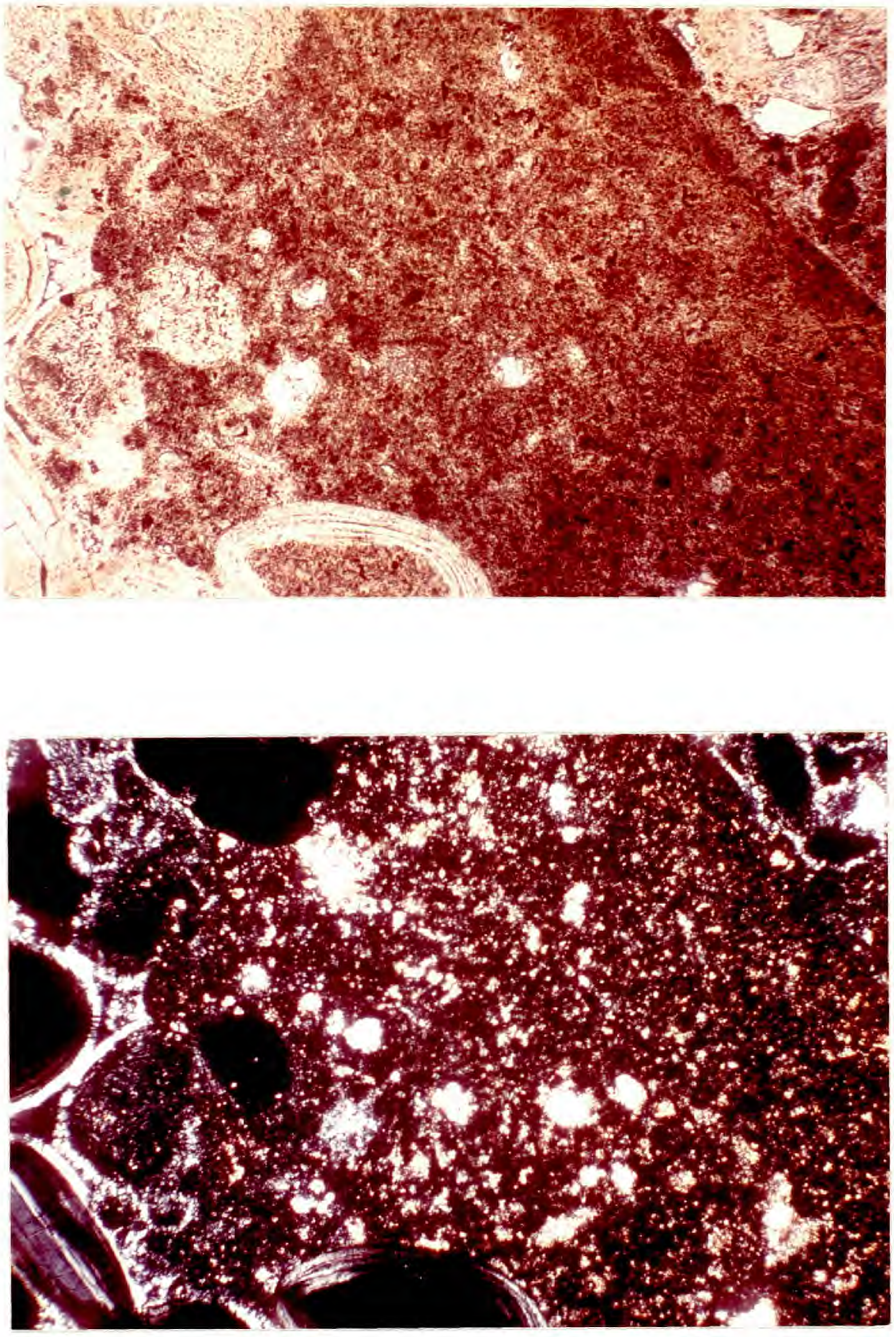


Fig.6.e. Photomicrograph of pelletal phosphatised limestone 961 (upper photo = plane polarised light; lower = crossed nicols). A muddy phosphatic pelletal sand (bottom left) is succeeded by a phosphatised lime mud which, at an erosional horizon, is intensely iron-oxide stained; this is followed (top right) by a second phosphatic pelletal sand.
Note:- oolitic pellet margins, turbid collophane-rich nucleii, later francolite development in sandy areas, incipient network structures in muddy areas, lack of replacement of larger calcite fragments, high degree of matrix turbidity.

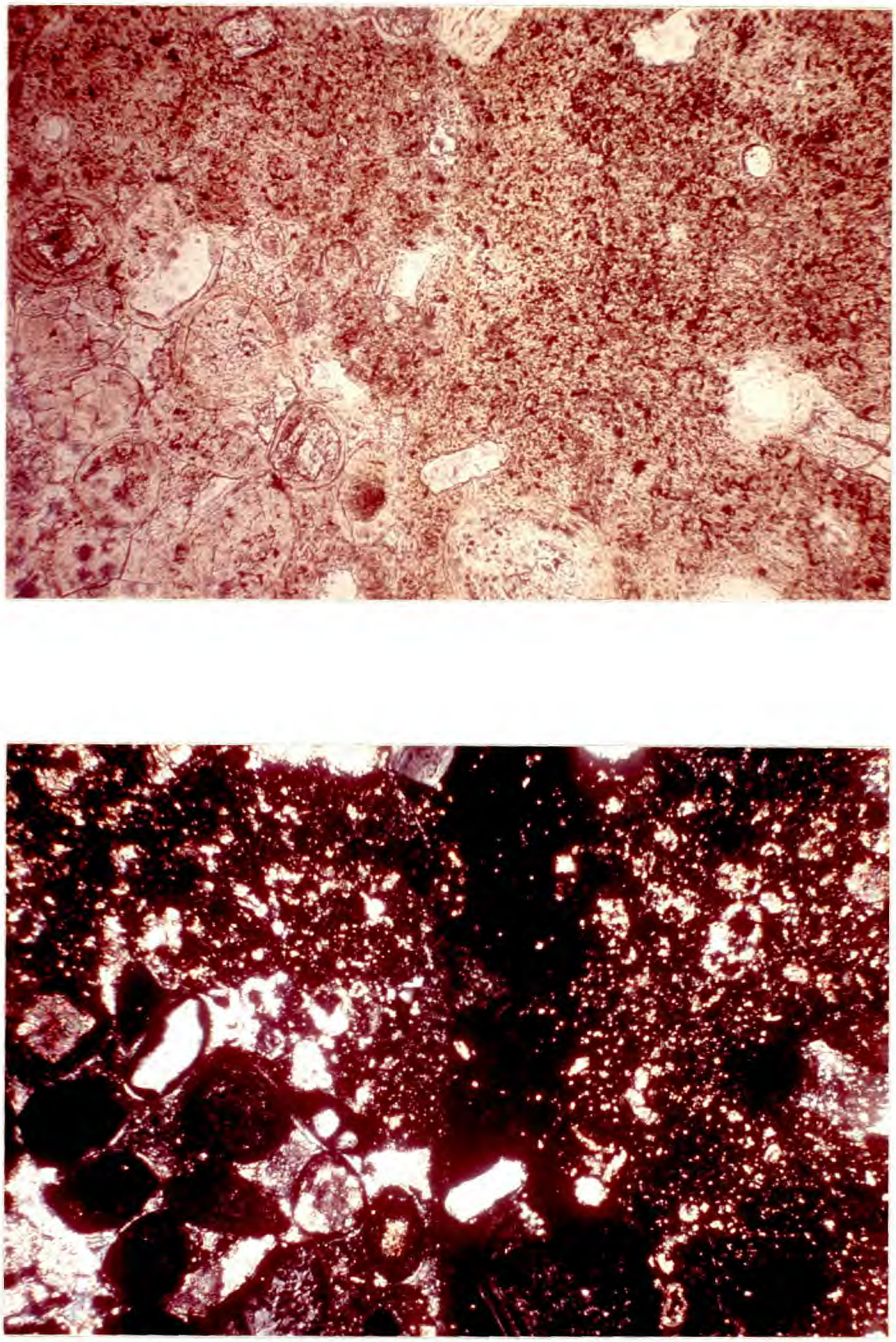


Fig.6.f. Photomicrograph of pelletal phosphatised limestone sample 982 (upper photo = plane polarised light; lower = crossed nicols). Left side = top of section. A poorly sorted, turbid, partly phosphatised, sandy lime-mud (right) containing sparse quartz, collophane pseudoolites, calcite grains and forams is cut by a highly phosphatised, slightly iron-stained erosion surface (centre). This is overlain by a poorly sorted muddy sand containing phosphorite pellets and pseudoolites with quartz, calcite or collophane nucleii. The mud matrix to these grains is not highly phosphatised. Note:- francolite rims, radial (?)shrinkage cracks, and local later calcite cement.

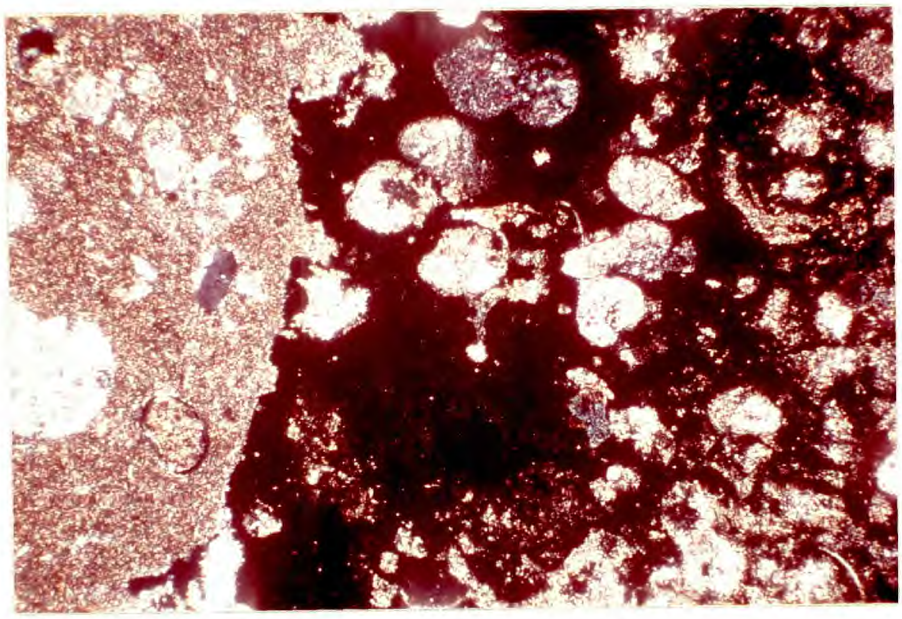


Fig.6g. Photomicrograph of partially phosphatised foraminiferal limestone 1016 (crossed nicols). Shows, left, burrow filled with unphosphatised foraminiferal limestone (containing on phoephorite pellet); shows, right, increasing intensification of phosphatisation of the burrowed limestone as the burrow wall is approached. Note:- most forams and calcite fillings remain unreplaced except locally (viz. top centre) after matrix is phosphatised.

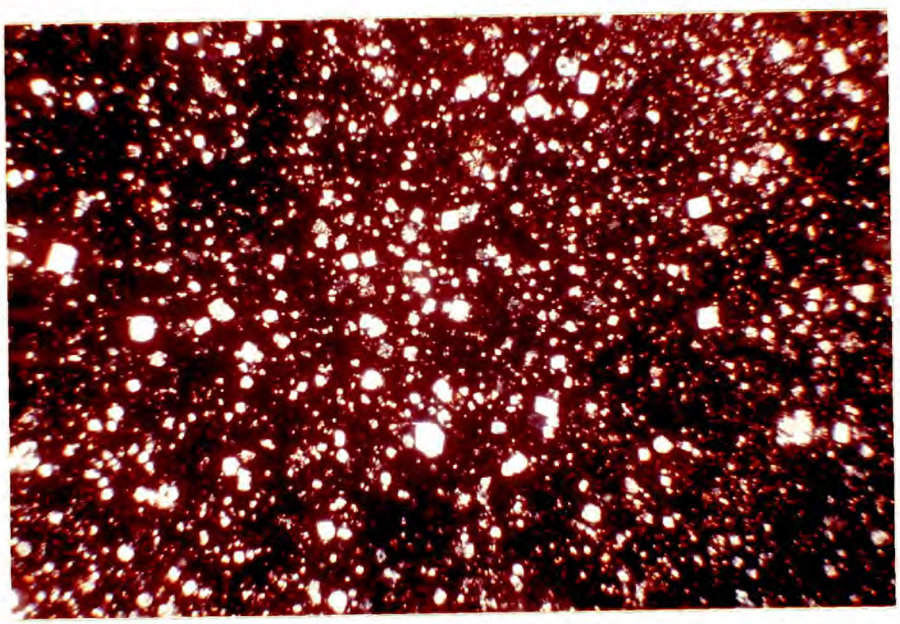


Fig.6.h. Photomicrograph of phosphatised limestone 157 (crossed nicols) showing abundant (?)dolomite rhombohedra set in a collophane-rich and iron rich lime-mud matrix.

complexity and history of phosphate mineralisation of the Moroccan continental margin to be unravelled. Mr. D. Carter very kindly set aside time for the palaeontological work involved.

From selected glauconitic phosphorites the writer was able to separate glauconites for K.Ar dating, kindly carried out by Dr. M. Dodson and Mr. D. Rex at Leeds (cf. Appendix 4).

6.4.1 Cretaceous Material

Soft upper Cretaceous mudstones showing no signs of phosphatisation and apparently not containing any detrital collophane are reported from sites 333, 860 and 862. Indurated, unphosphatised upper Cretaceous foraminiferal limestones were found at Sta. 964. At the same site and at Sta. 982, 1022 and 1038 were dredged pelletal conglomeratic phosphorites containing pebbles of upper Cretaceous foraminiferal limestone, moderately phosphatised throughout and with narrow highly phosphatised margins.

6.4.2 Tertiary Samples

The remainder of the dateable samples proved to contain Tertiary faunas. From the southern region, pebbles of probably Eocene (pre-Burdigalian) foraminiferal limestone were identified in conglomerate samples from sites 152 and 154. In each case the pebbles are moderately and uniformly phosphatised and apparently were so prior to incorporation into the conglomerate. The Eocene pebble from site 154 contains accessory silt sized detrital collophane. A similar age is obtained for the massive phosphatic foraminiferal limestone from site 148 and from the non-conglomeratic bedded phosphorite at site 156.

The glauconitic matrix of the southern samples locally contains abundant foraminifera closely resembling Orbuline universa d'Orbigny suggesting their formation after the 'Orbulina Datum' low in the Miocene (post-Burdigalian).

Radiometric age determinations using the K.Ar technique on separated glauconites, gave ages for sample 848 of 10.8 ± 0.5 m.y. and for two separate subsamples from 877, of 11.7 ± 0.5 m.y. and 11.0 ± 0.5 m.y. respectively, placing these samples in the upper Miocene.

Within northern province samples the massive patchily phosphatised foraminiferal limestone from site 958, containing both grains and oolites of collophane, has a probably Eocene (pre-Burdigalian) fauna. The same fauna is recognised in the massive moderately phosphatic limestones from sites 135, 136, 988 and 1016, all of which except 136 contain some accessory detrital collophane although they are not pelletal, and in pebbles of similar moderately phosphatic material incorporated into a pelletal conglomerate sample 139. Borings in samples 988, 135 and 1016 have been filled with pelletal phosphorite. Examination of many other pelletal samples gave no information to suggest that they were later Tertiary in age. However, the two pelletal foraminiferal sand samples 134 and 966, which are very different from all other pelletal samples in having mainly pellets formed around foraminiferal nucleii contain, both within the pellets and in the surrounding non-phosphatic foraminiferal sand, abundant Orbulina Universa D'ORB., and are therefore post lowermost Miocene (post Burdigalian).

6.5 Interpretation

6.5.1 Depositional Environments

Foraminiferal Limestones (Cretaceous-Eocene)

The homogeneous character of the fine grained Cretaceous and Eocene foraminiferal limestones, which are essentially bioaccumulates containing moderately sparse argillaceous and silt sized material, suggests an original stable depositional environment of moderate depth remote from sources of detrital clastics. The preponderance of silt-sized quartz among detritals

tends to imply deposition off a peneplained arid (?) coast where extremes of weathering resulted in production of mature quartzose silts. The origin of the lime mud comprising the fine grained matrix is obscure but could relate to benthonic faunal activity.

The presence of dolomite in certain phosphorites is thought by Rooney and Kerr (1967) and Strakhov (in Bushinsky, 1969, p. 158) to indicate formation in confined shallow basins or lagoons. The fine bedding of the dolomitic phosphatic limestones 156 and 157 would seem to indicate a moderately shallow water environment periodically agitated by currents but whether this was lagoonal or not remains to be seen.

In the phosphatised foraminiferal limestones and in other phosphatic facies, pyritic foraminiferal infillings are locally abundant attesting to the formation of reducing conditions in microenvironments but not on any large scale; allied with this, the absence of dark organic rich limestones or black shales in dredge hauls suggests that this was not a region of extreme biological productivity. The impregnation of many samples with iron oxide, particularly at bedding horizons, suggests that oxidising conditions were widespread during the time that these phosphatic limestones formed.

Pelletal Conglomerates (Probably Eocene)

On the basis that one of the pelletal phosphorites contains an Eocene matrix fauna it is suggested that the majority are of the same age; they certainly differ markedly from the two post Eocene pelletal foraminiferal sand samples 134 and 966. That they contain pebbles of Eocene foraminiferal limestones suggests a shallowing of the environment during the later Eocene. The prevalence of lime-mud within the matrix might suggest deposition at moderate water depths where wave and current agitation and turbulence was low. Equally, since most biogenic skeletal remains are broken, and coprolites are moderately common, the mud could be a biodiagenetic product

caused by benthic faunal activity. The admixture of pellets and pebbles of pelletal phosphorite and the frequent irregular bedding and local erosion surfaces tend to suggest that the deposit is of very shallow water origin and that the mud may be a biodiagenetic product. The above mentioned characteristics suggest that these deposits accumulated in coastal type flats or shallow lagoons in close proximity to a beach or bar whence coarser material could be derived.

The uniformity of size of the pellets, the degree of rounding of some of them and the frequent high degree of sorting of sand layers (Fig. 6e,f) suggest mechanical derivation from some source more or less within the high energy surf zone. Absence of inorganic detrital constituents of the same size (usually associated quartz is silt-sized) tends to suggest formation on an offshore bar rather than a beach where longshore transport of mature quartz sand might be expected to result in admixture of apatite pellets with similarly sized detritals as in fact is found in the onshore Eocene deposits (Salvan, 1952, Visse, 1948). Further evidence for relative remoteness from land is given by the abundance of argillaceous material and the only local silt sized quartz. The formation of apatite pellets is considered in detail later in text; suffice it to state here that it appears the pellets originate by phosphatisation, disaggregation and mechanical reworking of the phosphatic lime mud within which the pellets are now found. The narrow bedding and irregularity of erosional horizons suggests that storm waves may, by periodic disaggregation of the lime muds, have resulted in mechanical formation of phosphate pellets which, after concentration and mechanical sorting in offshore bars were irregularly swept seaward or shoreward by current activity and there incorporated into muddy sediments accumulating in quiet water. The abundance of iron oxide, particularly at erosional horizons tends to suggest formation in a prevailing oxidising environment.

Post-Eocene Pelletal and Glauconitic Phosphatic Sediments

Post-Eocene sediments are apparently widespread on the outer shelf and uppermost slope off Cap Sim but very restricted off Cap Blanc. At this northern site two samples (134 and 966) of pelletal foraminiferal sands seem to have been deposited in a current swept region moderately far from land since they do not contain any quartz or clay, nor are the foraminifera abraded as might be expected if deposited in a shallow water high energy region. The pellets (Fig. 6 d) are of phosphate-covered foraminifera sometimes attached to an original phosphatic lime mud matrix. Their perfect preservation and absence of any widespread signs of abrasion before or after phosphate coatings formed suggests that they were derived by the erosion of a soft sediment. The preservation of a foraminiferal sand such as this suggests winnowing, or the prevention of settling, of fines, probably by turbulence at or near an original shelf edge. It is argued that winnowing of nearby soft phosphatised foraminiferal ooze provided the coated specimens. Their contemporaneity with uncoated specimens is borne out by the presence of coated and uncoated specimens of Orbulina.

To explain the formation of the apparently Miocene glauconitic phosphatic conglomerate it is necessary to advocate a large scale change in the tectonic and depositional framework off Cap Sim following deposition of the Eocene foraminiferal limestones. It must be emphasised that while such a change may also have occurred off Cap Blanc there is at present no evidence to support this; the conglomerates there, being intraformational, are of a completely different type to that found off Cap Sim. Also stressed is the fact that the northern conglomerates only contain small pebbles, commonly with irregular margins, while the southern conglomerate resembles a breccia and contains a tremendous assortment of angular and subangular boulders cobbles and pebbles. It would appear that the combination of uplift and erosion directly offshore from the Atlas mountain belt in south

central Morocco gave rise in effect to a basal conglomerate or breccia in which phosphatic and non-phosphatic fragmented limestones form the chief constituents: the breccia is considered to lie more or less on an Oligocene erosion surface (cf. Chapter 5).

The pebbles were in many instances exposed, prior to contact with their present matrix, to a marine environment in which glauconitisation, phosphatisation and in some cases oxidation of their margins occurred. In some cases there is evidence that the pebbles were moved after this and prior to incorporation into the present matrix. The depositional history of this conglomerate is complex, as shown by the incorporation locally of pebbles of glauconitic lime mud, compositionally similar to the matrix and showing signs of having been rolled while soft, allowing the surface accretion of discrete grains of glauconite. The matrix composition is irregular, and silty, sandy and muddy patches are often visible within the same thin section; sometimes these differing types are clearly separated by an oxidised erosional horizon at which phosphatisation is more intense. This suggests the irregular operation of different current strengths, possibly under the influence of storms. These characteristics argue for deposition well out of reach of shallow water turbulence, probably on an open shelf under similar conditions to those where the rocks are presently found. The rarity with which composite pebbles are found tends to argue against any significant reworking after original formation of the breccia.

The lime mud is siltier nearer to land and becomes more foraminiferal offshore, suggesting that there has been no great palaeogeographic change as the same change applies to the Recent sediment cover. From its general appearance the lime mud would seem to represent a bioaccumulate which local benthic faunal activity has rendered very fine grained. As in the case of the northern province, the coarser components, in this case glauconite and

silt sized quartz, represent incursions resulting from intermittent current activity. The seaward gradation from silty to foraminiferal characteristics, and the fact that glauconite is only known to form on open shelves (Galliher 1935) suggests that these deposits did not form (as the northern deposits appear to have done) in a shallow coastal type environment. The characteristics of the glauconite suggest that it formed in some environment not exposed to seawater, probably within some muddy sediment, from which it was moved by current activity which, in that it allowed contact with seawater, favoured surface oxidation of large numbers of the grains. The glauconite, together with silt-sized quartz and lime mud was then deposited, or trapped, within the interstices of the breccia. The formation of glauconite during the Miocene requires that during much of this period this part of the continental margin was moderately stable, shallow, and far from land off a coast where supplies of terrigenous detritus were negligible. The origin of this sediment is further considered in the following discussion of phosphate mineralisation.

6.5.2 Phosphate Mineralisation

Within those specimens which contain collophane in the matrix, various phenomena tend to suggest that post-depositional phosphatisation has occurred. The presence of abundant calcite relics in the form of foraminiferal tests, and the presence of calcite rhombs indicating precipitation from a supersaturated solution within the phosphatised matrix, and the somewhat irregular margins of both calcite fragments and matrix impregnation by phosphate all argue against direct precipitation of phosphate from seawater. The most convincing evidence that phosphatisation took place more or less immediately after deposition is given by concentration of phosphate mineralisation immediately below bedding or erosional surfaces, where it is often associated with oxidation phenomena. It must be concluded that phosphatisation was more or less contemporaneous with sedimentation and that the

degree of exposure to seawater was critical in determining the degree to which phosphatisation occurred. This applies, it must be emphasised, to th_ Eocene foraminiferal limestones, the Eocene pelletal sediments and the Miocene glauconitic sediments. Rather than being an exclusively intra-sediment diagenetic process it appears that some diffusion mechanism must have operated such that contact with seawater enhanced the degree to which phosphate mineralisation occurred.

When individual pebbles are concerned, the apparent dissimilarity between their degree of phosphatisation and that of the matrix and even of their own margins suggests that they were phosphatised prior to incorporation into the conglomerate matrix. However, those that have intensely phosphatic margins (which in some cases are also glauconitised or oxidised) were evidently in contact with some phosphatising milieu for some considerable time. Since the pebbles are very rarely composite as would be expected had their phosphatisation come about via the interstitial solutions of some previous matrix as a result of diagenesis, it is concluded that seawater was the phosphatising milieu. It may be significant in this context to record that accretionary apatite pebble margins are extremely rare and can often be attributed to mineralisation within the present confining matrix. The seawater hypothesis tends to be particularly well borne out by the characteristics of burrow walls which are usually intensely phosphatised whether or not the interior of the pebble or the burrow fill exhibit any signs of phosphatisation (cf. Figs. 6 g). This type of phosphatisation is often accompanied by glauconitisation and even pyritisation, neither of which phenomena affect the burrow fill.

Further points arising from the study of phosphatised limestone pebbles are that

(a) their degree of phosphatisation is uniform except at pebble margins;

(b) they closely resemble massive non-conglomeratic varieties from the same or adjacent sites;

(c) they occur in association with unphosphatised limestones which can occur either as discrete boulders or, within the conglomerate, as pebbles with or without phosphatised margins;

(d) usually the phosphatic lithologies differ petrographically from the non-phosphatic varieties except in their degree of rounding and abrasion.

These data tend to stongly suggest that the degree of pebble phosphatisation, except at pebble margins, is not related to post erosional exposure on the seafloor but is an original characteristic. On the basis of these considerations the case is put forward for the formation on the continental margin during upper Cretaceous and Eocene times of moderately phosphatic foraminiferal limestones and phosphorites.

Abundant evidence has been presented to show that whether oolitic or structureless and whether completely or incompletely phosphatised, many of the phosphate pellets appear to have originated by the phosphatisation of original lime mud. Further evidence shows that although nucleation is not noticed in the present deposits, the erosion of the more phosphatised parts of the associated lime mud matrix could well have given rise to such granular phosphate fragments and thus the pellets could be local in origin. That they cannot have been transported over any great distance is attested by their relative angularity. Nucleation appears to have been a rare phenomenon in that only a few pellets contain quartz, calcite or foraminifera as specific nucleii. Fragments of teeth and bone are recognised but are not abundant. It is emphasised that the admixture of abundant irregular and often rather angular grains argues against the origin of pellets by alteration of coprolites, a mechanism proposed for many other pelletal

deposits by workers such as Bushinsky (1969) Cayeux (1941) and many others. In fact, where coprolites are observed in these sediments there is no difference in degree of phosphatisation between the coprolites and their surrounding matrix.

Some evidence pointing towards a possible mechanism of in situ nucleation is given by the post-depositional growth of francolite rims preferentially around grains in sandier parts of the sediment. Then again, the development of network structures within the surrounding groundmass reflects diagenetic segregation of clusters of impurities about specific centres; the subsequent mechanical disaggregation of the sediment might well result in fragmentation along the veinlets of the 'net', these being lines of potential structural weakness, eventually leading to formation of irregular pellets of collophane stuffed with impurities and with a clear collophane margin. Moreover, the coalescence of clear zones of network collophane around larger fragments such as foraminifera may represent a nucleation phenomenon explaining the generation of collophane ovules as primary constituents. A particularly interesting sample in this respect is 134 (Fig. 6 d), where stage 1 is represented by the coalescence of network structure about foraminifera resulting in formation of a thin, irregular collophane rim. In most cases the surrounding matrix has subsequently been removed but the forams have remained coated with a thin collophane pellicle which in many instances has grown by further accumulation possibly direct from seawater since there is no evidence for the incorporation of the pellets into a mud from within which further apatite growth could occur prior to the eventual deposition of pellets in their present non-phosphatic environment. Bushinsky (1969) has argued that the accretion of collophane on pellets by deposition from seawater is unlikely in view of the agitated environments in which the pellets seem to have originated. But in this particular case no other mechanism seems so readily to explain the facts.

The same mechanism may account for some of the oolites although the possibility that the pseudooolitic concentricity arose by marginal alteratic and segregation processes is considered a more likely origin. This mechanism definitely seems to account for the development of clear rims in angular to subangular grains (as it does for pebbles). In that these zones occur regardless of matrix phosphatisation, which can be non existant, this phenomenon may have resulted from contact with seawater prior to fixation in the present cement. In the majority of instances the matrix is poorly phosphatised except at the aforementioned erosional or bedding surfaces.

The basic characteristics of these pelletal phosphorites conform well with those of bedded pelletal phosphorites around the world (cf. Bushinsky, 1969, Rooney and Kerr, 1967, Cayeux, 1941). Slow or negligible sedimentation is attested by the relative lack of detrital sediments and the frequent erosional horizons; widespread reworking is signified by the development of composite and broken grains and of soft margined pebbles and several growth stages within individual oolites; diagenetic phosphate redistribution is indicated by network structures and nucleation phenomena, particularly of fibro-radial francolite. The phosphatic foraminiferal limestones, ferruginous limestones, and glauconitic conglomerates, are in many respects very similar to Agulhas Bank phosphorites as described by Parker (1970). Here again, Cayeux (1934) pointed out that the incorporation of pelagic foraminiferal limestones within a glauconitic conglomerate on Agulhas Bank reflected uplift and erosion, that the matrix of the conglomerate is a substitution product and not a primary precipitate, and that the nodules were not dependant on present day phenomena (Cayeux, 1934, p. 131).

6.5.3 Comparison with Onshore Moroccan Phosphorites

The onshore Moroccan phosphorites which are Maestrichtian-Eocene in age and have maximal development of about 100m, comprise, according to Salvan (1952,

1956) and Visse (1948, 1953), mainly well-sorted sands of phosphorite pseudo-ooliths and similarly sized quartz with a carbonate matrix low in argillaceous material and very rarely phosphatic. The uncoated 'exo-quartz' is reported to be the same size as associated phosphorite grains and is moderately abundant, its abundance increasing in the vicinity of crystalline massifs. Essentially the matrix has the qualities of a lime-mud and there is never any phosphate cememt. The pellets of the onshore deposit comprise mainly collophane with common calcite and quartz nucleii, the calcite being present either in finely divided form or as discrete rhombohedra, much as is found among the offshore deposits. Glauconite, similarly to the Cap Blanc group, is never present. Principal included faunal phases include foraminifera, radiolaria and diatoms. The same fauna exists in the matrix although in addition there are in the matrix abundant vertebrate remains. Visse and Salvan and Cayeux (1941) agree that the phosphate grains must have originated biochemically in a 'pelagic' region where biological productivity was very high, and that they were subsequently transported to a very shallow depositional area (the zone of accumulation) where they and associated sand sized quartz were well mixed and sorted and deposited together with some form of slightly argillaceous but non-phosphatic lime mud. They agree that the pseudoooolite shapes were not chemically, but mechanically induced in the main.

The discovery, immediately off the coast, of the Eocene phosphatised lime muds and associated mainly mechanically formed pellets suggests that here may be the origin of the pellets of the onshore deposits. Continual interaction of phosphate-rich seawater with shallow water lime muds, and irregular disaggregation of the phosphatised product by storm waves or tidal currents, followed by mechanical concentration and sorting of pellets on bars and shoreward migration caused in particular by tidal currents may well have given rise over a long period of time to some of the pelletal phosphorites

of Morocco. These muddy pelletal offshore phosphorites represent a shallow water facies; the deeper water facies may be represented by the phosphatic foraminiferal limestones. That there have not been any pelletal phosphorites found off Cap Sim, but only foraminiferal phosphorites or phosphatic limestones may reflect the enhanced erosion caused in this southern region by proximity to the Atlas uplift. The significance of the present findings with regard to palaeo-oceanography and the origin of phosphorites in general is discussed in Chapter 8.

CHAPTER 7

GEOCHEMISTRY OF PHOSPHATE-ROCKS

7.1 Introduction

Relatively few detailed studies have been made of the geochemistry of marine phosphorites or carbonate-apatites. Krauskopf (1955) and Gulbrandsen (1966), among others, have pointed out the marked enrichments in phosphorites of a number of otherwise trace elements. Average values calculated by the writer from data given by Swaine (1962) for land phosphorites of marine origin, and the averages for the Phosphoria Formation (Gulbrandsen, 1966) are given in table 7.1.1. Exceptionally high values quoted by Swaine for certain elements were discounted in the calculations; usually they had been determined by semi-quantitative methods of low accuracy. Comparison of all these averages and ranges with crustal abundances are made in Fig. 7.1.1. Where only the ranges of elemental abundances were given by Swaine, the median value of each range is arbitrarily used to give an indication of the abundance level. Following Nicholls (1967), element abundance ratios between 2:1 and 1:2 (Fig. 7.1.1) are not considered to reflect significant enrichment or depletion. In comparison with crustal abundances, average trace element values in phosphorites from all over the world (data from Swaine) show enrichment in As, I, Mo, Se, U, Cr, Sr, Sn, Pb, Cd and depletion in Cu, Ni, Li, Co, Ti, Mn: the elements V, Zn, Rb, B, Be are not significantly enriched or depleted. There is good agreement between these data and those from the Phosphoria Formation and Gulbrandsen's data (1966) also show these last phosphorites to be enriched in Ag and Sb and depleted in Sc, Ba and Zr relative to crustal abundances (Fig. 7.1.1). Further data on rare earth concentrations (table 7.1.1) show that La and Ce in certain submarine phosphorites are neither enriched or depleted relative to crustal

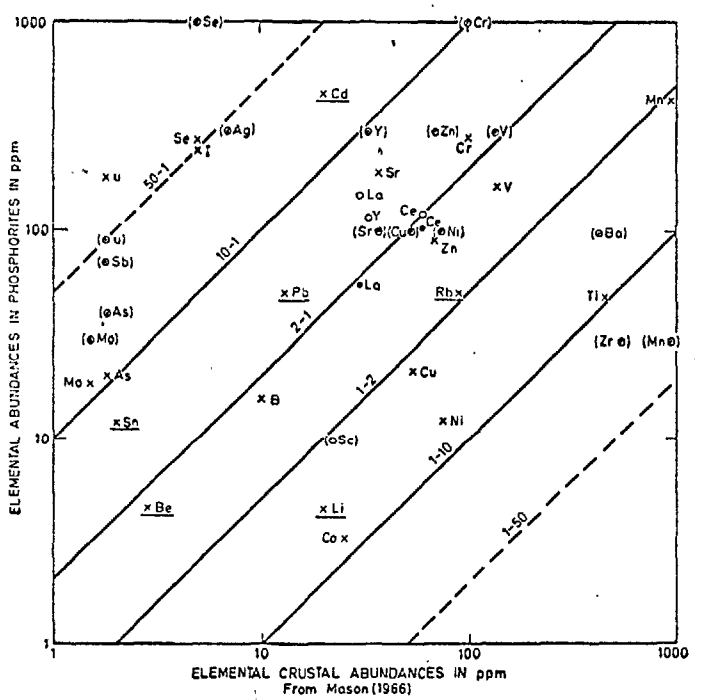


Fig.7.1.1.

Elemental abundances in phosphorites compared with crustal abundances; based on data given in table 7.1.1.: x = average abundance data derived from Swaine (1962); x̲ = median value of element abundance ranges (based on Swaine,1962); ⊙ = averages from Phosphoria Formation (Gulbrandsen,1966); ● = submarine phosphorite (data from Goldberg et al, 1963); O = carbonate-apatite (data from Altschuler et al,1967). All values for Ag,Se are x100; for Cd,I,Sb are x10; for Sr,Ti are ÷ 10.

abundances although La and Y are enriched in the Phosphoria Formation and in carbonate-apatites separated from phosphorites while Ce is not significantly enriched in the latter. In general it seems that the minor element assemblage of phosphorites is characterised by an enriched group comprising Ag, As, Cd, Cr, I, La, Mo, Pb, Sb, Se, Sn, Sr, U and Y; a depleted group comprising Ba, Co, Cu, Li, Mn, Ni, Sc, Ti and Zr, and a 'normal' group comprising B, Be, Ce, Rb, V and Zn. Krauskopf (1955) and Gulbrandsen (1966) invoke control principally by the organic fraction for the elements Ag, As, Cd, Cr, Mo, Sb, Se, of the enriched group, and Cu, Ni, V and Zn of the non-enriched groups in the Phosphoria Formation. But,it is here suggested that the origins of these variations and abundances will inevitably be complex functions of such factors as the availability of elements in seawater, the relative rates of detrital and other sedimentation, the lattice characteristics of apatite and associated minerals, sorption phenomena, the concentrating effects of organisms, and the physio-chemical characteristics of the environment. In that the minor element assemblage of authigenic mineral deposits may well be a function of the chemistry of the depositional environment, as is the case in marine manganese nodules (cf. Glasby, 1970), and as the origin of the geochemical assemblages typical of phosphorites has not been established beyond doubt, it was felt that a study was merited of the controls of these assemblages in phosphatic rocks from northwest Africa and elsewhere.

In this chapter a preliminary study is made of the geochemical characteristics and trace element partition in northwest African subsea phosphatic rocks in relation to other phosphatic deposits. Trace element partition in the Phosphoria Formation is examined using statistical techniques. Deductions are made concerning the controls of minor element assemblages in phosphatic rocks and the palaeoenvironmental significance of these findings is discussed.

7.2 Analytical Methods

The analytical methods are described in Appendix 2 and the data are presented in table 7.3.1 and 7.3.4. Semiquantitative geochemical analyses for Si, Ca, Al, Mg, K, Fe, Ba, Co, Cr, Cu, Ga, Mn, Ni, Pb, Sr, Ti, V were effected on 11 N.W. African subsea phosphatic rocks and 9 limestones together with selected offshore phosphorites from New Zealand, California and South Africa, and an onshore phosphorite from Morocco, using a Direct Reading Emission Spectrograph; wet chemical techniques were used to determine As, Sb, C_{org} and P_2O_5, and Hg analyses were carried out using a mercury spectrophotometer. The mineralogy of the samples was determined by the writer using X Ray Diffraction and petrographic analyses. Element dispersion in selected samples was studied using an electron microprobe. Mass spectrometric analysis for a large number of elements was carried out on apatite-rich separates from selected samples of subsea phosphate-rock.

Geochemical analyses from the Phosphoria Formation used in this work are derived from Gulbrandsen (1966).

7.3 Moroccan Offshore Phosphatic Rocks

7.3.1 Electron Microprobe Investigation (Fig. 7.3.1)

Although electron microprobe techniques have been widely used to study elemental dispersion in manganese nodules (Burns and Furstenau, 1966; Cronan, 1967; Glasby, 1970) they do not appear to have been used in the study of phosphorites except contemporaneously with this study, and on material supplied by the writer, by students in the Department of Mineral Technology, Imperial College (Ashcroft, 1969; Brock, 1967). In the present study an attempt was made using this technique to study elemental dispersion in certain subsea phosphatic rocks (136, 148 and 152 from Morocco, and D134 from New Zealand). Electronbeam scanning was carried without success for

the rare earths, Sr, Ba, V, Zn, Cd, Cr, and Cu, and it must be assumed that they are present in amounts less than 1000ppm and do not occur concentrated above this level in discrete minerals (Suddaby, pers. comm.). The elements Ca, P, Fe and Si were measured in nearly all samples, and Mg, Ti and S were measured in selected samples.

Petrographic examination shows the probed slides to comprise broken and unbroken calcitic skeletal debris and detrital quartz set in a fine grained matrix of cryptocrystalline apatite and microcrystalline calcite. The matrix was occasionally made turbid by the presence of finely divided iron minerals (presumed to be oxides), organic matter, and clay. Authigenic pyrite was tentatively identified in 136.1 and 152, and glauconite in 152 and D134. Considerable oxidation of pyrite and glauconite, however, made accurate mineral identification often impossible.

The identification of a strong Fe-S association in 136.1 shows the main iron phase in this sample to be pyrite which occurs either as segregations in the matrix or as infillings of foraminiferal tests. In sample 148, which has a more turbid matrix than 136.1, Fe is widely disseminated and not associated with Si; it is associated with Si in certain discrete brown segregations and foram infillings. These data suggest the presence of iron oxide in the matrix while either iron oxides and opal, or some oxidised iron silicate form segregations and infillings. S was not detected in this sample. In sample 152, a glauconitic conglomerate, Fe is irregularly distributed in both pebble and matrix; in the latter iron occurs associated with Si, mainly in sand sized fragments optically identified as glauconite. Fe is less common in the pebble where it occurs in segregations which are not usually Si-associated. These brown and black segregations probably represent pyrite or oxidised pyrite: S was not determined on this sample. Fe, Si and Mg are all associated in a narrow brown band on the margin of

the pebble; the association suggests that the pebble coating was originally glauconite, an Fe-Mg-K aluminosilicate, while the colour shows it has been subsequently oxidised. Analyses of New Zealand glauconitic phosphorite D134 show a similar widespread Fe-Si association attributed to glauconite despite the fact that optically much of the slide shows intense oxidation and unoxidised glauconite is only locally recognised. Background distribution of Fe in this sample is much more uniform that that of Si, suggesting the presence of finely disseminated non-silicate iron minerals, probably oxides. In this sample glauconite both fills foram chambers and replaces foram tests.

In each sample, Si, where not associated with Fe, usually occurs in discrete subhedral grains identified as quartz. The paucity of Si in the matrix signifies a general scarcity of fine-grained detrital silicates. As conjectured above, the local concentration of Si in foram chambers may reflect the formation there of authigenic opal. Differences in silicate mineral content between matrix and pebble in sample 152 are well brought out by the Si distribution; the matrix is evidently richer in finely disseminated Si-rich mineral phases, probably clays.

In each slide, apart from interruptions occasioned by the presence of non-calcareous detrital or authigenic phases, Ca is more or less uniformally distributed. P is much more irregularly distributed than Ca, being concentrated mainly in the spaces between calcareous biogenic skeletal fragments and mineral grains. Foraminiferal tests have therefore strongly resisted phosphatisation as suggested by optical data (Chapter 6). In sample 152 both matrix and pebble appear to contain similar amounts of P. However, at the pebble margin the depletion in Si and the just noticeable enhancement in P reflect a probably authigenic accretion of apatite subsequent to development of the Si, Fe, Mg zone and prior to incorporation into the

conglomerate matrix.

Numbers of small rhombohedral crystals in sample 148 proved to contain concentrations of Mg, supporting the suggestion that they are composed of dolomite. Mg concentrations were not found in sample 136.1 and D134. A search for Ti in all samples revealed in sample D134 a Ti concentration in a minute subhedral mineral grain, presumably rutile.

Using an electron microprobe Ashcroft (1969) also found Fe-Si, Ca-P, and Ca-Mg correlations in Moroccan subsea phosphate rock samples 139 and 148 and, in addition, Fe-S and Fe-Mg correlations in sample 139. In Tasman seamount phosphatic rock sample 3D, Brock (1967) found an Fe-Si association and in D134 found there to be identifiable siliceous skeletal remains.

In summary,

(1) Ca-P associations characterise the matrix and some foram fillings but do not occur in recognisable skeletal remains;

(2) Fe-Si associations are common, reflecting coexistence of pyrite and (?) opal, or the presence of Fe-silicates - often glauconite or oxidised glauconite. The Fe-Si association would not otherwise have been recognised in the more oxidised samples;

(3) Fe-S associations are less common and reflect the incidence of pyrite, chiefly in foram tests;

(4) Ca, Si, Mg and Ti respectively reflect the incidence of calcite, quartz, dolomite and (?) rutile.

(5) Unfortunately all other minor components searched for were not present in measurable quantities so minor element partition between different mineral phases could not be established.

The nature of the Fe and Si distribution tends to suggest that the dark coloured rather formless and extremely fine segregations noted in the matrix

Fig.7.3.1. Electron beam scanning photographs of back-scattered electrons (BSE) and selected characteristic elemental X radiation from sections of phosphorites.

Sample 1361 (x50) page 157b; showing a pyrite-filled foraminiferal test;

Sample 148: top = BSE photograph of the area shown on pages 157 d and 157 e. note foraminiferal remains, particularly that in centre field. lower = Mg radiation from a small rhombohedra (x ? 200). page 157c

Sample 148. page 157d. Elemental X radiation in the slide section shown on page 157c.

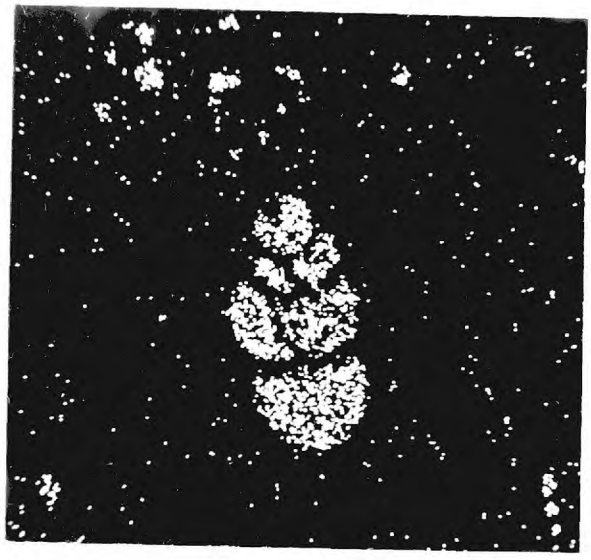
Sample 148. page 157e. (x100) An enlarged view of the foraminiferal test central to the photographs of page 157d

Sample 152. page 157f. (x15) A view of the contact between pebble (left) and matrix in a glauconitic phosphatic conglomerate; the Mg radiation(bottom left) is a slightly enlarged view of the pebble margin at upper left centre in adjacent photographs.

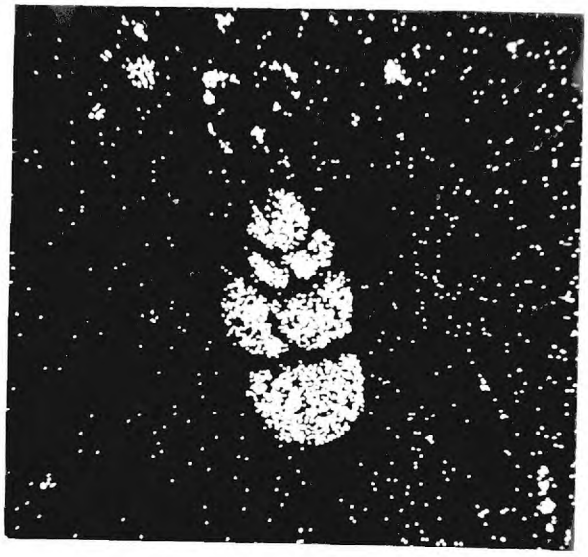
Sample D134 (New Zealand) page 157g. top = BSE photograph representing the area shown on page 157h. note foraminiferal remains (x20). lower = slightly magnified view of Ti radiation from a small angular anhedral mineral grain (x ? 200).

Sample D134. page 157h. (x20). Elemental X radiation from section shown in Fig. on page 157g. Foraminiferal remains often filled with Fe, Si.

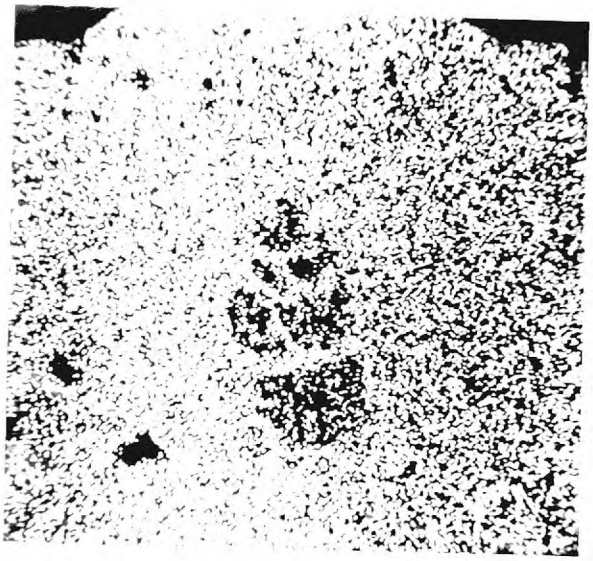
Sample D134. page 157i. (x20). Elemental X radiation from a partially oxidised region near the glauconitised margin of this sample.



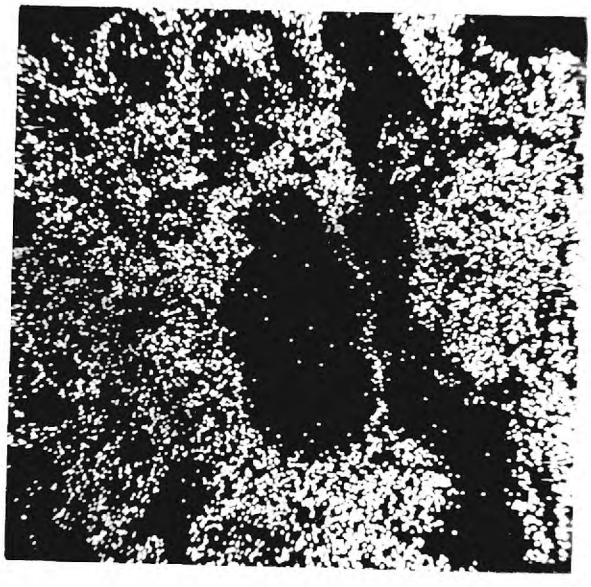
Fe



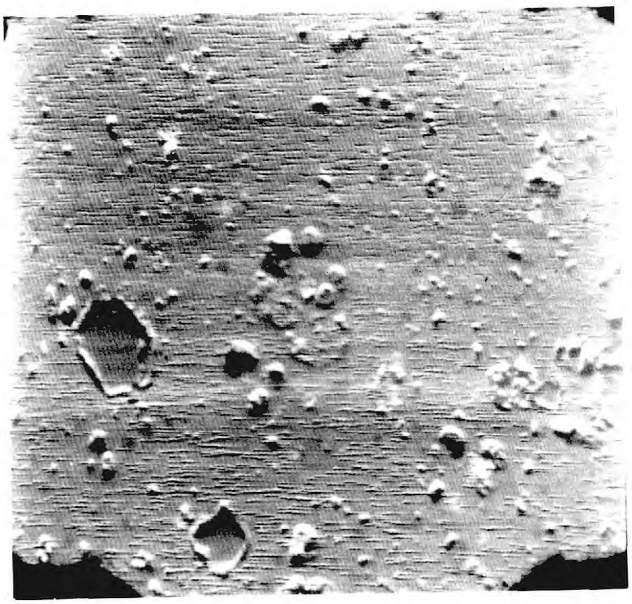
S



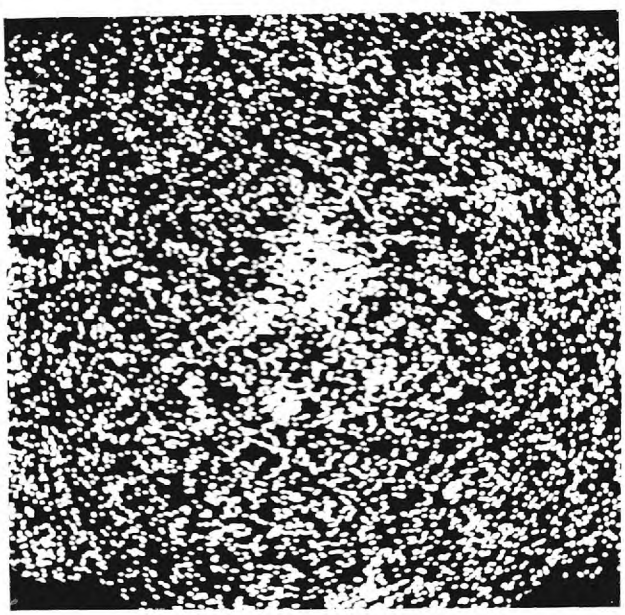
Ca



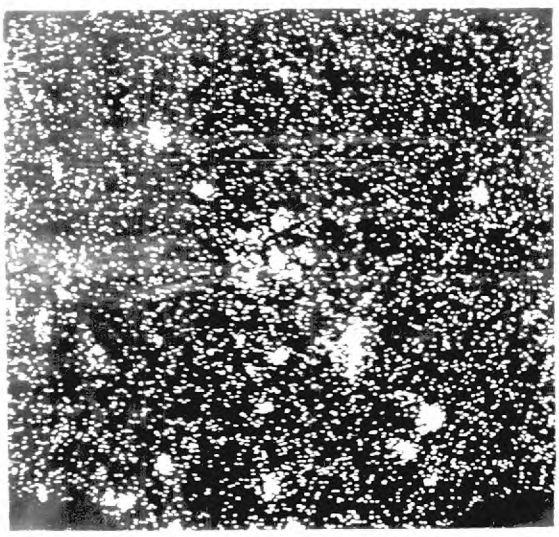
P



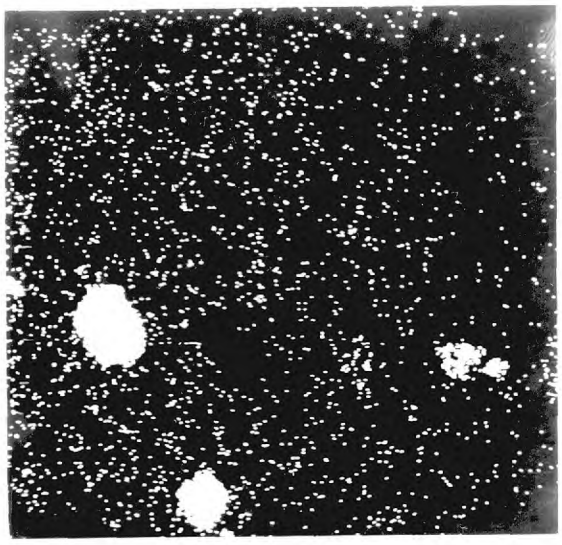
BSE



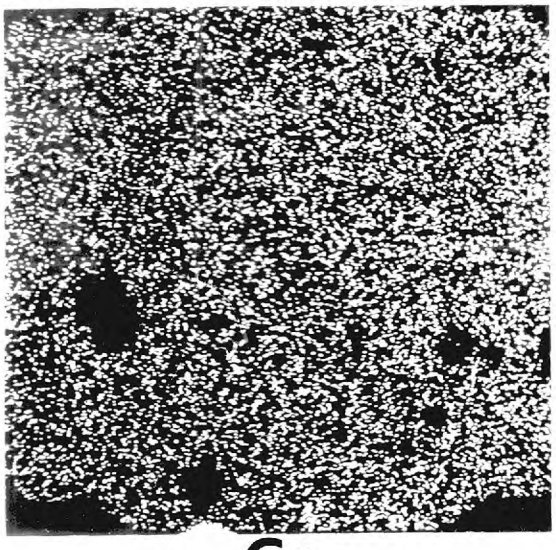
Mg



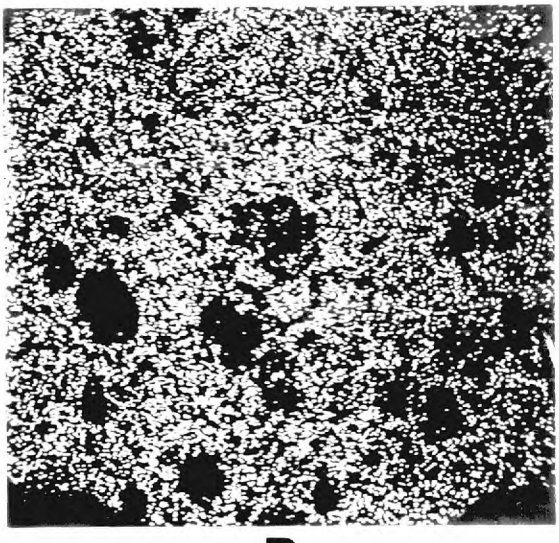
Fe



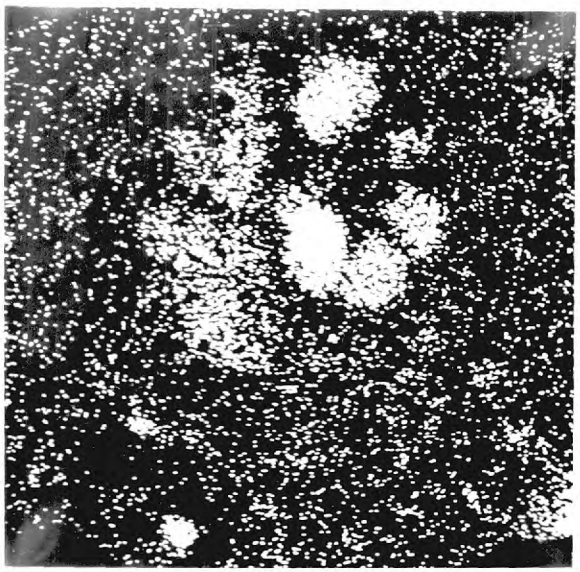
Si



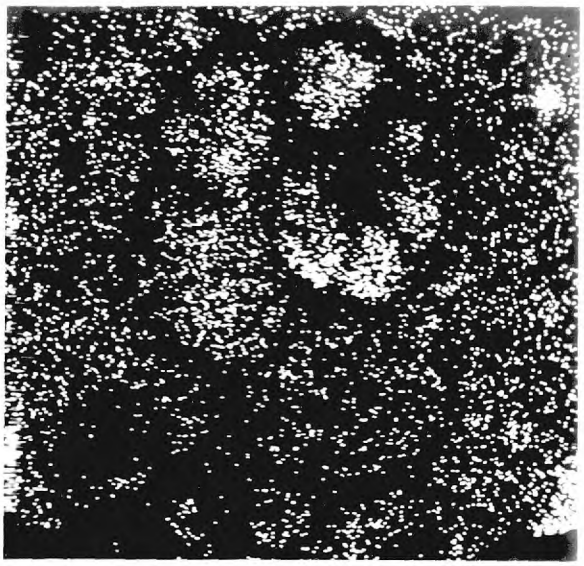
Ca



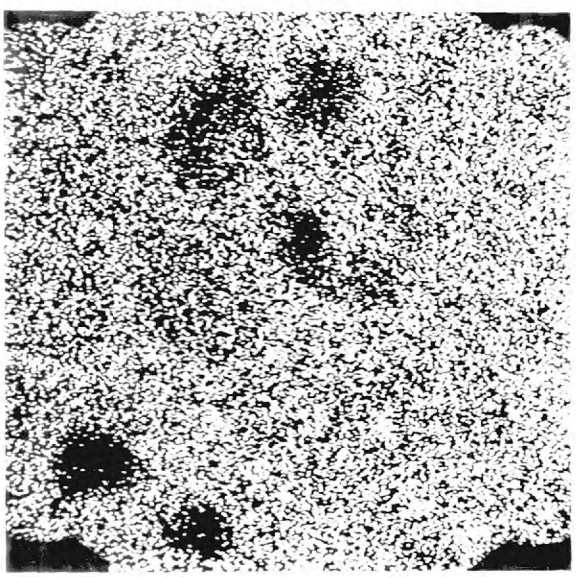
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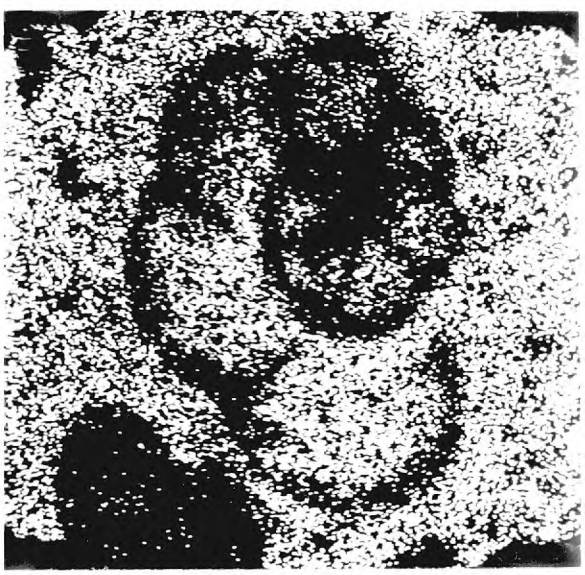
Fe



Si



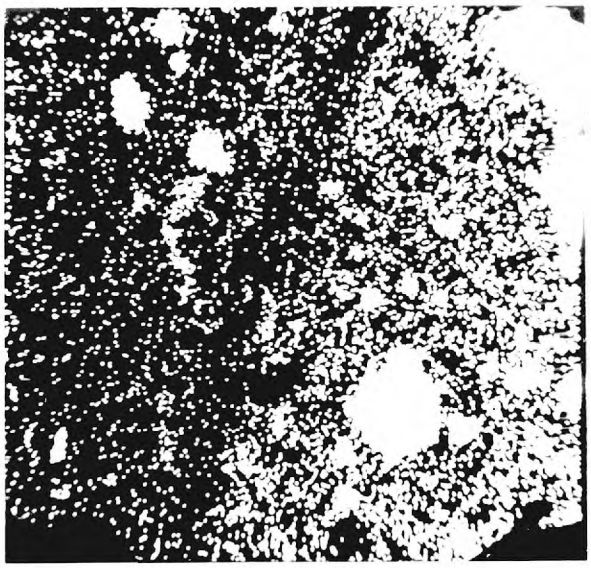
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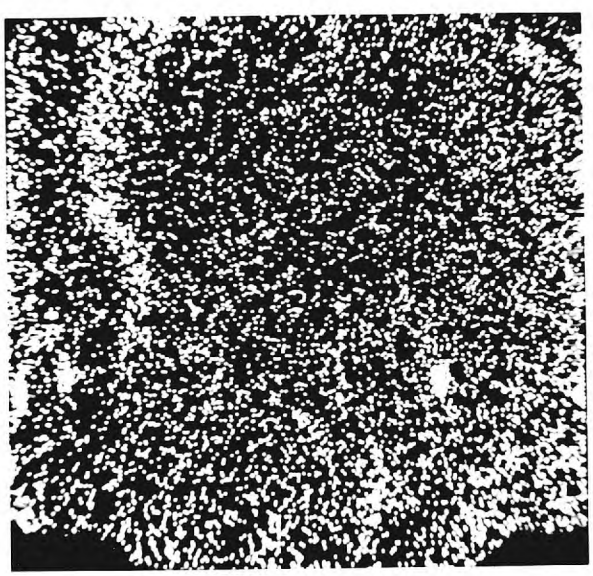
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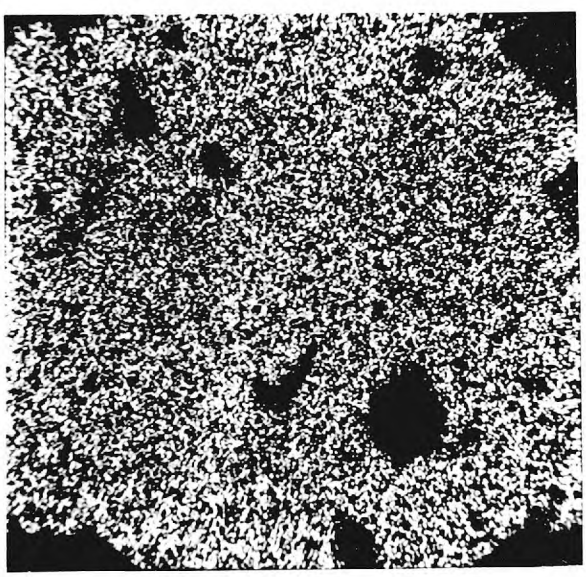
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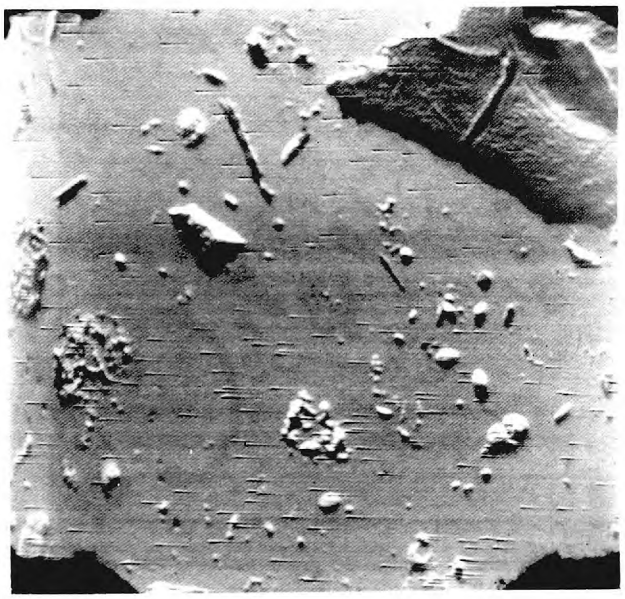
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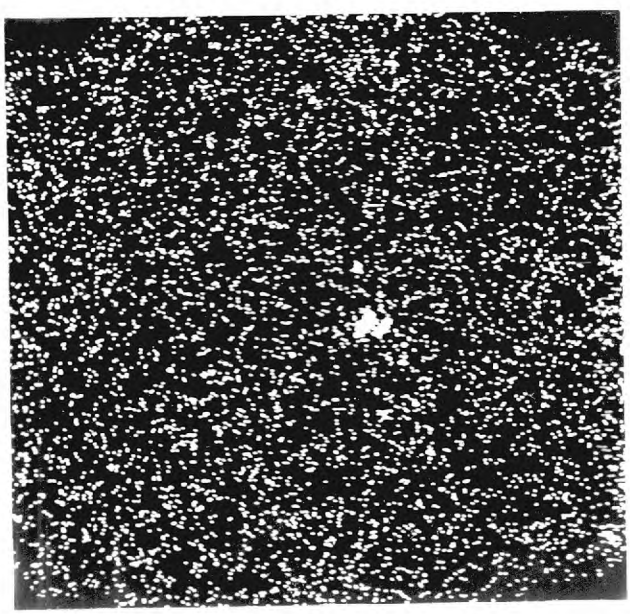
Mg



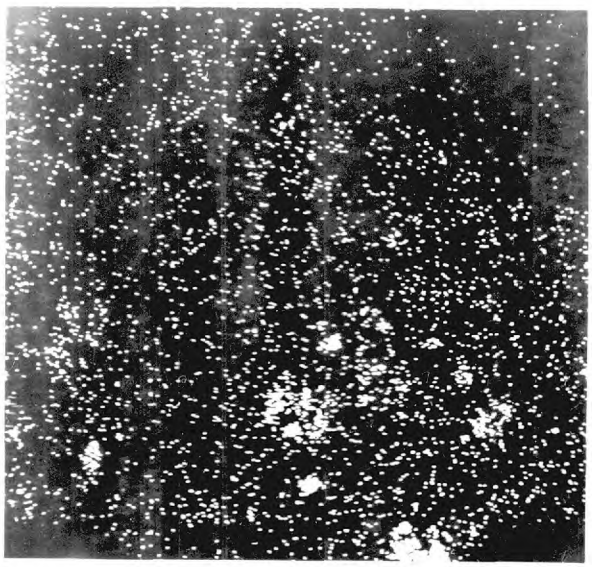
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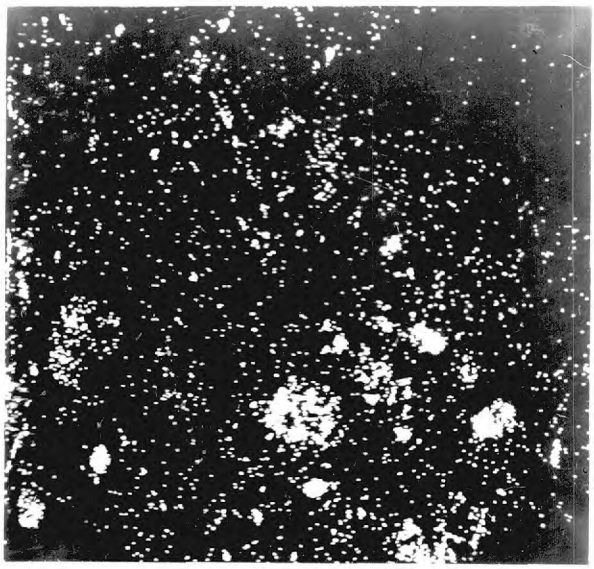
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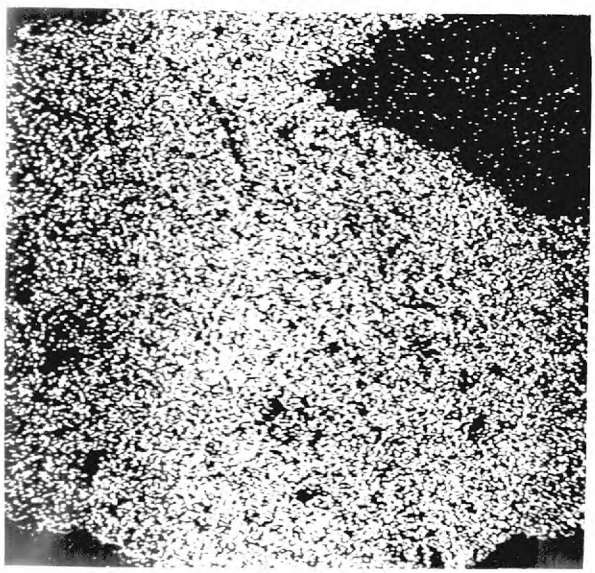
Ti



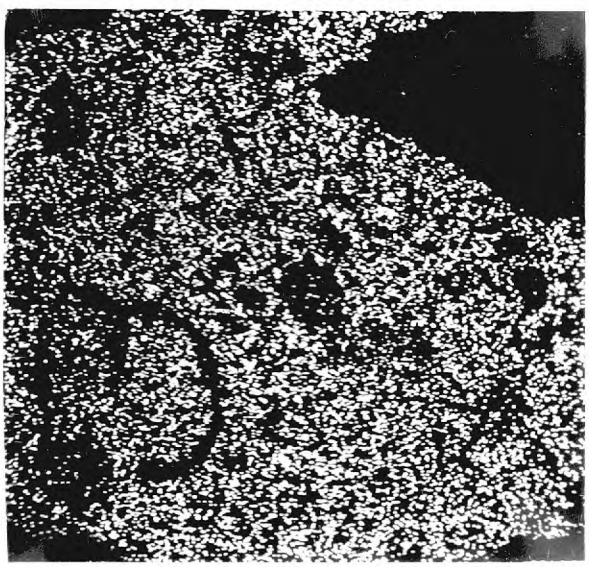
Fe



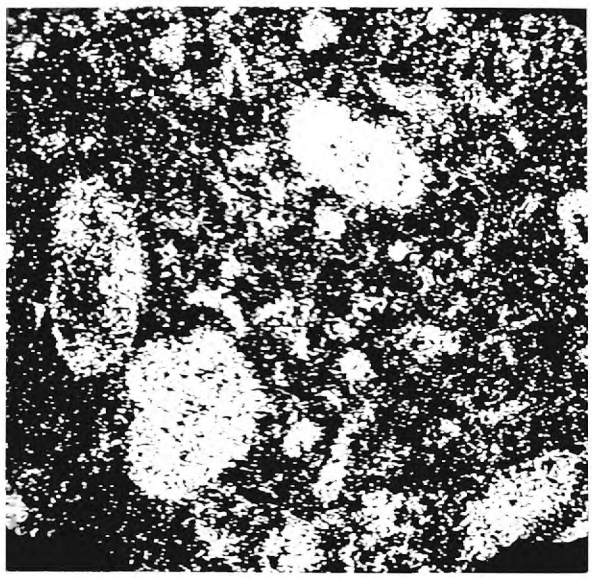
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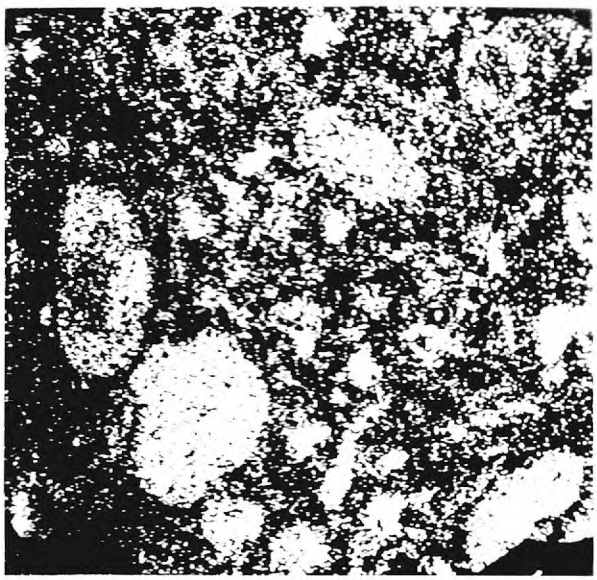
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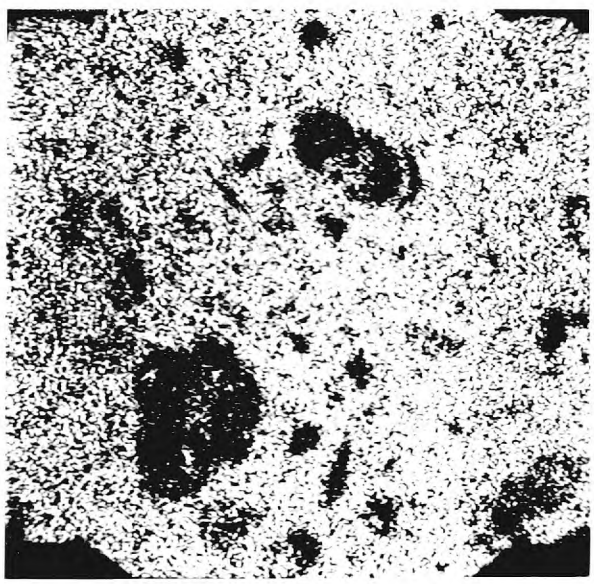
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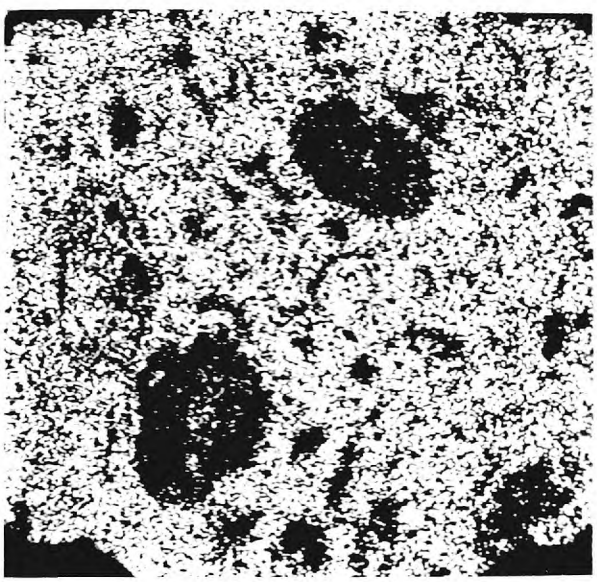
Fe



Si



Ca



P

(Chapter 6) are composed mainly of organic material rather than Fe oxides or clays. The more or less complete segregation of Fe from P argues against the presence of ferric phosphates, and the lack of any P-S or P-Si association tends to militate against any notable substitution of S or Si for P in the apatite lattice. The same cannot be said for Mg because instrumental interference (Suddaby, pers. comm.) resulted in very poor definition for this element. The clear mineralogical controls established by petrographic and electron probe analysis for dispersion of the major elements P, Fe, Si, S, Ti and Mg, suggest that these elements can be used to represent the major mineralogical controls in the following statistical analyses of the raw data.

7.3.2 Results of Whole Rock Analyses (Table 7.3.1 and Fig. 7.3.2)
Using Bushinsky's (1969) definition of phosphorites as rocks containing >18% P_2O_5, approximating to 50% apatite, many of the analysed offshore Moroccan phosphate-rocks can only be defined as phosphatic limestones; the sample richest in phosphate (139.1) contained only 25.3% P_2O_5, a level similar to other analysed offshore phosphorites (cf. Fig. 7.3.2) which usually contain on average c.29% P_2O_5 (Mero, 1965). The phosphatised limestone (148) and pelletal phosphatic rocks (135, 136, 139) are all phosphorites. The glauconitic or ferruginous-dolomitic phosphatic rocks (152, 154, 156, 157) and the Saharan phosphatised limestone (234), which was partially glauconitised, are all classified as phosphatic limestones.

This mineralogical differentiation is reflected in the geochemistry (Fig. 7.3.2), the iron-rich rocks being enriched in the mainly lithophile elements Si, K, Fe, Mg, Mn, Ti, Ga, Pb and possibly V and Co, whilst the phosphorites are enriched in P_2O_5, Ca, C_{org}, Sr, Cu and (?)Hg; the distribution of Ni, Ba, Cr, Sb and As is more or less even between the two groups. The Ga enrichment most probably reflects Al enrichment and indeed the sample

richest in Ga was found to contain a detectable amount of Al whereas the others did not. These data are interpreted to reflect general enrichment of the southern province in authigenic glauconite and dolomite and detrital minerals at the expense of calcite and apatite. Compared with offshore N.W. African limestones and sandy limestones the phosphatic suite are clearly richer in Ca, P_2O_5, C_{org}, As, Sb and Pb, and tend to be slightly richer in Sr, Cu, Cr, V and Ni. Such enrichment may be due to differences in detrital or authigenic mineralogy as well as to differences in the relative apatite and organic contents.

The compositions of the phosphorites are seen to be similar in many respects to those of other offshore phosphorites from the California Borderland, Agulhas Bank, and the seas around New Zealand. The Agulhas Bank sample, which is a glauconitic phosphorite, shows more affinities with the phosphatic limestones than with the phosphorites. Campbell Plateau sample F127 is very different from the remainder most probably because it contains disseminated Mn oxides. In marked contrast to worldwide averages and those from the Phosphoria Formation (cf. tables 7.1.1 and 7.3.1), the N.W. African deposit is notably depleted in As, Sb, Cu, Cr, Sr, V, Ba and Ni; it is also, perhaps significantly, depleted in C_{org}. Compared with crustal abundances, phosphorite sample 148 (taken as typical of the offshore phosphorites) is enriched in As, and weakly in Sr, and Pb, whilst Ni, Mn, Ti, Cu, Co, Ba are depleted and Sb, Cr and V are neither enriched or depleted (cf. tables 7.1.1 and 7.3.1). This relative impoverishment of subsea phosphorites in minor elements, compared with data from onshore deposits, may result from marked differences in the depositional environment of present day onshore and present day offshore deposits (see later).

Finally, in comparison with the offshore Moroccan phosphorites it is clear that the one analysed onshore Moroccan phosphorite (Fig. 7.3.2) is slightly

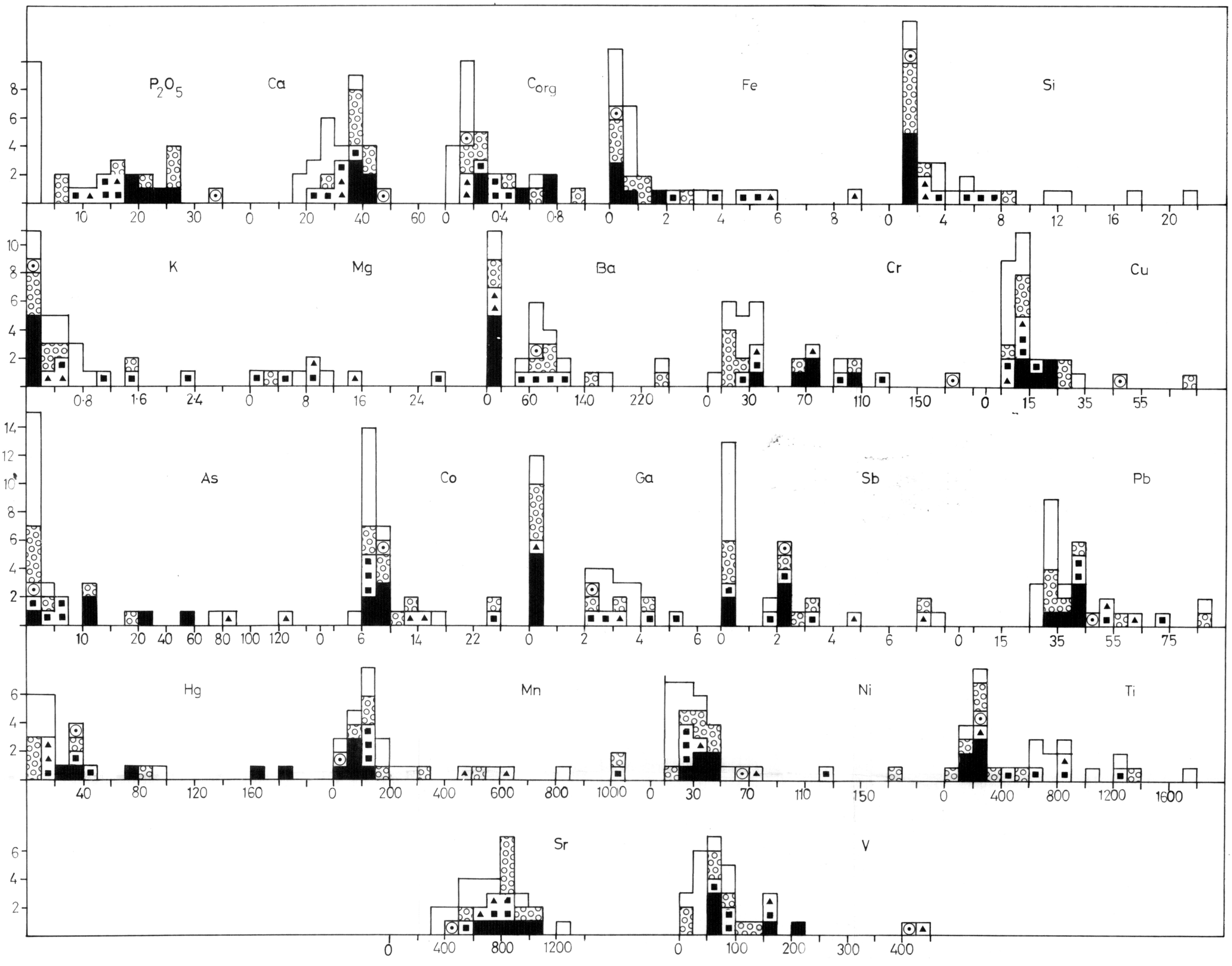


Fig. 7.3.2 Frequency distribution of individual elements in selected subsea phosphatic rocks and limestones.

■ = phosphorites 135, 136, 139, 148; ■ = glauconitic phosphatic limestones 152, 154, 155, 234; ▲ = ferruginous dolomitic phosphatic limestones 156, 157; = certain worldwide subsea phosphorites; ⊙ = onshore Moroccan phosphorite; □ = offshore limestones.

P_2O_5, Ca, C_{org}, Fe, Si, K, Mg expressed as per cent; all others as ppm except Hg (ppb)

enriched in Ca, P_2O_5, Cr, Cu, V, Ni, Ba, Ga, Pb and slightly depleted in C_{org}, Fe, As, Mn, Sr although its contents of Si, K, Ti, Co, Hg and Sb are similar. The similarities in Si, K and Ti suggest that the rate of detrital sedimentation was much the same. These differences would not seem to relate to organic carbon differences but may instead reflect differences in the depositional environment such as the concentration of minor elements in seawater or Eh, pH conditions. Examination of a range of onshore Moroccan samples is evidently required to substantiate and understand these variations.

In an attempt to establish possible mineralogical controls for the geochemical assemblage, statistical analyses were carried out on the raw data.

7.3.3 Interelement Associations

The data were subjected to product-moment correlation coefficient analysis and R-mode factor analysis, techniques described in Chapter 3. From the correlation coefficient matrix (Fig. 7.3.3) derived from a mixed population of offshore Moroccan phosphatic rocks and limestones, a number of correlations emerge which appear geologically meaningful. Strong correlation between the lithophile elements Si, K and Ti, and their pronounced antipathy to the essential constituents of apatite and calcite (Ca, Sr, P_2C_5) reflects the interplay of detrital and bio- or chemo- genic sedimentation and bears out the petrographic and electron microprobe investigations. Fe and Mn are closely correlated with K, which may be due to the presence in some samples of glauconite (Fe-K association) and in others of Fe and Mn rich clay. As shown in Chapter 3, Mn is not normally enriched in glauconite, nor associated with Fe in glauconitic sediments. The C_{org}-P_2O_5 correlation supports the raw data which showed phosphorites to contain more C_{org} than limestones. Only Cr and Cu are strongly correlated with C_{org} suggesting that the organic content has very little influence on the overall geochemical assemblage. The origin of the V-Ni-P_2O_5 correlation is obscure but may relate to the

association, within the present sample population, of glauconite and pyrite with phosphatic rocks as opposed to limestones.

To attempt further resolution of the data into associations with geological significance, the data were subjected to R-mode factor analysis. Factor model 5, explaining 93.3% of total sample variance provides the most geologically meaningful associations (table 7.3.2). Essentially the same elemental associations emerge as from correlation coefficient analysis. An organochemical association (Ca, Sr, P_2O_5, C_{org}) is opposed to a detrital mineral association (Si, Ti, K). A strong organo-metallic association appears to be further associated with apatite (Cu, Cr, C_{org}, P_2O_5, Sr). Most interesting is the resolution of the Fe, Mn, K correlation into three distinct factors. The Fe, P_2O_5, Cr, K association very closely resembles the glauconite factor derived from sediment studies (Chapter 3). The Co, Mn, Ni, V, Ca association closely resembles a manganese-iron oxide factor also derived from sediment studies (Chapter 3). Incorporation of Ca into this association may reflect the prevalence of oxidised mineral phases among limestones rather than phosphatic rocks, as might be expected. Finally, the Pb, Sr, K, Mn, Fe association may represent control by some admixed clay mineral phase. A separate factor with associations typical of the pyrite known to occur in some samples is not apparent probably because pyrite is never more than an accessory mineral and does not overtly influence the geochemistry.

Assessing the raw data for As, Sb, Ba and Hg (Fig. 7.3.2), which were not detected in enough samples to allow statistical analysis, it appears that

(1) Ba tends to be richest in glauconitic samples where it possibly follows K;

(2) Hg appears to be richest in organic and pyrite rich samples (viz. 139);

(3) As and Sb are richest in the iron oxide-rich dolomitic phosphatic lime-

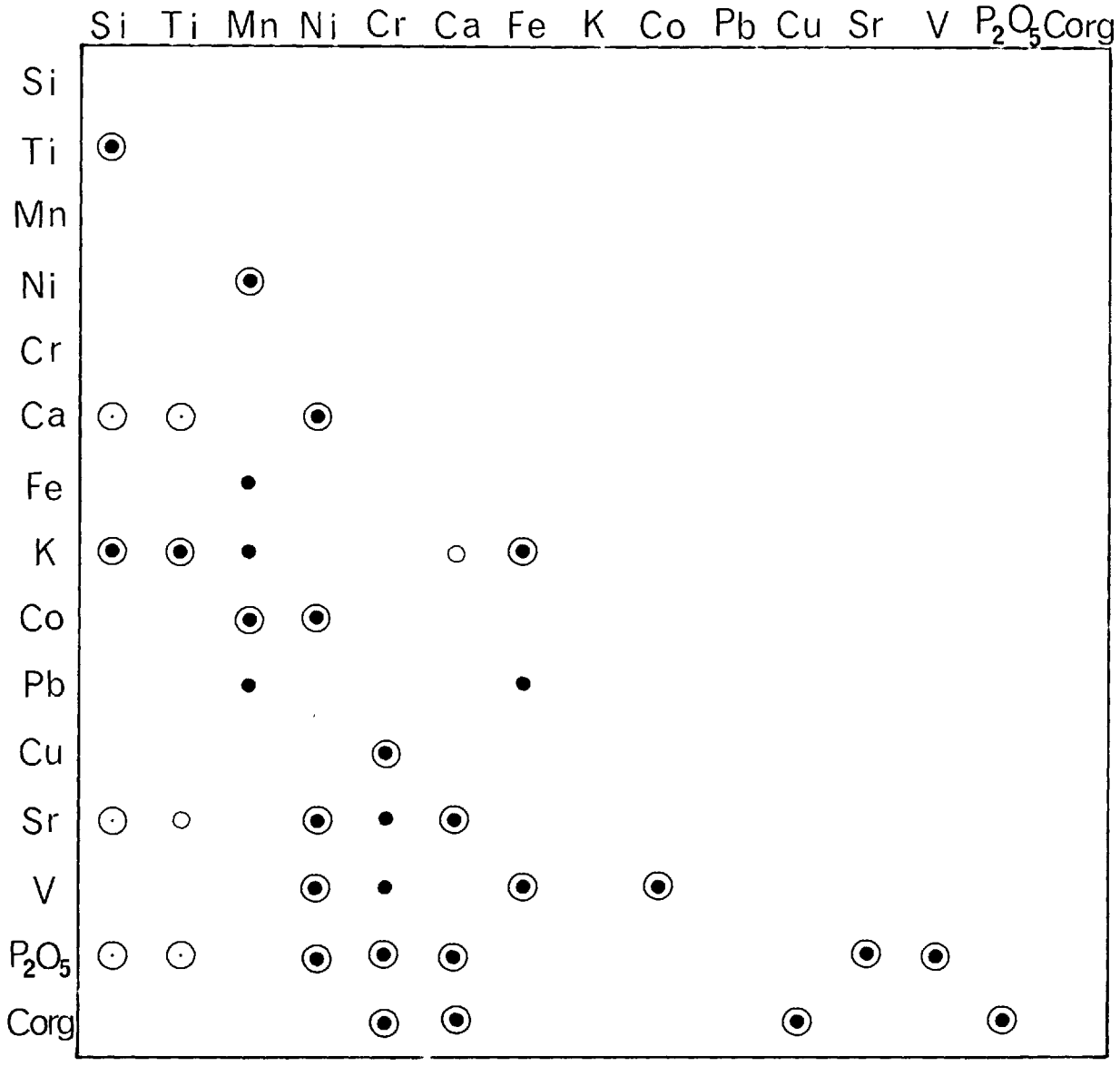


Fig.7.3.3. Product moment correlation coefficient matrix for Moroccan phosphatic rocks and limestones (data from table 7.3.1)
Significant + correlation = large heavy circle (99% confidence level), or small closed circles (95% confidence level); significant - correlation = large light circle (99% confidence level), or small open circle (95% confidence level).

stones 156 and 157 which are poor in pyrite and C_{org} and do not contain any glauconite.

These last data support the findings of Stow (1968) and Blissovsky et al (1968) that As in phosphorites usually tends to follow iron minerals, particularly oxides.

Evidently the use of statistical analyses allows a reasonably clear assessment to be made of the origins of geochemical assemblages and, for these rocks, shows that admixed authigenic and detrital minerals other than apatite and the organic phase provide the main geochemical controls. In order to assess the contribution of the apatite phase, an attempt was made to separate and analyse carbonate-apatites from selected phosphorites.

7.3.4 Analysis of Carbonate-Apatite Concentrates

Reluctance of analysts in the past to attempt separation of carbonate-apatite from the other constituents with which it is intimately admixed in phosphorites has in part contributed to the general lack of precise data regarding element partition and controls in these rocks. In this section are presented analyses of some carbonate-apatite concentrates from Moroccan offshore phosphorites 139 and 148 and, for comparative purposes, from Campbell Plateau phosphorite F127. Using a solid-source mass-spectrometer the abundances of the following elements were determined (in order of atomic number):-

U, Th, Pb, Lu, Yb, Tm, Er, Ho, Dy, Tb, Gd, Eu, Sm, Nd, Pr,
Ce, La, Ba, Cs, I, Sb, In, Cd, Mo, Nb, Zr, Y, Sr, Rb, Br,
As, Zn, Cu, Ni, Cr, V,

the technique is described in Appendix 2, and results are presented in table 7.3.4.

Results

a. The Rare Earth Elements

Compared with other data on rare earth abundances in crustal rocks (cf. tables 7.1.1 and 7.3.4) the rare earths are not markedly enriched in these carbonate-apatites. The rare earth elements (REE) substitute for Ca in the apatite lattice where they can reach concentrations between 100 and 1500ppm (Hill, Marshall and Jacob, 1932; Robinson, 1948; Altschuler et al, 1967; Gulbrandsen, 1966). Studies of the relative abundances of REE in carbonate-apatites separated from phosphorites by Altschuler et al (1967) show marked depletion of Ce (table 7.3.5). The fundamental nature of this depletion is attested by the present mass spectrometric analyses from two further phosphorite deposits (table 7.3.5). Similar results are obtained on the carbonate-apatite skeletal remains of pelagic fish (Arrhenius and Bonatti, 1965) and in phosphorite nodules from the Blake Plateau (Ehrlich 1968). The depletion parallels that observed in seawater (Goldberg et al 1963) and may thus reflect growth of the carbonate-apatite in the marine environment. Slight enrichment in the heavier lanthanons manifest in the present data, and noted before by Altschuler et al (1967), again parallels that observed in seawater (table 7.3.5). Contrasting data have been produced by Semencv, Kholodov and Barinskii (1962), Goldberg et al (1963) and others who find that REE abundances in phosphorites parallel crustal abundances and do not exhibit the newly observed Ce fractionation (see table 7.3.5). It is suggested here, and has been suggested also by Altschuler et al (1967), that the observed discrepancy between whole rock data and that from separated carbonate-apatites results from the presence in the whole rock of some Ce-bearing phase (? clay).

Goldberg et al (1963) also showed phosphorites to exhibit slight but according to them significant enrichment in Sm and Eu, rare earth elements

which according to them have ionic radii nearest to Ca. However, Sin'kova, Ivanov and Filippov (1968) point out that the ionic radii of the REE have yet to be sufficiently precisely determined to allow such arguments to be pursued with confidence.

b. Other Elements

Of the remaining elements the following are enriched relative to crustal abundance (cf. tables 7.1.1 and 7.3.4) in the Moroccan carbonate-apatite concentrates:-

U, I, Sb, Cd, Mo, Br, As, Cu, Cr and In; depleted are Pb, Ba, Zr, Rb, Zn, Ni, Th, Cs and Nb; Y is enriched with the REE in sample 139 and depleted with the REE in 148 (as also is Sr); V behaves in an opposite manner and its abundances are not too dissimilar from crustal abundances. It may be significant that these groupings are not much different from those noted among average phosphorites (see earlier).

In relation to the whole rock analyses of these Moroccan samples (table 7.3.4), enrichment of the separated carbonate-apatites in Cr and Cu, which are known to be C_{org} associated, implies that the separation of organic matter may have been imperfect. In relation to crustal abundance the I and Br enrichments may also be organically induced, these being strongly biophile elements (cf. Goldschmitt, 1954); however, as tetrabromethane was used in the separation proceedure (Appendix 2) the possibility of Br contamination cannot be ignored. Cf the other enriched elements, most are found enriched in organic-rich reduzate sediments (cf. Goldschmitt, 1954) and the possibility of organic contamination must be stressed. Although the present data tend to suggest inadequate separation of carbonate-apatite and admixed organic material, X-Ray diffraction analyses showed that removal of non-phosphatic detrital and authigenic minerals was complete. The elemental enrichments are therefore attributed to the operation of sorption processes involving apatite and organic material (see later).

7.3.5 Summary

In contrast to worldwide average phosphorites, subsea phosphorites from Morocco and elsewhere are not enriched in many trace elements relative to crustal abundances. The whole rock assemblage is controlled mainly by non-phosphatic inorganic mineral phases for most of the following:- Si, K, Fe, Mg, Mn, Ti, Ga, Pb, Co, Ni, V, Sb, As, Ba. The apatite phase appears the main control only for Ca, P_2O_5, the rare earths and Sr, and the organic phase the main control only for Cr and Cu (and ? Hg). The possibility exists that the concentrations of U, I, Sb, Cd, Mo, Br and As are also influenced by organic matter. As for the rare earths and Y, these appear present in proportion to their abundance in seawater and are probably controlled by the apatite phase. The present data do not greatly assist in resolving the origins of the geochemical assemblages characteristic of average phosphorites although they do suggest that by mineral separation and statistical analysis some understanding of elemental partition in these rocks can be obtained. More detailed work along the lines suggested in Chapter 10 is being carried out on phosphorites in the Applied Geochemistry Research Group by J. McArthur (PhD thesis, in preparation).

7.4 Elemental Controls in the Phosphoria Formation

To assess the validity of using multivariate statistical techniques in resolving the origins of phosphate-rock geochemistry, a product-moment correlation coefficient and an R-mode factor analysis were also carried out on data presented by Gulbrandsen (1966) from the Phosphoria Formation. It is assumed that the major elements represent the main inorganic mineral phases and that minor element variations should be mainly interpreted in terms of their relation to major elements and organic carbon. Results of the correlation coefficient analysis are presented in Fig. 7.4.1 and of the Factor Analysis, in table 7.4.1. Organic carbon correlates with a strongly

lithophile group of elements (K, Al, Ti, Na, Mg) usually taken to represent the hydrolysate fraction (cf. Goldschmitt, 1954). This suggests that C_{org} is mainly clay sorbed or bonded as is found in other sediments (cf. Curtis, 1966). For this reason the correlation of C_{org} with Ni, Cr, Zn, Cu, Mo, Ag and V cannot be simply interpreted in terms of control mainly by the organic phase. Gulbrandsen's (1966) assumption that As and Sb were principally controlled by the organic phase is contradicted by the correlation coefficient matrix determined from his own data. The correlation of Sb with Ti, Cr, Fe, K, Mo, V, U, Al is not fully understood but suggests a part control by the clay phase (by sorption ?) and possibly by pyrite which is known to be present in these rocks (Gulbrandsen, 1966) and might be expected to give rise to an Fe-Mo correlation (cf. Gad, Catt and Le Riche, 1969) and possibly an Fe-Sb association (cf. Goldschmitt, 1954). As correlates with Na, Zr and La: Gulbrandsen (1966) has shown that in these rocks the Na most probably substitutes for Ca in the apatite lattice; the substitution of rare earths (eg. La) for Ca has been discussed earlier; Arrhenius (1963) reports substitution of Zr for Ca in marine apatites; As substitution in sedimentary apatites is discussed by McConnell (1970). It seems probable that this group of elements are correlated by virtue of their principal control by apatite lattice characteristics in these rocks.

As expected, P_2O_5, representing carbonate-fluorapatite, correlates with Ca and F; Al, representing the hydrolysate fraction, correlates with both lithophile and organically controlled elements reflecting, as mentioned above, sorption of organic matter by clays; Fe correlates with a hydrolysate-detrital group of elements (Al, Si, K, Zr, Ti, Mn) and with Mo and Sb which, as suggested above, may reflect local pyrite control. All the minor elements except As, La and Sr are correlated with one or more major elements (i.e. with major mineral forming phases). But although correlation coefficient analysis suggests certain elemental partition controls, it

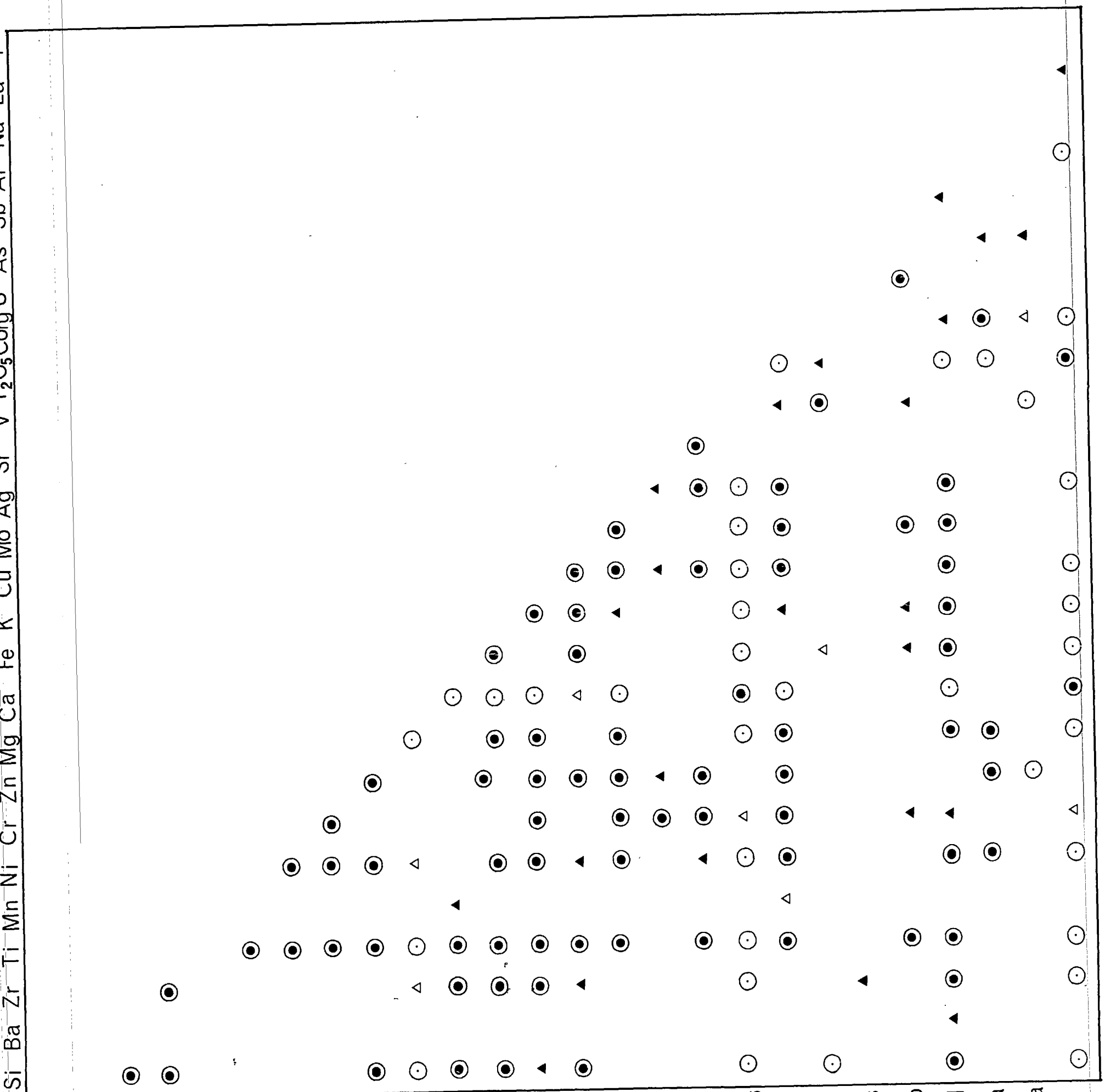
Fig.7.4.1. Product moment correlation coefficient matrix for data from the Phosphoria Formation (see text for details).

⊙ significant + correlation ; 99% confidence level

▲ significant + correlation ; 95% confidence level

⊙ significant − correlation ; 99% confidence level

△ significant − correlation ; 95% confidence level.



does not in this case provide an ideal means for distinguishing specific elemental associations related to discrete controls.

Accordingly, to assess the degree to which these elements are dispersed among the separate mineral phases, an R-Mode Factor Analysis (of the type described in Chapter 3) was carried out on the log-transformed data. Using this technique, elements are grouped into factors on the basis of the statistical associations extant between all the variables. The factors produced by this analysis appear to be geochemically significant (table 7.4.1). Up to and including factor model 7, strong factors which persist through three or more models are produced; beyond factor model 7, fragmentation of associations commences and impersistent and less geochemically meaningful factors are produced. Accordingly factor model 7 is used as an ideal representation of the system. It explains 76.4% of the total sample variance.

The most important factor, accounting for 31.1 % of total sample variance, basically illustrates the antipathy between the detrital aluminosilicate and heavy mineral phase represented mainly by the lithophilic group of elements Si, Al, K, Ti, Mg, Fe, Zr, and the authigenic phase represented by Ca, P_2O_5, F (apatite). The association of Ag and Cu with the detrital group may be due to some heavy mineral phase or preferential sorption onto a species of clay. The strong association of U with the apatite group of elements reflects its main location in place of Ca in the apatite lattice (Bowie and Atkin, 1956; Ames, 1960; Altschuler et al 1958; Clarke and Altschuler, 1958). A further 'detrital' factor is represented by the association of Al, K, Ti, Zr, within which Fe, Mo and Sb are also included. The absence of Si from this group is taken to reflect the independance of clays and quartz; Gulbrandsen (1966) has interpreted the Al-K association as indicative of control by muscovite and illite in these rocks, and he also suggested that lack of association of Al-K with Si indicates changes in the supply ratio

of detrital quartz/clay and authigenic or biogenic silica. As suggested earlier, the joint association of Fe with hydrolysate and reduzate elements indicates partition between clays and pyrite; the presence of two 'detrital' associations may reflect the local incidence of admixed black shale facies, presumed pyritic, as opposed to 'normal' shale admixtures (cf. Gulbrandsen, 1966; and McKelvey et al, 1959 for discussions of lithologies).

A metal-C_{org} association persists throughout the 9 studied factor models with the exception of model 8 where C_{org} has a factor loading$<\pm 0.300$, the presently used significance level. In the remaining models the loading of C_{org} on this factor is usually low suggesting a relatively weak relationship to associated variables. Common to this factor throughout the 9 factor models are Zn, Cu, Ag, Cr, V, Ti and less common are Ni, Sr, Mg, U, Na, Sb and Ba. Compared with previous work on the influence of the organic phase on sediment geochemistry (table 7.4.2) all elements of the first group are commonly associated with organic material except Ti which is an 'immobile' element always found in the hydrolysate fraction (cf. Goldschmitt, 1954). Of the second group, Ni, U and Mo are often found associated with the organic fraction (table 7.4.1) but Sr, Ba, Mg, Na and Sb are not; of this last group there is not even any significant correlation between C_{org} and Sr, U, Ba and Sb. Goldschmitt (1954) shows that Na and Mg are strongly clay-sorbed, not organically bonded in marine sediments and Lehr et al (1967) point to their common control by the apatite lattice in phosphorites. Furthermore, that these two elements form a strong association usually separate from C_{org} (table 7.4.1) suggests that they are not organically controlled. It is suggested that the minor element - C_{org} association represents a sorption factor controlled by the availability of suitable sorption surfaces (organic and inorganic) and does not represent either an organo-metallic association inherited from original organic matter, nor the exclusive sorption of associated elements by organic material although

undoubtedly the latter process is important.

The group of intercorrelated elements As, Zr, La, Na form an association with Ba which persists through several factor models. As discussed above these elements all substitute in the apatite lattice as also does Ba (Arrhenius, Bramlette and Picciotto, 1957) and it is difficult to envisage any other main control for this factor.

A further factor in which Mn is persistently antipathetic to C_{org} and Sb may be induced by local contrast between oxidised and organic-rich reduzate samples.

Finally a factor is developed in model 7 in which there is antipathy between Sr and As; the reasons for this are not at all clear although it may reflect the interrelation between these two elements within the apatite lattice.

In summary, a statistical evaluation of the geochemical assemblage of phosphorites from the Phosphoria Formation shows that the suggestion of Gulbrandsen (1966) that organic control is of primary importance in controlling the abundance of Ag, As, Mo, Ni, V, Zn, Cr, Cu and Sb is not well substantiated. Mo and Sb correlate best with Fe and are probably pyrite controlled. As appears mainly sorbed in apatites. The remaining metals show only weak associations and correlations with C_{org} and also show weak associations with the hydrolysate elements. It is deduced that sorption of organic matter onto clay, and of minor elements onto both clay and organic matter controls these associations. The conclusion that sorption processes are of great importance in governing the geochemistry of other sedimentary rocks has been reached previously by Curtis (1966), Nicholls and Loring (1962), Krauskopf (1956), and Vine and Tourtelot (1970) among others. Of the remaining elements, Ca, P_2O_5, F and U appear mainly apatite-controlled and apatite substitution appears to govern the dispersion of much of the

La, As, Na, Mg, Ba, Zr and possibly Sr, while detrital mineral phases appear to control mainly Si, K, Al, Ti, Zr, Mg, some of the Ag and Cu and part of the Fe.

7.5 Environmental Significance

With regard to the average phosphorite assemblage in which Ag, As, Cd, Cr, I, La, Mo, Pb, Sb, Se, Sn, Sr, U and Y are enriched, B, Be, Ce, Rb, V and Zn are 'normal' and Ba, Co, Cu, Li, Mn, Ni, Sc, Ti and Zr are depleted relative to crustal abundances, the foregoing analyses suggest that these relative abundances reflect a relative dearth of non-phosphatic detrital and authigenic minerals and are considerably influenced by sorption processes and to a lesser extent by carbonate-apatite characteristics. Van Wazer (1958) and Whippo and Murowchick (1967) quote possible substitutions in sedimentary apatites for Ca by Mg, Mn, Na, K, Pb, Sr, Zn, Cd, Fe^{2+}, Al H_3O and the Rare Earths; for F by OH, Br and Cl, and for P by As, V, C, S and H_4. The foregoing analyses do not support significant apatite lattice control for more than a fraction of these elements and although these substitutions may all occur to some degree, this mode of origin is not important with regard to the overall minor element assemblage. In particular, of the enriched group, As, La, Sr, U and Y together with Ba and Zr of the depleted group appear strongly apatite controlled.

The frequent presence, in phosphorites, of non-phosphatic detrital and authigenic minerals such as clays, glauconite and pyrite does not appear to contribute significantly to the enrichments in average phosphorites or those from the Phosphoria Formation although they are important controls in Moroccan and other subsea phosphorites. The depletion of average phosphorites in lithophile elements such as Li, Ti, Rb, Zr, is in keeping with a relative dearth of detritals but the possibility that Mo and Sb enrichments

are pyrite and not sorption controlled and that As enrichment is preferentially controlled by Fe oxides in many instances must be borne in mind.

Considering the relative availability of these elements in seawater it is strikingly apparent (Fig. 7.5.1 and table 7.5.1) that with few exceptions the same group of elements is enriched in seawater as in phosphorites, relative to crustal abundance, and those elements relatively depleted in phosphorites are similarly depleted in seawater. This suggests that sorption of elements from seawater in proportion to their abundance and availability there plays a considerable part in moulding the minor element characteristics of phosphorites. Some degree of fractionation is to be expected in view of the influences of apatite lattice characteristics, Eh, pH conditions, proportions of detrital and authigenic constituents, post depositional and weathering changes and so on.

Influence of Environmental Chemical Parameters

The presence of intimate admixtures of carbonate-apatite with such minerals as pyrite, glauconite, opal and organic matter indicates the prevalence during phosphorite formation of at least mildly reducing conditions (cf. Krumbein and Garrels, 1952). However, carbonate-apatite formation is pH, not Eh, dependent and it is believed normally precipitated at about pH 7 to 7.8 (cf. Kazakov, 1937; Ames, 1959; Krumbein and Garrels, 1952; Gulbrandsen, 1969) therefore only the mineralogy of such elements as are Eh, pH controlled can be used to indicated the chemistry of the environment of deposition. Krauskopf (1967) suggests that only the nature of the mineral phases gives a satisfactory empirical measure of the redox potential.

Goldberg (1965) has stressed that the reduction of U^{6+} (the common form of U- complexes in seawater) to U^{4+} (the common form of U in phosphorites) requires a negative redox potential of -0.4 to -0.5 volts. Arrhenius (1963) implies that the low U content of Pacific seamount phosphorites (which are

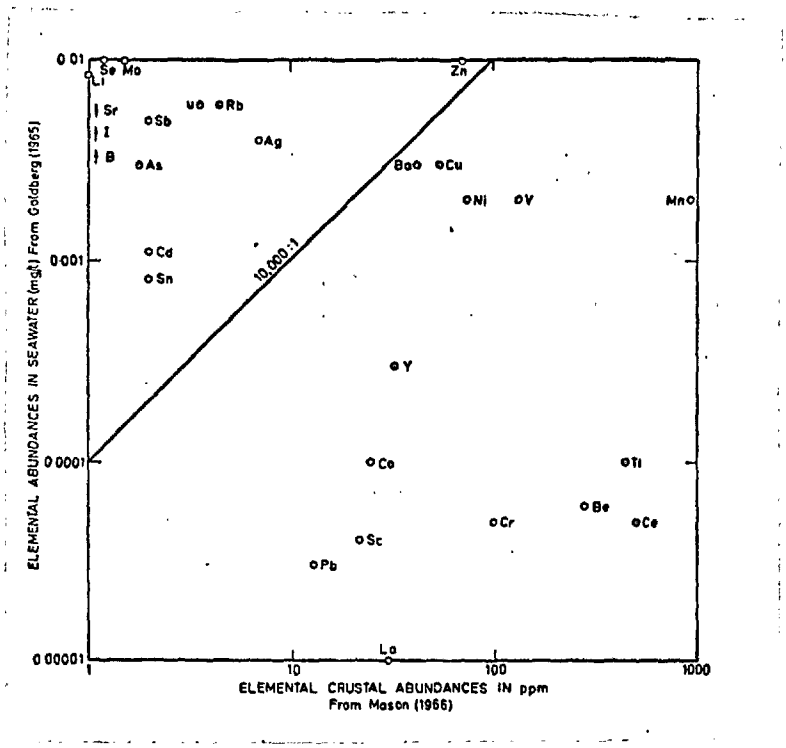


Fig.7.5.1.

Elemental abundances in sea water relative to crustal abundances; based on data given in table 7.1.1.: all values for Ag,Be are x100; for Cd,Ce are x10; for U are x2; for Ba,Ti are ÷ 10; for Li,Rb are ÷ 20; for Se are ÷ 400 :arrows represent direction of enrichment for elements highly concentrated in the sea.

often associated with Mn oxide minerals) reflects their formation under oxidising conditions. But, Manskaya and Drozdova (1968) show that the reduction of U^{6+} to U^{4+} can be accomplished by formation of organo-metallic complexes, regardless of the environmental Eh: this supports the arguments of Curtis (1966) that concentrations of U and certain other elements were Eh - independant functions related to the sorption of their organo-metallic complexes by organic material. Furthermore Cathcart (1968) shows U enrichment in U.S. Atlantic coastal plain phosphorites to reflect the degree of exposure of these sediments to seawater, U being particularly high in reworked sediments from presumably oxidising shallow water environments. Similarly, Altschuler et al (1956) find U in Florida phosphorites to be enhanced during weathering and leaching processes. Thus Uranium content need not be indicative of Eh conditions in the depositional environment but is more probably a function of kinetic rather than thermodynamic influences.

When Krauskopf (1956) suggested that Cr concentrations in reducing conditions were probably functions of the precipitation of insoluble hydroxide, the possibility that it might be concentrated by sorption of Cr-organic complexes onto organic matter was overlooked. Curtis's (1966) exposition of this problem implies that Cr does form organo-metallic complexes which may be concentrated in sediments by sorption processes under redox conditions different from those characterising ionic or anionic species of Cr.

Perhaps more pertinent evidence regarding environmental chemistry comes from comparison of elemental characteristics of phosphorites with those of manganese nodules which only form in highly oxidising environments. The relatively easily oxidised Ce is enriched relative to other rare earths in nodules (Goldberg, 1965; Glasby, 1970) whereas it is depleted relative to La in carbonate-apatite. Similarly Co is enriched relative to Ni in

highly oxidising environments (Goldberg, 1965); such enrichment does not characterise carbonate-apatites, which are also generally depleted in Mn another element normally concentrated in oxidising environments (cf. Gulbrandsen, 1966). Furthermore the enrichment of phosphorites in many minor elements requires that some significant concentration process be operative. Vine and Tourtelot (1970) and Brongersma-Sanders (1969) argue that for similar concentration in black shales, one process may be via the concentration and decay of large quantities of organic matter; marine life forms such as plankton are notably enriched in minor elements (Goldberg, 1961). Brooks, Presley and Kaplan (1968) have shown that in the region of maximal organic decay, immediately below the sediment water interface, there are notable enhancements in the metal contents of interstitial waters of marine sediments. Concentrations of organic matter, where ineffectively oxidised, may give rise to reducing conditions which would influence element dispersion; they would also give rise to metal rich interstitial waters and hence, possibly, to the elemental enrichments noted for phosphorites.

Concerning the Moroccan and other subsea phosphorites and phosphatic rocks, the restriction of pyrite and the local abundance of glauconite and iron oxides attest to mildly reducing or slightly oxidising conditions in the depositional environment. The relative metal concentrations being far less than in average phosphorites tends to suggest that conditions were sufficiently oxidising to prevent considerable organic and hence metal accumulations within the sediments. In this context, geochemical studies provide a useful supplement to mineralogical investigation.

In summary, the minor element assemblage of phosphorites appears influenced by the abundance (and hence supply rates) of different minerals, the abundance of suitable sorptive surfaces (in particular of organic matter) and the rate of supply, availability, and species of elements in solution

as well as the chemical characteristics of the environment. The influence of this last factor is most difficult to ascertain since the form in which the various elements originally occurred in sea- or interstitial water is but poorly known. At present it is probably more valid to say that the assemblage is very strongly kinetically controlled but that the rate of supply of elements may be indirectly correlated with the Eh, pH characteristics of the environment through the medium of organic matter and its decay.

CHAPTER 8

THE GENESIS OF PHOSPHORITES

8.1 Environment of Deposition

8.1.1 Subsea Phosphorites

Present day subsea phosphorites (table 8.1 and Fig. 8.1) are generally found (1) in depths less than 1000m on continental margins or offshore banks in regions where sedimentation is slow or negligible, and (2) they appear most concentrated in the middle latitudes along the western and often arid coasts of continents, in association with divergent upwelling from depths of 100 - 200m of phosphate-rich water which supports a rich organic life (cf. McKelvey, 1963, 1967; Brongersma-Sanders, 1957; Kazakov, 1937; Sheldon, 1964 a; Strakhov, 1960; MacPherson, 1945). The association with west-coast-continental divergent upwelling is not ubiquitous in that east coast phosphorites are widely known (table 8.1 and Fig. 8.1) and the extensive onshore U.S. Atlantic coastal plain Miocene phosphorites, for example, are an east coast phenomenon (cf. Cathcart, 1968). The significance of the apparent association between upwelling and subsea phosphorites is obscure since, paradoxically, although the impression has been given by McKelvey (1963) that most of these deposits are Recent, such is not the case (table 8.1). In many instances not only are the phosphorites themselves ancient but they have subsequently been coated with other authigenic minerals such as ferromanganese oxides or glauconite (cf. Murray and Renard, 1891; Pratt and Manheim, 1967; Norris, 1964; Summerhayes, 1967, 1969) showing that their present environments are not suited to phosphorite formation. Recent geochemical studies by Kolodny (1969) and Kolodny and Kaplan (1970) of the U234/238 disequilibrium ratios in selected seafloor phosphorites from the California Borderland, Baja-California, Agulhas Bank, Chatham Rise,

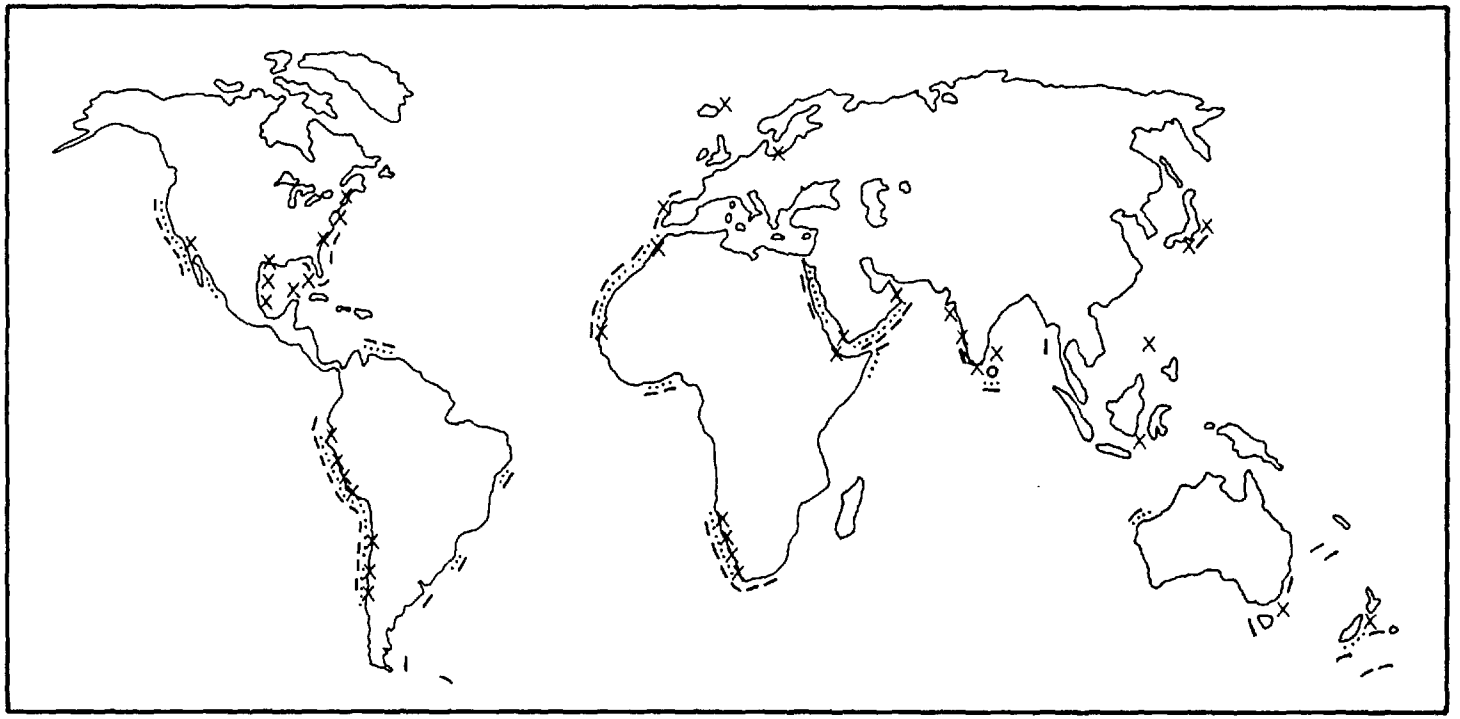


Fig.8.1. Distribution of phosphorite in relation to upwelling and associated phenomena (modified from Brongersma-Sanders, 1957, and McKelvey, 1967):-
..... = upwelling water; ----- = known subsea phosphorites; xxxx = recorded plankton concentrations (resulting in red-water), mass mortalities of fish and other creatures, or diatom ooze. Sources of geological information given in table 8.1.

Blake Plateau, the Tasmanian coast and a North Tasman guyot top show that all are older than 800,000 years, the limit of this radiometric dating technique. The North Tasman guyot phosphatic rocks (Menard, 1969) are found by the writer to be phosphatised corals presumably formed near sea-level. Phosphatisation has been followed by manganese mineral encrustation as at other sites showing, in agreement with the geochemical data, that the phosphatisation is not Recent; the dredging of Miocene and Pliocene foraminiferal oozes from nearby guyots (Connolly, 1969) suggests that phosphatisation was a Tertiary phenomenon. In addition to these previous studies, the present study confirms that there appears to be no interrelation between present day upwelling and the age or distribution of phosphorite off northwest Africa.

The limited evidence for contemporaneous formation of carbonate-apatite on the seafloor in specific areas is given (1) by d'Anglejan (1968), who found phosphatisation of Recent faunal remains at depth in one sediment core taken off the Californian coast; (2) by Baturin (1970, in press) who finds large scale carbonate-apatite formation in the organic rich sediments from the southwest African coast; (3) by Goldberg and Parker (1960) who found submarine phosphatisation of wood fragments to be occurring in the Gulf of Tehuantepec. Although there seems little doubt that phosphorite deposition and upwelling phenomena are in some instances closely related the restriction of geologically Recent phosphorite formation casts some doubt on the significance of the association.

8.1.2 Marine Phosphorites Now On Land

That the majority of marine phosphate deposits now on land are believed to have formed in moderately high energy shallow water environments is not a subject for dispute (cf. Cayeux, 1941; Visse, 1948; Rooney and Kerr, 1967; Gibson, 1967). Bushinsky (1966) and Gulbrandsen (1969) further argue that

the high content of apatite-bonded SO_4 in many phosphorites indicates enhanced salinity such as is found in lagoons; the argument that associations between dolomite and apatite in phosphorites also suggests lagoonal formation has been put forward by Rooney and Kerr (1967) and Strakhov (in Bushinsky, 1969, p. 158). For various reasons a lagoonal origin has been proposed in this study for the Moroccan offshore pelletal phosphorite deposits. By contrast, the glauconitic Moroccan offshore phosphorites appear to have formed on an open shelf and the incidence of Recent phosphorite in open shelf sediment off S.W. Africa (Baturin, 1970, in press), of Eocene lacustrine authigenic carbonate apatite deposits (Love, 1964) and of authigenic carbonate apatite deposits in Nile valley alluvium (Chumakov, 1967) militate against any generalisation being drawn regarding the environments appropriate to phosphorite formation.

It is generally agreed that the main requirement is a concentration of phosphate such that in a system such as the ocean - near saturated with $CaCO_3$ and apatite, the formation of apatite results in the solution becoming undersaturated with respect to $CaCO_3$ (cf. Gulbrandsen, 1969). The main source of phosphorus is thought by some (Kazakov, 1937; McKelvey, 1963, 1967; MacPherson, 1945 and others) to be coastal upwelling but Bushinsky (1964, 1966, 1969) and Pevear (1966, 1967) favour a predominantly estuarine type of environment in which phosphorus derives in considerable part from continental run-off.

That there is an association of phosphorite with features indicative of high biological productivity is undisputed. Organic matter, although usually in amounts less than 2%, is a ubiquitous associate of phosphorite; other commonly associated minerals are chert, pyrite and glauconite all of which tend to form in regions of high organic productivity where decaying organic matter gives rise, even if only locally, to reducing conditions. The formation

of phosphorites on a large scale in reducing environments is not likely in that oxidation of organic matter is a prerequisite to the release of phosphate; Gulbrandsen (1969) has argued that nearshore downwelling of oxygenated surface water is a prerequisite to the decomposition of seafloor accumulations of organic matter and the resultant accumulation of phosphate required for phosphorite formation. Other than the fact that most old phosphorites are of moderately shallow water origin and may derive their phosphate via some means of organic preconcentration there is no conclusive evidence in favour of marine upwelling as a dominant control on phosphorite formation (cf. Bushinsky, 1969).

3.1.3 Palaeoenvironmental Changes

The present northwest African shelf fulfils many of the criteria apparently requisite to phosphorite formation and was suitable for phosphorite formation during the upper Cretaceous, Eocene, Miocene and Lower Pliocene. The absence of Oligocene phosphorites is a reflection of the tectonism of this period but the question naturally arises why should there be none forming at present. Quaternary and Recent palaeogeography of the region appears very similar to the Mio-Pliocene palaeogeography (cf. Choubert and Marcais, 1962). Thus it seems unlikely that palaeogeographic changes, invoked elsewhere as factors influencing the occurrence of phosphorites (Salvan, 1957) and responsible for the different distribution patterns of the widespread Eocene and restricted Miocene Moroccan phosphorites, have caused the present environment to be unsuitable for phosphorite formation.

That changes in ocean basin circulation have occurred in the past is suggested by the history of the ocean basins; Le Pichon (1968) has shown that the Artic Basin must have been closed and the Straits of Gibralter much wider during the Eocene than since. As the Atlantic has opened and the Mediterranean closed, the oceanic circulation pattern has undoubtedly changed.

Such changes in addition to possible oceanic chemical changes related to seafloor spreading episodes have been invoked to explain the occurrence of widespread Eocene chert in the deep Atlantic (Peterson et al 1970). Although there is no such narrow time stratigraphic restriction on Atlantic phosphorites, the possibility that the widespread Cretaco-Eocene phosphorites around North Africa may have received, indirectly via enhanced ocean productivity, some boost in phosphorus from oceanic volcanic sources cannot be entirely ruled out. Equally, as Salvan (1957) suggests, the widespread nature of these deposits may be more a reflection of locally ideal palaeogeographic conditions.

Associations between periods of phosphorite formation and periods of volcanism have been postulated by Ronov and Korzina (1960), Mansfield (1940), Rooney and Kerr (1967) and Gibson (1967). Volcanic activity is undoubtedly a source of phosphorus in seawater (cf. Buljan, 1955) but Bushinsky (1966, 1969) and Cathcart (1968) find there to be no satisfactory direct evidence for a genetic relationship between specific phosphate formations and volcanism; Bushinsky (1969) further points out that the local concentration of phosphorites at certain periods in the geological record is more probably a function of sampling than volcanism. Nevertheless, the possibility that volcanically induced oceanic chemical changes do have a long term effect particularly on biogenic sedimentary components has been pointed out by Nicholls (1965) and would also be expected to be reflected in phosphorite accumulations.

In view of the decrease of apatite solubility with rising temperature (cf. Kramer, 1964; Valashko et al, 1968) it has been suggested (Summerhayes, 1967, 1969; Kolodny and Kaplan, 1970) that apatite precipitation may have been more widespread from the warm seas of the Tertiary in which temperatures were possibly some 10 degrees higher than at present (cf. Arrhenius, 1963).

This might explain the fossil nature of the phosphorite. However, the occurrence of present day phosphorite formation on the S.W. African shelf shows that other factors may be of equal or greater importance than oceanic temperature changes.

In summary, the fossil nature of most subsea phosphorites is taken to indicate widespread environmental changes detrimental to the large scale formation of phosphorite at present. Temperature, current, geographic, and possibly oceanic chemical changes appear responsible for this state of affairs: it is not possible with any confidence to decide which is the most important.

8.2 Mechanics of Formation

The considerable controversy concerning the mechanisms of phosphorite formation is due to the fact that (1) present day formation on any large scale has only just been discovered (Baturin, 1970, in press) and as a consequence even the nature of the initially precipitated phase is not accurately known although it seems to be a gel, and, partly as a result, (2) the absolute degree of saturation of the sea with appropriate calcium phosphate species cannot yet be determined (cf. Pytcowicz and Kester, 1967).

In principal the major theories polarise into those favouring direct inorganic precipitation or phosphatisation from seawater and those favouring a biogenic-diagenetic origin.

8.2.1 Inorganic Precipitation

The purely inorganic precipitation thesis derives from two main observations: (1) that the majority of phosphorites in the geological record are composed dominantly of structureless pellets (or nodules) some of which have an accretionary aspect, and (2) because from experimental and theoretical

work various investigators have found evidence to suggest the near saturation of seawater with some form of calcium phosphate (cf. Kazakov, 1937; Dietz, Emery and Shepard, 1942; Smirnov, Ivnitskaya and Zalavina, 1958; Sillen, 1961; Kramer, 1964, 1966; McConnell, 1965; Roberson, 1966; Pytcowicz and Kester, 1967; Gulbrandsen, 1969). McConnell (1965, 1970) and Bushinsky, (1969) criticise much of the earlier work for, among other things, not considering in calculations of the solubility products of calcium phosphate species the true nature of the precipitated phase, and it appears that only Kramer (1966) McConnell (1965) and Roberson (1966) infer that the bulk of seawater is near saturated with carbonate-apatite, a situation appropriate for phosphorite formation. That some direct precipitation does occur is evinced by the presence of apatite encrustations on other minerals (Altschuler, 1965; d'Anglejan, 1967). Furthermore synthesis of carbonate-apatite by precipitation has been carried out (Simpson, 1964; Legeros, 1965; Legeros et al, 1968; McConnell, Frajola and Deamer, 1961) showing that such a process is feasible in the natural environment. Whether it occurs on any notable scale remains to be seen. With regard to the structureless pellets, another school of thought argues that they are of replacement or mechanical origin and not functions of direct precipitation (Cayeux, 1941; Salvan, 1952; Visse, 1948; Bushinsky, 1964, 1966, 1969, and others).

The popularly suggested mechanism for direct inorganic precipitation, modelled on Kazakov's (1937) work is that the ascent of phosphate-rich water in regions of upwelling is associated with a decrease in partial pressure of CO_2 and a consequent pH increase resulting in phosphorite supersaturation and precipitation of carbonate-apatite (cf. MacPherson, 1945; McKelvey, Swanson and Sheldon, 1953; McKelvey et al, 1959; McKelvey, 1963; Kramer, 1964; Roberson, 1966; Gulbrandsen, 1969). Inorganic colloidal precipitation of apatites is also favoured by Dietz, Emery and Shepard (1942)

and Emery (1960). Below pH of about 7.8, apatite only will precipitate, but above this pH, where seawater is saturated with calcite and apatite, both will precipitate unless there is excess phosphate present such that apatite precipitation results in the solution becoming unsaturated with respect to $CaCO_3$ (cf. Gulbrandsen, 1969).

The inorganic precipitation thesis relies on inadequate chemical data regarding the nature and concentration of dissolved phosphate species and the nature of the precipitated phosphate phase. It also relies on an interpretation of the origin of structureless pellets which is open to question. Furthermore, Bushinsky (1964, 1966, 1969) argues that the precipitation of carbonate-apatite, necessarily as a gel in the first instance, would prevent its accumulation in the agitated waters which must have characterised zones of pellet accumulation. In the present study direct precipitation of apatite from seawater was not found to be of the least importance as far as the origin of offshore northwest African phosphorites was concerned.

8.2.2 Inorganic Replacement

Murray and Renard (1891) were among the first to note the pseudomorphing of calcareous skeletal material by apatite on the seafloor; subsequent reports of phosphatised calcareous material and rocks are widespread (d'Anglejan, 1968; Dietz, Emery and Shepard, 1942; Hamilton, 1956; Hutchinson, 1950; Summerhayes, 1967, 1969). Phosphatised siliceous skeletal remains are also recognised (Carozzi, 1960; Baturin, 1970, in press) and Goldberg and Parker (1960) have found phosphatised wood fragments. Replacement of coprolites is widely reported (Cayeux, 1941; Bushinsky, 1964, 1966, 1969). The experimental conversion of calcite to carbonate-apatite has been achieved by Ames (1959) and Simpson (1964) among others, and it has been suggested for example by Pevear (1966, 1967) that this is the only

suitable mode of origin of phosphorites on a large scale. Certainly in the present work the evidence seems weighted in favour of replacement of calcareous rocks and sediments as the prime origin of Moroccan offshore phosphorite. The question remains as to whether, in the role of concentrators of phosphate in marine sediments, organisms have a significant role to play.

8.2.3 Role of Organisms

It is widely known (Rittenberg, Emery and Orr, 1955; Kaplan and Rittenberg, 1963; Rochford, 1951; Seshappa, 1953; Brooks, Presley and Kaplan, 1968; Bushinsky, 1969) that due to decay and dissolution of trapped organic matter the phosphate content of interstitial sediment water is higher than in the overlying water by one or more orders of magnitude (Bushinsky, 1966, quotes values 50 - 100 times higher than seawater). Undoubtedly such conditions are more favourable to the diagenetic formation of authigenic carbonate-apatite than are those in seawater. Even though the resulting concentration of phosphate may still be lower than theoretically required for the precipitation of carbonate-apatite, Baturin (1970, in press) proposes that diffusion mechanisms within the sediments may establish concentration gradients about nucleation centres and thus give rise to carbonate-apatite precipitation and, ultimately, phosphorite formation.

The aforementioned association of phosphorite with organic matter strongly suggests to some that organisms are the main source of phosphorite phosphorus. They propose that organic decay and dissolution provides the main means whereby phosphate precipitation or phosphatisation of other material can be effected (cf. Murray and Renard, 1891; Cayeux, 1941; d'Anglejan, 1967; Bushinsky, 1966, 1969; Gulbrandsen, 1969). The present data strongly suggest that this may account for the homogenous phosphatisation of many offshore Moroccan samples, particularly foraminiferal limestones. But, in

those cases where erosion surface, pebble margin or burrow wall phosphatisation is concerned it appears to be the degree of exposure to seawater which is critical. In these cases the concentration of phosphate immediately beneath the sediment -water interface implies the operation of a diffusion mechanism whereby phosphate is continually supplied from the overlying water to the sediment. In spite of the above suggestions regarding organic concentration there is no visible evidence to support the influence of organic material on this non-uniform process of phosphatisation. In fact in coprolites where some organic concentration of phosphate might be expected there is no enhancement of phosphate over that observed in the generally poorly phosphatised matrix of the samples.

8.3 Summary

The prime requisites for phosphorite formation appear to be shallow water, a warm arid climate with slow or negligible detrital sedimentation, a moderately alkaline pH (7.0 - 7.8) and in particular an adequate supply of phosphate over the amount that can be held in solution (cf. Gulbrandsen, 1969). Although special environments such as estuaries, lagoons or shallow shelves in upwelling regions are invoked as prerequisites by different investigators, there seems to be no specifically characteristic site of formation. It seems most likely that concentration of phosphate in interstitial sediment water and in overlying seawater by dissolution of organisms is a major direct source of phosphorite phosphate. Direct inorganic precipitation of apatite from seawater does not seem to be of major importance but the inorganic phosphatisation of rock and sediment in prolonged contact with circulating phosphate-rich seawater may be an important source of phosphorites. Diagenetic carbonate-apatite formation may proceed within the sediments either by direct precipitation or by phosphatisation of pre-existing material; diffusion mechanisms and concentration gradients may play

an important part in these processes, and in the migration of phosphate from bottom waters into the sediment.

The rate of decay of sinking organic remains in the sea places a constraint on the depths at which maximal sediment phosphate accumulation can occur via the medium of organic concentration; optimal depths appear to be rather less than 200m. A further constraint is that circulation of oxygenated water must be sufficient to oxidise (decay) much of the dead organic material in order to release PO_4; nearshore downwelling has been proposed as a suitable mechanism (Gulbrandsen, 1969).

The formation of pelletal deposits appears a function of mechanical shallow water concentration of material derived from some nearby quiet water region (lagoon, open shelf etc.) where phosphate is diagenetically accumulating.

Finally, with regard to the apparent scarcity of present day subsea phosphorite formation it appears that minor palaeogeographic, palaeo-oceanographic and palaeo-climatic changes since the Tertiary are probably responsible; to invoke only temperature changes does not entirely solve the problem and each deposit should in fact be considered on its own merits. In the case of the northwest African deposits considered in this thesis, combinations of ocean current and palaeographic changes account for the difference between earlier and later Tertiary, while the Quaternary-Recent global temperature drop may significantly have affected phosphorite formation.

CHAPTER 9

MINERAL EXPLORATION AND CALCULATION OF RESERVES

9.1 Phosphorite Prospecting Using a Scintillation Counter

9.1.1 Introduction

It is generally accepted (cf. Overall, 1968, b; and 'Mining', 1968, an annual review published by the Mining Journal, London) that land phosphate reserves can satisfy demand at least until the year 2000. It is also accepted that at some stage in the future, subsea phosphorites will be mined (cf. Mero, 1965; Overall, 1968, a, b; Tooms, 1967, a, b) but the discovery and proving of such deposits using traditional oceanographic sampling techniques is slow and expensive. The possibility has therefore been investigated in this project of detecting such deposits through the location of anomalous seafloor radioactivity resulting from the high uranium content of many phosphorites. Phosphorites outcropping on land normally contain between 0.005 and 0.02 per cent uranium (McKelvey and Nelson, 1950; Davidson and Atkin, 1953; Sheldon, 1959) compared to averages of 0.0004, 0.00005 and 0.0002 per cent for shales, sandstones and carbonates respectively (Turekian and Wedepohl, 1961).

The application of radiation measurements to phosphorite prospecting on land has included gamma-ray logging in Turkey (Sheldon, 1964 b), North Carolina and the Spanish Sahara (Notholt, 1967) and ground and aerial scintillation surveys in Africa (Bollo and Jaquemin, 1963), the U.S.A. (Moxham, 1954) and Turkey (Sheldon, 1964 b). No attempts appear to have been made to apply the same techniques at sea where the use of submersible scintillation counters has largely been restricted to the study of sediment movement (Courtois, 1966; Hazelhoff-Roelfzema, 1968; Smith and Parsons, 1967).

In this chapter are described the results of an investigation, suggested by the writer, into the use of scintillation counters in the detection of subsea phosphate deposits off Morocco: a part of this work, covering a survey of parts of the seafloor north of Safi, has been described by Nutter (1969).

9.1.2 Detection Equipment

The instrument used (Fig. 9.1), provided by the Wantage Research Laboratory of the United Kingdom Atomic Energy Authority, was a conventional sodium iodide scintillation counter housed, together with a high tension supply, in a sealed cylindrical container. A conventional N.I.O.-type pinger, fixed some six feet above the counter allowed the depth to be monitored as the equipment was lowered to the seafloor. Measurements of natural seafloor radioactivity were made on the seafloor with the ship hove-to. Electrical impulses were relayed to the ship through a one-quarter inch diameter waterproofed and armoured cable on which the counter was lowered. Radiation levels were recorded on a battery operated ratemeter to which a monitor dial was attached to allow readings to be made on deck. The counter stability was checked between stations using a ^{60}Co source. Seafloor counts were measured over a period of two minutes before, or more generally, after dredge, grab and core stations.

During the initial reconnaissance cruise on R.R.S. 'John Murray' in 1968, radiation measurements were made by Dr. B.H. Hazelhoff-Roelfzema in the ship's laboratory by surrounding the counter with a unit amount of either wet, unground sediment or dry rock fragments the size of small pebbles, placed in a makeshift container. Subsequently, during the 1969 cruise, a thick aluminium casing with three-quarter inch walls capable of withstanding pressures at depths down to 1000 metres was provided enabling subsea determination to be made by the writer and colleagues.

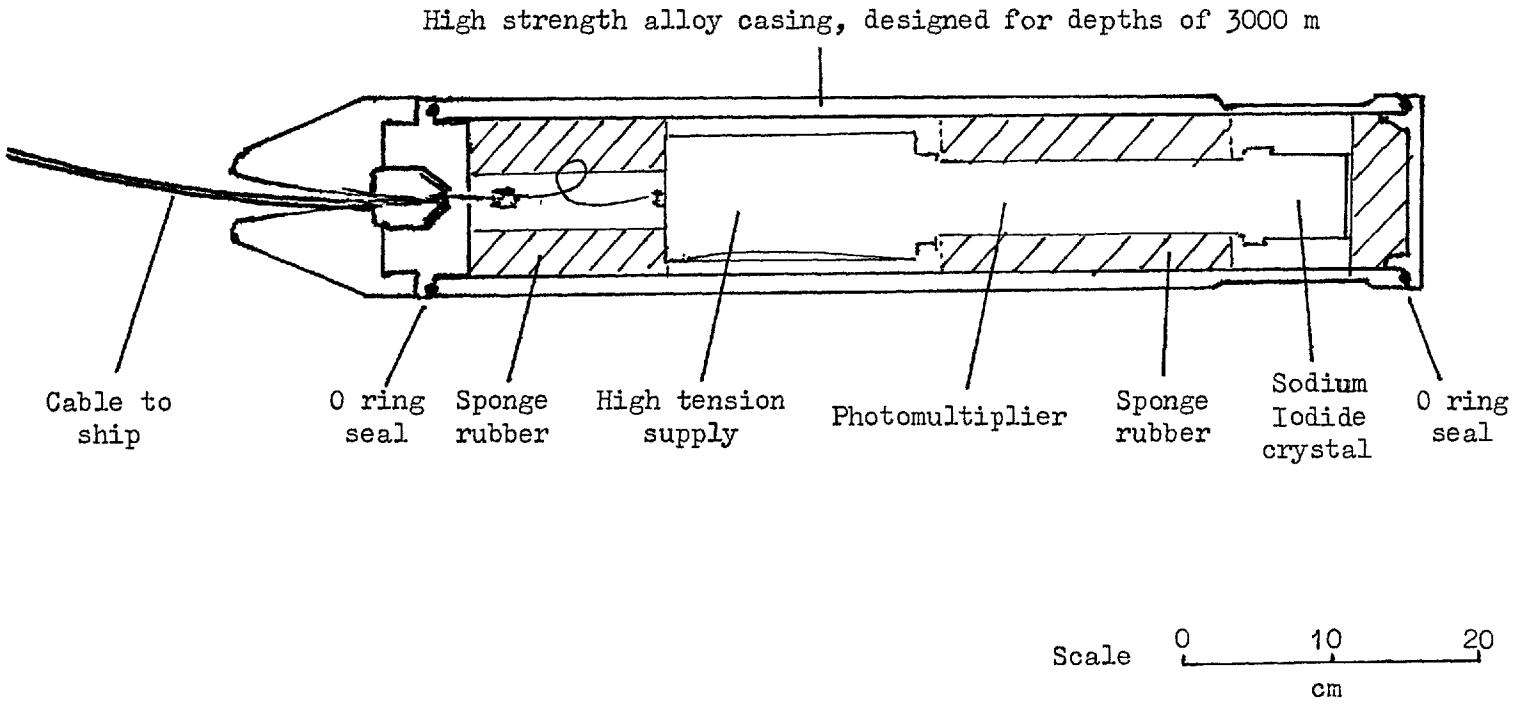


Fig.9.1. Submersible scintillation detector

In order to identify the radioactive component of the phosphorite, selected rock and sediment samples were examined by Mr. D.B. Smith at the Wantage Research Laboratory using a two-inch diameter sodium iodide crystal and 100 channel pulse height analyser. The complex spectrum was then compared with that of uranium to establish whether this was the principal source of radioactivity in the specimen.

9.1.3 Results:

9.1.3(a) Laboratory Radiation Determinations

The initial survey was carried out on samples from the three 1968 reconnaissance traverses between Agadir and Rabat. Both shipboard and laboratory radiation measurements on selected rock and sediment samples demonstrated that radiation increased with increasing phosphate content (table 9.1: Figs. 9.2 and 9.3). The laboratory radiation determinations, made by D.B. Smith of U.K.A.E.A. on samples of dry sand sized material, differ by an order of magnitude or more from shipboard determinations both because of the differing environmental and geometric conditions of measurement, and the difference in sample preparation (Smith, pers. comm.).

Gamma spectrum analyses (undertaken by D.B. Smith of the Wantage Research Laboratory, U.K.A.E.A.) of selected samples show that high radiation levels are due to uranium and its decay products (Fig. 9.4). This was confirmed by the close correlation between the sample spectra and that of a sample of pitchblende. The most active sample (136R) is found to contain approximately 0.06 per cent uranium. Independent confirmation that the samples contain substantial amounts of uranium is provided by mass spectrometric analysis of carbonate apatites separated from samples 139 and 148 which contain 0.004 and 0.014 per cent uranium respectively, and only very small amounts of thorium (Chapter 7). Samples containing less than 1.0 per cent P_2O_5 show some background scatter of radiation which is due to low uranium content

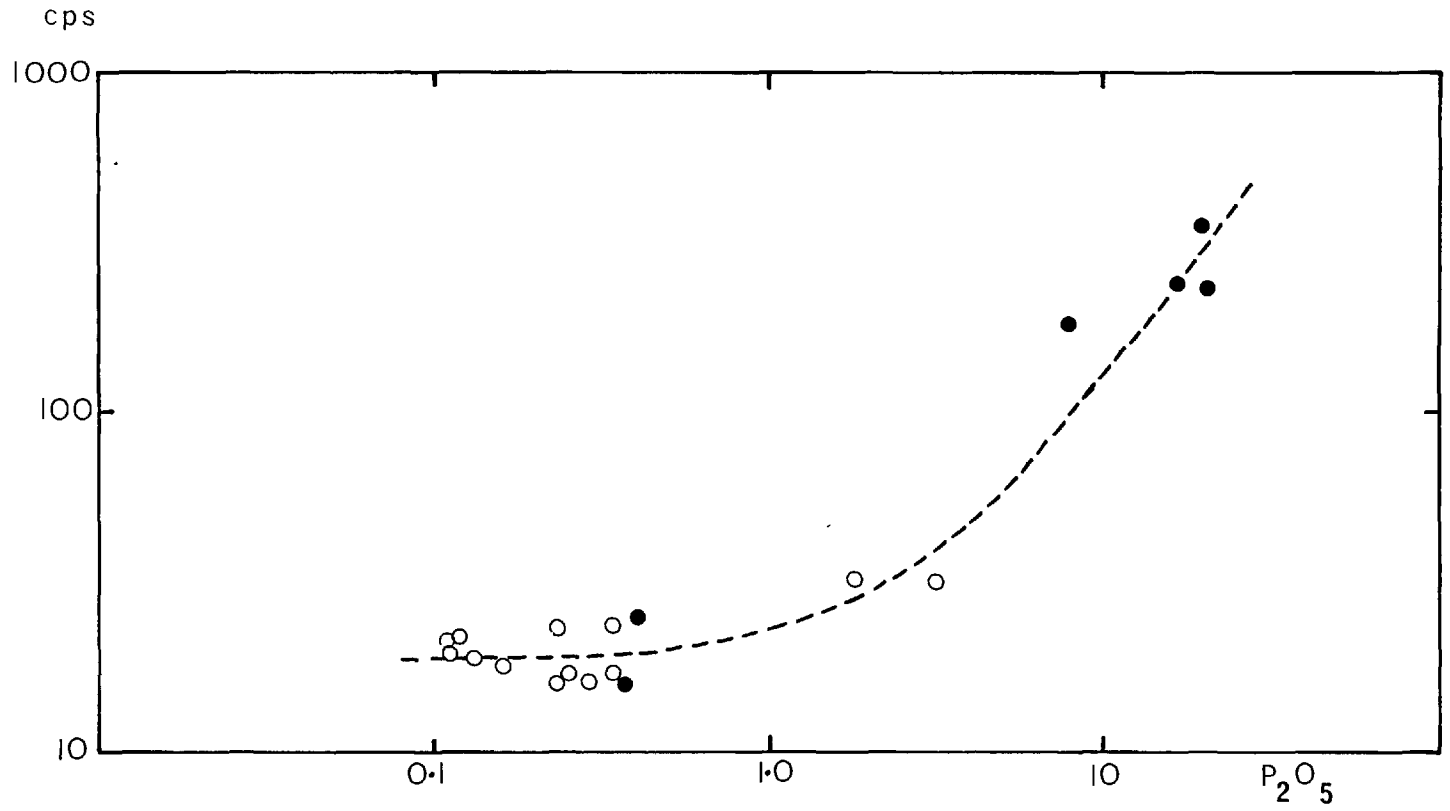


Fig.9.2. Radiation levels (determined on ship by Hazelhoff-Roelfzema) vs % P_2O_5 content (determined by the writer). Rock samples = closed circles; sediments = open circles; data from table 9.1.

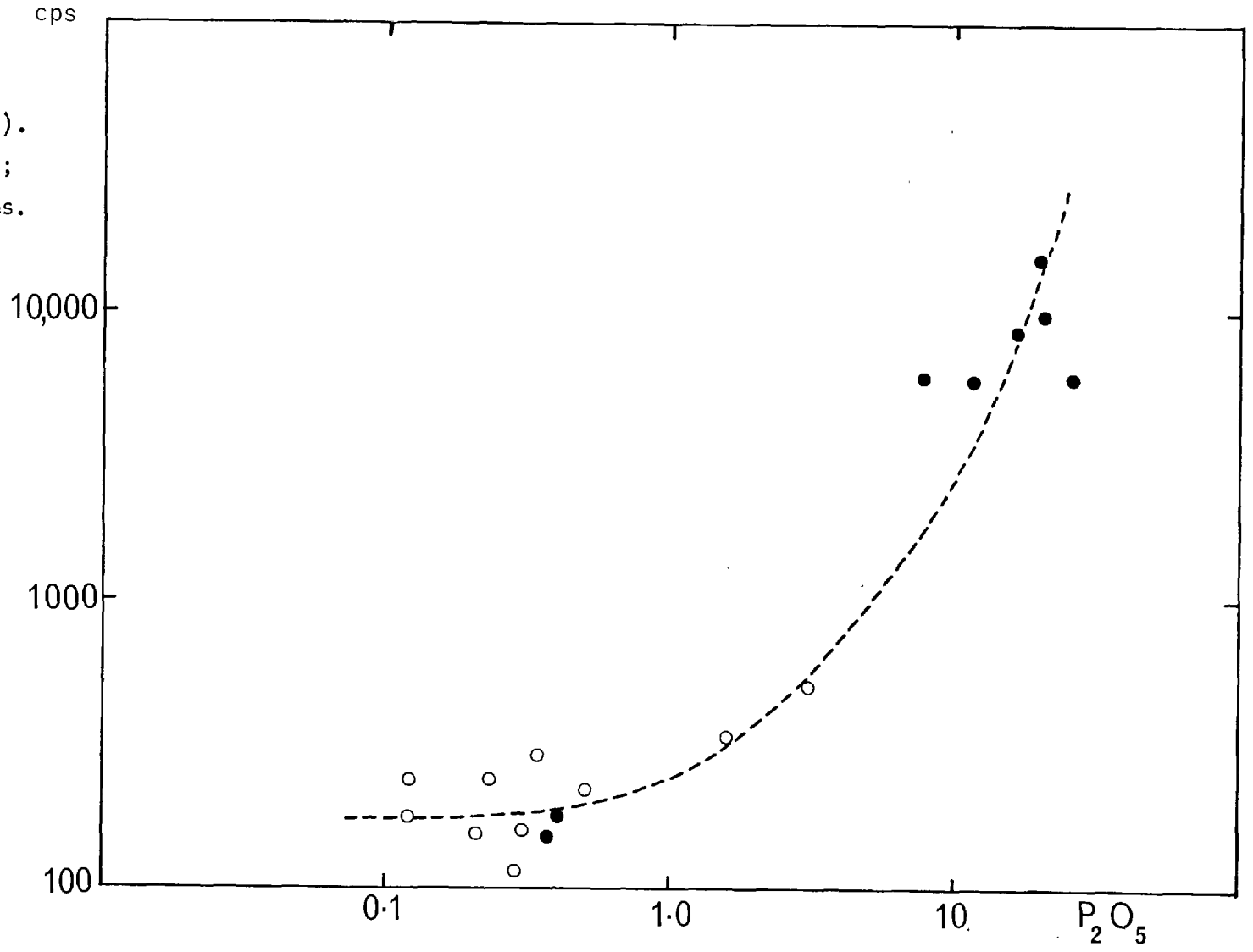
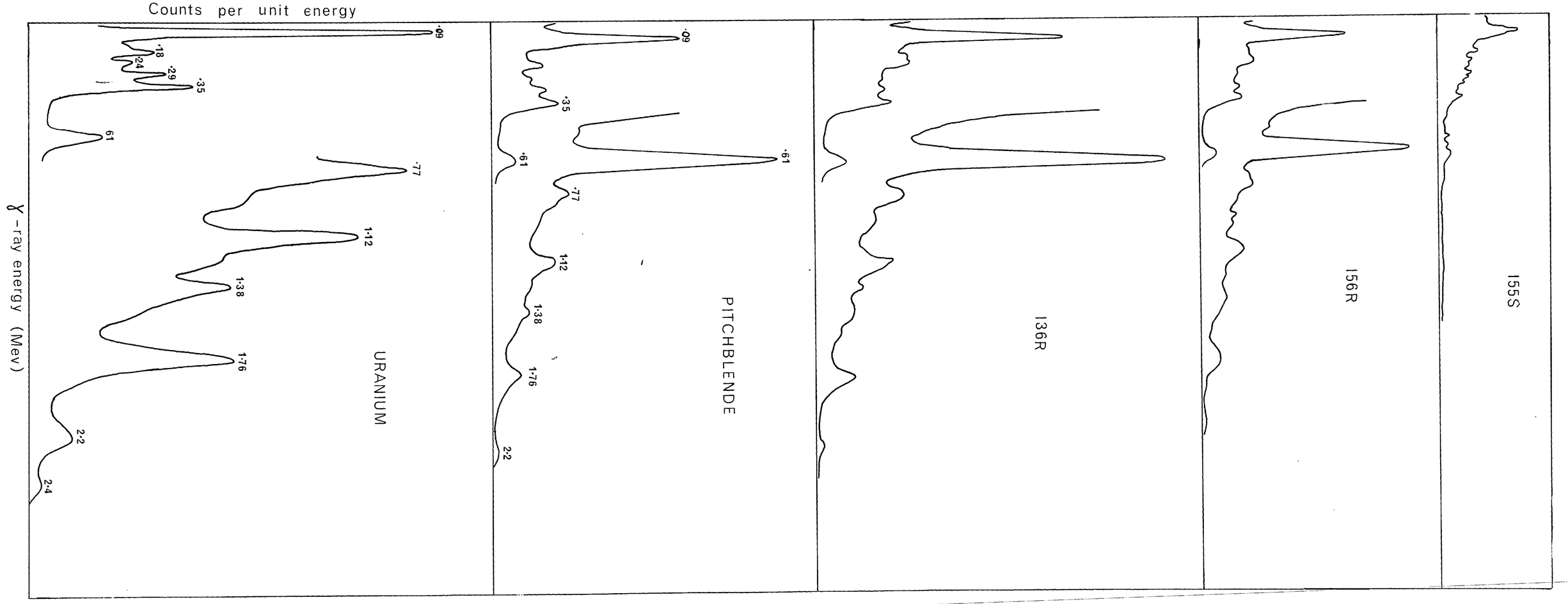


Fig.9.3. Radiation levels vs.% P_2O_5 (data from table 9.1). Rock samples = closed circles ; Sediment samples = open circles.

Fig.9.4. Gamma spectra of selected rock and sediment samples, compared with control spectra of uranium and pitchblende ore samples. Data from D.B.Smith (U.K.A.E.A.).



as shown by a spectrum of sediment sample 155 (Fig. 9.4). The interrelation between radiation levels and phosphate content is therefore probably governed by the increasing abundance of uranium with increased phosphate. Considering the sample spread it seems that this effect is not geographically restricted.

9.1.3(b) Subsea Data

During the 1969 follow-up cruise of the R.R.S. 'John Murray' subsea prospecting was carried out for the first time. With a counter of the type employed, the geometric relation between counter and seafloor must vary from site to site as the counter will probably sink into mud, be partly submerged, or lie on the surface of sand, and may not be wholly in contact with rock outcrops. The attenuation of radiation by seawater absorption will vary in these three cases. Other variations can be introduced by the difference in gamma activity caused by sediment density changes, the amount of material, and thus the radiation emmitted per unit volume being different for wet mud, sand and rock. The results presented here are thus semi-quantitative.

Seabed radioactivity was generally determined after sampling operations. The sediment at all the counting sites contained less than 2.0 per cent P_2O_5. The radiation levels are more or less normally distributed, being concentrated between 10 and 20 counts per sec, and very slightly skewed toward high levels (Fig. 9.5). Two radiation determinations are completely anomalous with respect to the rest. One is from a dredge site at which phosphorite rock was obtained, and the other is within one mile of a recorded phosphorite outcrop. However, at eight other sites, in whose general vicinity phosphorites had been dredged, radiation levels do not differ significantly from the general background, being scattered between 9 and 42 counts per second.

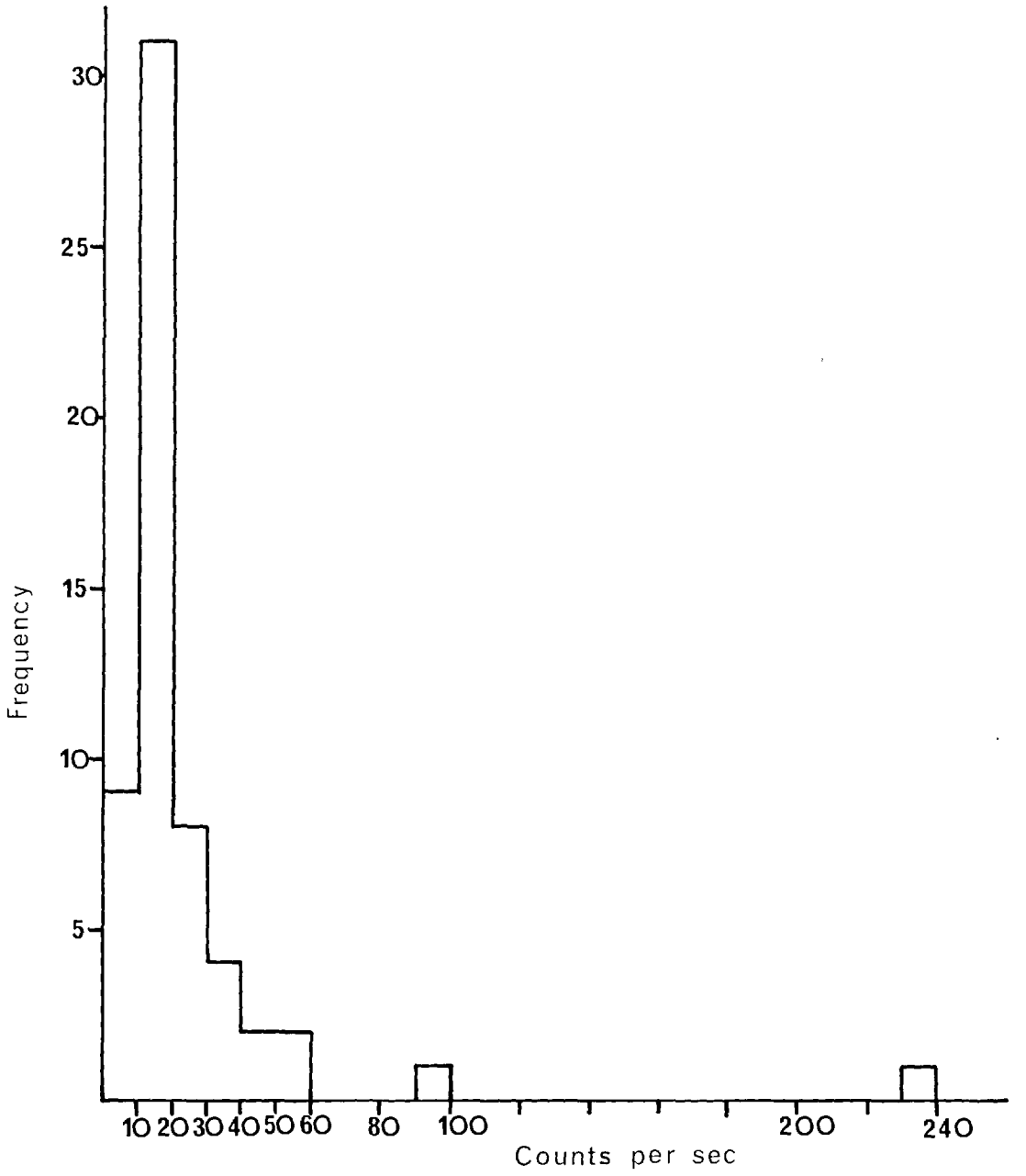
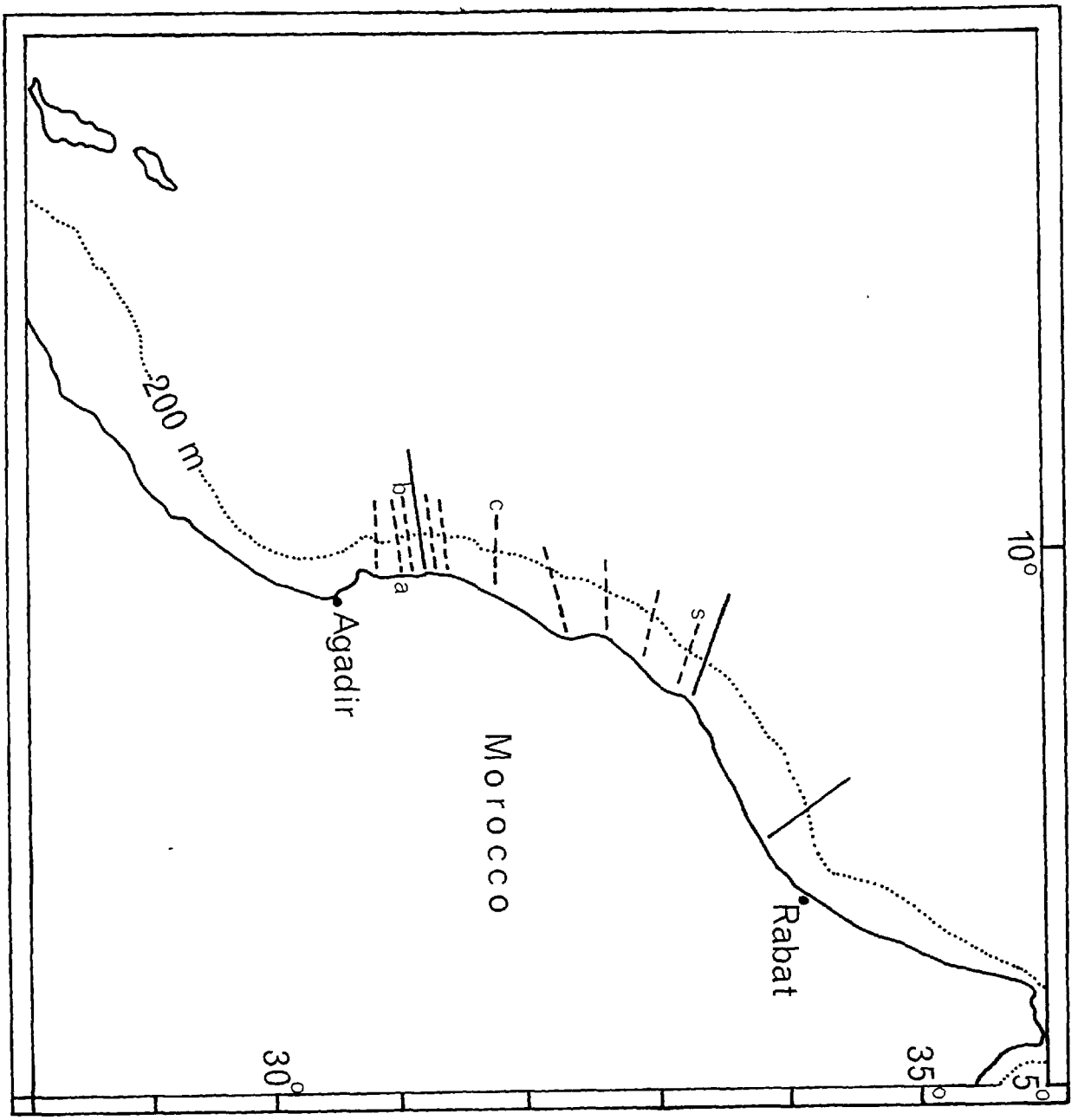


Fig.9.5. Frequency distribution of seabed radiation from 1969 traverses shown in Fig.9.6.a., with the exception of data from the detailed traverse 's', which is displayed in Fig.9.8.

The complexity of interrelation between radiation level and phosphate content introduced by the prospecting method used is illustrated by the results for three traverses across the continental shelf and upper continental slope (Fig. 9.6). In Fig. 9.6b.a some degree of correlation is observed between changes in radiation level and changes in sediment phosphate content. Similarly in Fig. 9.6b.b the general background radiation levels of less than 30 counts per sec correlate reasonably well with phosphate. However, the very high counts are considerably higher than could have been expected from the phosphate content of the sediment at dredge station 848, or even the overlapping station 847. It is considered probable that this high radiation is due to phosphatic rock outcrops, phosphorite rock having been recovered in dredge haul 848. These results do illustrate the difficulties of correlating point counts with dredge stations. This lack of correlation is even more marked on Fig. 9.6b.c.

If the radiation counts are compared with locations where rock phosphorites were dredged, correlation is essentially non-existent, only the phosphate at station 848 being associated with a high radiation count. This surprisingly poor correlation, considering the laboratory results, is almost certainly due to the fact that counting was done after the sampling operations. At dredge stations the counting was normally carried out .1 to .3ml from the location from which phosphatic rocks were dredged. Even at grab or core sites (i.e. sediment, but not rock stations) the radiation measurement may be, due to drift, many metres or even hundreds of metres from where the sediment was collected. Ideally, detailed counting should have been undertaken on a reverse traverse across the phosphorites, and it is intended to allow time for this operation on a future cruise. The lack of correlation between phosphate outcrop and counts does indicate that there are rapid changes in lithofacies or that local burial by sediment obscures the occurrence of outcropping phosphorite within distances of as little as 0.1 miles

Fig.9.6.9. General research area, showing traverses along which radiation determinations were made in 1968 (solid line) and 1969 (dashed line). Subscripts a,b, and c refer to traverses shown in Fig.9.6.b.; subscript s refers to the traverse shown in Figs.9.7. and 9.8.



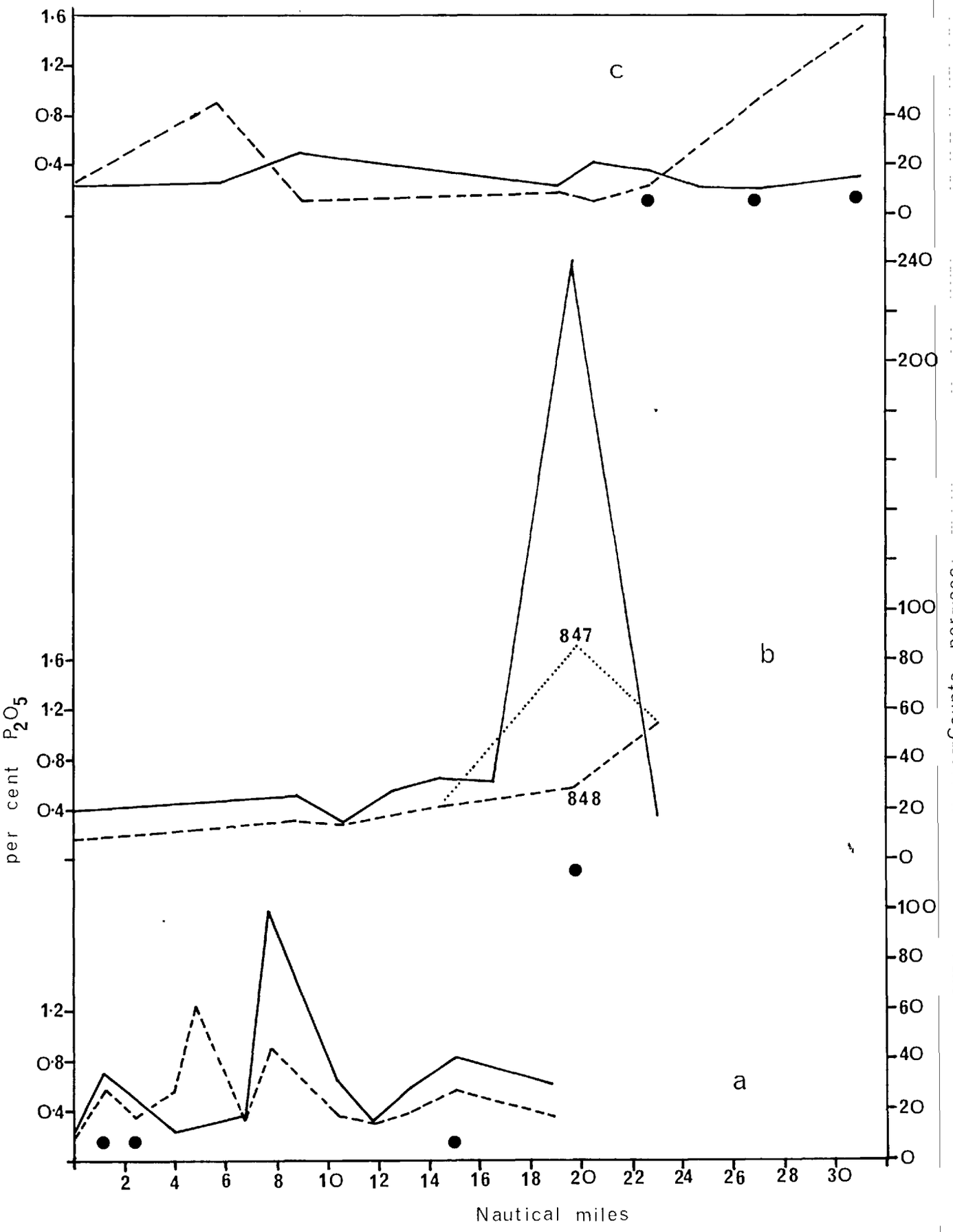


Fig.9.6.b. Phosphate (dashed line) and radiation (heavy line) levels along traverses a, b, and c (cf.Fig.9.6.a.); phosphorite rock dredgings are solid dots.

from the dredged outcrop. In practice it has been demonstrated that this is the case (cf. Chapter 5); the outcropping phosphorites are interbedded with limestones and mudstones and patchily overlain by a thin veneer of recent sediment which may, or may not, be phosphatic.

In addition to the above traverses, radiation determinations were made at approximately half-mile intervals along a previously sampled traverse on which both phosphorite and phosphatic sediment had been obtained (Fig. 9.7). This detailed close-spaced point counting survey described by Nutter (1969) showed (Fig. 9.8) that a general background radiation level of about 15 counts per sec corresponded to a background phosphate level of about 0.3 per cent P_2O_5, and that values above this level, although only between 20 - 40 counts per sec, correlated closely with a zone in which phosphate levels rose to 0.5 - 0.8 per cent P_2O_5. Two isolated radiation peaks occur seaward of the main phosphatic sediment zone and do not appear to correlate either with phosphate in the sediment or with the outcrop of phosphorite. These peaks may represent nearby restricted outcrops of phosphorite protruding through, or just buried, by the thin veneer of recent and virtually non phosphatic sediment. Phosphorites were dredged on this traverse, but since radiation levels do not exceed 35 counts per sec, it seems unlikely that they were detected by the counter which suggests that the area of outcrop is not widespread. It should be noted that the counting traverse and sampling traverse do not exactly coincide, although since both outcrop strike and the strike of sediment zones are parallel to the coast, similar characteristics are to be expected at similar distances from the coast on such closely adjacent traverses.

9.1.3.c Summary

Although further trials need to be carried out the present reconnaissance data show that a submersible scintillation counter can be used to locate

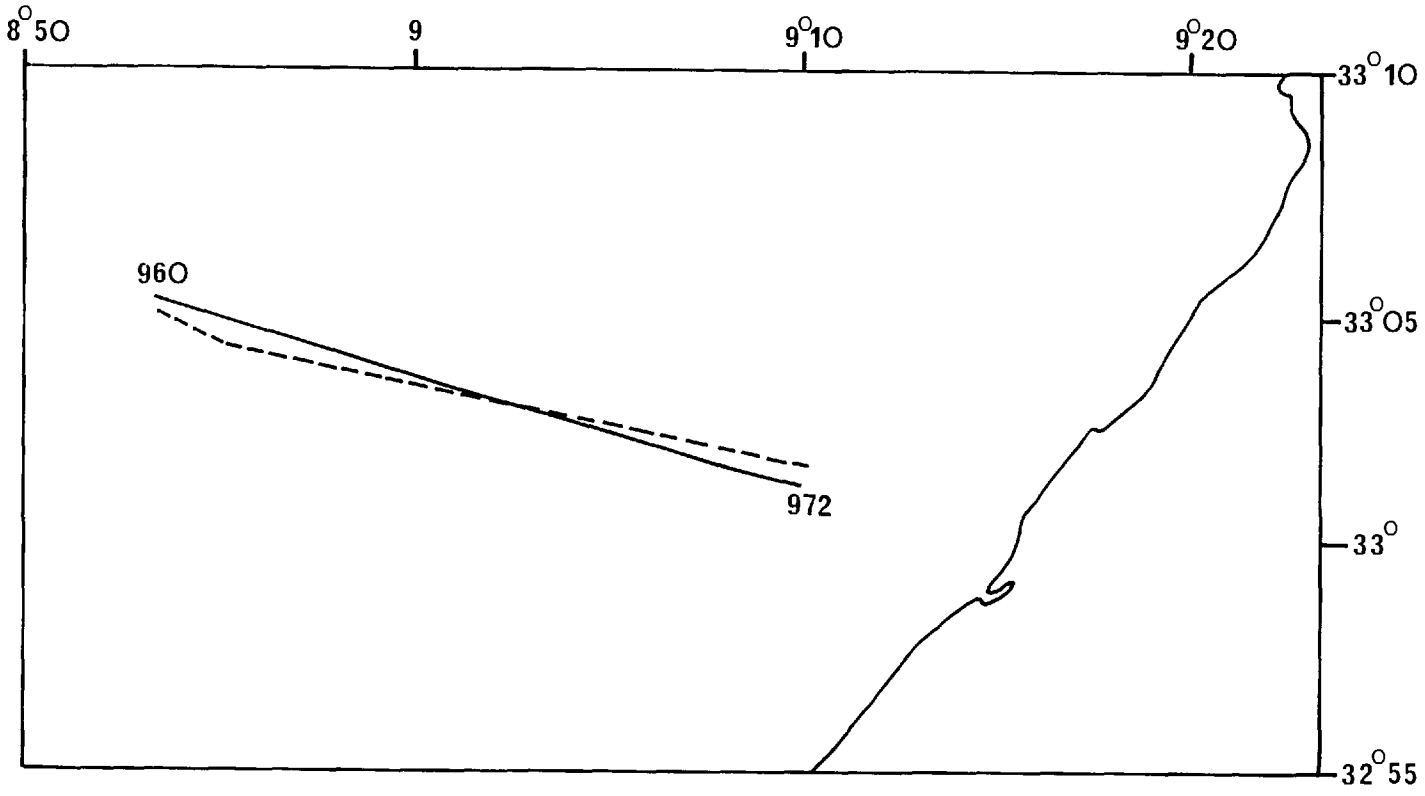


Fig.9.7. Location of sampled traverse 's' (shown in Fig.9.6.a) between sample sites 960 and 972, in relation to a later close-spaced point counting subsea radiation survey represented by the dashed line.

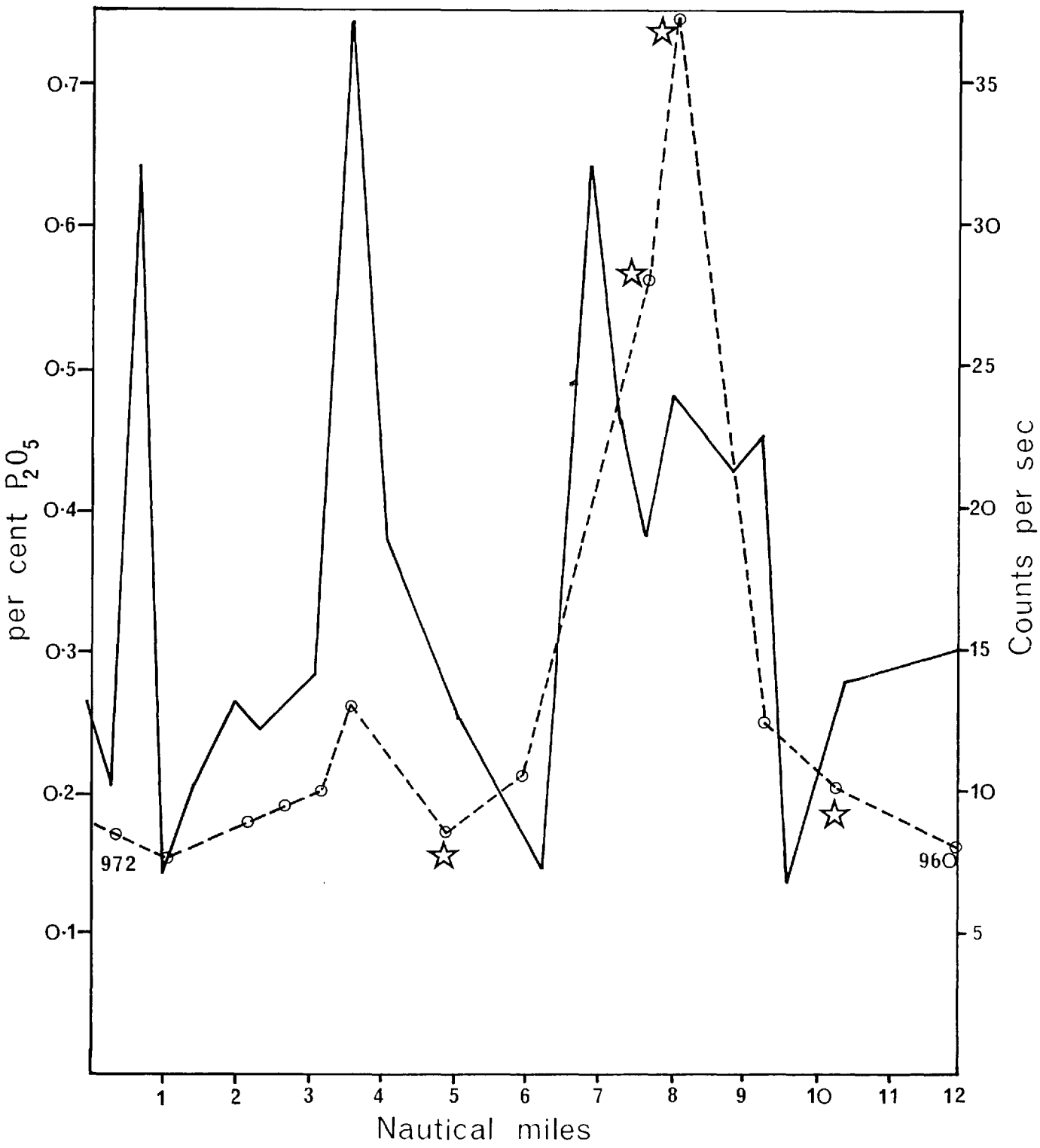


Fig.9.8. Phosphate (dashed line) and radiation (solid line) levels from the two complementary traverses shown in Fig.9.7. and designated s in Fig.9.6.a. dredge hauls of phosphorite are shown by star symbols.

subsea deposits of phosphorite and this promises to be the most useful method yet used to prospect rapidly for such deposits. Trials show that the blanketing of phosphorite outcrops by recent non-phosphatic sediment, and the interbedding of phosphorite with relatively non-phosphatic, non-uraniferous sedimentary rocks, necessitate continuous profiling techniques for the best results. Experiment shows, however, that close-spaced point counting techniques can be used satisfactorily in areas such as that investigated where the incidence of rock outcrop militates against use of a towed instrument due to the liklihood of snagging and loss of equipment. From the bulk of radiation determinations at randomly selected sites, it seems that there is sufficient radiation from rocks and sediments containing more than 2.0 per cent P_2O_5 to regard this as a threshold in the detection of seafloor phosphorites. That deposits with so little phosphate can be adequately detected by such a remote sensing method instead of by slow conventional methods involving the collection and shipboard chemical analysis of samples, makes the scintillation counter a prospecting tool of considerable interest. Such remote-sensing techniques could be used rapidly and effectively to determine the occurrence and distribution of phosphate off the coasts of developing countries with agricultural economies and no fertiliser resources. However, it should be emphasised that further work is required on developing towed counter and counter probes, etc.; such work is presently being carried out by the Applied Geochemistry Research Group in conjunction with U.K.A.E.A. and N.I.O.

9.1.4 Morrocan Offshore Phosphate Reserves

Assuming that (1) phosphate sediments containing $\geq 0.5\%$ P_2O_5 cover an area north of Safi of 2500sq.km. (Nutter, 1969) and, south of Safi, of 850sq. miles, (2) the average phosphate content of these sediments is 1% P_2O_5, (3) the average thickness of the deposit is 5m, and (4) that the mean

specific gravity of the sediments is about 2.6, then the total reserves of the Moroccan shelf sediment deposit are

$$(5 \times 3300 \times 10^4 \times 2.6) = 4.3 \times 10^8 \text{ metric tons } P_2O_5$$

The deposit is much smaller than the Phosphoria Formation (1.7×10^{12} metric tons according to McKelvey et al, 1953) but of a similar size to the phosphatic sand deposit off Baja, California (1.5×10^9 metric tons according to d'Anglejan, 1967).

Estimation of the bedrock reserves is rather more difficult in the absence of stratigraphic control in the form of drill cores and the recovery of so few phosphatic-rock samples from such a large area. If it is assumed (1) that phosphatic rocks outcrop continuously along the 300 miles of shelf from which they were often dredged, (2) that their average outcrop width is 10km, (3) that their thickness is that of the onshore deposit - 100m, (4) that the average phosphate content is 20% of P_2O_5, and (5) that the average specific gravity of phosphorite is 2.8, then there are $100 \times 300 \times 10^4 \times 2.8 \times 20 = 1.7 \times 10^{11}$ metric tons of P_2O_5 buried beneath the shelf. This compares favourably with the size of the Phosphoria Formation.

Despite the magnitude of these subsea deposits their economic potential is rated very low for the following reasons: (1) Morocco has very large terrestrial phosphorite resources which make that country now, and likely to be for a considerable time, one of the world's chief phosphate exporters; (2) substantial untapped reserves of phosphorite exist in the nearby Spanish Sahara (Mining Magazine, 1970). Large parts of both deposits are granular poorly consolidated surface deposits which are easy to mine and beneficiate. The disadvantages of the offshore deposits are (1) their low grade, necessitating extensive beneficiation (maximal recorded rock phosphate content is about 25% P_2O_5, and sediment phosphates do not exceed 8.0% P_2O_5); (2) their situation mainly in water depths greater than 300 feet, the present limit of

hydraulic dredging, and which would make eventual mining costs relatively expensive; (3) the fact that the major part of the reserve comprises bedrock or associated breccia which would be extremely difficult to mine. It seems unlikely under these circumstances that the offshore deposits will be competitive with those onshore until such time as onshore mining becomes difficult or onshore reserves are worked out. The possibility that the locally phosphate-rich inshore sand belt may be an economically viable proposition cannot be overlooked; but, at this stage, this deposit is only poorly defined by a very few samples and much more detailed investigation is required before any sound suggestions can be made.

CHAPTER 10

SUMMARY OF MAIN CONCLUSIONS, AND RECOMMENDATIONS FOR FUTURE RESEARCH: BEDROCK

10.1 Summary of Main Conclusions

1. The northwest African continental margin developed by upbuilding and outbuilding on a subsiding basement apparently characterised by the same basins and gulfs as recognised onshore.

2. Subsidence was terminated by Oligocene epeirogenic and tectonic events definitely related to the Atlas orogeny and possibly to an interruption in Antlantic seafloor spreading; subsidence has only continued on a notable scale in the Souss Trough and northern Aaiun Basin.

3. Reduced Miocene and, locally, Pliocene sediments were deposited on an erosional shelf which originated in the Oligocene; the main locus of post-Oligocene deposition has been the continental slope - rise complex.

4. Moroccan upper Cretaceous subsea phosphorites are usually phosphatised foraminiferal limestones, as are Moroccan Eocene subsea phosphorites from the supposed 'gulf' off Essaouira; Eocene pelletal phosphorites from the more northerly 'gulf' off Cap Blanc, are presumed to have been deposited in much shallower water.

5. Moroccan Miocene glauconitic phosphatic limestones represent a basal conglomerate transgressive onto the Oligocene erosional shelf and formed in an open sea environment probably at moderate depths (cf. 100 - 300m).

6. The incidence of Lower Pliocene subsea phosphorites in the northern Aaiun Basin implies a slowing of subsidence and sedimentation at this time.

7. The phosphorites and phosphatic limestones appear to have originated by the phosphatisation of pre-existing lime-muds. The degree of phosphatisation appears to have been critically dependant on the degree of exposure of surficial sediments to seawater and it is envisaged that diffusion mechanisms allowed some concentration gradient to be set up between bottom water and interstitial water such that under suitable conditions concentration of phosphate could occur in the surficial sediments. In general all relatively coarse calcareous skeletal material (such as foraminifera) have resisted phosphatisation.

8. Phosphate pellets appear to have arisen by the mechanical disaggregation of phosphatised lime muds, probably by storm waves; through contact with seawater they have become more phosphatic than the parent material, probably during periods of continued reworking on offshore bars.

9. Although there is evidence for internal migration of phosphatic fluids and the formation of intrasediment apatite segregations, there is no evidence for intrasediment pellet formation.

10. The parent material for the pellets appears to have formed in a lagoonal or mud-flat type of environment subject to occasional wave activity and sited far from land; the pellets characterising the onshore Eocene pelletal deposits may have originated in this environment.

11. Both the glauconitic and pelletal deposits appear to have formed in oxidising environments.

12. Widespread environmental changes detrimental to the large scale formation of subsea phosphate deposits have occurred since the Pliocene. Temperature, current, geographic and possibly oceanic chemical changes may be responsible, but the post-Tertiary temperature decline has probably had the greatest effect so far as most subsea deposits are concerned.

13. The geochemical assemblages of average phosphorites suggest that they were formed from seawater, usually not under strongly oxidising and probably under slightly reducing conditions. The role of different minerals in controlling different chemical elements can be reasonably determined using multivariate statistical analyses.

14. Becuase of the high uranium content of phosphorites, submersible scintillation counters can be used as remote sensing tools to locate subsea phosphorite deposits; a threshold value of 2% P_2O_5 is indicated at present.

15. The economic potential of the northwest African phosphatic rocks and sediments is suspect in view of their low grade, the form in which they occur, and their situation usually in water depths 300 feet: present studies indicate that total reserves may be in the vicinity of 1.7×10^{11} metric tons P_2O_5 in bedrock, and of 4.3×10^{8} metric tons P_2O_5 in sediment.

The main advances achieved in this study have been the discovery and delimitation of widespread Tertiary subsea phosphatic rock deposits off northwest Africa, and the determination of their probable modes and environments of origin particularly in relation to the vast onshore deposits. Other notable advances include establishing in more detail than before the geological framework of the northwest African continental margin; critical examination of the upwelling theory of phosphorite formation as deus ex machina; the successful testing of a submersible scintillation counter for phosphorite prospecting; and the use of multivariate statistical techniques to determine probable controls of phosphorite geochemistry.

10.2 Recommendations for Future Research

1. Sidescan sonar traverses, seismic profiling, drilling and precision dredging should be carried out to more accurately ascertain the geology of the Moroccan phosphatic rock deposits; further reconnaissance

dredging should be carried out off the northern Sahara to determine the extent and nature of the Pliocene phosphorites which apparently crop out there.

2. Trials should be carried out on the use of a towed scintillation counter for rapid remote-sensing phosphorite prospecting.
3. To determine in detail the geochemical characteristics of carbonate-apatites, total chemical analyses of this mineral should be attempted using electron micro-probe analysis to surmount the difficulties of separating apatite from admixed organic and inorganic mineral phases.
4. Attempts should, nevertheless, be made to isolate the various organic and inorganic phases of these rocks to further establish the origin of the geochemical assemblage.
5. The phosphatisation process should be examined at erosion surfaces, pebble and burrow margins, and in oolites and pellets by electron micro-probe analysis to determine the attendant geochemical changes.
6. Structural carbonate and sulphate substitutions in carbonate-apatite should be determined (a) as an aid in identifying coupled substitutions with other minor elements (such as Na-Ca: SO_4 - PO_4), and (b) in order to ascertain possible mineral facies differences between the carbonate-apatites of different deposits (such as between Moroccan onshore and offshore deposits and between offshore Miocene and Eocene deposits). The differences in these two constituents may reflect important differences in the temperature or salinity of the original depositional environments. Similarly, differences in other geochemical characteristics may signify differences in oxidation and reduction potential of importance in understanding the origin of the deposits both here and elsewhere in the world.
7. At the same time, attempts should be made to establish the effect of weathering in the sea on the geochemical assemblage of subsea phosphorites.

8. On the grounds that modern muds cover virtually the entire shelf north of Rabat (McMaster and Lachance, 1969), that the shelf between Agadir and Cap Juby is cut into Cretaceous strata (cf. Dillon, 1969), and that modern and Pleistocene biogenic sediments blanket most of the southern Saharan shelf, it is recommended that future geological effort be concentrated in the Agadir-Al Jadida region and the Villa Cisneros-Cap Juby region as far as phosphorite prospecting is concerned.

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APPENDIX 1

SAMPLE PREPARATION AND MINERAL SEPARATION

A1.1 Sample Preparation

a. Sediments

After removal of pebbles and coarse shells, surface sediment samples were mixed, then coned and quartered to obtain four 50-100gm. subsamples. Cores were split horizontally, one half being retained in its plastic liner for reference purposes; from the remaining half, 2cm wide subsamples were collected at approximately 6cm intervals, care being taken to leave untouched the 0.5cm thickness of possibly smeared sediment against the wall of the plastic liner. Surface sediment subsamples were dried at 60°C for 48 hours, ground in a tungsten carbide Tema mill or automatic agate mortar and pestle to pass an 80 mesh nylon sieve, and homogenised on a sample shaker. Core samples were similarly treated but were hand ground in a porcelain mortar and pestle; separated size fractions and mineral concentrates were ground in agate or porcelain mortars. Dr. S.H.U. Bowie gave permission to use the I.G.S. Tungsten Carbide Tema, and assistance in its operation was given by Mr. J. Elston, I.G.S. To minimise salting between samples, grinding equipment was washed with dilute acid and deionised water. Subsamples of the ground powders were obtained when required for chemical analyses, by using an automatic rotary sample splitter.

b. Rocks

Rock samples were broken up with a tungsten carbide hammer and anvil; organic and mineral encrustations, and obviously weathered portions, were removed, and the remainder ground in an automatic agate mortar (sometimes a porcelain mortar) to pass a 125 mesh nylon sieve before homogenising on a sample shaker.

A1.2 Granulometric Analysis and Size Fraction Separations

The sand fraction was separated from fines by wet sieving; a standard pipette method was used to determine percent silt (<4phi, >8phi) and clay (<8phi), and the dried sand fraction was sieved into fractions at one phi intervals representing Wentworth grades. By this method the writer analysed samples 144, 150, 151, 153, 154, 155 from the detailed study area, samples 255, 256, 258 and 277 from the Sahara, and samples 125, 126, 127, 129, 133, 134, 137, 140 from north Morocco (the data from north Morocco have been presented by Nutter, 1969). Median diameters and sorting parameters were calculated by the writer, using Inman's method, on all samples analysed here and by Nutter (1969) (table 1.4.2).

To separate silt and clay for chemical analysis a suspension of the <4phi fraction was mixed with a peptiser, allowed to stand overnight, stirred and then centrifuged at 1500 r.p.m. for 15 minutes. The material in suspension, representing the <2phi (clay) fraction, was decanted and dried out at $<100^{o}C$. This process was repeated until sufficient material was obtained. The remaining material, a silt and clay mixture, was suspended in one litre of water in a graduated cylinder and left to stand for 24 hours; the material in suspension was siphoned off and the proceedure repeated until the supernatant liquid remained clear; the remaining material was of silt size only. The writer treated in this manner samples 125*, 126*, 127*, 133*, 134*, 137*, 140*, 144, 150, 151, 153, 154 and 155; there was too little clay in samples 153 and 134 to allow an adequate amount to be separated for analysis. The writer's P_2O_5 analyses of asterisked samples have been presented by Nutter (1969).

A1.3 Mineral Separations:

a. Sediments

A Franz magnetic separator and a Cook micropanner were used to separate

glauconite from each sand sieve fraction of samples 151, 154, 155, 832, 833, 834, 836, 837, 873 and 882, using instrumental settings of 0.35 - 0.5 amps, horizontal inclination of 22° and vertical settings of 8° - 20° on the Franz. Very coarse sand fractions were hand-picked. Further purification of the glauconite fractions of sample 155 was achieved using tetrabromethane and acetone (s.g. 2.7).

A micropanner was used to separate detrital mineral grains, and foraminifera containing glauconite casts, from biogenic skeletal debris in subsamples of the non-magnetic fractions of different size grades. Other subsamples were treated with 25% vol acetic acid for 24 hours to remove calcareous biogenic skeletal remains and rock fragments; the fine part of the residues was decanted; the coarser part was treated with Franz and micropanner to separate glauconitic material and detrital fragments; quartz was separated from other components using a micropanner.

Subsamples were obtained using an automatic rotary sample splitter. All fractions and subsamples were qualitatively examined using a binocular microscope to monitor progress.

Acid insoluble residues of surface sediments were obtained for spectrographic analysis by leaching them in excess 25% vol acetic acid for 48 hours; the dried insoluble residues were ground to pass an 80 mesh nylon sieve and homogenised using an agate mortar and pestle. P. Guise assisted in the preparation of the residues.

b. Rocks

Fragments of the glauconitic matrix of glauconitic-phosphatic-conglomerates 848 and 877 were broken down to about 20 mesh size using a jaw crusher; an automatic agate mortar and pestle was then used to crush the sample to pass an 80 mesh nylon sieve; periodically during this process the fines were

washed into suspension and decanted and the coarse residual samples were passed, when dried, through the Franz magnetic separator to concentrate glauconite grains. Many of the grains were composite and it proved impossible even using heavy liquids to effect a complete separation from associated apatite; nevertheless, the resulting concentrates were at least 95 per cent pure glauconite. These samples were used for K.Ar analysis.

A series of powdered whole rock samples selected for apatite separations, included Moroccan offshore samples 139, 148 and 154, and New Zealand offshore samples Z1037, F127 and D134. Calcite was removed from powdered samples using a tri-ammonium citrate leach as described by Silverman et al (1952): X-Ray diffraction analyses showed no detectable calcite in the residues. Minerals heavier than s.g. 2.9 were separated by centrifuging the dried residues in tetrabromethane and were discarded without examination (usually this fraction was minute). Minerals lighter than s.g. 2.7 (mainly quartz) were effectively separated by centrifuging in a mixture of tetrabromethane and acetone. This light mineral fraction was much darker in colour than the remaining apatite concentrate and is assumed to also be enriched in separatable organic material although this was not checked. The apatite concentrate and light mineral fractions were examined by X-Ray diffraction. The above s.g. limits were chosen on the basis of d'Anglejan's (1967) findings that the s.g. of phosphorite pellets was about 2.8. Unfortunately this happens to be similar to glauconite, which could not be separated from samples Z1037, D134 and Morocco 154 by this method. Since the samples were at this stage extremely fine grained it also proved impossible to remove glauconite by magnetic separation and these samples were discarded. The apatite concentrates from F127 and Morocco-139 and 148 were analysed by mass spectrometry.

A1.4 Iron Staining Investigation of Selected Sediments

Certain samples from that group rich in soluble Fe and Mn were selected for investigation and sieved into sand, and silt and clay fractions prior to binocular microscope examination. An automatic rotary sample splitter was used to obtain subsamples. Sand fraction subsamples were leached for a day in excess 25% vol acetic acid to remove carbonate skeletal material; fine residual material resulting from this treatment was decanted from suspension and separately collected: both coarse and fine fractions, when dried, were examined using a binocular microscope. Unleached and leached coarse and fine subsamples were then bleached for a day in a 10 per cent Na-dithionite solution to reduce and dissolve Fe and Mn oxides and hydroxides; dried residues were examined using a binocular microscope. An interesting feature not followed up through lack of time was the discovery, after dithionite treatment, that shell, rock and mineral fragments in some samples (904, 906, 933) were covered with some apparently crystalline colourless mineral giving their surfaces a distinctly sugary appearance; conceivably this is a secondary carbonate or (?) opal. The samples examined were 904, 906, 933, 950, 961, 962, 963, 972, 973, 974, 985 and 986. In almost every case shell material and rock fragments were coated or impregnated with an orange brown to dark brown mineral which disappeared after dithionite treatment; similarly coloured dendritic structures and also foram casts disclosed by acetic leaching were bleached by dithionite treatment, as were the unleached fine fractions of these samples. Further work on the secondary minerals in these sediments is recommended.

APPENDIX 2

CHEMICAL ANALYTICAL METHODS

A2.1 Instrumental Methods

a. Optical Spectrography

The spectrographic method used in the analysis of acetic acid insoluble residues of Moroccan sediments was that described by Nichol and Henderson-Hamilton (Trans.Inst.Mining and Metall. v.74, part 15, pp 955-961, 1965) and in current use in the A.G.R.G. for soil and stream sediment analyses. The analyst was Mrs. E. Bannerjee; the instrument was a Hilger E742 large quartz emissionspectrograph. Prior to analysis, the samples were ignited in a furnace at 450°C for 3 hours to oxidise organic matter and eliminate combined water. Samples were analysed for Fe_2O_3 (representing total Fe), Pb, Sn, Ga, Bi, V, Mo, Cu, Zn, Ti, Ag, Ni, Co, Mn, Cr, Ba and Sr. Of these elements, Bi was always below the detection limit of 5ppm; Sn was also below the 5ppm detection limit in all samples except 1082 (40ppm), 976 (10 ppm), 819 (5ppm) and 802 (6ppm); and Ag was always below a detection limit of 0.2ppm with the exceptions of samples 117 (0.2ppm), 934 (0.2ppm), 847 (0.6ppm), 819 (0.2ppm), 893 (1.6ppm); therefore these elements were not further considered.

In this method a synthetic rock base standard, approximating to intermediate rock composition and containing varying amounts of the different elements, is used to determine, by comparison, the composition of the samples. The assumption is made that typical soils and stream sediments do not differ significantly from average intermediate rocks to warrant matrix corrections provided it is accepted that the results are no better than semi-quantitative: this philosophy is accepted here with respect to marine sediment samples from

which carbonates have been removed. A series of previously analysed control soil and stream sediment samples were run with these samples by the analyst. Further control is given by the analysis of the international rock standards G1 and W1 and the writer included also a series of 20 samples analysed previously by direct reading emission spectrography for a comparison of method (cf. table A2.1). The accuracy and reproducibility of the method are described later.

b. Direct Reading Emission Spectrography

This spectrographic technique has been in use in the A.G.R.G. since 1968 and is the subject of A.G.R.G. internal reports by Newman and Foster (1968) and Young (1970). Apart from its use in the routine analysis of soil and stream sediment material, it has also been used in the A.G.R.G. by Glasby (1970) in the analysis of Mn nodules; Glasby has further detailed the analytical proceedures and these will thus not be repeated here.

Analyses of the acetic insoluble residues of sediments from Morocco and the Spanish Sahara were carried out on an ARL 2900B Quantometer Direct Readout Spectrograph by A.G.R.G. technical staff; samples were ignited prior to analysis, as for optical spectrography. Again, G1 and W1 were used as standards and a series of samples of known composition (known as the Statistical Series) were run as controls. Corrections for analytical drift were assessed by the writer by determining for each element in the Stat. Series, the ratio of mean daily values (dz) to the mean values for the previous month (Mz) (table A2.2). Analyses were carried out on the 11th 13th and 17th December, 1968 and the previous month's averages were determined for the period 28.10.68 - 25.11.68. On certain days, and for certain elements, it was found that the difference between dz and Mz exceeded 30 per cent; significant analytical drift was assumed to have occurred (Foster, pers. comm., ex-chief analyst, A.G.R.G.) and elemental determinations were corrected by the ratio dz/Mz in these cases. The causes of

analytical drift and a discussion of this problem is given by Young (1970, A.G.R.G. Internal Report). In this method, the instrument is calibrated with synthetic rock base standards and it is assumed that the composition of the predominantly silicate mineral sediment samples is not sufficiently different from the rock base to warrant matrix corrections provided it is accepted that the results are semi-quantitative. The accuracy and reproducibility of the method are discussed later.

This technique was also used to provide semi-quantitative analyses for a series of subsea phosphatic rocks to allow a preliminary assessment of subsea phosphorite geochemistry. Because of the high Ca content of these rocks it was necessary to make a correction for matrix effects due to Ca on the contents of Ba, Sr and V. To obtain some idea of the validity of these analyses (matrix effects due to large amounts of phosphorus were not investigated for example) three samples from the Phosphoria Formation were analysed at the same time; these were supplied by R.A. Gulbrandsen of the U.S.G.S., who had published previous analyses of these samples (Gulbrandsen, 1966). Results are discussed later.

c. Atomic Absorption Spectrophotometry

Moroccan sediment samples were leached for 48 hours in 25% vol acetic acid and the filtrate was analysed for Fe and Mn by L. Brown and P. Guise using a Perkin Elmer 303 Atomic Absorption Spectrophotometer. Because of known interference of Ca with certain elements and as the samples contained amounts of $CaCO_3$ ranging from 10 - 95%, approximate corrections for interference were applied as follows. Solutions of analar grade $CaCO_3$ equivalent to sediments containing 30%, 50%, 70% and 90% $CaCO_3$, were made up in 25% vol acetic acid; a range of Mn and Fe standards were made up from these solutions and calibration curves were obtained for the different strength carbonate solutions (cf. Fig. A2.1). Filtrates were divided into batches

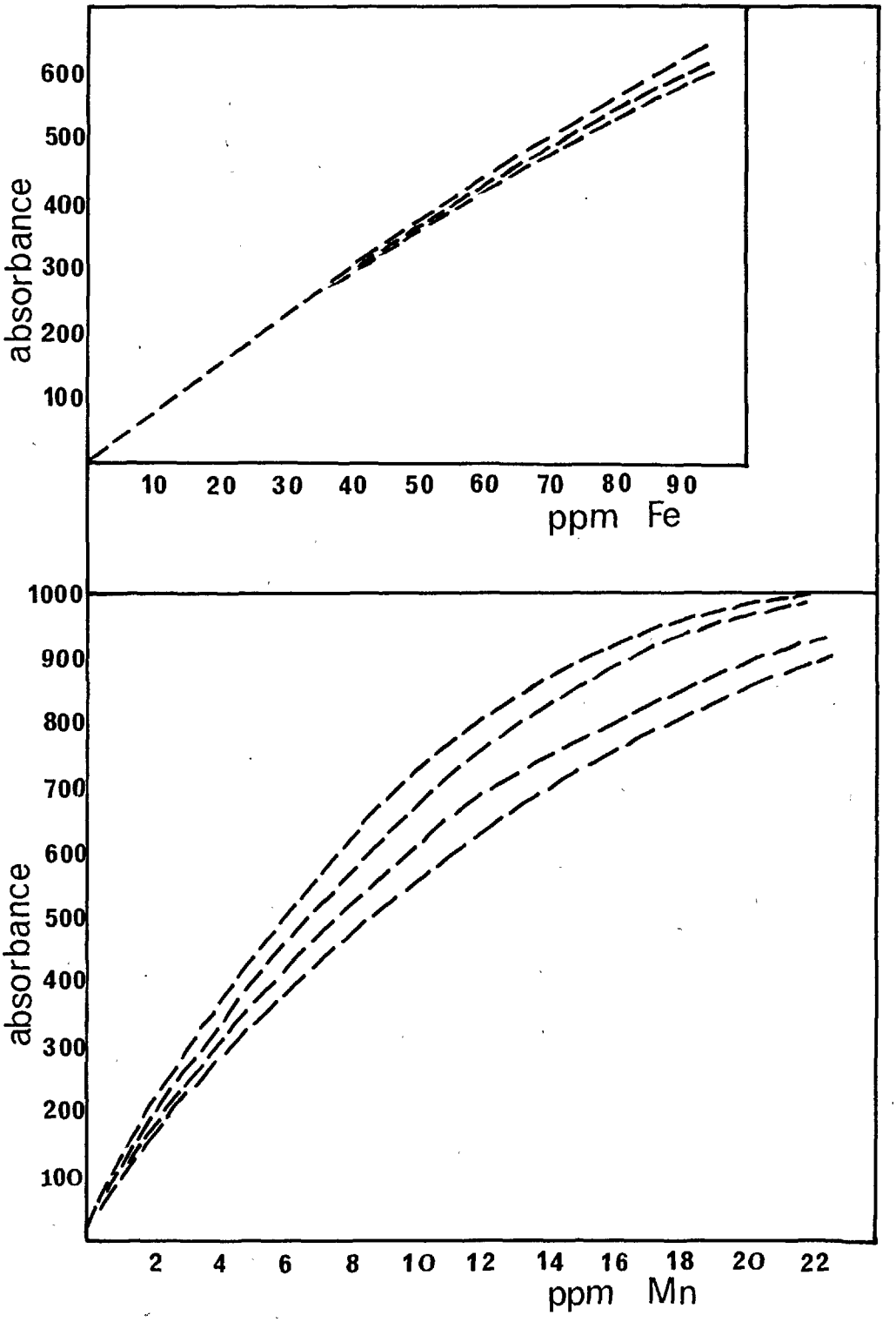


Fig.A.2.1. Calibration curves used in the determination by atomic absorption, of Fe and Mn in the acetic acid soluble fraction of Moroccan sediments.

Fe : top line represents solutions with 0%, 30% and 50% $CaCO_3$; middle line represents solutions with 70% $CaCO_3$; lower line represents solutions with 90% $CaCO_3$. Mn : as above, but upper line = 0% $CaCO_3$; line two = 50 and 30% $CaCO_3$; line three = 70%$CaCO_3$ and line four = 90% $CaCO_3$

to represent sediments containing 15 - 40%, 40 - 60%, 60 - 80% and 80 - 99% carbonate, and their Fe and Mn values were determined from the 30%, 50%, 70% or 90% standard carbonate curves respectively. The results, although not highly accurate, are reasonable quantitative estimates within fairly narrow limits (cf. Figs. A2.1a and b).

Zinc and Mg analyses were carried out by A. Forster on the filtrate from a 1N HNO_3 warm leach of all rock samples. No corrections were made for Ca interference which, in the case of Zn is likely to be considerable. However, in that the sample analysed were of fairly constant matrix, results are expected to be internally consistent. No duplicates or replicates were analysed.

d. Mercury Analyses:

Mercury analyses of selected rock samples were carried out by Dr. P.M.D. Bradshaw using a method described by James and Webb (1964, Trans.Inst. Mining and Metall. v.73, part 9, pp 633 - 641). Essentially, the Hg content of the vapour phase of heated samples is determined by measuring the absorption, by the vapour, of ultra-violet light at a specific frequency.

e. Infra-Red Spectral Analysis

Dr. R. Chester of the Oceanography Department, Liverpool University, obtained infra-red spectra of most of the phosphatic rock samples discussed in text. According to Dr. H. Elderfield, Geology Department, Leeds University, (pers. comm.) the spectra suggest the presence of structural carbonate within the apatite lattice.

f. X-Ray Diffraction Analysis

Samples were ground extremely fine in an agate mortar and then analysed on a Phillips Proportional Counter X-Ray Diffractometer with wide angle

goniometer, using CuK radiation. By this means, using equipment in the Geology Department, University of Manchester, the writer analysed smear-mounted whole rock and mineral separation samples of 136.1, 139.1, 148, 154, 156, 235, D134, Z1037, F127, TAS 3D, and TAS 41D during preparation of purified carbonate-apatite for mass spectrometric analysis. Operating conditions were a scan speed of 1°/min, a slit of 1°, a ratemeter setting of 200c/s and chart speed of 1600 mm/hr.

Samples of the acetic acid insoluble residues of selected sediment samples were analysed, in cavity mounts, by R. Curtis in the Geology Department, Imperial College. Operating conditions were: scan speed 2°/min; time constant - 1 sec; scale factor - 8 x 1; divergence (α) - 1; slit - 0.1mm. Qualitative results determined by the writer from diffraction data are presented in table A2.4.

g. Redox Potential Determinations

Redox potential measurements were made on board ship, by the writer, on selected surface sediment samples and at approximately 1 foot intervals down cores immediately after their collection. Measurements were made using specially shaped long electrodes supplied by Analytical Measurement Limited, in conjunction with a portable battery operated (pocket) meter. A mixed solution of M/300 potassium ferrocyanide and M/300 potassium ferricyanide, developing an Eh of $^{+}183$mv was used as a standard, and all Eh values were corrected with respect to the standard hydrogen electrode. Readings were taken at 0, 2, 5, 10, 15 and 20 minute intervals and it was found that, in each case, equilibrium was reached after about 10 minutes, so all quoted readings are from 10 minutes after electrode insertion. Core measurements were taken by inserting the electrodes through holes drilled through the plastic liner; the holes were sealed with plasticene while readings were being taken.

h. Electron Microprobe Analysis

Highly polished sections of selected phosphorite samples were prepared using techniques similar to those described by Glasby (1970) and, prior to analysis, these were coated with a thin film of carbon. Excitation of a small area of the sample by an electron beam produced a continuous spectrum containing X-Radiation characteristic of each element present in the sample. Using a spectrometer and pulse-height analyser, radiation characteristic of chosen elements was selected and the distribution pattern of its intensity was reproduced on an oscilloscope screen and photographed using Polaroid Land Film, type 47. Back scattered electron distribution was measured in the same way to give a picture of the sample surface; scattering differs according to surface topography and the atomic numbers of the elements present. The areal distribution patterns so measured were achieved by electron beam scanning of a small area of the sample surface; scale measurements were not always taken butthe scale can be assessed from the size of recognisable foraminiferal skeletons. Elemental distributions are represented on the photographs by a series of white dots, the intensity and density of which are functions both of concentration and exposure time; their density thus gives only a semi-quantitative picture of the elemental distribution. All the instrumental work was carried out by Dr. P. Suddaby, Geology Department, Imperial College, using a Cambridge Instruments Geoscan.

i. Mass Spectrometric Analysis

Carbonate-apatite separates from samples 139, 148 and F127 were analysed by the writer using the A.E.I. MS 7 mass spectrograph in the Geology Department, University of Manchester; the operations were supervised by Dr. G.D. Nicholls, whose technical staff and students provided valuable assistance. The techniques used are essentially identical to those described by Nicholls et al, 1967 (Analytical Chem. v.39, pp 584) and Glasby (1970), so are not described here in any detail. The method involves the introduction of Re into the

sample as an internal standard, and comparison of the intensity of selected element lines with the intensity of the standard Re line. The samples were drymixed with an equal amount of rock base containing 21.1ppm atomic Re prepared by Glasby (1970). The resultant powder was then mixed with an equal weight of Ringsdorf spec-pure graphite, ground for 30 minutes in an agate mortar and pestle, and pressed into electrodes ready for analysis.

In this work, exposures in the range 0.3 to 1500 x 10^{-9} coulombs were used, enabling elements to be determined to 0.5ppm. Where extrapolation of the calibration curve was required to determine the abundance of certain elements, the data in tables 7.3.4 and 7.3.5 are starred. Instrumental settings and operating conditions were as described by Glasby (1970, table 31, p.440) and the R-values used in determining elemental abundances were the same as those quoted by Glasby (1970, table 32, p.444). There was not sufficient time for more than one analysis per sample, and consequently no precision calculations can be made. However, on analysis of dry-mixed manganese nodules, Glasby (1970) obtained precision levels of the order of ± 25%, and similar figures are reported by McArthus (PhD thesis, in preparation, University of London) from the analysis of dry-mixed phosphorites. As far as accuracy is concerned the present results, agree within reasonable limits, with analyses by McArthur of related material from adjacent sample sites, and furthermore the rare-earth ratios compare favourably with those determined on similar material by other workers using other analytical techniques (cf. table 7.3.5).

A2.2 Wet Chemical Analytical Techniques: Sediments

a. Colorimetric Phosphate Analyses

Colorimetric phosphate analyses were carried out using a method based on A.G.R.G. Tech. Comm. 52 (modified from a method by Ward, Lakin and Canney, U.S.G.S. Bull. 1152, p 66, 1963). All Moroccan samples from traverses 5,

15 and 21 collected during 1968, and the different size fractions of those samples from traverses 5 and 15 which had been separated into size grades, were analysed by the writer; core samples and total sediment samples collected during 1969 from the detailed study area south of Safi were analysed by Miss B. Clavering as were Saharan surface samples and mineral separations.

The modified method is briefly described:-

(1) A 0.1gm sample in a test tube is leached for 1 hour with 2ml of 4M HNO_3 on a sand tray;

(2) when cool the solution is diluted to 10ml with water, mixed, and allowed to settle before a 5ml aliquot of the clear solution is pipetted into a test tube calibrated at 5, 7 and 10ml;

(3) 2ml of ammonium metavanadate-molybdate solution is added and the solution diluted to 10ml with water, mixed, and allowed to settle for 30 minutes;

(4) the colour of the solution is visually compared with a standard series to determine its phosphate content.

Shipboard colorimetric phosphate analyses were carried out by the writer on the 1968 cruise, and by the writer and Nutter on the 1969 cruise, in order to monitor sampling progress at sea. A volumetric scoop was used to obtain approximately 0.1gm of sediment or crushed rock, which was then leached overnight in cold dilute nitric acid and analysed by the above technique the following day. Reagents required on board ship were weighed out, prior to the cruise, into plastic vials or polythene bags and an adequate supply of deionised water was obtained using a deionising column and distilled water supplied for the ship's batteries. Results compare favourably with those obtained subsequently in the laboratory (Fig. A2.2) thus proving the viability of this method as a field analytical tool.

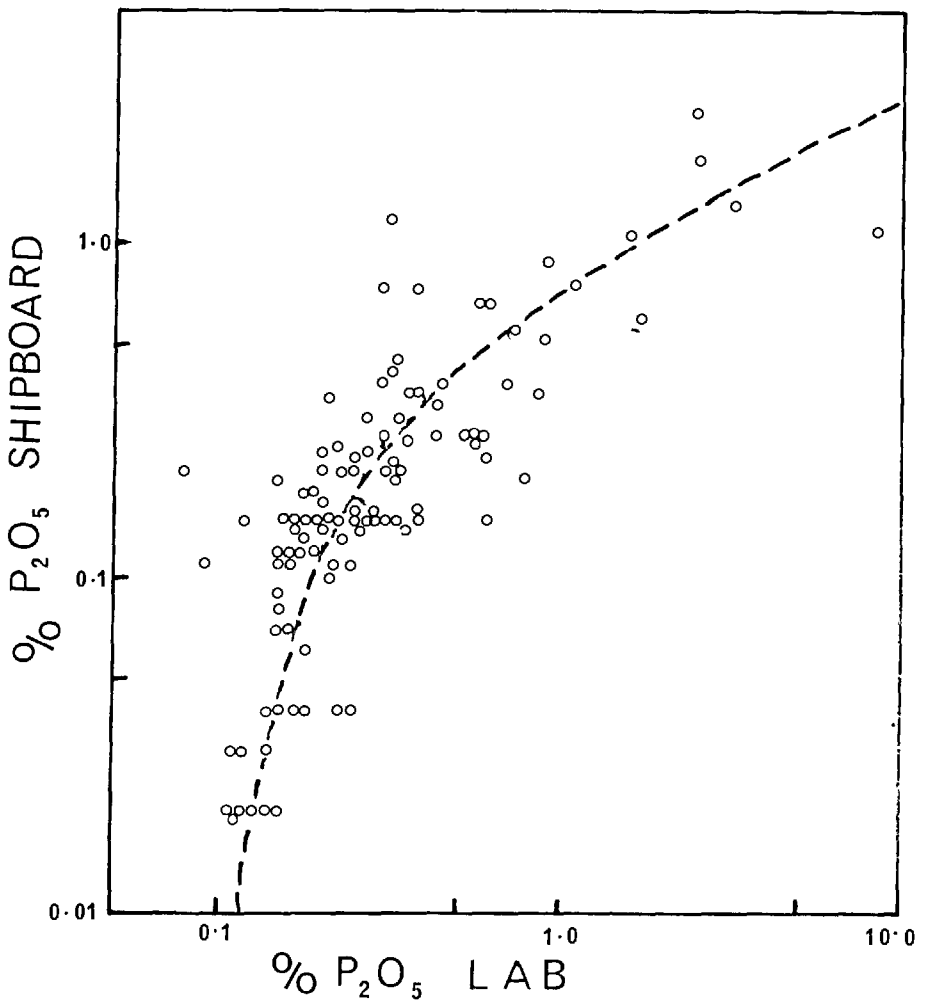


Fig.A.2.2. Comparison of reconnaissance shipboard phosphate analyses with later laboratory analyses carried out on different subsamples.

Reproducibility of the method is discussed later.

b. Carbonate Analyses

Carbonate analyses were carried out by Miss B. Clavering on all surface sediment samples and size fractions, using a method based on that described in A.G.R.G. Tech. Comm. 53 for the analysis of soils and stream sediments. Certain modifications were made to the proceedure to account for the high carbonate content of the marine sediments and a brief description of the modified method is given below.

(1) A 0.1gm sample in a testtube is leached for 1 hour with 10ml of 0.2N HCl in a boiling water bath;

(2) when cold the solution is diluted to 10ml with water, mixed and allowed to settle before a 5ml aliquot of clear solution is pipetted into a 100 - 250ml conical flask;

(3) the solution is diluted to 50ml with water, a few drops of phenolphthalein indicator are added, and the excess acid is titrated against 0.2N NaOH;

(4) knowing the titre and the blank, the concentration of carbonate can then be calculated.

c. Organic Carbon Analyses

All surface sediments were analysed for organic carbon by P. Guise, using a method devised for soils and stream sediments and described in A.G.R.G. Tech. Comm. 32 (based on Schollenberger, 1927, Soil. Sci. v.24, p.65). Briefly, samples are oxidised by a mixture of K-dichromate and H_2SO_4; excess H_2SO_4 is determined by titration against ferrous ammonium sulphate solution and, knowing the titre, organic carbon can be calculated.

A2.3 Wet Chemical Analytical Techniques: Rock Samples

Arsenic analyses were carried out on selected rock samples by Mrs M. Clemens, using a method described in A.G.R.G. Tech. Comm. 49. Briefly,

the method, known as the Gutzeit method, involves the evolution of arsine gas which, when adsorbed onto $HgCl_2$, gives rise to a colour complex the intensity of which is proportional to As content.

Using a method described in A.G.R.G. Tech. Comm. 17 Mrs. Clemens also carried out Antimony analyses on these same samples. The method involves the formation of a distinctively coloured organo-metallic complex whose intensity is proportional to Sb content.

Mrs. Clemens also carried out organic carbon analyses on these rock samples, using the method described in A.G.R.G. Tech. Comm. 32.

Volumetric phosphate analyses were carried out by the writer using a method devised for phosphate rocks and described in detail by Bennett and Hawley (Methods of Analysis of Silicate Rocks, 2nd Ed., 1965, Academic Press, London, pp 259 - 260). In brief, the method involves obtaining an ammonium molybdate precipitate which is then dissolved in NaOH; the excess NaOH is determined by back titration with HNO_3 and, knowing the remaining reacted NaOH, the P_2O_5 content can be calculated. All these analyses were carried out in duplicate.

APPENDIX 3

ANALYTICAL PRECISION AND ACCURACY

Duplicate and replicate analyses on randomly selected samples were carried out by each analytical method to enable precision calculations to be made. Usually between one third and one half of any batch of samples were analysed in duplicate and one in twenty samples in replicate. Calculation of precision from duplicate analyses was carried out using a method described by Khaleelee (1969):-

The percentage deviation of each duplicate analysis from the mean of each pair of determinations is given by:-

$$X_{pi} = \left[\frac{x_i - x_{ii}}{2} \Big/ \frac{x_i + x_{ii}}{2} \right] \times 100$$

where x_i and x_{ii} represent the two determinations.

The mean percentage deviation for all duplicates is given by:-

$$\bar{X}_p = \frac{\sum X_{pi}}{N}$$

where N represents the number of duplicate pairs.

The standard deviation of the individual percentage deviations (X_{pi}) about the mean percentage deviation ($\bar{X}_p$) is given by:-

$$\sigma^2 = \frac{\sum (X_{pi} - \bar{X}_p)^2}{N - 1}$$

At the 95 per cent confidence level, if individual percentage deviations are normally distributed about the mean, the precision may be estimated thus:-

$$P = \pm (\bar{X}_p \pm 2\sigma) \text{ per cent.}$$

Where five or more replicate determinations were carried out on one sample, precision was estimated using the following standard calculation:-

$$P \text{ (at the 95\% confidence level)} = \pm \frac{200}{\bar{X}} \sqrt{\frac{\sum X^2 - N.\bar{X}^2}{N - 1}}$$

where X = each determination; $\bar{X}$ = the mean of all determinations, and N = the number of determinations.

Where several different precision values were available for different batches analysed at different times, a mean precision figure was calculated: analytical precisions were as follows for wet chemical analytical methods:-

(1) colorimetric phosphate: ± 11% (mean of several duplicate and replicate values;

(2) volumetric phosphate: ± 11% (replicate analyses);

(3) titrimetric carbonate: ± 5% (mean of several duplicate and replicate values);

(4) atomic absorption: ± 13% (duplicates of soluble Fe); ± 23% (duplicates of soluble Mn);

(5) As, Sb and C_{org}: respectively ± 33%, ± 25%, and ± 14% (based on duplicates).

There were no duplicate or replicate analyses for Zn or Mg atomic absorption analyses, nor for Hg analyses, but other A.G.R.G. workers regularly attain precisions of better than ± 25% in the analyses of these elements by the techniques used here.

Precisions obtained for spectrographic analyses are quoted in table A2.8. Precision for most elements analysed by optical emission spectrography is between ± 30% and ± 40%, the most notable exceptions being Zn (± 65%) and Co (± 52%). For most elements analysed by direct reading emission spectrography mean precision is between ± 12% and ± 28%, the notable exception being Zn (± 52.5%).

Compared with accepted values or ranges for the international rock standards G1 and W1 (table A2.7) the present direct reading emission spectrographic analyses of these standards gave results for most elements more or less within the limits of analytical error (approx. ± 30%). Cobalt values are

very slightly low and Pb and Zn high for W1; in the case of G1, Ba is slightly low, while Ti and V are high. Precisions often notably decrease for very low elemental abundances, which may explain the divergence for Ti and V in G1 and of Pb in W1. Glasby (1970) also notes that spectral line characteristics for Zn and Pb give rise to bad precisions. In general, it seems that this instrumental method is reasonably accurate for semi-quantitative work in the range of abundances represented by the presently analysed sample population. Matrix effects have not been considered but are unlikely to be significant for semi-quantitative analyses of the types of materials analysed here in which there is not much matrix variation and where the matrix approaches average silicate rocks.

Optical emission spectrographic analyses (table A2.7) of W1 show Sr analyses to be slightly low and V analyses to be slightly high ($> \pm$ 40% deviation); Sr is low and V high also for G1 and, in addition, Ba is slightly low and Pb slightly high in G1. The consistancy of the Sr depletion and V enhancement suggests instrumental error; the effects of this on data processing should be insignificant since all samples were analysed in one batch and under the same instrumental conditions. The G1 data tend further to suggest that Pb and Ba analyses may be unreliable at relatively high concentration levels but not to sufficient of an extent to materially affect the present semi-quantitative analyses.

Direct reading and optical emission spectrographic results on the same acetic acid insoluble residues of sediments (samples 111, 112, 113, 114, 115, 116, 117, 119, 120, 121, 125, 126, 127, 137, 144, 150, 151, 153, 154, 155) were compared to ascertain the degree of reproducibility. The mean ratios of D.R. determined to optically determined spectrographic abundances for each element were:- Pb (0.89), Ga (0.64), V (1.00), Cu (0.87), Zn (0.79), Ti (0.97), Ni (0.75), Co (0.54), Mn (1.11), Cr (0.84), Ba (0.65), Sr (1.33).

Clearly, although results in no case diverge by more than ± 50%, direct comparison between the sets of results obtained by the two methods is not realistic; the direct reader results are consistently low by about 15% on average.

To determine the feasibility of using the wetchemical techniques and the direct reading emission spectrographic method as set up - for silicate rock analyses - to give meaningful semi-quantitative analyses of phosphatic whole rocks, three previously analysed Phosphoria Formation phosphorites were analysed by this method (table A2.6). Mean abundance ratios (A.G.R.G. analyses/U.S.G.S. analyses) showed that Sr, V, Cr, C_{org} and As are between 30 and 50 per cent low and Sb is a little over 50% low, while Fe is between 30 and 50% high and Mn, Pb, Ca and Zn are more than 50% high. The remaining elements are within ± 30% of previously determined values. It is argued that as both A.G.R.G. and U.S.G.S. analyses were semi-quantitative, those results within ± 50% may be considered to give a reasonable semi-quantitative estimate of minor element abundances in these rocks. Ca is but slightly over 50% different, and varies consistently with previously determined Ca variations (table A2.6) so its use in data processing is acceptable. Mn, Pb, and Zn results however are far from reliable and their use in data processing should be treated with extreme caution. In summary, the fact that the matrix of the chosen rock sample population is fairly constant suggests that the results should be internally consistent; the fact that most elements are within ± 50% of previously determined values on phosphorite standards suggests that the present analyses give a meaningful estimate of phosphatic rock geochemistry.

Lastly it should be pointed out that, in data processing, where only trace amounts (below detection limit) of certain elements were recorded, values equivalent to half the quoted detection limit for those elements were used to represent trace concentrations.

APPENDIX 4

LITHOLOGICAL AND AGE DATA

Results of visual and petrographic analyses of rock samples are listed in table 5.1. A number of Moroccan samples (mainly phosphatic) were palaeontologically analysed by Mr. D. Carter, Geology Department, Imperial College, and a further number (mainly non-phosphatic) were analysed by F. Deres and D. Fournie of the Société Nationale des Pétroles d'Aquitaine, Pau, France (their results are quoted by arrangement with Mr. Bhat of S.N.P.A.). In most cases the data on which identifications were based was not given in any detail.

Mr. Carter found that pelletal foraminiferal limestones 134 and 966 contain Orbulina universa D'ORB and are therefore younger than the 'Orbulina Datum' low in the Miocene and may be of Miocene age. Orbulia universa D'ORB., was also recognised in the matrix of glauconitic phosphatic conglomerates; a Miocene age for these last samples is corroborated by K.Ar dating and it is assumed that all glauconitic phosphatic conglomerates are of this same age.

Mr. Carter also dated the following Saharan samples; 257, a fine grained sandy limestone, and 259, a fine grained shelly limestone, were found to be probably lower Miocene; sample 273, a shelly limestone, was found to be probably upper Miocene.

Mr. S. Rye, Geology Department, Imperial College, found soft Saharan limestone sample 252, and unconsolidated sand samples 256, 258 and 277, to contain Recent faunas mixed with a phosphatised, derived lower Pliocene fauna characterised by abundant Globorotalia truncatulinoides.

K.Ar Determinations (table 5.2)

K.Ar analyses were carried out by Dr. M. Dodson and D. Rex of the Geology Department, Leeds University, on whole rock samples 234 and 154, and on glauconites separated from certain rock and sediment samples. A concentrate of subrounded to subangular black to light green glauconite grains, some showing syneresis cracks, was obtained using a magnetic separator and heavy liquids, from the 250-125 micron size fraction of continental slope sediment sample 155. A concentrate of smooth, black, subrounded and cracked glauconite grains was obtained, using a magnetic separator, from the 500-250 micron fraction of continental slope sediment sample 882. A concentrate of moderately light green angular to subangular 'knobbly' grains of glauconite was magnetically obtained from the same size fraction of continental shelf sample 833; several of the grains in this sample appear to be partly glauconitised rock fragments; these could not be separated without considerable difficulty. The method of concentration of glauconite from rock samples 848 and 877 has already been described. Whole rock sample 234 consisted of a partially glauconitised phosphatic limestone; whole rock sample 154 consisted of a glauconitic phosphatic conglomerate.

Table 5.1 Summary of Geological Data Pertaining to Rock Samples

Column 1 = sample types: p represents pebbles and r represents cobbles, boulders and bedrock. Columns 2, 3 and 4 represent rock types: F = flint, C = conglomerate, L = limestone, S = sandstone, St = siltstone, M = mudstone, Ph = phosphorite, G = glauconitic, Sy = silty, Calc = calcareous, Sh = shelly, P = phosphatic, Pl = pelletal. Where a rock is (say) a silty limestone, it will be defined thus - Sy,L. Where two rock types were dredged at the same site the symbols for each type are separated by a semicolon thus:- sandstone and glauconitic, phosphatic, conglomerate are

represented by S;G,P,C.

Column 2 represents phosphatic rocks; column 3 represents other lighologies; column 4 represents rock types which proved dateable; column 5 lists palaeontologically determined ages. Ages marked with + were determined by Mr. D. Carter; the unmarked ages were determined by M. Deres and M. Fournie.

Phosphatic rocks examined in thin section by the writer are marked with an asterisk.

Sample No.	1	2	3	4	5
813	p	G,P,C.*	Calc,St		
815	r		G,Sh,L.	L	?Palaeocene (Landinian) +
817	r	Ph	Calc,M.	M	Eocene (Lutetian?)
818	r	Ph	Sy,L.		
819	r	P,L.*	M	M	Eocene (Lutetian ?)
820	p	P,Calc,S*			
821	p		L		
823	p		L;St	St	Up.Cret.(Turonian-low,Senonian)
826	p		Calc,St		
829	r		L;St	St	Up.Cret (?)
830	p		Sy,L		
831	r		L;Calc,M	M	Up.Cret(above Danian)
832	p	Ph	L		
833	r	G,P,C.*	M	M	Up.Cret.(Turonian) +; Up.Cret. (Ceromanian-Santonian)
834	r		Sy,L;F;M	M	Eocene
836	r		L;Sh,St		
837	r		S		
841	p	G,P,C.*	Calc,St		
847	r	G,P,C.*			
848	r	G,P,C.*			
855	r	P,L.*	L;Calc,M	M	Up.Cret.
856	r		Sh,L;M		
859	p		St		
860	p		M	M	Up.Cret.(Turonian) +; Up.Cret. (Santonian-Campanian)
862	p		M;Calc,St	M	Up.Cret.(Santonian-Campanian)+
864	p		M;Calc,St		
865	r	G,P,C.*			
871	r		Sh,L	L	Cretac.
873	p		M		
875	r	G,P,C.*	P,Calc,St*		
876	r		Calc,M;St		
877	r	G,P,C*		C	Tertiary
880	r		St		
882	r		Calc,M		
883	r	G,P,C.*	Sy,L		
151	r	Ph	L;M		
152	r	G,P,C.*	L	Ph	Eocene+ (pebbles)

154	r	G,P,C.*		Ph	Eocene^{+} (pebbles)
892	r		Calc,St		
893	r	G,P,C	L;M	M	Palaeocene-Eocene
894	r		M;S		
895	r		M		
896	r	G,P,C.*	St;M	M	? Eocene
898	r	G,P,C.*	M		
899	r	G,P,C.*	L		
149	p		St		
148	r	Ph;G,P,C*		Ph	Eocene+ ; Tertiary
157	r	Ph;G,P,C*			
902	p		St		
904	p		S;St;L		
906	r		F;S;L		
907	r		St;Sy,L		
908	r		M		
909	r		Sh,L;M;S		
910	r		S		
911	p		S		
914	r		M;L	L	Low.Cret.(? Neocomian)
915	r	Ph	M		
916	r		M;Sy,L		
922	r	Pl,P,C*	S;M	S	? Eocene
923	r	Pl,P,L*	St,S		
924	r	Pl,P,L*	M;Sh,L	Sh,L	Low.Cret.(Barremian-Aptian?)
930	r		S		
931	r	Pl,P,L*	L;Sy,M		
932	r		L		
933	r	Pl,P,L*	M;Sh,M	M	Up.Cret.(above Danian)
942	p		St		
948	r		Calc,M		
949	r		Sh,L		
950	r	P,L			
952	r		Sy,L		
954	r	P,L*	M		
958	r	Pl,P,C*	S;L		
959	r	Pl,P,L*		Ph	Eocene^{+}
960	r		M		
961	r	Pl,P,C*	Sh,L	Ph	Tertiary with Up.Cret.Pebbles
963	r	Pl,P,L*	L;M	L	Up.Cretac. ?
964	r	Pl,P,C*	S;M	Ph	Up.Cret.pebbles^{+}; S = Tertiary
965	r		St		
966	p	Pl,P,C*	Calc,M	Ph	?Miocene^{+}; M = Eocene(Lutetian)
972	p		St		
973	r	Ph	L		
974	p		Sh,L	L	Eocene (Lutetian)
976	p		M;S		
978	r		M;L		
979	r		M		
980	r		M;Sh,M	M	Up.Cret.(above Danian)
982	r	Pl,P,C*	L;Sy,L	Ph	Up.Cret.pebbles^{+}
985	r		S		
987	r		M;S		
988	r	Pl,P,L*	M	Ph	?Early Tertiary^{+}
989	r	Pl,P,C*	L;St	St	Up.Cret.- low.Tertiary
996	r		Sy,M		
997	r	Ph			
1001	r		S		
155	r	Ph	M;L		
156	r	Ph;G,P,C*		Ph	Eocene^{+}

903	p	G,P,C*	M;St		
1004	r	Pl,P,C*	L,M	Ph	Up.Cret.-low.Tertiary+; M = Up.Cretac.(above Danian)
1006	p	Pl,P,C*			
1014	p		Sy,L		
1015	r		Calc,M		
1016	p	Pl,P,C*	Sy,L	Ph	Eocene+; M = Up.Cret.(above Danian)
1017	p		Sy,L		
1020	p		L		
1022	p	Pl,P,C*	St	Ph	Up.Cret.(?Senonian)+
1028	r		S	S	Tertiary
1031	p		S		
1033	r		L		
1035	r	Ph	L		
1037	p	Ph			
1038	r	Pl,P,C*	L	Ph	Up.Cret.pebbles+
1040	r		L	L	Up.Cret.(above Danian)
1055	r		L		
1056	r	G,Ph*		Ph	?Miocene
1070	p		L		
134	r	Pl,P,L*		Ph	?Miocene+
135	r	Pl,P,L*		Ph	Eocene+; Ph = Tertiary
136	r	Pl,P,L*	L	Ph	Eocene+
139	r	Pl,P,C*		Ph	Eocene pebbles+; Ph = Tertiary

Table 5.2 K.Ar Analyses Carried Out by Dodson and Rex, Geology Department, Leeds University.

The Vol.^{40}Ar is expressed in rad.scc/g x 10^{-6}.

Sample	No.	%K	Vol.^{40}Ar	%^{40}Ar rad.	Age m.y.
Whole Rock	154	2.12	4.33	67.3	49.1 ± 3
Whole Rock	234	0.46	4.10	67.1	210 ± 10
Rock Glauconite	848	5.04	2.17	33.9	10.8 ± 0.5
Rock Glauconite	877a	4.88	2.14	44.0	11.0 ± 0.5
Rock Glauconite	877b	4.73	2.21	42.1	11.7 ± 0.5
Sed. Glauconite	155	6.88	3.98	55.1	14.4 ± 0.5
Sed. Glauconite	833	3.96	1.68	25.6	10.6 ± 0.5
Sed. Glauconite	882	6.94	3.66	60.9	13.1 ± 0.5

APPENDIX 5

TABLES

Table 1.4.1 Binocular Microscope examination of different size grades. A = Abundant, C = Common, R = Rare. Symbols in parentheses represent variables noted only in acetic acid insoluble residues. Samples 837,154,155 and 882 are from the continental slope; the rest are from the continental shelf.

Sample No.	Mudstone	Limestone	Sandstone	Phosphorite	Mollusca	Shark Teeth	Glauc. Grains	Glauc. Coatings	Echinoid Spines	Coral	Forams.	Sponge Spicules	Quartz	Detrital Minerals	Bryozoa	Glauc. casts	Fishbones
Very Coarse Sand																	
150																	
832	A			C	R			C									
833	A			C	R												
834	A			C	C			C									
151	C	C		C	R			C									
153	R	R		R		A	C										
836	C			R	A	R											
873	A			C				C									
837				C	A		R										
154				R	A		R		R	C	R						
155	R	R	R	R	C	R	C										
882	C			C	R	R	A	C	R								
Coarse Sand																	
150																	
832	A			R			A										
833	A			R	R		A				R	R		R			
834	A			C	C		A										
151	C			R	R		C	C									
153	R			R	C		A	C									
836				R	A		R		R		R				R	R	
873	C			R			A	R									
837				R	A		A	C					R			R	
154				C	A			C		C	(R)(R)		(C)				
155		R	C	C	C	R	A	C			R					(C)	
882		R		R			A	R			A						
Medium Sand																	
150																	
832	A			R			A										
833	C			(R)C			A				C	R	R			(R)	
834	C			(R)C			A	C			C		R			R	
151	R			(R)R			A		R		R					R	R
153	C			(R)C			A				R						
836				(R)C			C		R		C	R				R	R
873				R			A	R									
837				R	R		C	R			R		R			R	R
154				C	C		C		R		A(R)R					R	R
155		B	C	C	R		C				A(R)(R)					.R	
882				(R)	(R)C						A		.			(R)	
Fine Sand																	
											A	R	C	C		R	
R				(R)R		C					A		R			R	
R				(R)R	(R)C			R			A(R)(R)					R	
				(R)R	R	C					A(R)		R			R	
				(R)R		C					A	R	R	R			
				(R)R		C					A						
				(R)R		C		R			A(R)R	R				C	
				R		C					A					R	
R				(R)		A		R			A	R(C)R				R	
				R	R	A		R			A(R)(R)	R				A	
				R	(R)A						A(R)(R)	R				A(R)	
				(R)	(R)A						A(R)R(R)					C	
Very Fine Sand																	
											C	C	A	R			
				(R)R		C					A(R)					C	
				(R)R		R					A(R)R	R				C	
				(R)		C					A	R	R			C	
				(R)R		C		R			A	R	R			R	
				(R)		C					A	R				R	
				(R)R		C					A	C	R			C	
R				(R)		C					A(C)C	R				C	
				(R)R		C					A	C	R			C	
				(R)R		C		R			A	R	R	R		C	
				(R)R		C		R			A	R	R			C	
				(R)		C					A(R)R	R				C	

Table 1.4.2 Granulometric characteristics of some Moroccan and Saharan sediments (phi units). Column 1 = Md total sediment; 2 = Md carbonate fraction; 3 = Md detrital fraction; 4 = Md phosphatic fraction; 5 = sorting of total sediment; 6 = sorting of carbonate fraction; 7 = sorting of detrital fraction; 8 = sorting of phosphate fraction.

Sample No.	1	2	3	4	5	6	7	8
125	4.4	4.35	4.6	4.4	0.32	0.35	0.32	0.27
126	4.1	4.02	4.5	4.15	1.40	1.40	0.47	0.95
127	4.3	4.2	4.45	4.10	0.60	0.77	0.32	0.55
133	2.0	1.95	2.00	2.40	1.10	0.55	1.01	0.85
134	1.4	1.2	1.90	2.20	2.10	1.40	1.96	1.55
137	3.0	2.95	3.0	3.10	0.55	0.60	0.45	0.57
140	3.1	2.98	3.8	3.3	0.90	1.25	0.87	0.35
144	4.4	4.25	4.62	4.45	0.57	0.82	0.36	0.45
150	4.6	4.5	4.60	4.62	0.30	0.27	0.31	0.40
151	2.9	2.9	4.40	1.50	2.40	2.35	2.57	2.35
153	2.2	2.5	1.10	0.80	1.77	1.00	1.62	1.70
154	2.85	2.5	4.32	2.12	1.55	1.85	0.72	1.35
155	3.00	3.9	4.2	2.42	1.55	1.40	1.00	1.45
922	1.45	1.32	2.10	1.92	1.32	1.22	1.69	1.25
923	1.10	1.10	1.40	1.68	1.27	1.20	1.55	1.4
926	1.50	1.30	3.70	1.30	1.15	1.30	1.97	1.55
927	3.15	2.60	3.42	3.20	0.80	0.85	0.41	0.70
931	1.35	1.20	2.10	1.20	1.25	1.10	1.95	1.30
936	4.15	3.90	4.25	4.10	0.80	1.25	0.55	0.80
937	1.00	0.95	2.75	1.92	1.00	0.75	0.2	0.9
986	0.50	0.45	0.75	0.70	0.60	0.60	2.35	0.7
987	-0.10	-0.10	0.00	0.00	0.50	0.45	2.25	0.6
989	3.10	2.20	4.5	2.05	1.80	1.85	1.07	2.00
991	3.70	2.55	4.2	3.2	1.50	1.45	1.12	1.55
992	2.00	1.80	2.85	2.20	1.30	1.40	1.45	0.50
993	2.40	2.20	2.90	2.90	1.10	1.00	0.95	0.55
998	2.70		3.00	2.30	1.40		1.30	0.50
999	0.70	0.70	0.25	0.00	1.15	1.15	1.23	1.25
1079	2.75	2.50	2.85	2.80	0.62	0.75	0.55	0.40
1080	2.90	2.70	3.10	2.90	1.0	0.85	1.01	0.65
1081	4.60	4.40	4.80	4.60	0.5	0.60	0.47	0.60
1083	4.75	4.60	4.78	4.80	0.35	0.4	0.35	0.35
1085	4.60	4.40	4.70	4.60	0.45	0.75	0.39	0.55
1086	4.10	3.40	4.35	4.20	1.10	1.10	0.91	0.60
1088	2.55	2.30	2.92	3.05	1.30	0.95	1.26	0.85
255	1.7							
256	1.2							
258	0.5							
257	2.3							

Table 1.4.3 Redox potential measurements on some surficial sediments; all readings are positive.

Sample No.	Eh(mv)	Sample No.	Eh(mv)	Sample No.	Eh(mv)
110	133	224	365	250	387
125	399	225	115	251	127
126	367	226	147	252	367
127	267	227	277	256	377
128	<67	228	147	257	425
133	<67	230	<67	258	407
134	385	232	137	259	392
137	202	233	<67	260	419
140	97	234	365	262	422
141	97	235	449	263	367
143	162	237	389	264	297
144	102	238	389	272	389
155	383	239	377	273	365
154	132	240	357	270	430
153	385	241	402	274	117
151	197	242	345	275	345
150	87	244	367	278	122
221	<67	245	337	279	155
222	<67	246	327	281	155
223	<67	247	384	282	97
		249	500		

Table 2.2.1 Granulometric characteristics of the phosphatic and detrital components of the sand fraction of selected sediments (phi units). Column 1 = Md detrital components; 2 = Md phosphatic components; 3 = sorting of detritals; 4 = sorting of phosphatic components. Values for 151, 154 and 155 were calculated on a glauconite-free basis.

Sample No.	1	2	3	4	Sample No.	1	2	3	4
125	2.3	2.7	0.67	0.81	936	3.25	3.08	0.20	0.46
126	1.85	2.9	1.05	0.9	937	2.65	1.90	0.17	0.92
127	2.68	3.2	0.93	0.27	986	0.38	0.67	0.45	0.75
133	1.95	2.4	1.01	0.82	987	-0.2	-0.1	0.6	0.53
134	1.70	2.2	1.50	1.55	989	2.65	1.6	0.67	1.61
137	3.00	3.08	0.45	0.57	991	2.45	2.35	0.77	0.84
140	3.1	3.2	0.42	0.25	992	2.18	2.15	0.66	0.45
144	2.62	2.95	0.7	0.65	993	2.40	2.15	0.75	0.52
150	3.22	3.25	0.17	0.18	998	2.58	2.25	1.05	0.90
151	-0.1	0.1	1.5	1.35	999	0.22	-0.1	1.15	1.25
153	0.85	0.70	1.6	1.57	1079	2.85	2.80	0.4	0.37
154	3.05	1.90	1.0	0.87	1080	2.85	2.90	0.5	0.51
155	2.60	2.18	1.5	1.37	1081	3.12	3.12	0.28	0.27
922	1.72	1.85	1.20	1.32	1083	3.15	3.15	0.23	0.21
923	1.30	1.60	1.43	1.30	1085	3.02	3.06	0.37	0.36
926	1.70	1.00	1.37	1.12	1086	2.97	3.12	0.52	0.37
927	3.20	3.05	0.21	0.47	1088	2.45	3.02	0.57	0.60
931	1.90	1.15	1.45	1.26					

Table 2.2.2 Phosphate contents (per cent P_2O_5) of selected mineral fractions from different size grades of shelf and slope sediments off Cap Sim.

Sample No.	Separated Biogenic Debris				Glauconite				Pebbles and Granules	Unleached	
	Coral and Mollusca	Mainly Foraminifera								Silt	Clay
	0 phi	2 phi	3 phi	4 phi	1 phi	2 phi	3 phi	4 phi	(0 phi)		
154	0.08									0.26	0.38
155	0.08								4.5	0.34	0.45
832			0.10	0.10			0.15	0.14	13.5		
833		0.17	0.10		0.20	0.14	0.18	0.17	4.5		
834			0.13	0.16				0.19	1.3		
836			0.11				0.16	0.22	1.5		
837			0.13	0.14				0.20	9.0		
873				0.22					3.6		
882									19.1		
Mean	0.08	0.17	0.11	0.13	0.20	0.14	0.16	0.18	7.0	0.30	0.41

Table 2.2.3 Phosphate contents (per cent P_2O_5) of acetic acid insoluble residues of the non-magnetic fractions of selected sediment samples.

Sample No.	Separated detrital concentrates					Separated glauconite		
	(1) with fines removed		(2) decanted fine material			green casts		brown casts
	3 phi	4 phi	2 phi	3 phi	4 phi	3 phi	4 phi	2 phi
154	10.36		0.18	0.20	0.37	0.97		
155	8.6	2.7	0.29	0.32	0.54	3.15	1.76	
833	2.61	0.56		0.22	0.29	0.45	0.23	
834				0.32				
836				0.39		0.56		
882		3.38	0.17	0.22	0.32			0.27
Mean	7.2	2.2	0.21	0.28	0.38	1.28	1.00	0.27

Table 2.2.4 Phosphate content (per cent P_2O_5) of purely biogenic fractions of north Moroccan sediments (from Nutter, 1969).

Sample No.	Size Fraction	Per Cent P_2O_5
125	1 phi	0.03
927	0 phi	0.08
	1 phi	0.09
937	0 phi	0.09
	1 phi	0.10
1088	1 phi	0.14

Table 3.3.1 Elemental abundances in different size fractions of Moroccan sediments.

Element	C.Sim: C.Blanc (mean clay)		C.Sim: C.Blanc (mean silt)		% Difference clays : silts		Shale av.	Ratios to Al C.Sim: C.Blanc clay : clay	
Zn	118	120	75	81	1.7	7.4	95	0.86	0.89
Ti	2226	2182	8371	8502	2.0*	1.5	4600	16.2	16.3
Sr	52	49	95	108	5.8*	12.0	300	0.38	0.36
Mn	262	322	356	390	18.6	11.3	850	1.90	2.40
Ni	49	50	45	40	2.0	11.1*	68	0.36	0.37
Cr	120	125	87	89	4.0	2.2	90	0.87	0.93
Co	8.7	9.7	10.3	11.1	10.3	7.2	19	0.063	0.072
Ba	199	166	252	232	16.6*	7.9*	580	1.45	1.23
V	160	184	145	178	13.0	18.5	130	1.16	1.37
Pb	32.6	30.8	21.9	21.9	4.9*		20	0.24	0.23
Cu	113	94.3	41.2	42.4	16.5*	2.8	45	0.82	0.70
Ga	19	18.6	14.5	14.1	2.1*	2.8*	19	0.14	0.14
Si	21.0	20.6	32.8	31.0	1.9*	5.5*	7.3	1526	1529
Mg	2.13	2.44	1.34	1.84	1.3	27.2	1.5	155	181
K	3.78	3.67	3.65	3.52	2.9*	3.7*	2.66	275	274
Fe	4.14	4.39	2.9	3.14	5.7	7.6	4.72	301	328
Ca	0.79	0.73	0.83	1.05	7.6*	20.9	2.21	57	54
Al	13.76	13.4	7.54	8.29	2.6*	9.0	8.0		
P_2O_5	0.34	0.15	0.3	0.3	55.9*		0.16	24.7	11.1

Elemental abundances were determined by direct reading emission spectrography on the acetic insoluble fraction of the sediment; P_2O_5 values are calculated on a carbonate-free basis. Abundances for minor elements are given in ppm; for major elements Si, Al, K, Mg, Ca, Fe, and P_2O_5 abundances are given in per cent. Each silt and clay mean was determined from five samples, the individual abundance levels in which are given in table 3.3.1a; for Cap Sim the samples used were 144, 150, 151, 154, 155, and for Cap Blanc were 125, 126, 127, 137 and 140. The presence of an asterisk denotes enrichment off Cap Sim; absence of an asterisk in the same columns denotes enrichment off C. Blanc. For convenience the ratios to Al have been multiplied by 1000. Average shale abundances have been derived from Turekian and Wedepohl, 1961.

Table 3.3.1.a Direct reading emission spectrographic analyses of the acid insoluble residues of some Moroccan and Saharan sediments. All values are expressed in ppm, except Si, Mg, K, Fe, Ca, Al and P_2O_5, which are given in per cent. P_2O_5 values are expressed on a carbonate-free basis.

Sample No.	Zn	Ti	Sr	Mn	Ni	Cr	Co	Ba	V	Pb	Cu	Ga	Si	Mg	K	Fe	Ca	Al	P_2O_5
111	83	5018	86	316	38	110	9	116	172	24	27	12	26.1	1.9	3.0	3.6	1.6	5.6	1.43
112	108	4150	83	410	34	146	11	137	269	40	29	13	22.9	3.1	3.1	8.0	1.4	9.3	1.02
113	77	4741	74	527	42	136	12	148	318	49	62	15	23.1	2.5	3.0	7.6	1.2	10.8	0.67
114	83	4349	64	427	35	119	9	166	241	38	35	14	22.5	1.5	3.0	5.5	0.9	11.0	0.47
115	233	9064	95	345	75	163	14	24	284	37	45	19	24.7	1.3	3.3	3.0	0.4	15.5	0.18
116	72	6429	59	291	47	126	11	17	214	27	38	17	27.6	1.4	3.4	3.4	0.7	10.2	0.16
117	55	6641	42	366	37	103	10	121	176	22	29	11	36.8	2.2	2.5	3.0	0.9	5.9	0.17
119	89	5130	70	666	43	99	13	274	190	28	61	16	25.0	1.7	3.1	3.6	0.8	12.0	0.20
120	79	5635	79	272	41	114	9	300	225	22	53	16	29.5	3.2	3.3	3.8	1.1	11.6	0.24
121	97	5019	67	447	42	104	12	166	186	29	42	14	27.2	1.9	2.9	4.0	1.2	8.6	0.59
125	101	5022	80	563	53	100	13	297	175	30	58	18	24.4	1.9	3.6	4.1	0.6	11.1	0.11
126	109	5345	72	766	49	104	16	276	188	24	51	17	29.4	2.9	3.6	4.3	0.7	12.4	0.26
127	86	4538	75	349	39	99	10	269	166	17	49	16	25.1	1.7	3.5	3.7	0.8	12.1	0.33
129	109	3402	412	507	49	176	19	209	315	55	39	12	14.2	3.0	3.0	7.4	5.9	9.9	8.50
133	135	2669	765	339	36	146	12	198	194	54	38	10	12.5	5.3	2.7	8.0	13.3	7.7	19.00
134	106	2387	608	388	35	106	10	191	170	48	31	8	11.7	6.1	2.1	6.5	12.6	8.0	18.80
135	88	3337	181	762	35	97	12	203	247	48	36	13	23.9	7.8	2.7	5.2	3.7	10.0	1.60
137	85	3162	68	394	21	106	8	163	170	53	27	11	21.1	1.8	3.2	8.0	1.2	8.8	0.91
139	70	1717	113	999	27	63	15	234	261	96	23	7	16.8	1.7	2.1	9.2	6.9	4.9	0.80
140	64	4100	151	424	22	86	8	154	154	27	22	9	21.5	5.7	2.3	3.6	3.6	4.8	4.60
144	146	5900	78	369	61	112	13	299	198	24	54	19	29.4	1.8	4.1	5.7	0.7	11.4	0.13
150	74	5610	61	342	42	100	10	244	187	28	34	16	28.2	0.7	3.6	3.1	0.7	10.6	0.22
151	64	3002	63	154	27	101	5	151	112	29	27	11	25.7	1.5	5.0	9.8	1.0	4.8	0.41
153	66	1625	66	150	20	98	4	404	99	37	14	8	20.6	3.0	3.7	15.3	1.1	3.0	1.29
154	163	3168	79	189	32	173	7	169	151	25	29	15	23.9	1.9	5.1	7.0	1.0	7.6	0.68
155	175	2310	69	146	31	240	4	192	202	25	28	11	24.9	2.7	5.4	9.7	1.1	3.9	1.21

Table 3.3.1.a (Contd.)

Sample No.	Zn	Ti	Sr	Mn	Ni	Cr	Co	Ba	Y	Pb	Cu	Ga	Si	Mg	K	Fe	Ca	Al	P_2O_5
221	25	3947	75	225	42	72	5	220	86	18	33	10	40.6	0.5	2.3	2.1	0.7	4.9	0.18
223	25	4735	83	212	38	138	4	187	84	21	27	10	38.2	0.9	2.3	1.8	0.7	3.8	0.23
224	149	4264	78	198	62	200	5	143	236	43	67	13	39.5	0.9	2.4	5.2	0.8	5.2	0.38
225	55	5500	92	240	62	111	5	163	120	21	53	10	42.2	1.0	2.0	2.0	0.9	4.5	0.67
226	25	3136	50	95	19	36	1	99	69	15	19	5	41.8	0.8	0.6	0.8	0.6	1.9	0.64
227	25	7009	55	86	40	86	4	134	92	53	40	9	52.1	1.2	0.8	1.8	0.5	2.1	0.41
228	25	2142	41	53	41	87	3	109	56	46	34	9	47.3	1.4	0.8	1.4	0.4	2.2	0.12
230	25	6474	68	208	52	108	7	171	99	46	74	12	36.3	0.8	2.1	1.9	1.3	3.7	0.77
234	137	3853	72	146	80	210	9	135	130	48	132	17	25.1	0.8	2.8	7.6	1.1	7.6	0.73
237	175	4905	90	193	87	298	10	180	290	65	100	15	28.5	0.8	2.2	7.7	1.7	7.4	0.25
238	155	4504	71	166	92	227	9	140	173	56	92	14	33.7	0.9	2.0	5.1	1.3	4.6	0.29
239	190	4204	92	173	100	431	8	176	336	73	112	17	25.6	0.8	2.1	10.0	1.9	7.6	0.29
240	101	4416	69	134	108	295	7	119	250	65	78	13	42.0	1.0	1.6	5.3	1.2	4.0	0.13
241	25	5047	55	121	62	140	5	137	157	50	62	10	42.9	0.8	1.6	2.3	1.1	2.7	0.50
242	99	4638	76	141	84	344	8	111	284	63	112	14	39.9	0.8	1.7	4.2	1.5	5.1	0.15
245	92	4506	57	133	67	291	8	120	224	60	129	13	47.1	1.0	1.4	3.9	1.0	4.5	0.14
246	25	3230	34	62	33	50	1	95	38	43	31	7	43.7	0.6	0.3	0.6	0.4	1.4	0.04
247	25	2359	57	23	27	41	1	10	58	40	21	7	40.9	0.9	0.1	0.3	0.1	0.6	0.03
249	133	8154	74	497	78	118	17	348	186	54	72	17	27.5	0.8	2.7	3.9	1.0	7.4	0.31
250	140	8255	68	524	76	121	18	289	175	57	73	17	28.8	0.7	2.6	4.0	0.9	7.1	0.33
252	160	5688	69	467	79	162	24	169	229	53	61	15	28.8	0.6	2.9	5.7	1.2	5.8	2.00
255	222	2996	434	185	66	350	17	136	238	73	38	8	10.6	0.9	1.6	12.9	16.8	3.4	1.81
256	112	3076	153	178	67	241	10	141	253	67	44	10	13.4	1.2	1.5	12.3	5.9	4.1	32.00
257	141	3573	105	231	74	153	10	175	291	76	66	13	18.8	0.9	2.2	7.6	3.4	6.6	2.30
258	177	2932	144	175	59	183	9	148	271	77	48	11	18.1	2.1	2.1	9.8	5.8	3.7	24.30
259	174	2545	105	177	55	161	9	192	234	79	51	11	18.8	2.6	1.9	10.3	5.3	3.7	2.20
260	25	1773	109	141	42	124	6	150	149	58	30	7	13.0	5.0	1.4	5.2	10.5	1.8	2.40
262	76	3581	87	170	53	130	8	196	185	71	53	11	14.0	4.6	2.1	4.3	7.3	4.5	0.86
263	68	2961	87	206	55	223	8	183	393	108	54	11	16.1	4.0	1.8	8.8	6.4	4.6	0.25
264	25	2418	43	88	40	98	4	98	178	58	50	8	41.3	1.6	0.9	3.0	2.4	0.8	0.36

Table 3.3.1.a (Contd.)

Sample No.	Zn	Ti	Sr	Mn	Ni	Cr	Co	Ba	V	Pb	Cu	Ga	Si	Mg	K	Fe	Ca	Al	P_2O_5
266	25	4819	47	155	43	57	6	164	104	41	29	12	44.6	0.4	2.7	1.9	0.3	4.2	0.14
267	204	3339	91	177	59	177	6	162	527	128	54	11	14.6	1.3	1.8	22.3	2.2	5.2	1.45
268	167	3968	83	193	61	184	8	217	458	100	277	13	18.8	1.5	2.1	17.2	2.3	6.4	0.92
269	162	3940	75	200	62	284	9	157	602	103	66	11	15.4	1.0	1.9	20.7	2.1	4.6	1.07
270	87	3795	94	346	170	217	11	224	662	103	85	11	14.1	1.2	1.7	19.5	3.2	5.2	1.92
271	179	3420	86	256	65	222	10	175	556	90	72	11	19.9	1.3	1.7	19.8	3.4	4.3	1.64
272	144	3220	56	211	61	180	8	162	321	82	49	13	26.6	1.7	2.0	9.4	2.3	5.1	0.75
273	179	3635	77	183	58	191	7	134	202	75	44	13	20.2	1.0	2.5	11.5	2.1	4.7	0.90
274	138	3786	47	156	57	171	7	101	118	55	37	12	25.0	0.6	2.9	8.4	1.1	3.7	1.00
275	210	3611	54	171	58	144	6	137	112	51	49	12	26.0	1.0	2.2	5.9	1.6	3.4	1.09
276	181	3556	106	217	63	217	9	176	317	75	51	14	16.1	1.4	2.2	11.6	3.0	6.2	1.63
277	278	4255	122	207	65	172	9	178	206	70	53	14	23.6	1.0	2.5	8.2	3.1	5.1	24.40
280	114	6937	64	270	85	127	13	302	191	56	81	21	24.4	0.8	3.1	4.2	0.7	10.0	0.12
283	130	8413	72	605	108	138	16	287	214	62	78	19	23.4	0.9	2.9	4.2	0.8	8.8	0.18
284	177	9055	72	886	109	145	19	268	210	60	80	20	23.9	0.9	3.1	4.2	0.7	8.7	0.16
285	115	6068	57	254	81	120	12	265	171	51	117	19	21.0	0.3	2.8	4.5	0.6	8.5	0.12
125 silt	62	8800	146	406	40	87	11	273	152	22	42	14	27.8	1.3	3.6	2.7	1.3	7.9	
125 clay	60	2357	50	331	44	111	9	191	164	24	96	17	18.5	1.8	3.3	4.1	0.8	13.3	
126 silt	108	9427	122	445	39	88	12	261	205	16	39	15	34.5	2.5	3.9	3.2	1.0	9.2	
126 clay	107	2137	42	374	50	123	11	179	184	30	107	19	21.8	2.8	3.6	4.8	0.7	13.8	
127 silt	59	9321	108	423	36	78	10	263	169	14	36	14	32.3	2.1	3.4	2.8	1.1	9.6	
127 clay	204	2049	62	306	40	120	9	171	184	20	92	19	19.4	2.7	3.9	4.3	0.8	13.8	
133 silt	144	8746	140	360	63	109	12	210	200	30	72	15	41.0	2.7	3.2	3.7	1.4	8.3	
134silt&clay	136	5629	75	297	57	121	10	211	191	34	91	19	25.3	1.3	3.8	3.8	0.5	1.2	
137 silt	71	6900	68	323	32	88	10	147	152	27	44	13	31.9	1.1	3.1	3.5	0.7	6.6	
137 clay	111	2061	30	263	68	146	10	134	219	31	89	20	21.9	2.4	3.8	4.4	0.4	12.8	
140 silt	106	8062	98	352	55	106	13	217	213	31	53	15	28.7	2.2	3.6	3.5	1.2	8.3	
140 clay	121	2307	59	334	49	125	10	156	167	50	88	19	21.3	2.6	3.8	4.4	0.9	13.3	

Table 3.3.1.a (Contd.)

Sample No.	Zn	Ti	Sr	Mn	Ni	Cr	Co	Ba	V	Pb	Cu	Ga	Si	Mg	K	Fe	Ca	Al	P_2O_5
144 silt	104	10,000	106	409	47	89	12	272	166	20	41	15	35.1	2.0	3.8	2.9	0.9	8.7	
144 clay	155	2720	59	308	57	127	11	200	175	33	131	22	22.6	2.0	4.2	4.1	0.6	15.0	
150 silt	61	8147	84	347	44	83	10	214	135	23	40	14	33.1	0.9	3.4	2.8	0.7	6.4	
150 clay	99	2305	42	260	50	134	9	159	180	45	108	20	20.0	0.9	3.9	3.9	0.6	13.7	
151 silt	78	8199	90	351	50	92	11	244	167	27	43	16	30.8	0.9	3.8	3.2	0.8	7.9	
151 clay	110	2062	46	239	46	123	7	176	165	31	122	19	20.0	1.7	3.8	4.0	0.7	13.3	
154 silt	67	7941	82	345	42	91	9	267	123	14	38	14	31.6	0.8	3.5	2.7	0.7	8.2	
154 clay	111	2227	63	235	45	102	8	269	128	18	108	16	20.0	1.8	3.5	3.6	1.0	14.4	
155 silt	66	7568	111	326	44	81	10	263	131	27	44	14	33.6	2.1	3.6	3.0	1.0	6.6	
155 clay	116	1817	49	269	50	115	9	191	150	36	96	18	22.7	4.2	3.4	5.0	1.0	12.5	
153 silt & clay	127	6192	64	337	53	112	10	342	169	29	80	18	29.8	0.6	3.8	4.1	0.4	9.3	

Table 3.3.1.b Chemical analyses of Moroccan continental margin sediments (see text for descriptions of methods). Soluble Fe and Mn, and P_2O_5 values are expressed on a carbonate free basis but C_{org} values are not: all other determinations were made on acid insoluble residues. P_2O_5, C_{org}, and Fe_2O_3 values are expressed in per cent; all other values are in ppm.

Sample No.	Fe_2O_3	Pb	Ga	V	Cu	Zn	Ti	Ni	Co	Mn	Cr	Ba	Sr	Mo	Sol. Mn	Sol. Fe	C_{org}	P_2O_5
110	9.2	20	30	160	50	200	5000	60	30	400	200	300	60				0.3	0.60
111	11.8	30	20	200	40	200	5000	60	30	300	200	200	85		7.2	67.8	0.23	1.43
112	17.5	50	30	300	40	200	5000	60	20	300	200	300	85		11.4	64.4	0.21	1.02
113	14.0	35	20	300	62	215	4000	50	20	350	115	145	35	2	13.2	80.2	0.34	0.67
114	17.1	35	25	400	40	200	6000	60	25	500	180	250	55		8.8	51.7	0.46	0.47
115	8.9	30	30	250	55	125	6000	60	25	300	180	300	50		5.2	40.8	0.67	0.18
116	8.5	30	33	190	52	150	5800	66	20	350	145	275	50		4.9	40.3	0.67	0.16
117	8.2	20	18	140	40	75	4250	58	22	380	107	150	25		4.3	40.9	0.38	0.17
119	7.7	33	33	210	70	200	5300	53	27	666	120	370	63	2	6.6	26.5	0.24	0.20
120	7.0	21	27	220	57	155	6000	65	23	255	155	400	60		7.2	44.7	0.13	0.24
121	7.0	20	17	115	33	183	4000	43	15	330	97	173	37	5	13.9	42.5	0.26	0.59
125	10.0	30	30	200	50	50	5000	60	20	500	130	400	50	2	6.2	22.5	0.30	0.11
126	9.3	30	20	200	40	50	5000	60	20	300	130	400	50	3	8.2	22.5	0.30	0.26
127	7.2	20	30	175	50	200	5000	57	22	300	20	375	57		4.0	21.3	0.35	0.33
128	23.5	45	20	400	35	75	4000	68	28	400	250	200	350					
129	16.6	62	18	315	45	138	3500	65	34	452	209	321	310		14.2	44.9	0.23	8.50
133	9.4	30	30	300	60	160	6000	85	30	400	300	400	60		9.3	190.4	0.28	19.00
134	14.5	54	13	170	36	134	2461	47	19	346	126	294	457		16.3	98.1	0.23	18.80
135	11.6	53	20	247	41	111	3440	46	22	680	115	312	136		21.2	38.2	0.15	1.60
137	14.0	43	19	163	30	175	3300	40	16	300	115	175	40		9.8	110.8	0.38	0.91
138	9.0	40	30	300	50	160	6000	60	30	400	200	400	60					
139	20.0	108	11	261	26	88	1770	36	27	220	75	360	85		29.1	50.4	0.19	0.80
140	8.0	30	13	154	25	81	2461	47	19	346	126	294	457		19.7	126.3	0.26	4.60
141	3.4	17	10	50	1	25	1150	15	2	160	50	60	150		4.7	34.0	0.10	2.02

Sample No.	Fe_2O_3	Pb	Ga	V	Cu	Zn	Tl	Ni	Co	Mn	Cr	Ba	Sr	Mo	Sol.Mn	Sol.Fe	C_{org}	P_2O_5
143	9.4	30	40	200	60	200	5000	60	30	400	160	400	60		2.2	19.5	0.57	0.13
144	7.6	17	28	170	55	187	5500	66	24	300	134	400	62		1.9	18.5	0.45	0.13
149	2.6	16	16	60	30	25	1600	30	13	200	60	160	40		2.4	32.3	0.10	0.27
150	8.3	30	30	177	43	270	5700	60	18	300	105	330	50		2.4	23.1	0.94	0.22
151	19.8	22	18	130	20	50	3300	50	11	110	110	230	43		0.9	39.3	0.63	0.41
153	43.0	40	16	173	14	67	2070	40	8	187	170	600	65		1.9	64.8	0.33	1.29
154	13.8	15	20	140	27	100	3700	47	14	140	187	195	43		0.9	28.0	0.45	0.68
155	18.0	14	18	210	22	117	3000	47	9	161	270	200	50		1.7	47.4	0.38	1.21
802	9.6	20	35	200	60	50	6000	85	20	300	130	550	85		1.4	13.5	0.80	0.30
803	8.1	20	35	145	50	50	5500	60	16	300	115	400	60		1.2	16.6	0.80	0.20
804	9.2	10	16	50	13	50	1600	20	5	160	85	100	30		0.8	21.3	0.33	0.39
805	29.0	16	13	100	6	25	1300	20	5	85	130	85	20		0.8	45.4	0.41	0.75
806	9.0	30	30	160	60	100	6000	60	20	300	130	400	50		2.9	29.8	1.10	0.22
809	7.6	20	30	160	55	75	5500	60	17	300	115	450	50				0.77	
810	8.5	16	20	100	50	50	5000	50	13	200	100	300	40		1.2	17.2	0.66	0.20
811	15.7	8	18	107	23	150	3500	55	16	115	165	160	30		1.5	20.6	0.69	0.37
812	24.0	13	15	107	1	25	550	18	3	45	230	25	15		0.9	31.4	0.24	0.76
813	29.0	30	20	300	16	100	1600	40	3	85	400	100	40		0.4	47.7	0.32	0.64
814	18.5	8	20	85	13	100	2000	40	5	130	160	130	20		0.6	19.8	0.35	0.33
815	20.0	13	16	85	8	100	1600	20	3	130	130	130	50		0.7	41.3	0.41	0.88
817	19.0	20	16	100	13	100	3000	30	10	160	100	200	60		3.0	81.0	0.40	0.57
818	15.9	16	23	93	9	125	1800	30	12	215	115	250	45		1.1	46.7	0.41	0.45
819	11.4	45	25	165	45	100	3500	50	23	450	130	1600	40		27.7	136.6	0.37	0.75
820	8.0	40	20	130	40	160	4000	50	20	400	130	400	200		12.8	90.4	0.45	1.69
821	14.5	16	30	130	30	50	5000	50	13	200	130	400	60		1.8	55.9	0.75	0.44
822	21.0	20	30	130	30	200	5000	50	20	300	160	200	60		1.7	55.4	0.51	0.28
823	11.8	30	20	300	30	50	5000	60	20	200	200	300	100		5.1	72.4	0.22	0.10
824	9.6	18	30	180	40	215	5500	55	25	350	150	350	73		2.7	37.2	0.40	0.10
826	15.8	40	30	300	40	200	5000	50	20	500	200	300	85	2	8.7	73.3	0.40	0.48
827	15.2	20	23	130	23	125	4000	50	15	200	107	300	55		1.9	42.9	0.58	0.20
829	14.2	18	19	124	18	25	4000	40	10	260	118	260	127		5.4	110.8	0.52	0.30

Sample No.	Fe_2O_3	Pb	Ga	V	Cu	Zn	Tl	Ni	Co	Mn	Cr	Ba	Sr	Mo	Sol.Mn	Sol.Fe	Corg	P_2O_5
830	10.0	16	20	100	13	25	4000	30	6	160	60	200	40		8.6	169.8	0.34	0.30
831	20.5	30	25	130	25	50	5000	45	12	250	145	350	100		2.9	73.5	0.53	0.34
832	23.0	28	16	100	18	100	2200	40	15	130	110	250	43		0.8	32.4	0.34	0.82
833	25.0	18	17	107	13	25	3000	30	9	145	115	900	40		1.2	44.8	0.39	0.54
834	16.8	25	12	73	9	25	1000	25	3	115	107	725	70		2.2	51.5	0.42	1.09
835	23.7	18	15	93	6	25	925	23	3	55	250	95	20		0.9	62.2	0.24	1.71
836	23.3	23	23	130	25	150	3000	43	13	190	130	233	78		2.1	48.0	0.28	0.79
837	18.1	19	20	145	21	115	2700	46	17	230	140	163	59		2.6	50.1	0.26	2.44
838	25.0	12	16	55	1	50	750	13	3	100	180	40	18		0.4	37.6	0.16	0.42
839	10.0	2	13	40	1	25	1000	10	3	60	100	60	16		0.4	28.9	0.32	0.37
840	47.0	1	21	103	8	90	1480	30	9	75	280	78	28		0.4	26.4	0.26	0.47
841	18.8	18	21	150	20	25	2600	46	14	170	160	133	114		0.5	14.3	0.41	0.72
842	22.3	8	15	73	1	50	400	30	10	30	250	20	20				0.18	0.39
843	16.0	20	30	200	60	100	5000	100	30	300	160	400	60				0.56	
844	7.2	12	25	160	40	100	5500	60	16	250	115	300	45				0.48	
846	22.8	40	16	200	40	100	1300	50	16	160	400	50	40	2			0.26	1.73
847	31.0	30	13	300	20	200	2000	60	30	300	200	130	100	2	7.7	37.5	0.22	7.18
848	20.0	40	30	400	50	300	6000	60	30	400	300	300	85		10.5	53.3	0.26	2.84
851	18.0	9	15	68	2	25	500	18	3	50	230	40	15		0.3	25.7	0.28	0.44
852	24.0	16	16	85	16	50	1300	40	8	100	200	200	50		0.9	43.9	0.34	0.57
853	22.2	30	20	110	20	50	2500	35	9	180	150	1150	90		3.4	77.9	0.36	0.83
854	15.7	15	18	80	17	25	2300	35	9	215	143	1450	80		1.2	61.8	0.34	0.64
855	24.5	30	20	215	25	75	3000	45	13	250	180	500	73		6.2	79.6	0.40	1.02
856	7.4	30	30	160	40	200	4000	60	30	100	130	300	50		1.7	20.6	0.94	0.18
857	10.5	30	30	300	50	50	6000	60	16	300	160	400	85		1.8	24.9	0.92	0.18
859	11.0	40	40	200	40	200	6000	85	20	500	200	400	60		2.0	35.3	0.58	0.32
860	33.0	30	16	160	13	100	2000	50	10	300	300	400	60		1.2	39.8	0.36	0.47
861	10.1	25	30	165	35	175	5500	60	25	400	160	400	68		1.1	27.6	0.86	0.21
862	29.5	35	16	85	9	25	2000	30	3	160	145	230	30		0.9	38.1	0.54	0.72
863	20.5	20	13	50	1	25	400	30	3	60	100	130	20				0.22	0.41
864	25.0	30	16	85	12	25	1800	30	9	350	130	7500	70		5.9	57.8	0.38	0.70
865	10.0	23	26	178	36	130	5400	52	22	280	118	340	50		1.8	32.4	0.66	0.21

Sample No.	Fe_2O_3	Pb	Ga	V	Cu	Zn	Tl	Ni	Co	Mn	Cr	Ba	Sr	Mo	Sol.Mn	Sol.Fe	C_{org}	P_2O_5
866	12.5	20	13	100	13	50	2000	30	8	130	130	160	50	2	4.4	134.0	0.22	1.24
867	20.1	30	16	85	13	90	1800	25	3	160	93	230	55	2	6.5	92.8	0.70	0.66
868	6.9	12	30	165	55	100	5500	73	18	350	108	400	55				0.52	
869	7.2	30	35	145	45	115	5500	60	23	350	160	350	40		2.3	36.8	0.98	0.21
870	7.7	25	30	180	35	100	4000	40	17	300	100	300	45		1.6	31.2	0.50	0.27
871	14.2	30	20	130	20	50	3000	40	13	300	85	130	50		2.8	62.5	0.40	0.50
872	6.0	20	30	100	20	100	4000	40	20	200	85	300	40		1.7	26.6	0.96	0.18
873	35.7	40	17	107	10	25	1650	25	3	115	180	350	35		0.8	46.8	0.50	1.16
874	30.0	40	13	85	8	50	2000	40	13	160	160	400	40		1.1	34.8	0.09	0.88
875	33.0	40	20	200	20	200	3000	60	13	400	300	160	100		1.4	32.0	0.34	1.50
876	34.0	50	20	300	30	300	4000	85	30	500	200	500	130		4.3	59.9	0.18	0.60
877	22.2	40	16	160	30	300	3000	60	20	400	130	160	85		11.0	140.5	0.18	2.50
878	25.0	20	20	145	22	125	2000	35	12	130	200	1300	50		1.2	58.0	0.34	1.24
879	7.8	20	20	100	40	200	4000	50	16	300	100	500	30		1.8	29.7	0.84	0.26
882	13.5	5	16	160	16	50	1000	40	10	85	200	130	50		2.2	21.2	0.26	1.90
885	9.2	30	16	160	20	200	8500	40	16	600	85	300	60		2.5	23.4	0.14	0.27
886	5.0	20	20	93	30	25	3000	40	12	250	60	250	35				0.22	0.43
887	12.5	85	16	300	20	25	2000	50	30	2000	160	300	85	13			0.09	2.60
888	7.1	40	16	160	30	50	2000	30	10	200	85	300	85				0.32	0.18
889	7.9	30	13	160	30	25	2000	30	6	400	85	200	85				0.18	0.14
890	6.7	18	20	100	35	180	4000	45	20	300	73	300	35		1.5	29.1	0.54	0.20
891	14.0	25	23	73	23	100	3500	35	5	230	60	300	35		1.1	35.2	0.38	0.22
892	16.8	50	20	300	40	200	4000	50	20	500	130	300	6		10.3	65.3	0.14	0.14
893	25.8	25	25	130	30	100	3000	50	15	200	115	600	55		2.0	52.0	0.40	0.38
894	29.0	50	20	200	50	100	3000	50	16	400	200	1000	200		7.5	127.4	0.30	2.70
895	55.0	60	16	500	10	100	3000	60	20	500	300	400	200		5.3	41.5		1.90
896	21.0	40	20	160	30	100	4000	50	13	400	130	300	85		7.0	52.8	0.28	3.70
897	24.0	50	16	400	13	200	2000	50	20	200	500	130	85				0.24	1.18
898	12.0	30	10	200	16	25	1000	40	16	160	100	9000	50	2	12.9	49.6	0.14	11.50
899	22.2	40	40	400	85	200	6000	85	30	400	160	600	130		2.5	25.3	0.36	1.40

Sample No.	Fe_2O_3	Pb	Ga	V	Cu	Zn	Ti	Ni	Co	Mn	Cr	Ba	Sr	Mo	Sol.Mn	Sol.Fe	C_{org}	P_2O_5
901	12.5	40	13	130	30	100	2000	30	10	300	85	200	100		21.5	117.9	0.16	4.60
902	12.7	40	13	200	20	25	2000	50	30	600	60	300	60	13	98.9	163.9	1.26	0.56
903	6.5	30	16	160	20	50	1600	20	16	500	85	400	85	5	40.2	67.4	0.09	1.41
904	5.6	40	16	160	13	100	3000	40	20	1300	60	300	60	16	67.4	40.0	0.09	0.15
905	10.2	40	20	200	30	50	4000	40	20	500	100	300	100	2				
906	8.5	50	16	300	30	50	3000	40	20	1000	60	200	60	16	122.1	62.8	0.09	0.23
907	20.5	100	20	400	50	50	5000	60	20	500	100	300	50	30	104.4	138.9	0.10	0.28
908	11.0	85	30	400	50	200	6000	60	20	600	200	300	100		33.1	69.4	0.14	0.10
909	11.0	160	16	130	40	100	4000	50	30	400	85	300	100	6			0.18	7.06
911	16.5	40	20	300	13	50	2000	50	30	400	60	150	50	10	50.1	121.5	0.12	0.50
912	5.6	20	20	130	16	100	4000	30	16	300	60	300	60		1.2	16.2	0.10	0.20
913	3.6	10	16	50	8	50	2000	20	5	200	50	160	30		1.2	48.4	0.18	0.12
914	11.8	30	16	200	30	100	3000	50	16	400	130	300	85		19.2	79.5	0.34	1.11
915	10.2	30	30	160	60	200	6000	60	16	300	160	400	100		2.8	31.8	0.76	0.37
918	7.7	20	30	160	50	160	6000	60	20	300	160	500	60		3.1	63.1	0.56	0.16
921	7.8	17	30	160	45	300	5000	68	25	400	115	300	55		2.0	27.0	0.60	0.16
922	15.2	35	18	180	40	225	5000	45	10	200	150	300	75		4.6	100.4	0.26	3.41
923	12.3	30	20	160	30	100	3000	40	16	300	100	130	100		8.7	138.3	0.22	7.02
924	17.5	40	20	400	30	100	5000	50	20	850	100	200	60	2	47.1	252.0	0.16	2.70
925	10.7	28	30	180	35	150	5000	55	20	350	115	250	50		10.5	54.5	0.18	0.31
926	9.4	30	25	300	35	180	4500	50	25	250	130	250	50		2.1	21.6	0.36	0.15
927	4.5	18	23	110	28	75	3500	45	15	230	85	165	40				0.22	0.13
928	5.8	12	17	60	17	50	2500	30	13	200	110	165	45		1.4	30.0	0.18	0.16
929	20.5	50	20	400	50	50	4000	50	30	2000	130	200	85	10			0.20	0.87
930	11.0	60	20	300	40	50	4000	60	30	1600	130	300	50	5	67.6	141.0	0.20	0.24
931	11.6	40	16	250	40	100	5000	45	23	350	85	197	70		54.3	138.2	0.36	0.35
932	6.4	40	20	130	40	100	5000	40	20	850	100	400	50	2	140.0	281.8	0.12	0.91
933	17.5	60	16	300	40	50	6000	40	30	850	130	200	50		55.6	138.2	0.14	0.91
934	22.0	60	16	500	30	50	4000	50	20	600	160	300	85	6	30.4	170.9	0.10	1.01
935	16.5	60	20	160	40	200	4000	50	20	400	160	200	130		19.8	438.0	0.20	1.52
936	3.6	13	16	60	16	50	3000	30	5	200	60	160	20		2.4	31.6	0.46	0.20
937	26.0	50	13	160	30	50	2000	20	5	300	85	160	60	2			0.12	
939	7.2	20	30	130	50	50	5000	50	16	600	100	400	50		3.1	23.6	0.45	0.22

Sample No.	Fe_2O_3	Pb	Ga	V	Cu	Zn	Ti	Ni	Co	Mn	Cr	Ba	Sr	Mo	Sol.Mn	Sol.Fe	C_{org}	P_2O_5
940	6.5	35	30	150	40	175	4500	55	27	1150	100	350	45	2	17.2	23.1	0.42	0.21
941	7.5	16	25	150	38	75	5000	55	16	280	125	280	72		2.8	47.2	0.12	1.15
942	10.7	40	20	300	40	25	3500	50	12	250	200	300	550		6.8	67.8	0.28	10.70
943	9.3	40	23	180	40	25	3500	45	10	250	180	300	350	2			0.50	4.75
944	26.7	50	16	500	16	50	4000	60	40	3000	100	2000	100	13	46.8	82.3	0.16	1.65
947	9.3	40	30	200	50	200	4000	50	20	400	130	300	60	6			0.22	0.28
950	40.0	60	16	400	20	50	3000	30	20	600	130	160	40	2	36.7	219.4	0.14	5.83
951	9.6	30	20	100	20	300	4000	40	20	200	85	160	50		3.9	84.9	0.30	0.36
952	7.4	30	30	100	40	200	5000	50	20	300	85	300	50		2.8	47.2	0.48	0.24
953	19.0	50	18	450	35	150	4000	50	23	450	93	130	55				0.24	0.87
954	18.5	60	10	300	10	50	1600	30	20	1600	60	130	60	10	500.0	447.1	0.09	15.30
956	16.0	40	20	200	40	400	3000	60	30	200	200	300	60		2.8	37.7	0.28	1.14
957	25.0	35	18	300	25	100	3500	55	20	250	250	250	400				0.21	
958	6.3	20	13	100	16	25	1300	40	13	400	85	160	500		9.1	76.6	0.24	18.80
959	15.0	40	25	250	50	25	4500	50	13	300	180	350	300		13.8	85.2	0.15	2.10
960	15.5	73	20	400	35	125	4500	110	45	3500	200	400	105	8	55.2	133.3	0.17	1.43
961	32.0	60	20	500	20	300	4000	60	30	1300	100	200	30		56.4	189.1	0.15	2.00
962	36.0	60	30	600	50	300	4000	100	50	1600	300	300	100		106.3	149.7	0.23	2.03
963	34.0	50	16	300	20	100	5000	50	20	400	130	200	100	3	19.6	87.8	0.23	4.39
964	22.5	30	20	400	40	200	5000	60	40	400	200	200	100		8.2	82.4	0.29	2.35
965	21.0	50	20	400	40	100	4000	60	20	400	200	300	60	2	13.8	77.7	0.83	0.66
966	8.8	30	20	160	40	50	4000	60	30	300	85	300	50				0.43	0.36
967	4.0	13	16	85	16	50	3000	30	13	130	60	200	40				0.60	0.36
968	8.2	20	30	100	30	100	4000	50	10	200	100	200	40		4.3	46.6	0.56	0.29
969	16.5	30	30	300	50	300	6000	85	30	400	300	400	50	2	4.8	63.2	0.70	0.27
970	15.0	55	30	350	55	200	5500	55	25	850	130	350	50	13	78.8	111.1	0.33	0.50
971	10.0	50	16	160	30	100	1600	40	20	600	85	160	60	2			0.27	0.28
972	47.0	160	30	600	60	100	5000	85	40	4000	200	400	85	16	103.3	244.0	0.19	2.33
973	9.0	30	5	100	5	25	1000	30	30	4000	30	200	85	5	1000.0	1000.0	0.09	13.30
974	33.5	100	13	600	10	50	3000	50	60	10,000	60	300	60		148.1	141.1	0.15	3.16
975	21.0	85	16	400	130	130	4000	60	30	4000	130	300	60	13			0.19	0.96

Sample No.	Fe_2O_3	Pb	Ga	V	Cu	Zn	Tl	Ni	Co	Mn	Cr	Ba	Sr	Mo	Sol.Mn	Sol.Fe	C_{org}	P_2O_5
976	7.9	30	30	250	50	100	5500	60	25	250	145	350	55		5.5	80.6	0.68	0.31
977	10.5	20	30	200	40	100	5000	50	20	300	130	300	60		5.0	77.3	0.73	0.75
978	13.5	30	30	300	40	100	5000	60	30	300	160	300	100		7.7	135.8	0.43	0.59
979	12.0	20	20	300	30	50	4000	50	10	200	130	200	50		10.1	65.9	0.33	0.49
980	29.0	45	20	300	30	50	5000	55	25	250	200	300	100		7.7	145.7	0.33	1.62
981	34.0	85	16	400	30	50	5000	50	16	400	300	200	200		9.4	110.0	0.31	3.04
982	19.0	50	20	600	40	25	4000	60	20	600	300	200	130		45.5	216.5	0.17	1.95
985	37.0	100	13	400	20	50	3000	50	40	8500	85	300	40	16			0.09	4.00
986	65.0	85	10	500	5	100	2000	30	40	1600	130	100	60	13	332.3	290.3	0.09	7.70
987	13.0	40	16	400	30	50	5000	50	30	600	160	160	30		71.4	216.1	0.12	1.40
988	8.7	25	30	250	45	250	4500	55	18	230	93	130	63		8.3	70.6	0.37	3.50
989	11.0	30	20	160	30	300	4000	50	16	400	100	200	60		6.2	94.3	0.40	2.40
991	7.1	16	30	160	30	130	5000	50	16	300	160	300	40		5.6	73.3	0.40	0.40
992	15.5	40	18	180	35	50	3000	45	20	300	180	250	450		9.6	104.6	0.27	15.10
993	16.0	50	18	250	30	75	4000	30	15	300	200	250	300		8.5	113.2	0.21	7.78
998	11.6	40	25	300	50	200	4500	55	30	350	150	250	200		15.3	126.3	0.31	7.81
999	11.2	35	15	250	35	25	2800	45	17	400	145	230	500		27.7	142.7	0.19	19.90
1C00	14.0	60	20	200	100	50	4000	100	20	300	160	200	200	2			0.37	2.12
1C02	17.0	60	20	300	40	200	5000	60	20	400	200	300	400		23.4	109.2	0.19	7.76
1C03	17.0	85	30	400	50	200	5000	85	30	400	300	300	400		28.1	102.9	0.25	6.70
1C05	23.5	60	13	500	16	50	3000	100	40	4000	160	300	400		154.4	108.8	0.09	5.60
1C07	24.0	85	13	600	30	100	5000	130	60	3000	200	400	200		189.5	172.8	0.17	3.00
1C16	11.5	30	30	200	50	100	6000	85	30	300	160	300	60				0.66	
1C17	6.3	30	20	100	40	200	4000	50	13	300	130	300	40				0.70	0.17
1C18	8.6	30	30	200	40	130	6000	60	20	400	160	300	60		5.4	49.3	0.59	0.59
1019	13.5	30	20	200	40	160	5000	50	16	400	160	300	50		7.7	84.4	0.31	0.76
1020	25.5	85	20	300	30	160	4000	40	30	600	160	200	60	2	8.4	58.6	0.35	0.78
1021	14.0	60	30	300	30	100	4000	50	16	1300	160	300	60	2	65.9	59.1	0.09	0.40
1022	17.6	500	20	300	40	300	4000	60	18	550	180	400	55	2	34.5	125.9	0.09	1.60
1023	16.6	45	16	300	35	100	3000	55	25	450	180	180	350		38.2	303.1	0.09	10.00

Sample No.	Fe_2O_3	Pb	Ga	V	Cu	Zn	Ti	Ni	Co	Mn	Cr	Ba	Sr	Mo	Sol.Mn	Sol.Fe	C_{org}	P_2O_5
IC26	14.0	40	30	300	60	25	5000	60	20	500	160	300	200	2			0.09	1.32
IC27	16.0	85	13	300	40	25	1300	85	30	3000	100	400	400	13			0.17	
IC28	9.2	160	13	200	20	50	1600	60	30	500	160	200	600		51.8	141.1	0.21	25.70
IC29	13.1	30	16	200	30	25	1300	50	20	400	200	200	1600		7.0	140.1	0.38	23.90
IC30	5.5	45	13	107	25	25	800	35	8	250	160	180	2500		4.5	60.2	0.33	28.50
IC31	15.0	93	15	300	30	25	1650	50	15	350	130	230	700		38.4	120.0	0.25	24.30
1032	18.0	40	16	300	30	25	2000	50	20	400	100	130	85	2	52.5	93.9	0.21	9.10
1033	16.2	85	30	400	40	100	4000	60	30	2000	130	300	85	8	157.2	221.4	0.23	5.18
1034	21.5	40	20	400	40	200	5000	60	30	500	160	300	85	2	17.5	89.9	0.25	2.10
1035	16.3	40	20	200	40	50	5000	40	16	400	160	300	130		22.2	83.8	0.36	6.95
1036	29.0	50	16	400	30	50	3000	60	30	600	85	300	85		63.6	125.0	0.38	3.93
1037	16.0	40	30	400	50	50	6000	60	16	500	160	400	100		18.0	84.4	0.35	0.58
1038	12.3	20	20	300	45	200	4500	60	30	400	165	250	50		9.7	75.5	0.50	0.34
1039	9.0	30	30	300	50	50	6000	60	20	300	160	300	60		4.6	37.1	0.78	0.22
1040	7.5	20	25	180	40	125	5000	55	20	250	115	250	55		17.5	44.1	0.75	0.24
1046	4.5	40	16	85	20	100	4000	40	20	300	100	300	40		4.4	36.1	0.32	0.15
IC47	6.8	60	20	160	40	50	5000	60	30	400	100	200	40		4.4	36.9	0.25	0.17
IC48	6.2	20	16	100	30	50	5000	60	30	300	130	300	50		3.7	44.2	0.23	0.17
IC49	6.2	20	20	130	40	100	4000	60	20	200	100	200	30				0.31	
IC50	5.7	40	20	160	40	160	5000	60	30	400	130	300	40		4.4	39.8	0.69	0.17
IC51	6.4	30	20	100	40	200	4000	60	20	300	100	200	40		4.9	40.2	0.77	0.17
IC52	9.5	30	20	200	50	300	6000	60	30	300	160	300	40		5.0	38.6	0.82	0.16
IC53	7.8	30	20	200	50	200	5000	60	20	300	100	300	50		11.2	35.4	0.69	0.17
IC54	10.8	40	20	300	60	200	6000	60	20	600	200	300	60		0.8	24.1	0.65	0.43
IC56	16.5	40	20	300	30	160	4000	50	30	500	160	300	200		24.4	70.7	0.23	3.07
1057	25.0	40	10	200	5	25	1000	20	5	200	200	40	300	2			0.25	6.84
1058	16.2	20	6	200	2	25	1000	30	13	160	130	50	200	2			0.21	5.29
1061	7.5	20	20	160	50	100	4000	50	16	300	130	300	60				0.35	
1062	8.2	30	30	160	60	300	4000	50	20	400	160	300	40		3.8	21.2	0.29	0.37
1063	7.2	20	16	160	40	200	6000	50	20	600	130	130	40		3.8	36.4	0.21	0.40
1064	8.2	20	16	130	30	50	4000	50	13	300	100	130	40		5.1	25.4	0.27	0.18
1065	5.7	30	25	130	40	150	4500	55	20	300	130	230	40		3.7	35.5	0.42	0.15

Sample No.	Fe_2O_3	Pb	Ga	V	Cu	Zn	Tl	Ni	Co	Mn	Cr	Ba	Sr	Mo	Sol.Mn	Sol.Fe	C_{org}	P_2O_5
1066	7.8	35	30	180	45	100	6000	60	20	400	180	300	60		4.5	36.7	0.54	0.14
1067	7.6	30	40	160	40	200	5000	60	20	300	160	300	60		4.6	35.0	0.59	0.16
1068	8.7	30	30	160	30	100	6000	60	16	300	160	300	50		5.1	34.4	0.66	0.16
1069	9.6	40	30	130	40	200	5000	60	20	300	100	300	50		7.0	47.9	0.51	0.25
1070	11.8	50	30	300	40	200	6000	60	20	400	200	300	85				0.51	0.29
1071	11.0	30	16	200	20	50	3000	40	13	300	85	130	30				0.44	0.64
1072	16.7	45	25	300	35	105	4500	55	19	350	215	215	55	2	9.9	47.9	0.30	0.83
1073	8.0	20	13	100	10	15	1600	20	5	200	85	60	40		9.6	62.3	0.28	1.26
1075	18.0	30	20	300	30	100	4000	60	20	200	200	160	85	2			0.29	
1077	15.5	30	20	300	40	300	5000	85	40	400	200	200	60				0.27	
1078	14.0	100	20	200	40	50	3000	60	30	600	130	130	85	2	24.3	69.3	0.30	1.72
1079	11.7	30	16	300	40	100	8500	60	20	850	200	85	85		10.8	61.3	0.26	3.37
1080	7.4	40	30	200	40	100	5000	60	20	400	160	200	60		5.7	43.0	0.30	0.60
1081	8.7	40	40	200	50	200	6000	60	20	300	200	300	60		4.5	35.0	0.85	0.19
1082	6.6	30	40	100	20	100	6000	60	20	300	100	200	50		4.5	40.1	0.90	0.17
1083	10.2	30	30	200	50	400	5000	60	30	300	160	300	50		4.5	34.6	0.90	0.15
1084	11.5	60	40	300	40	300	6000	60	20	400	300	300	60		5.9	45.5	0.64	0.25
1085	7.0	30	30	200	40	400	5000	60	30	200	130	200	60		4.8	32.5	0.72	0.16
1086	16.5	50	40	300	50	200	8500	60	20	400	200	300	60	10	6.4	51.1	0.49	0.45
1087	18.0	50	16	400	20	25	4000	40	20	400	130	100	30	2			0.32	0.77
1088	24.1	60	20	500	30	200	5000	50	30	400	300	200	60	8	10.5	78.4	0.23	1.50
1089	9.0	20	30	200	40	200	5000	60	30	300	160	200	50				0.23	
1090	33.0	50	16	400	16	200	1600	40	20	500	400	60	60				0.32	1.46

Table 3.4.1 Statistical analyses of different population subsets; degree of skew of sample populations: * denotes significant at 95% confidence level; ** denotes significance at 99% confidence level; - denotes presence of negative skew. All data were logtransformed except that represented by column 4.

Column 1: names of variables. Column 2: population subset (1). Column 3: population subset (2). Column 4: population subset (2) (untransformed data). Column 5: population subset (4). Column 6: population subset (3). Column 7: Northwest African phosphatic rocks and limestones population. Column 8: variables of the Phosphoria Formation sample population. Column 9: skew of Phosphoria Formation population.

1	2	3	4	5	6	7	8	9
Zn	-**	-**	**	-**	-		Si	-*
Ti	-	-**	-	-**	-	-	Ba	**
Sr		**	**	**	**	-	Zr	
Mn	-	**	**	**	*	*	Ti	-*
Ni	-		**		-	*	Mn	-**
Cr	-		**	-	-**		Ni	-**
Co	-**	-**	**	-**	-*	**	Cr	
Ba	-**	**	**	**	-		Zn	-**
V	-	-	**	-	-		Mg	-**
Pb	-	-*	**	-*	-	**	Ca	-*
Cu		-**	**	-**	-**		Fe	-
Ga	-	-	**	-			K	-
Si	-						Cu	-
Mg							Mo	-**
K	-**					-	Ag	
Fe	-**					-	Sr	-**
Ca						-	V	-*
Al	-						P_2O_5	-
P_2O_5	**	**	**	**		-	C_{org}	-
Fe_2O_3			**		*		U	-**
Sol.Fe				**			As	-**
Sol.Mn				**			Sb	
% Sand					-**		Al	-
% Silt					-		Na	-*
% Clay					-		La	
C_{org}						-	F	-

Table 3.5.1 Trace element associations indicated by R-mode factor analysis of the log-transformed data from population subset 3 (Moroccan sediments). Variables in parentheses are antipathetic to the remainder of the factor association; factors are designated A, B, C etc.

Variance and Model	A	B	C	D	E	F	G	H
91.8% : 8	Cu, Ni, Tl, Ga (Sand, Fe)	Clay, Silt, Ga (Sand, P_2O_5)	Cr, Fe_2O_3, V	V, Mn, Co, Pb, Fe_2O_3	Sr, P_2O_5 (Tl, Ga)	Ba	Zn	Ni (Pb)
89.3% : 7	Cu, Ni, Tl, Ga, Co (Fe, Sand)	Clay, Silt, Ga (Sand, P_2O_5)	Cr, Fe_2O_3, V	V, Mn, Co, Pb, Fe_2O_3	Sr, P_2O_5 (Tl)	Ba, Mn	Zn	
85.2% : 6	Cu, Ni, Tl, Ga, Ba, Co (Fe, Sand)	Silt, Clay, Ba, Ga (P_2O_5, Sand)	Fe_2O_3, Cr, V, Pb	Mn, Co, V, Pb, Fe_2O_3, (Ba)	Sr, P_2O_5, Ba, Pb (Tl)		Zn	
80.9% : 5	Cu, Ni, Tl, Ga, Zn, Ba, Co (Fe, Sand)	Clay, Silt, Ba, Zn, Ga (Sand, P_2O_5)	Cr, Fe_2O_3, V, Pb	Mn, Co, V, Pb, Fe_2O_3 (Ba)	Sr, P_2O_5, Ba, (Tl)			
73.9% : 4	Cu, Ni, Tl, Ga, Zn, Co, Ba (Fe, P_2O_5, Sand)	Clay, Silt, Zn, Ga, Ba (Sand, P_2O_5)	V, Mn, Co, Pb, Fe_2O_3, Cr, P_2O_5		Sr, Ba, P_2O_5, Cr, Pb			
65.1% : 3	Cu, Ni, Tl, Ga, Ba, Zn, Co (Fe, Sand)	Silt, Clay, Zn, Ga (Sand, P_2O_5, Sr)	V, Pb, Co, Mn, Fe_2O_3, Cr, P_2O_5					
54.1% : 2	Ga, Tl, Ni, Cu, Silt, Zn, Clay, Ba, Co	(Sand, P_2O_5, Fe_2O_3, Sr)	V, Pb, Co, Mn, Fe_2O_3, Cr, P_2O_5, Sr (Silt)					

Table 3.5.2 Trace element associations indicated by R-mode factor analysis of the log-transformed data from population subset 2 and factor model 6 from the analysis of population subset 4 (Moroccan sediment analyses). Elements in parentheses are antipathetic to the remaining elements in the factor associations; factors are designated A, B, C etc.

Variance and Model	A	B	C	D	E	F	G	H
92.1% : 8	Ga, Cu, Ni, Cr (P_2O_5)	Sr, P_2O_5	Ba	Mn, Co, V, Ni, Pb, Cu.	Fe_2O_3, Cr, V	Tl	Zn	Pb
89.3% : 7	Ga, Cu, Ni, Cr, Co (P_2O_5)	Sr, P_2O_5	Ba	Mn, Co, Pb, V, Ni, Cu	Fe_2O_3, Cr, V	Tl, Zn	Zn, Co	
86.3% : 6	Ga, Ni, Cu, Cr, Co, Zn (P_2O_5)	Sr, P_2O_5	Ba	Mn, Co, Pb, V, Ni, Cu	Fe_2O_3, Cr, V	Tl, Zn		
80.6% : 5	Ga, Cu, Ni, Ba, Co, Zn, Cr (P_2O_5, Fe_2O_3)	Sr, P_2O_5, Ba		Mn, Co, Pb, V, Ni, Cu	Cr, Fe_2O_3, V, P_2O_5	Tl, Zn		
73.0% : 4	Ga (P_2O_5, Sr, Pb, Mn, V, Fe_2O_3, Co)			Ni. Cu, Co, Ga, Mn, V, Pb, Ba, Zn	Cr, Fe_2O_3, V	Tl, Zn		
64.6% : 3	Ga, Cu, Ni, Zn, Co, Cr (P_2O_5)			Mn, Pb, V, Co, Sr, Ni, P_2O_5, Cu, Ba	Cr, Fe_2O_3, V, P_2O_5 (Tl. Ba)			
53.6% : 2	Ga, Cu, Zn, Ni, Co, Ba, Tl (P_2O_5, Fe_2O_3)			(V, Pb, Mn, Co, Ni, P_2O_5, Sr, Fe_2O_3, Cu, Cr)				
85.3% : 6	Ni, Cu, Ga, Co, Cr, Zn, V	Sr, P_2O_5, Sol.Fe	Ba	Sol.Mn, Mn, Sol.Fe Pb, V, Co, Ni, P_2O_5	Fe_2O_3, Cr, V	Tl, Zn	Factor model 6 from population subset IV	

Table 3.5.3 Trace element associations indicated by R-mode factor analysis of the log-transformed data from population subset I (Moroccan and Saharan sediments). Elements given in parentheses are antipathetic to the remaining elements in the factor association. Factors are designated A, B, C etc.

Variance and Model	A	B	C	D	E	F	G	H	I
94.1% : 10	Sr, Ca, P_2O_5, Mg, Co (Si, Ti)	Pb, Fe, V, Ca, Zn (Si, Ti)	Cu, Ni, Cr, Ga, Ti, Pb, V, Zn, Co (Mg)	Cr, Fe, K	Mn, Al, Co, K, Ga, Ti, Zn, V, Ba	Ba, K	Mg (Ni)	P_2O_5	Zn
92.7% : 9	Sr, P_2O_5, Ca, Mg, Fe, Co (Si, Ti)	Pb, V, Fe (Si)	Cu, Ni, Cr, Ga, Pb, V, Ti, Zn, Co (Mg)	Fe, Zn, Cr, K, V (Si)	Mn, Al, Co, K, Ga, Ti, Zn, V, Ba	Ba, K	Mg		
91.2% : 8	Sr, P_2O_5 Ca, Mg, Fe, Zn, Co (Si, Ti)	Pb, V, Fe (Si)	Cu, Ni, Cr, Pb, Ga, V, Ti, Zn, Co (Mg)	Fe, Cr, Zn, K, V	Al, Mn, Co, Ga, K, Ti, Zn, V, Ba	Ba, K	Mg		
88.7% : 7	Sr, Ca, P_2O_5, Mg, Fe, Co (Si, Ti)	Pb, V, Fe, Ca (Si)	Ni, Cu, Cr, Pb, Ga, Ti, Zn, V, Co (Mg)	Fe, Zn, Cr, K, V	Al, Mn, Co, K, Ga, Ti, Zn, V, Ba	Ba, K	Mg		
85.7% : 6	Ca, Sr, P_2O_5, Mg, Fe, V, Pb, Co (Si, Ti, Ga)		Ni, Cu, Pb, Cr, V, Ga, Zn, Co (Mg)	Fe, Zn, Cr, K, V	Al, Mn, Co, Ga, K, Ti, Zn, V, Ba	Ba, K	Mg		
88.2% : 5	Ca, P_2O_5, Sr, Mg, Fe, Pb, V (Si, Ti, Ga)		Cr, Ni, Cu, Pb, V, Zn, Fe, Ga, Co		Al, K, Mn, Co, Ga, Ti, Zn, Ba, V (Pb)	Ba	Mg	(Ti, Ni)	
77.8% : 4	Ca, P_2O_3, Sr, Mg, Fe, V, Pb, Zn (Si, Ti, Ga)		Ni, Cr, Cu, Pb, V, Zn, Fe, Ga, Co (Mg)		Al, Mn, K, Co, Ga, Ti, Ba, Zn, V	Ba,Fe		(Ti)	
72.4% : 3	Ca, P_2O_5, Sr, Mg, Fe, V, Pb (Si, Ti, Ga)		Ni, Cu, Cr, Pb, V, Zn, Fe, Ga, Co (Mg)		Al, Mn, K, Co, Ga, Ti, Ba, Zn, V, Fe				
57.8% : 2	Ca, P_2O_3, Sr, Fe, Mg, V, Pb, Zn, Cr, Co (Si, Ti)		Ga, Co, Al, Ni, Zn, K, Cu, Ti, Mn, V, Cr, Fe, Ba						

Table 3.5.4 List of R-mode factor scores for 7 factor model of population subset 1 (see table 3.5.3 for associations of factors A, B, C etc.); the following designations have been given to each factor:- A (phosphate), B (iron oxide), C (Ga-hydrolysate), D (glauconite), E (Al-hydrolysate), F (barium), G (magnesium). Sediment texture, phosphate content and presence of glauconite are indicated in table A2.5.

Sample	E	A	C	G	F	D	B
0111	.611	-.181	-1.091	-1.275	-.625	-.001	.851
0112	.930	.042	-1.284	-.429	-.684	-.515	-.724
0113	1.151	.274	-.464	-.204	-.405	.236	-1.304
0114	.864	.564	-.923	.644	-.045	-.236	-.631
0115	1.893	.477	.154	-.781	-3.989	-.518	.386
0116	1.413	.812	-.747	-.275	-3.707	-.398	-.054
0117	1.811	1.097	-1.565	-1.059	-1.111	.601	-.446
0119	1.401	.375	-.191	1.080	.568	.771	-.180
0120	1.135	.099	-.274	1.591	.230	.340	.294
0121	.978	.121	-.463	.893	-.083	.272	.120
0125	1.410	.406	-.009	1.329	.564	.579	-.051
0126	1.721	.228	-.314	1.355	.331	.574	.022
0127	1.106	.235	-.580	1.136	.491	-.000	.899
0129	.822	-2.479	.098	-.034	-.200	.499	.396
0133	.256	-3.627	-.093	.507	-.317	.490	1.174
0134	.163	-3.512	-.569	.369	-.213	.999	.734
0135	1.211	-1.489	-.642	1.908	-.271	1.163	-.890
0137	.361	.393	-1.728	.521	.341	-.606	-.924
0139	.066	-.484	-1.710	-.780	1.465	1.211	-2.865
0140	.578	-1.308	-1.898	-1.965	-.435	.992	.311
0144	1.360	.476	.098	1.323	.423	-.162	.591
0150	.911	.906	-.484	.290	.693	.046	.570
0151	-.282	.793	-1.897	-.589	.556	-1.428	.477
0153	-1.134	.307	-2.690	.727	2.182	-1.706	-.164
0154	.273	.170	-1.174	1.238	-.112	-2.075	1.204
0155	-.576	.195	-1.512	1.342	.230	-2.912	.905
0221	-.278	.776	-.771	-1.562	1.265	.962	1.646
0223	-.356	.450	-.760	-1.514	.548	.640	1.796
0224	-.261	.621	.381	-.542	-.307	-.930	.633
0225	-.143	-.056	.254	-.783	.186	.853	1.935
0226	-1.848	.650	-1.957	-.547	.088	1.336	1.295
0227	-1.121	.593	.333	.311	.051	1.692	.487
0228	-1.857	.900	-.343	1.113	-.058	.752	.260
0230	-.263	.192	.628	-1.497	.754	1.636	1.000
0234	-.210	.171	1.173	.026	-.054	-1.058	1.122
0237	-.009	.258	1.366	-.526	-.177	-.714	.087
0238	-.337	.309	1.265	-.557	-.277	-.459	.588
0239	-.242	.172	1.679	.116	-.307	-1.299	.018
0240	-.659	.441	1.642	1.364	-.614	-.428	-.017
0241	-.997	.460	.831	.502	.410	.937	.419
0242	-.467	.291	1.857	1.464	-.791	-.386	.133
0245	-.575	.586	1.633	1.535	-.602	-.166	-.062

Table 3.5.4 (contd.)

Sample	E	A	C	G	F	D	B
0246	-2.401	1.341	-.335	.119	-.060	2.025	.303
0247	-2.775	.981	-.609	.539	-4.357	2.082	-.192
0249	1.011	.451	.959	-1.293	1.069	.997	.244
0250	.976	.540	1.017	-1.003	.904	.887	.256
0252	.603	.182	.780	-1.016	.383	-.156	.548
0255	-.826	-2.463	.844	-1.378	-.461	-.599	.816
0256	-.899	-1.686	.440	-.937	.024	-.765	.557
0257	-.207	-.540	.762	-.061	.303	-.280	-.230
0258	-.715	-1.578	.309	-.164	-.082	-.840	.309
0259	-.668	-.933	.156	.552	.258	-.567	-.691
0260	-1.422	-1.722	-.558	1.588	.446	.960	-1.096
0262	-.227	-1.074	.152	.877	.103	.802	-1.071
0263	-.311	-.443	.172	.744	-.156	.311	-2.634
0264	-1.979	.403	-.017	.984	.158	.938	-1.205
0266	-.320	1.607	-.528	-.354	1.027	.837	.584
0267	-.556	.240	-.185	-1.814	-.098	-1.199	-2.123
0268	-.247	.061	1.260	-.266	.434	-.374	-1.717
0269	-.439	.408	.188	-1.745	-.114	-1.288	-1.927
0270	-.219	-.258	1.173	-1.999	.624	.224	-2.097
0271	-.408	-.063	.397	-.828	.124	-.865	-1.698
0272	-.291	.432	-.021	-.339	-.037	-.777	-1.365
0273	-.457	.211	-.059	-.942	-.089	-1.348	-.202
0274	-.762	.689	-.129	.212	.112	-1.694	.740
0275	-.760	.170	.211	.779	.226	-1.136	.820
0276	-.147	-.471	.352	.053	-.089	-1.002	-.513
0277	-.381	-1.019	.637	-.744	.267	-1.136	1.402
0280	.856	.731	1.257	1.026	.780	.375	.089
0283	1.235	.515	1.322	-.427	.655	.974	-.201
0284	1.525	.542	1.357	-.406	.492	.919	-.145
0285	.404	1.044	1.430	.479	1.161	.111	.401

Table 7.1.1 Trace Element abundance data in phosphorites, apatites, seawater and the earth's crust (ppm). I Crustal abundances (Mason, 1966); II Seawater abundances (Goldberg, 1965); III Phosphoria Formation averages (Gulbrandsen, 1966, table 3 p.774); IV Worldwide phosphorite averages (calculated from data in Swaine, 1962); V Ranges of worldwide phosphorite analyses (given in Swaine, 1962); VI Rare earth determinations on Californian continental shelf phosphorite nodule (Goldberg et al, 1963); VII Rare earth determinations on carbonate apatite separated from Florida phosphorite (Altschuler et al, 1967).

	I	II	III	IV	V	VI	VII
Ag	0.07	.00004	3		1-50		
As	1.8	.003	40	20.5	.4-188		
B	10.0	4.6		16.0	3-33		
Ba	425.0	.03	100		1-1000		
Be	2.8	.0000006			1-10		
Cd	0.2	.00011			1-10		
Ce	60.0	.000005				102	120
Co	25.0	.0001		3.3	.6-11.8		
Cr	100.0	.00005	1000	285	7-1600		
Cs	3.0						
Cu	55.0	.003	100	21.7	.6-394		
I	0.5	.06		24.1	.15-280		
In	0.1						
La	30.0	.00001	300			56	150
Li	20.0	.17			1-10		
Mn	950.0	.002	30	428.0	0-10000		
Mo	1.5	.01	30	18.7	1-138		
Nb	20.0						
Ni	75.0	.002	100	12.5	1.9-30		
Pb	13.0	.00003			0-100		
Rb	90.0	.12			0-100		
Sb	0.2	.0005	7		1-10		
Sc	22.0	.00004	10		10-50		3
Se	0.05	.0004	10	2.7	1-9.8		
Sn	2.0	.0008			10-15		
Sr	375.0	8.0	1000	1900	1800-2000		
Th	7.2						
Ti	4400.0	.001		476	100-3000		
U	1.8	.003	90	190	8-1300		
V	135.0	.002	300	167	20-500		
Y	33.0	.0003	300		0-50		110
Zn	70.0	.01	300	90	4-345		
Zr	165.0		30		10-500		

Table 7.3.1 Elemental abundances in selected subsea phosphatic rocks and limestones and in certain terrestrial phosphorites. Si, Mg, Ca, Fe, K, P_2O_5, C_{org} expressed in per cent; other values in ppm.

Sample No.	Si	Ba	Ti	Mn	Ni	Cr	Zn	Mg	Ca	Fe	K	Co	Pb	Cu	Ga	Sr	V	P_2O_5	C_{org}	As	Sb	Hg
CAL.1	2.7	150	359	76	42	66	25	0.10	38.0	0.78	0.26	7	39	25	2	1075	129	25.0	0.93	19	2	<10
AGUL.1	8.1	84	1317	104	35	103	25	0.10	26.0	2.68	1.46	7	34	25	4	918	60	25.0	0.44	10	0.5	80
US.22	5.6	94	737	132	134	326	1075	0.41	40.0	1.36	0.33	22	123	71	3	414	107	27.0	1.60	20	3	
US.47	3.9	125	908	110	202	871	860	0.06	50.0	2.43	0.37	11	65	71	4	874	77	31.9	2.00	30	2.5	
US.41	2.6	82	667	127	270	1205	3500	0.14	51.0	0.68	0.32	12	76	109	4	624	5360	32.1	2.80	<2.5	4.5	
TAS.3D	1.0	10	50	313	18	14	35	0.73	36.0	0.04	0.02	8	33	8	tr	809	10	5.3	0.14	<2.5	3	
TAS.41D	1.0	10	158	525	40	15	60	0.82	35.0	0.02	0.02	10	31	10	tr	581	23	5.1	0.14	<2.5	2.5	
TAS.43D	1.1	10	132	113	16	9	30	1.94	27.0	0.02	0.02	7	27	6	tr	1221	14	0.4	0.10	2.5		
MOR.1	1.4	73	216	32	65	343	310	0.18	45.0	0.05	0.07	8	47	46	2	445	400	33.6	0.18	<2.5	2	30
F127	1.7	1840	566	3196	477	23	185	0.40	40.0	1.24	0.21	285	179	121	3	895	110	25.3	0.60	2.5	9	<10
D134	1.5	72	286	116	35	17	40	0.38	39.0	0.47	0.15	12	55	14	tr	831	69	21.9	0.28	<2.5	<0.5	35
Z1037	1.9	91	247	192	22	14	40	0.40	42.0	1.32	0.55	8	41	11	tr	882	77	16.2	0.20	<2.5	<0.5	<10
120	3.6	68	725	259	18	30	60	0.68	26.0	0.76	0.71	6	142	12	3	714	30	0.4	0.09	<2.5	11.0	15
135	2.0	10	243	77	36	72	35	0.48	37.0	0.32	0.14	8	40	14	tr	762	211	18.9	0.25	10	2	30
1361	1.2	10	155	45	42	71	70	0.37	35.0	0.10	0.06	8	34	21	tr	832	55	19.8	0.73	<2.5	<0.5	70
1362	1.3	10	249	157	17	14	20	0.70	35.0	0.04	0.09	7	33	7	tr	589	25	0.3	0.10	<2.5	<0.5	<10
1391	1.3	10	211	77	40	107	70	0.48	36.0	0.41	0.11	6	37	21	tr	1067	67	25.3	0.70	10	2	165
1392	1.4	10	153	90	31	62	70	0.45	42.0	0.59	0.09	7	40	19	tr	995	68	24.6	0.52	50	<0.5	180
148	1.5	10	207	111	29	35	55	0.32	42.0	1.75	0.18	9	44	10	tr	682	161	20.1	0.27	25.0	2	20
151	12.6	167	837	183	20	90	40	0.83	25.0	0.88	0.50	7	31	31	3	524	77	0.4	0.67	<2.5	1.5	<10
152	5.7	80	601	116	27	90	75	2.50	25.0	4.72	1.53	6	50	11	3	771	88	13.6	0.32	2.5	<0.5	15
154	7.3	63	893	102	24	128	65	1.63	23.0	5.08	2.29	7	44	13	4	835	96	15.3	0.46	5	2	40
155	6.7	103	1248	2609	127	38	85	1.90	36.0	3.83	1.01	38	73	18	5	816	173	13.4	0.33	3.7	3	
156	2.5	tr	854	453	79	74	95	2.25	30.0	8.56	0.52	15	63	11	3	739	430	16.6	0.10	89	9	18
157	2.0	tr	251	604	37	37	105	3.90	32.0	5.52	0.24	13	53	9	tr	672	158	11.1	0.10	125	4.5	10
227	21.8	75	672	45	17	16	25	0.23	16.0	0.13	0.26	6	25	12	2	625	28	0.3	0.02	<2.5	<0.5	
234	3.0	47	452	115	22	25	20	7.56	32.0	2.21	0.51	7	40	7	2	590	52	7.9	0.25	5	1.5	30
252	3.1	75	761	809	53	28	25	0.16	33.0	0.61	0.67	16	36	9	2	95	62	0.8	0.09	<2.5	<0.5	90
257	5.3	51	687	239	19	28	30	0.88	29.0	0.70	0.35	6	31	7	2	474	43	0.8	0.14	<2.5	<0.5	
259	11.7	87	1031	100	17	38	40	1.20	24.0	0.88	0.62	7	31	10	3	339	45	0.4	0.13	<2.5	<0.5	15
264	17.8	1455	1700	93	14	28	80	2.69	15.0	0.45	0.54	7	29	9	3	353	43	0.2	0.08	<2.5	<0.5	<10
273	4.7	111	1270	555	25	32	50	3.25	22.0	3.04	0.93	8	31	7	3	614	77	0.5	0.10	75	<0.5	10

Table 7.3.2 Trace element associations indicated by R-mode factor analysis of the log-transformed subsea Moroccan phosphatic rock and limestone analytical data. Elements given in parentheses are antipathetic to the remaining elements in the factor association. Factors are designated A, B, C etc.

Variance and Model	A	B	C	D	E	F
93.3% : 6	Ca, P_2O_5, Sr, C_{org}, (Si, Ti, K)	Fe, V, P_2O_5, Cr K, Ni	Co, Mn, Ni, V, Ca	Pb, Sr, K, Fe, Mn	Cu, Cr, C_{org} P_2O_5, Sr	C_{org}, (Sr)
89.6% : 5	Ca, P_2O_5, Sr, C_{org}, (Si, Ti, K)	Fe, V, P_2O_5, Cr, K	Co, Ni, Mn, V, Ca	Pb, Sr, K, Mn, Fe	Cu, Cr, C_{org}, P_2O_5, Sr	
83.9% : 4	Ca, P_2O_5, Sr, C_{org}, Ni (Si, Ti, K)	Fe, K, V, Pb, P_2O_5, Cr, Mn	Co, Mn, Ni, V, Pb, Ca		Cr, Cu, C_{org}, P_2O_5, Sr, V, Ni	
76.8% : 3	Ca, Sr, P_2O_5 (Ti, Si, K, Fe)	Co, Mn, Ni, V, Fe, Pb, P_2O_5, Sr, Ca			Cr, C_{org}, Cu, P_2O_5, Sr, V, (Mn)	
62.9% : 2	Ca, P_2O_5, Sr, C_{org}, Cr, Ni, Cu, V, (Ti, Si, K)	Fe, Mn, Co, Ni, V, K, Pb, Ti, P_2O_5				

Table 7.3.4 Elemental abundances in carbonate-apatites separated from subsea Moroccan phosphorites (ppm); * denotes extrapolated value; tr denotes trace. Analyses by M.S.7.

Element	139	148	F127	Element	139	148	F127
U	36.0	146.6	3.0*	Y	141.9	9.2	
Th	1.7*	tr		Sr	1298.2	1754.1	
Pb	3.0*	tr		Rb	3.4	2.1	
Ba	5.0	3.5		Br	1314.0	1311.2	
Cs	1.3	0.7		As	68.8	50.9	
I	565.3	312.4		Zn	63.0	39.4	
Sb	5.8	3.3		Cu	558.6	356.4	
In	1.2	0.3*		Ni	58.4	28.9	
Cd	13.5*	8.1*		Cr	289.7	105.0	
Mo	3.7*	1.8*		V	74.6	150.8	
Nb	0.7*	0.5		La	48.4	3.8	42.4
Zr	4.1	3.1		Ce	25.9	3.5	22.4

Table 7.3.5 Relative atomic abundance of lanthanons in marine apatite, seawater, phosphorite, and shale (normalised to lanthanum): I Phosphoria Formation, U.S.A. (Altschuler et al, 1967); II Moroccan phosphate from Khouribga (Altschuler et al, 1967); III Bone Valley Formation, Florida (Altschuler et al, 1967); IV Seawater (Goldberg et al, 1963); V Eastern Europe and Kazakhstan (Semenov et al, 1962); VI Californian offshore nodule (data from Goldberg et al, 1963); VII Composite shale; * extrapolated values.

	Carbonate Apatite Concentrated From Phosphorite						Sea-water	Phosphorite Whole Rock		Shale
	148	139	F127	I	II	III	IV	V	VI	VII
La	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ce	0.91	0.53	0.54	.54	.64	.81	.44	2.05	1.81	1.94
Pr	0.18	0.25	0.15	.12	.21	.21	.22	.45	.25	.26
Nd	0.66*	0.71	0.44	.69	1.39	.47	.74	1.43	.98	.92
Sm				.10	.24	.18	.14	.31	.18	.17
Eu		0.05	0.06	.03	.04	.03	.04	.04	.04	.05
Gd	0.85*	0.30	0.84	.14	.27	.10	.18	.33	.24	.14
Tb		0.04	0.03*	.03	.04	.03	-	.04	.03	.03
Dy		0.18	0.13	.08	.23	.10	.22	.20	.19	-
Ho		0.05	0.02*	.03	.07	.03	.06	.04	.05	.03
Er		0.15	0.08*	.07	.18	.14	.17	.12	.14	.09
Tm		0.02*	0.01*	.02	.08	.01	.04	.02	.02	.01
Yb		0.07	0.05*	.07	.17	.05	.14	.13	.10	.07
Lu		0.01*	0.01*	.01	.02	.02	.03	.02	.02	.01

Table 7.4.1 Trace element associations indicated by R-mode factor analysis of the log-transformed data from the Phosphoria formation (original data from Gulbrandsen, 1966). Elements in parenthesis are antipathetic to the remainder of the factor association. Factors are designated A, B, C etc.

Variance and Model	A	B	C	D	E	F	G	H	I
82.7% : 9	P_2O_5, Ca,F,U (Si,K,Al,Ti,Mg,Zr,Fe,Ag)	Cr,Cu,Ni,Ag,Zn,C_{org}, V,Ti,Sr,Mg,U	Na,Mg,Zn,Ni (Sb)	La(Zn,V)	Mn(Sb)	Mo,Fe,Sb,Al, K,Ti,Zr	Sr(As,K, Mg,Al)	Ba,Sr, V,Zr	Fe(U, Zr,V)
79.6% : 8	Ca,P_2O_5,Fe (Si,Al,K,Ti,Zr,Mg,Fe Ag, Cu)	V,U,Cu,Zn,Ag,Ba,Ti, Sb,Cr	Ni,Zn,C_{org}, Mg,Na,Cu, Ag,Ti,Cr (La)	La,As,Na, Zr,Ba	Mn,Ba, Al(Sb, C_{org})	Mo,Fe,Sb,Al, K,Ti,Zr	Sr,Cr (As)	Cr(Zr, Na)	
76.4% : 7	Ca,F,P_2O_5,U (Si,Al,K, Ti,Mg,Fe,Zr,Ag,Cu)	V,U,Cu,Ag,Cr,Ti,Zn, Sb,C_{org},Ba	Ni,Na,Mg,Zn, C_{org},Ag,Cu, As, (P_2O_5)	La,As,Ba, Zr,Na(Zn)	Mn,Ba, (Sb, C_{org})	Mo,Fe,Sb,Al, K,Ti,Zr	Sr,Cr (As)		
72.6% : 6	P_2O_5,Ca,F,U (Si,Al, K,Ti,Mg,Ag,Fe)	V,Cu,Cr,Ag,Sr,Zn,U, C_{org},Ni,Ti,Ba	Na,Mg,Ni,C_{org} Zn,As,Ag (P_2O_5)	La,As,Ba, Zr(Zn)	Mn,Sr (Sb,U, C_{org})	Fe,K,Al,Ti,Mo, Sb,Zr,Si,Cu			
67.8% : 5	Ca,P_2O_5,F,U(K,Al,Si,Fe, Ti,Mo,Zr,Mg,Cu,Ag)	Zn,Cu,Ni,Ag,C_{org},Cr, V,Sr,Mg,Na,Ti (La)	Na,Mg(Sb,U, V,Mo,P_2O_5)	As,La,Na, Zr	Ba,Ti,Sr La,Zr (C_{org})				
62.3% : 4	Ca,F,P_2O_5,U (K,Al,Si, Fe,Ti,Mo,Zr,Mg,Cu,Ag)	Zn,Cu,Ni,C_{org},Ag,Cr, V,Na,Mg,Sr,Ti,U	Na,Mg(Sb,U, V,P_2O_5)	La,As,Ba, Zr,Mn (C_{org})					
55.6% : 3	Ca,P_2O_5,F,U (K,Al,Si Fe,Ti,Zr,Mo,Mg,Cu,Ag)	Zn,C_{org},Ni,Ag,Cu,Cr, V,Mg,Ti,Sr(La,P_2O_5, F)	Mg,Na(Sb,U,V, Ba,Zr,P_2O_5, Cu,Ti)						
45.8% : 2	P_2O_5,Ca,F,U (Si,K,Al, Fe,Ti,Zr,Mo,Mg,Cu)	Zn,C_{org},Cu,Ag,Ni,V,Cr, Ti,Sr,Mg,U,Na,Mo (La)							

Table 7.4.2 Previously determined correlations of different elements with organic carbon in sediments and sedimentary rocks.

Element	Zn	Cu	Ag	Cr	V	Ti	Ni	Sr	Mg	U	Na	Sb	Ba	Mo
Degens, Williams and Keith (1957)	*	*	*		*		*							*
Arrhenius, Bramlette and Picciotto (1957)	*	*	*				*							
Gad, Catt and Le Riche (1969)		*	*		*		*							*
Le Riche (1959)		*			*		*							*
Baturin et al (1967)					*		*			*				*
Nicholls and Loring (1962)							*							
Hirst (1962b)			*											
Tourtelot (1964)	*	*		*	*									
Curtis (1966)		*		*	*		*			*				*
Vine and Tourtelot (1970)	*	*	*	*	*		*							*
Present work: correlation coefficient results.	*	*	*	*	*	*	*		*		*			*
Present work: number of factor models in which each variable is carbon - associated (max. number of models examined = 9)	9	9	9	9	9	9	6	6	5	5	3	2	3	1

Table 7.5.1 A comparison between those elements enriched, normal or depleted in phosphorites relative to the crust and those elements relatively enriched or relatively impoverished in seawater. Data from table 7.1.1 and Figs. 7.1.1 and 7.5.1.

PHOSPHORITE: ENRICHED >2:1	SEAWATER ENRICHED >10,000:1	PHOSPHORITE: DEPLETED <2:1	SEAWATER: RELATIVELY IMPOVERISHED <10,000:1	PHOSPHORITE: "NORMAL"
Ag	Ag	Ba	Ba	B
As	As	Co	Co	Zn
Cd	Cd	Cu	Cu	Rb
Cr		Mn	Mn	
I	I	Ni	Ni	
La		Sc	Sc	
Mo	Mo	Ti	Ti	
Pb		Zr		
Sb	Sb		Be	Be
Se	Se		Ce	Ce
Sn	Sn		Cr	
Sr	Sr		La	
U	U		Pb	
Y				
	B		V	V
	Zn		Y	
	Li	Li		
	Rb			

Table 8.1 Locations and ages of the principal known subsea phosphorite deposits, and sources of information. R = Recent; Q = Quaternary; M = Miocene; E = Eocene; T = Tertiary; C = Cretaceous. Northwest African subsea phosphorites of Eocene, Miocene and Pliocene ages (possibly with some few Cretaceous samples) have been found in the present study.

Locality	Age	Source of information
Agulhas Bank	T(? M)	Parker (1970); Cayeux (1934; Murray and Renard (1891)
S.W. Africa	T & R	Baturin (1970)
N.W. Africa	T	This work
Gulf of Aden	T	Gevork'yan and Chugunnyy (1969)
Arabian Coast	?	see McKelvey and Chase (1966
Andaman Islands	?	Siddiquie and Murthy (1966)
E. Australia	M	Von der Borch (1970)
W. Australia	?	Murray and Renard (1891)
Tasmania	pre-R	Kolodny and Kaplan (1970)
Chatham Rise, N.Z.	M	Reed and Hornibrook (1952); Norris (1964)
Campbell Plateau, N.Z.	T	Summerhayes (1969)
California Borderland	M + Q pre-R	Dietz, Emery and Shepard (1942) Kolodny and Kaplan (1970)
U.S.A. Eastern Shelf	M	Pevear and Pilkey (1966); Gorsline (1963); Gorsline and Milligan (1963); Lutenaur and Pilkey (1967)
Blake Plateau	M	Manheim, Pratt and McFarlin (1968); Pratt and McFarlin (1965)
Pacific Seamounts	C E ?pre-R	Hamilton (1956) Hamilton and Rex (1959) Bezrukov et al (1969)
Tasman Seamounts	? up-T	this work, and Menard (1969)
Japan	?	see McKelvey and Chase (1966)
S. America	?	ditto
Baja, California	pre-R	d'Anglejan (1967); Kolodny and (1970)
India (low grade mud and sand)	?	Seshappa (1953); Murthy, Reddy and Varadachari (1968)

Table 9.1: Radiation and phosphate determinations made during 1968.

ROCK SAMPLES (L and P differentiate between limestone and phosphorite from the same dredge hauls)

Sample No.	Per Cent P_2O_5	COUNTS PER SEC Shipboard	COUNTS PER SEC Laboratory	Spectral Analysis
120	0.37	16	156	
136 P	19.84	350	15,502	*
139 L		25		
139 P	25.26		5,942	
148	20.14	230	9,604	
151	0.40	25	178	
152 P	13.56			
156	16.59	240	8,482	*
157	11.16		5,829	
234	7.90	180	6,021	
SEDIMENT SAMPLES				
111	.34	17		
112	.28	16	115	
113	.23	16		
114	.25	17		
116	.16	18		
117	.13	19		
119	.11	20		
120	.12	22	178	
121	.23	23	245	
125	.11	21		
126	.12		239	
129	1.58		339	
133	3.04	32	505	
134	1.80	33		
135	.21		157	
137	.30		161	
151	.34	24	299	
155	.50		223	*

Shipboard radiation determinations by B.H. Hazelhoff Roelfzema.

Phosphate analyses by C.P. Summerhayes.

Laboratory Radiation analyses by D.B. Smith.

Table A2.2 Mean ratios of daily average (d_z) to monthly average (M_z) of all variables from the Statistical Series used as external standards during direct reading emission spectrographic analysis of the acid insoluble residues of Moroccan and Saharan sediments. * denotes those ratios used as correction factors for determinations of certain variables made on specific days.

Element	17.12.68	13.12.68	11.12.68
Zn	0.92	1.00	0.95
Ti	1.04	1.00	1.68*
Sr	1.17	1.60*	1.07
Mn	1.28	0.86	1.27
Ni	1.09	0.99	0.90
Cr	1.21	0.82	0.87
Co	0.97	0.88	0.97
Ba	1.22	1.05	1.16
V	1.04	0.98	1.02
Pb	1.06	1.04	0.99
Cu	1.01	1.01	0.95
Ga	1.06	1.03	0.96
Si	0.95	1.06	1.26
K	0.93	1.03	1.27
Fe	1.02	1.00	1.40*
Ca		0.67*	1.02
Al	1.06	0.92	1.11

Table A2.3 Volumetric Phosphate Determinations (averages of duplicates); previous analyses of US 22, 41 and 47 by Gulbrandsen (1966), of D134 and F127 (different subsamples) by Summerhayes (1969), and of MOR.I by Fisons Laboratories.

Sample No.	% P_2O_5	± % Range	Sample No.	% P_2O_5	± % Range	Previous Analysis
120	0.37	0.13	259	0.44	0.10	
135	18.84	0.02	264	0.21	0.02	
136.1	19.84	0.04	273	0.56	0.03	
136.2	0.25	0.04				
139.1	25.26	0.06	Z1037	16.19	0.02	
139.2	24.6	0.08	D134	21.85	0.01	23.1
148	20.14	0.07	F127	25.29	0.05	26.2
151	0.40	0.02	TAS. 3D	5.28	0.10	
152	13.56	0.00	TAS. 41D	5.09	0.14	
154	15.33	0.03	TAS.43D	0.37	0.06	
155	13.42	0.08				
156	16.59	0.16	US 22	27.01		26.4
157	11.16	0.05	US 41	32.08		32.4
227	0.33	0.15	US 47	31.81		31.4
234	7.90	0.06	MOR. 1	33.57		33.5
252	0.78	0.14				
257	0.79	0.00				

Table A2.4 Qualitative assessment of X-Ray diffraction analyses of acetic acid insoluble residues of the non-magnetic fractions of selected sediment samples. Batch 1 = coarse fraction (after decantation of suspended fines) re-franzed to remove residual glauconite. Batch 2 = decanted fines from different size fractions. Batch 3 = magnetic concentrates obtained by the re-franzing of coarse fractions from Batch 1. Batch 4 = micropanned concentrates of brown foram casts obtained by the treatment of magnetic concentrates from Batch 3. Q = Quartz; Gl = Glauconite; F = Feldspar; I = Illite; Ch = Chlorite; K = Kaolinite; A = Carbonate-Apatite. Size fractions are given in phi units; asterisks denote mineral recordings.

Batch No.	Sample No.	Fraction	Q	Gl	F	I	Ch	K	A
1									
	154	2 - 3	*	*	*				*
	154	3 - 4	*	*	*	*		*	*
	155	2 - 3	*		*				*
	155	3 - 4	*	*	*				*
	833	2 - 3	*		*				*
	833	3 - 4	*	*	*	*		*	*
	836	2 - 3	*	*	*				*
	882	1 - 2	*		*				*
	882	2 - 3	*		*				*
	882	3 - 4	*		*	*		*	*
	280	3 - 4	*		*				
2									
	154	0 - 1	*	*	*	*	*	*	
	154	1 - 2	*		*	*	*	*	
	154	2 - 3	*		*	*	*	*	
	154	3 - 4	*	*	*	*	*	*	
	155	0 - 1	*		*	*	*		
	155	1 - 2	*		*	*		*	
	155	2 - 3	*		*	*		*	
	155	3 - 4	*	*	*	*	*	*	*
	832	3 - 4	*		*	*	*	*	
	833	2 - 3	*		*	*	*	*	*
	833	3 - 4	*		*	*	*	*	
	834	2 - 3	*		*	*	*	*	
	836	2 - 3	*		*	*	*	*	
	882	1 - 2	*		*	*		*	
	882	2 - 3	*		*	*		*	
	882	3 - 4	*	*	*	*	*	*	*
3									
	154	3 - 4	*	*	*	*		*	
	155	2 - 3	*	*	*	*			*
	155	3 - 4	*	*	*				*
	833	2 - 3	*	*	*	*			
	834	2 - 3	*	*	*				
	836	2 - 3	*	*	*	*			
4									
	833	2 - 3	*	*					
	833	3 - 4	*	*	*			*	
	834	2 - 3	*	*	*	*			
	837	2 - 3	*	*	*	*		*	
	873	3 - 4	*	*	*	*	*	*	
	882	1 - 2	*	*	*				

Table A.2.5 Sediment samples from the detailed study area off south central Morocco, and from the Spanish Saharan region. Column 1 = per cent P_2O_5; 2 = per cent $CaCO_3$ (corrected for soluble phosphate); 3 = metres water depth; 4 = sediment type (st = silt, ms = silty sand or sandy silt, sd = sand); 5 = sampling gear (g = shipek grab, d = pipe dredge, c = gravity core); 6 = notes on the presence of glauconite (*).

Sample No.	1	2	3	4	5	6	Sample No.	1	2	3	4	5	6
143	0.11	53.9	940	st	c		818	0.30	43.2	115	st	d	*
144	0.11	61.9	718-703	ms	d		819	0.16	90.7	92	sd	g	
145			622	sd	g	*	820	0.38	82.3	85	ms	g	
146			573	sd	g	*	821	0.20	70.3	98	st	d	
147			537	sd	g	*	822	0.15	68.4	98	ms	g	
149	0.17	58.8	15	sd	g		823	0.10	80.1	90-92	st	d	
150	0.18	32.8	90	st	g		824	0.09	73.9	90-75	ms	d	
151	0.32	28.8	126-121	ms	d	*	825	0.16	54.3	70	sd	g	
153	0.60	57.5	132	sd	g	*	826	0.22	66.7	55	ms	d	
154	0.34	57.6	414-340	ms	d	*	827	0.15	50.6	83-85	ms	d	
155	0.72	43.9	495-433	ms	d	*	829	0.17	63.3	85	ms	d	
802	0.20	50.3	1053	st	c		830	0.15	76.8	98	ms	d	
803	0.16	39.0	558	st	c		831	0.21	56.2	107	ms	d	*
804	0.27	41.4	256-222	ms	d	*	832	0.60	30.5	122	ms	g	*
805	0.58	26.5	121	sd	g	*	833	0.35	42.6	124	ms	d	
806	0.19	23.2	90	st	g		834	0.56	53.4	124	ms	d	*
809	0.14		586	st	c		835	1.24	29.4	122	sd	g	*
810	0.16	45.2	486-469	st	d		836	0.31	69.5	132	ms	d	*
811	0.24	46.5	399	ms	c	*	837	0.90	66.0	175	sd	d	*
812	0.45	47.5	260	sd	g	*	838	0.36	19.0	264	sd	g	*
813	0.41	47.5	234-219	sd	d	*	839	0.29	30.3	294	sd	c	*
814	0.25	36.9	186	sd	g		840	0.37	28.0	305	sd	g	*
815	0.56	41.4	143	ms	c	*	841	0.56	26.6	320-324	ms	d	*
817	0.36	45.8	128	ms	d	*	842	0.35	15.4	448	ms	g	*

Sample No.	1	2	3	4	5	6
843	.13		512	st	c	
844	0.18		558	st	c	
846	1.13	36.9	477	sd	g	*
847	1.69	77.6	305-309	sd	d	
848	0.56	83.1	294-256	sd	d	
849			309	sd	c	*
850	0.41	14.4	328	sd	g	*
851	0.36	22.9	267	sd	g	*
852	0.31	56.3	211	sd	g	*
853	0.26	78.3	132	ms	g	
854	0.25	71.7	128-121	ms	d	*
855	0.34	73.4	121	ms	d	*
856	0.16	28.2	111	st	d	
857	0.16	28.2	98	st	d	
859	0.22	46.7	87	st	d	*
860	0.31	42.0	96	st	g	
861	0.18	28.2	119	st	g	
862	0.56	26.6	132	ms	d	
863	0.31	30.9	132	sd	g	*
864	0.34	60.0	138	ms	g	*
865	0.18	28.1	139	sd	d	*
866	0.32	80.6	188-313	sd	d	
867	0.29	66.6	595	sd	g	*
868	0.14		895	st	c	
869	0.18	30.4	73	st	g	
870	0.20	41.4	83	st	g	
871	0.23	69.6	79-83	sd	d	
872	0.15	32.6	117	st	d	
873	0.90	24.6	132	ms	d	*
874	0.68	26.5	132	ms	g	*
875	0.86	46.0	136	ms	d	
876	0.24	71.8	136	sd	d	
877	0.38	88.4	151-138	sd	d	

Sample No.	1	2	3	4	5	6
878	0.86	33.1	603	ms	g	
879	0.17	53.8	906	st	c	
880	0.45		921-912	sd	d	*
882	1.13	42.4	753	ms	d	*
883	0.26		888-815	ms	d	*
885	0.25	25.3	19	sd	g	
886	0.13	83.6	32	sd	g	
887	0.90	96.8	38	sd	g	
888	0.11	89.0	38	sd	g	
889	0.10	92.6	41	sd	g	
890	0.14	36.1	73	st	d	
891	0.18	36.0	98	ms	d	*
892	0.11	85.3	105	sd	d	
893	0.23	55.6	200	ms	d	
894	0.56	82.1	134	ms	d	
895	0.68	67.7	130	ms	d	
896	0.93	76.9	136	ms	d	
897	0.74	40.3	301	sd	g	
898	1.46	88.1	143	sd	d	
899	0.51	69.2	316	st	d	
219	0.21	35.0	1600	st	g	
221	0.13	55.2	1278-1422	sd	d	
222	0.14	48.3	888	sd	c	
223	0.15	60.0	593-511	sd	d	
224	0.12	92.0	219-134	sd	d	
225	0.14	94.0	83	sd	g	
226	0.16	89.0	57	sd	g	
227	0.21	63.7	53-41	sd	d	
228	0.11	43.2	40	sd	g	
229	0.31	71.9	23	sd	g	
230	0.30	69.5	30	ms	g	

Sample No.	1	2	3	4	5	6
232	0.16	47.7	961	st	c	
233	0.17	58.8	738	st	c	
234	0.17	89.0	256-222	sd	d	*
235	0.06	94.0	211-132	sd	d	*
237	0.11	92.0	109	sd	g	
238	0.11	93.0	104	sd	d	
239	0.11	93.0	85-79	sd	d	
240	0.10	92.0	60	sd	g	
241	0.12	94.0	60	sd	d	
242	0.06	94.0	36	sd	g	
243	0.07	93.4	32	sd	c	
244	0.07	94.0	30	sd	g	
245	0.08	93.0	23	sd	g	
246	0.08	69.7	25	sd	g	
247	0.06	61.9	20	sd	g	
249	0.13	84.3	1371-1307	ms	d	
250	0.16	76.4	1038-1000	ms	d	
251	0.22	63.4	1044	ms	c	
252	0.28	90.8	674-591	sd	d	
255	5.40	74.1	213	sd	g	*
256	8.30	78.0	141	sd	g	
257	0.32	89.9	107	sd	g	
258	4.20	86.0	87-83	sd	d	*
259	0.31	89.9	85	sd	d	
260	0.33	89.8	79-72	sd	d	
262	0.15	92.9	60-47	sd	d	
263	0.11	92.0	36-32	sd	d	
264	0.13	89.1	28	sd	d	
266	0.11	36.8	19	sd	g	
267	0.25	88.9	38	sd	g	
268	0.20	88.1	41	sd	g	
269	0.24	86.3	43	sd	g	
270	0.32	88.0	47	sd	g	
271	0.27	88.9	40	sd	g	
272	0.15	92.0	51-60	sd	d	
273	0.18	90.0	79	sd	d	
274	0.21	88.1	90	sd	g	
275	0.21	89.0	102	sd	g	
276	0.27	88.9	105	sd	g	
277	5.20	82.0	313-107	sd	d	*
278	0.14	63.0	672	ms	c	
279	0.15	59.3	879	st	c	
280	0.11	58.0	959-918	st	d	
281	0.13	51.8	1077	st	c	
282	0.11		1101	st	c	
283	0.13	60.0	1083-1072	st	d	
284	0.12	67.7	1210-974	st	c	
285	0.11	65.8	1300-1053	st	c	
6561	0.13	91.9		sd		*
6564	0.07	94.0		sd		
6566	0.07	94.0		sd		
6567	0.06	94.0		sd		
6568	0.05	94.0		sd		
6569	0.05	94.0		sd		
6570	0.45	92.5		sd		*
6585	0.17	93.9		sd		
6588	0.09	94.0		sd		
6590	0.31	79.7		sd		*
6591	0.10	92.9		sd		*
6592	0.10	94.0		sd		*
6621	0.14	94.0		sd		*
6624	0.12	58.9		sd		*
6626	0.13	94.0		sd		*

Table A2.6 Comparison of semi-quantitative analyses carried out by the A.G.R.G. and the U.S.G.S. on phosphorites from the Phosphoria Formation. Batch 1 = elements determined in A.G.R.G. by direct reading emission spectrography. Batch 2 = elements determined in A.G.R.G. by wet chemical methods or atomic absorption.

Element	US 22 AGRG	US 22 USGS	US 41 AGRG	US 41 USGS	US 47 AGRG	US 47 USGS	US 22 AGRG/ USGS	US 41 AGRG/ USGS	US 47 AGRG/ USGS	AGRG/ USGS Mean Ratios
(Batch 1)										
Sr	414	1000	624	1000	874	1000	0.41	0.62	0.87	0.63
V	108	300	536	1000	78	100	0.36	0.54	0.78	0.56
Ba	95	100	83	100	125	100	0.95	0.83	1.25	1.01
Ti	737	960	667	960	908	960	0.77	0.69	0.94	0.80
Mn	132	100	127	30	110	100	1.32	4.23	1.10	2.22
Ni	134	100	270	300	202	300	1.34	0.90	0.67	0.97
Cr	326	1000	1205	3000	871	1000	0.33	0.40	0.87	0.53
Co	22	30	12	<10	12	<10	0.73	>1.2	>1.2	?
Pb	123	30	76	<10	65	<10	4.10	>7.6	>6.5	?
Cu	71	100	109	100	71	100	0.71	1.09	0.71	0.84
Ga	2.7	<10	4.7	<10	4.5	<10	-	-	-	?
Si	5.61	8.6	2.65	3.19	3.93	5.21	0.65	0.83	0.75	0.74
Ca	40.77	29.7	51.05	32.4	50.52	31.7	1.37	1.58	1.59	1.52
Fe	1.36	0.77	0.68	0.53	2.43	1.82	1.77	1.28	1.34	1.46
K	0.33	0.37	0.32	0.21	0.37	0.30	0.89	1.52	1.23	1.21
(Batch 2)										
Zn	1075	300	3500	300	860	100	3.58	11.66	8.60	7.94
Mg	0.41	0.46	0.14	0.16	0.06	0.07	0.89	0.88	0.86	0.88
P_2O_5	27.01	26.4	32.08	32.4	31.81	31.4	1.02	0.99	1.01	1.01
C_{org}	1.6	1.4	2.8	5.2	n.d.	2.1	1.14	0.54	-	0.56
Sb	3	5	4.5	10	2.5	7	0.60	0.45	0.36	0.47
As	20	30	<2.5	<10	30	50	0.67	-	0.60	0.62

Table A2.7 Minor element analyses of international rock standards W.1 and G.1. Columns 1 and 5 are analyses of W.1 and G.1 from Fleischer and Stevens (Geochim. Cosmochim. Acta v.26, 1962, pp 525-543); columns 2 and 3 are means of 5 replicate direct reading emission spectrographic analyses of W.1; column 6 contains means of 5 replicate analyses of G.1 (same method); columns 4 and 7 represent duplicate optical emission spectrographic analyses of W.1 and G.1.

Element	1 G.C.A.	2 11.12.68	3 13.12.68	4 O.E.S.	5 G.C.A.	6 11.12.68	7 O.E.S.
Zn	60-85	127.4	144.2	75.0	20-95	tr	75.0
Ti	6400	5900	6907	8500	1500	2600	1150
Sr	170-310	155.6	98.5	55	250-389	228	72.5
Mn	1320	1340.6	974.5	1600	230	226	180
Ni	80	68.6	96.2	92.5	1-2	tr	<5
Cr	92-165	106.8	129	145	8-32	15	16
Co	52	28.7	31.9	60.0	2.3	tr	<5
Ba	130-225	122.4	116.4	115	1100-1500	532	400
V	240	256	263	350	16	45.8	23
Pb	8	14	47.8	7.5	49	65.4	72.5
Cu	80-153	132	164.4	150	10-22	18.6	18.0
Ga	13.6-22	14.2	17.0	18	14-25	18.8	30

Table A2.8 ± Precision values at 2 standard deviations (95% confidence level) determined from 5 replicate direct reading emission spectrographic analyses of acid insoluble residues of the total sediment, the silt fraction and the clay fraction of sample 144, and of the unleached international rock standards G.1 and W.1; precisions determined from duplicate optical emission spectrographic analyses of several sediment samples are also presented.

Element	144 Total Sed.	144 Silt	144 Clay	W.1 11.12.68	W.1 13.12.68	G.1 11.12.68	Mean	C.E.S.
Zn	35.8	61.0	29.3	57.3	79.1	n.d.	52.5	65
Ti	26.8	1.0	20.3	21.1	25.1	19.0	18.9	33
Sr	34.9	13.8	36.5	34.8	25.1	18.7	27.3	45
Mn	12.7	21.7	11.4	29.3	19.0	8.4	17.0	37
Ni	33.5	12.4	22.3	27.9	17.3	n.d.	22.6	34
Cr	23.5	6.4	23.3	12.6	16.8	58.9	23.6	43
Co	29.4	5.4	24.7	16.8	13.5	n.d.	18.0	52
Ba	12.8	26.5	23.9	28.3	19.8	18.2	21.6	43
V	26.5	14.9	25.0	16.7	15.2	61.4	26.6	38
Pb	29.1	23.4	9.0	20.2	8.9	10.4	16.8	33
Cu	18.1	8.1	3.8	6.8	9.6	90.5	22.8	36
Ga	12.6	6.1	9.0	13.9	15.6	17.6	12.5	31
Si	47.6	3.3	7.4	23.3	14.9	29.7	21.0	
Mg	30.8	22.1	49.4	20.1	17.5	n.d.	24.0	
K	15.8	2.6	18.3	15.3	23.4	11.2	14.4	
Fe	9.8	10.8	13.0	28.8	14.8	66.8	24.0	36(Fe_2O_3)
Ca	31.8	26.1	17.9	38.0	9.6	18.9	23.7	
Al	9.2	16.9	13.0	15.9	17.4	17.4	15.0	