THE PETROGRAPHY AND MAJOR ELEMENT GEOCHEMISTRY OF THE PHOSPHORITE NODULE DEPOSITS ON THE AGULHAS BANK, SOUTH AFRICA

by

R.J. PARKER

Thesis submitted in fulfilment of the requirements
for the degree of M.Sc. at the University of Cape Town

Department of Geology,
University of Cape Town

May 1971

CONTENTS.

FIGURES

TABLES

PLATES

ABSTRACT

Dredging operations carried out on the Agulhas Bank have proved the existence of a widespread phosphorite nodule deposit, considered to be essentially in situ.

The pebble to boulder sized nodules recovered have been classified into two conglomeratic and three non-conglomeratic classes. The latter classes comprise (i) phosphatized microfossiliferous limestones (N 1 class); (ii) phosphatized highly ferruginous microfossiliferous limestones (N 11 class); and (iii) nodules composed of a poorly sorted mixture of quartz, glauconite and microfossil grains set in a micrite/collophane cement (N 111 class). Surface to centre phosphatization effects have been observed in some N 1 nodules. The first conglomeratic variety (C 1 class) is noted for abundant, often highly irregularly shaped, enclosed N 1 class phosphorite pebbles set in a matrix that is similar to the N 111 phosphorite type. The second conglomeratic variety (C 11 class) is similar to the first, but it is characterised by the inclusion of pebble sized microfossiliferous internal cast of macrofossils, as well as the presence of macrofossil shell debris.

X-Ray diffraction studies have shown that the prime phosphate mineral present is francolite, a carbonate fluorapatite, while optically this mineral has been identified as collophane. An X-Ray diffraction peak-pair technique has indicated an average 5.5% CO_2 concentration in the apatite phase of the phosphorites.

Studies on the major element geochemistry of the various phosphorite classes has shown that the bulk geochemistry of the nodules corresponds to the dominant mineralogy and that variations in the bulk geochemistry of the nodules from within a given group reflects variations in the concentration of diluent allogenic minerals. A sympathetic relationship exists between the Na and S concentrations in the phosphorites, and this has been related to substitution effects in the phosphate mineral phase. The average P_2O_5 concentration determined for the Agulhas Bank phosphorites is 16.18%.

The N 1 and N 11 phosphorite classes are considered to have originated as a result of limestone phosphatization involving a calcite-to-francolite replacement process.

Many of the sedimentological features exhibited by the texturally heterogenous N 111, C 1 and C 11 class nodules are incompatible under normal hydrodynamic conditions, suggesting an unusual depositional environment. In order to explain these features it has been proposed that the nodules were originally lime mud rich sediments and that the conglomeratic varieties were deposited by submarine transporting agencies such as mud-flows, turbidity currents and/or tidal/storm wave surges. Bioturbation may have been responsible for the mixing of lime mud and coarser material to produce the poorly sorted non-conglomeratic N 111 phosphorite class. Replacement of the calcitic lime mud by francolite is considered to be the prime mechanism responsible for the phosphate mineralization and lithification of these N 111, C 1 and C 11 class phosphorites.

CHAPTER I.

INTRODUCTION.

In 1967 the Marine Geological Research Group in the Department of Geology, University of Cape Town (sponsored by the South African National Committee for Oceanographic Research (SANCOR)) commenced a reconnaissance marine geological survey of the South African continental shelf between Cape Town and Port Elizabeth and north of latitude 36° S (i.e. the northern part of the Agulhas Bank). Since 1969 one of the projects undertaken by this group has been the systematic investigation of the extensive sea floor phosphorite and phosphatic rock deposits located in this area.

The results of the petrographic and geochemical research carried out on these phosphate rich rocks by the writer, as part of this project, is presented in this thesis.

Other sedimentological, stratigraphical, structural and bathymetric studies on the Agulhas Bank have provided a firm geological framework for the investigations into the phosphorite deposits.

The term "phosphorite" is strictly speaking reserved for those rocks of sedimentary origin containing more than 18% P_2O_5 (i.e. equivalent to 50% apatite, Bushinsky, 1969). The term will however be used in a general sense, in this thesis, for sedimentary rocks enriched in P_2O_5 as well as for true phosphorites. The prime phosphate mineral present in Agulhas Bank phosphorites is francolite, a carbonate fluorapatite which forms authigenically in the marine environment.

The first descriptions of phosphorite rock deposits date back to the middle of the 19th century (see Gulbrandsen, 1969, for a historical review) and from the beginning the study of these unusual rocks has resulted in scientific controversy and debate. The Challenger Expedition of 1873 - 76 (Murray and Renard, 1891) recovered the first examples from the present day sea floor, off the South African coast. Since this discovery sea floor deposits have been reported from many other regions of the world, and as a result a considerable amount of scientific effort has gone into elucidating the nature of these rocks.

Apart from the study of Dietz, Emery and Shepard (1942) on the Californian offshore phosphorites and that of Summerhayes (1970) on the N.W. African phosphorites, the number of in depth studies of submarine phosphorite nodule deposits are relatively few, and much remains to be learnt about the mode (or modes) of origin of phosphorite rocks.

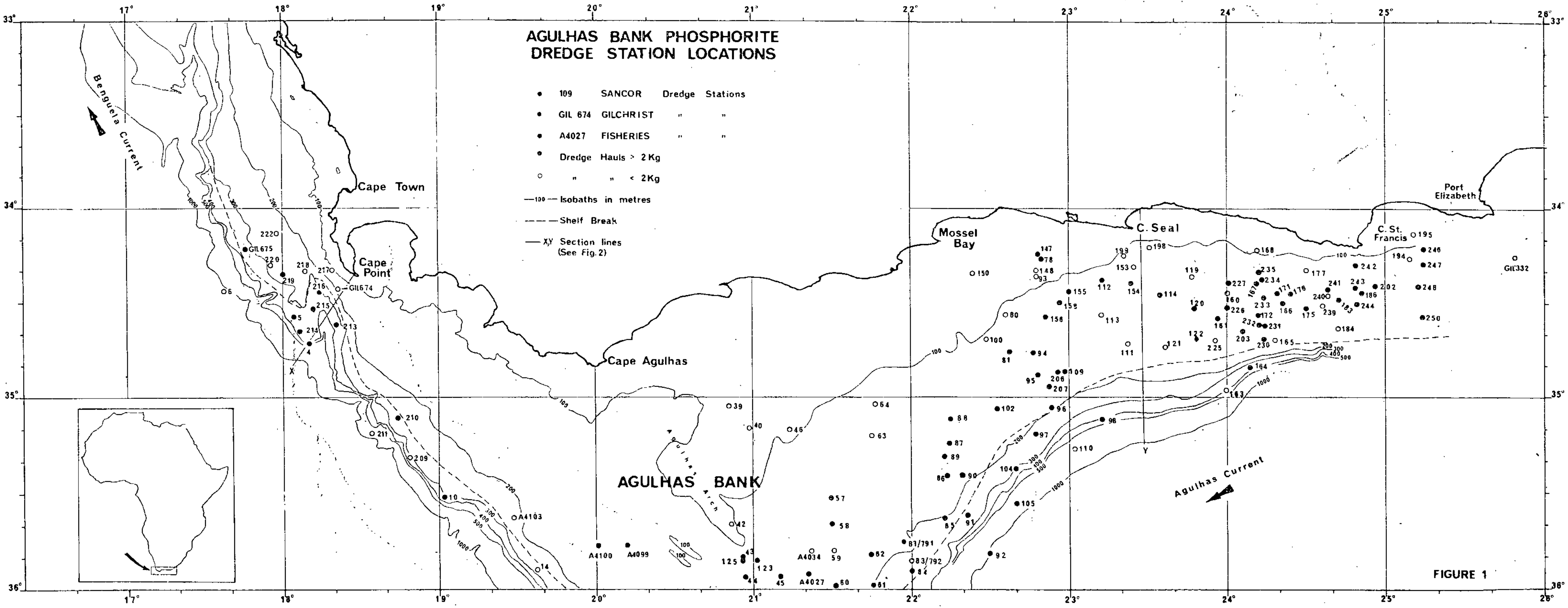
The initial work carried out on the Agulhas Bank phosphorites by Murray and Renard (1891) and later by Cayeaux (1934) clearly showed that the Agulhas Bank was potentially a phosphorite area of great interest. The present study has proved the presence of a rich and widespread phosphorite deposit on the Agulhas Bank and the results of the detailed petrographic and geochemical investigations into these rocks, presented in this thesis, represents an important contribution to the data on phosphorites.

The academic interest shown in submarine phosphorite deposits is also matched in no small measure by an economic interest in these deposits as potential source material for fertilizers. In view of the ever increasing demands made on agriculture to satisfy the food requirements of a rapidly expanding world population, this economic interest is sure to be sustained if not increased. Pot plant fertilizer tests conducted by the Phosphate Development Corporation (Phalaborwa, South Africa) have proved encouraging. These tests have shown that powdered Agulhas Bank phosphorite is comparable, as a fertilizer, to the best natural rock phosphate found on land in South Africa, and is only surpassed by artificially prepared "super-phosphate" fertilizer.

Phosphorite rock samples have been recovered from 127 dredge stations on the Agulhas Bank (see Figure 1 and Appendix B). The SANCOR phosphorite samples (see Figure 1) studied in this work were collected as a result of systematic dredging operations carried out on a roughly ten square mile grid on the South African continental shelf and Agulhas Bank between Cape Town in the west and Port Elizabeth in the east. Dredging operations were not carried out south of latitude 36° S due to navigational uncertainties. The Gilchrist and Fisheries phosphorite samples (see Figure 1) were collected prior to the inception of the SANCOR project by the University of Cape Town and the Division of Sea Fisheries respectively. The weight of phosphorite recovered from individual dredges varied from less than 1 kg to over 100 kg. All in all many hundreds of kg's of phosphorite have been recovered and this wealth of material has provided an ideal opportunity to investigate these unusual rocks, especially as the nodules are considered to be essentially in situ.

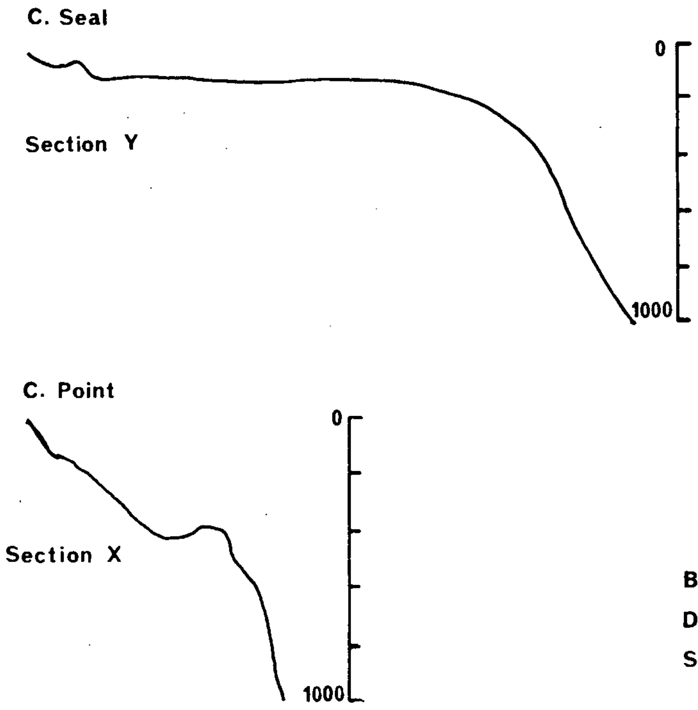
The primary objectives of this study were firstly to determine the dominant petrographic and bulk geochemical characteristics of the nodules and secondly to interpret these characteristics in terms of their origins. Secondary objectives included delineating the areal extent of the deposit and its relationship to the regional geology, bathymetry and physical oceanography of the continental shelf and Agulhas Bank.

The petrography of the nodules was studied in hand specimen, in thin section and by x-ray diffraction techniques, while various instrumental and wet chemical methods were used to determine their major element geochemistry.



AGULHAS BANK PHOSPHORITE DREDGE STATION LOCATIONS

FIGURE 1



Bathymetric profiles.
Depths in metres, vert. exag. x60
See Fig. 1 for locations

FIGURE 2

After Dingle, SANCOR 1971

CHAPTER II.

GEOLOGICAL AND OCEANOGRAPHICAL SETTING.

The purpose of this section is to briefly describe the relationship of the phosphorite nodules to the geology, bathymetry and physical oceanography of the Agulhas Bank.

The regional "hard" rock geology of the Agulhas Bank has been described in some detail by Dingle (1970), Dingle, Gerrard, Gentle and Simpson (in press) and Siesser (1970, and, in prep.). For the purposes of this study it is sufficient to note that the Agulhas Bank is primarily composed of a seaward thickening sequence of consolidated Cretaceous, Tertiary, and occasionally Quaternary carbonate rocks which unconformably overlie a "basement" sequence of lower Palaeozoic quartzites and shales. These basement rocks have been provisionally correlated with the onland Table Mountain Series (quartzites) and Bokkeveld Series (shales). An unconformity separates the Cretaceous and Tertiary limestone strata. Unconsolidated sediments of relict and recent origin mantle these "hard" rock sequences (Rogers, 1971; Birch, in prep.).

The preliminary investigations into the phosphorites and the underlying "hard" rock geology has shown that the distribution of the nodules may be roughly correlated with the outcrop of the Cretaceous and Tertiary carbonate rocks. Geophysical evidence indicates however that the distribution of the nodules is not related to any particular stratigraphic horizon within the Createaceous or Tertiary, except for a tendency for the phosphorite to be found in regions of upper Tertiary outcrop (R.V. Dingle, SANCOR Marine Geology Group, University of Cape Town, personal communication). The systematic study of the carbonate rocks of the Agulhas Bank by Siesser (in prep.) has established the petrography of these rocks in some detail, and he has shown that occasionally well rounded (i.e. reworked) pebbles of phosphorite are present in a few limestone samples tentatively dated as Quaternary in age, while enclosed phosphorite is absent in those carbonates considered to be Cretaceous and Tertiary in age. These stratigraphic relationships suggest that the Agulhas Bank phosphorite may be late Tertiary or early Quaternary in age. Kolodny and Kaplan (1970) have shown by uranium isotope studies that certain Agulhas Bank phosphorites are older than 800,000 years which is compatible with the above suggestion. An upper Tertiary age for these phosphorites would be in keeping with the Tertiary age reported for most of the of the world's sea floor phosphorites (Tooms, Summerhayes and Cronan, 1969).

The accurate dating by paeleontological means of the Agulhas Bank phosphorites is a subject that certainly warrants further attention, while K - Ar dating of the glauconite grains found within the phosphorites and in the associated sediments should also prove to be a fruitful field of future research.

The angularity and large size of many of the phosphorite nodules recovered, suggesting absence of transportation for any great distance, and the similarity of the sedimentary components found within the nodules to the surrounding unconsolidated sediments suggests that these Agulhas Bank phosphorites were formed essentially <u>in situ</u>. Murray and Renard (1891), in their pioneering studies on the Agulhas Bank phosphorite came to the same conclusions.

A major pre-Cretaceous structural feature separates the eastern and western Agulhas Bank into bathymetrically different areas. This feature, the Agulhas Arch, comprises an elongated upwarp of sea floor exposed basement rock trending in a south easterly direction from Cape Agulhas to approximately latitude 36° S. The bathymetry of the Agulhas Bank east of the Agulhas Arch is noted for its low seaward gradients and the shallowness of the major portion of the shelf (100 - 140 metres) and shelf break (ca. 150 metres), in comparison to the higher seaward gradients and greater average shelf (150 - 400 metres) and shelf break (200 - 400 metres) depths, found on the western side of this structural feature (see Figures 1 and 2). The significance of these bathymetric differences with respect to the phosphorite deposits found in these two areas, will be noted in later chapters.

The physical oceanography of the Agulhas Bank is dominated by two ocean currents. The warm (>20°C) Agulhas Current flows south westwards down the eastern coast of South Africa and it is deflected further out to sea by the southerly extension of the Agulhas Bank (Bang, 1970). Under its influence the eastern half of the Agulhas Bank is supplied with relatively warm surface waters. The western half of the Agulhas Bank is however influenced by the colder ($<20^{o}C$) Benguela Current (as defined by Bang, 1971) which flows northwards along the western coast of South Africa.

Upwelling of nutrient (i.e. phosphate) rich and biologically productive water is an important feature along the South African west coast (Brongersma-Sanders, 1957; Bang, 1971) and the western margins of the Agulhas Bank are similarly affected (Bang, 1970), while east of Cape Agulhas this phenomenon is important during summer and is linked to high biological activity in this area (Zoutendyk, 1970).

The supply of terrigenous material to the Agulhas Bank is relatively small as there are few large sediment laden rivers entering the sea along the coastline bordering the Agulhas Bank area (Rogers, 1971). This is in keeping with the generally low rainfall (less than 15 inches per annum) prevailing over most of the inland and coastal areas bordering the Agulhas Bank.

CHAPTER III.

PETROGRAPHY.

III.1 : Introduction.

Previous petrographic investigations on the Agulhas Bank phosphorite deposits are those of Murray and Renard (1891), Collet (1905), Cayeaux (1934) and Haughton (1956). The findings of these workers, while indicating the area as potentially of great interest, were incomplete with respect to the following : The studies were based on samples recovered from a limited number of stations, located predominantly on the continental slope, and gave no real idea of the extent of the phosphorite distribution and the richness of the deposit, as discovered on the continental shelf (i.e. the Agulhas Bank) in the present work. Furthermore, examples of the conglomeratic phosphorite type, now know to be the most important type, had not been recovered, except for some conglomeratic nodules found north of Cape Town (Haughton, 1956) i.e. outside the study area.

As noted above, dredge hauls containing phosphorite nodules have been recovered from 127 widely distributed stations on the Agulhas Bank (see Figure 1 and Appendix B). Representative examples of the phosphorite from each of these dredge hauls were examined and briefly described in hand speciment. On the basis of these descriptions, microscopic and x-ray diffraction (X.R.D.) studies, involving 80 thin sections and 30 X.R.D. pellets, were carried out on 60 selected phosphorite samples. The results of these petrographic investigations are presented in this chapter.

The X.R.D. studies (Chapter IV) have shown that francolite (a carbonate fluorapatite) is the primary phosphate mineral present. Optically however this mineral is identified as collophane, and in the petrographic (i.e. mainly microscopic) descriptions that follow this latter term will be used. Deer, Howie and Zussman (1962) note that collophane is a "sack" name for a variety of crypto-crystalline marine apatite minerals, including francolite.

The phosphorite nodules from the Agulhas Bank fall into two broad groups, on compositional and textural grounds :

(i) Non-conglomeratic Group.

(ii) Conglomeratic Group.

The non-conglomeratic group is further sub-divided into three sub-groups or classes, while the conglomeratic group is sub-divided into two classes. Cayeaux (1934) has put forward a classification of the limited number of Agulhas Bank phosphorites that were at his disposal. His classification however does not include the important and widespread conglomeratic group of nodules. Haughton (1956) has on the other hand noted that conglomeratic and non-conglomeratic phosphorite nodules have been recovered from isolated areas on the continental shelf bordering the western coast of South Africa north of Cape Town.

The terms "cement" and "matrix", used extensively in the petrographic descriptions that follow below, are here defined :

Cement : This refers to the collophane and/or micrite and/or goethite intergranular mixture which cements the enclosed silt, sand and gravel grains together.

Matrix : This refers to a mixture of silt and sand sized grains and cement. It excludes the pebble sized fraction found enclosed in the conglomeratic phosphorites.

Quartz and felspar are the principle terrigenous detritals. Quartz grains usually predominate over felspar by a factor of 10 : 1; and in view of the difficulty of accurately identifying the minor quantities of felspar present in the very fine sands and silts, the term quartz will be used in the petrographic descriptions to describe these principle detritals.

The term "sparry" calcite is used in place of "drusy" calcite. This is in keeping with the terminology proposed by Folk (1962). Sparry (or drusy) calcite refers to clear coarsely crystalline $CaCO_3$ typically found as a secondary cement infilling pore spaces. The term micrite, widely used in carbonate rock petrography, refers to an opaque microcrystalline calcite cement considered to have originated as lime mud (Folk, 1965).

A visual method (Folk, 1951) was used for estimating the percentages of the different components seen in thin section. A number of point count determinations on selected sections were made to check these estimates, with satisfactory results.

III.2 : Petrography of the Agulhas Bank Phosphorites.

Non-Conglomeratic Group.

III.2.1 : Class NI.

A. Summary.

Class NI nodules are composed of variable quantities of intact and fragmented sand sized microfossils (forming 40% - 70% of the rock) and macrofossil fragments (5 - 10%) set in a collophane/micrite cement. Silt sized angular quartz may be present in amounts ranging from 1% to up to 3 - 5%.

Examples from the Agulhas Bank of this class of phosphorite have been described by Cayeaux (1934, p. 111) while Murray and Renard (1891) have also described similar nodules recovered from a dredge station 100 miles to the southeast of the Agulhas Bank.

B. Morphology.

The nodules assigned to this group are irregularly tabloid in shape and their mean size is in the cobble range (Plate 1). The surface texture is rough and pitted due to the action of boring organisms, while the surface colour of the nodules is partly hidden by organic growths (e.g. Bryozoans), the nett effect being a mottled grey brown.

C. General Petrographic Characteristics.

(a) Allogenic Components.

The primary rock forming components are vitreous, porcelanous and agglutinous foraminiferal microfossils (Plate 2). Bryozoans are important in some nodules (i.e. DR - 10), while bi-valve macrofossil fragments are enriched in others. Echinoid plates and spines may be present. The size of the microfossils varies from 0.1 mm to approximately 1.00 mm, with an average value in the medium sand range. The macrofossils form large platy fragments up to 3 cm long, some of which exhibit algal borings.

The state of preservation of the microfossil tests is variable, ranging from intact and well preserved to corroded and broken. The tests are usually infilled by collophane-micrite while either goethite, pyrite or glauconite may sometimes form the infilling material.

(b) Authigenic Components.

In most of the nodules examined in thin section collophane is the dominant cement component, but occasionally micrite dominates. The colour of the cement is dependent on the relative proportions of collophane to micrite. Collophane rich cements are pale to moderate yellow, while an increase in the micrite content produces a grey coloured cement, as seen in thin section.

In certain of the nodules from this class there is a distinct, but gradational, colour change from the outer margins of the rock to the centre (Plate 1). The outer margins are a yellowish brown (10YR 5/2)+ in contrast with the central area, which is yellowish grey (5Y 7/2)+. This central area is usually offset to the sea floor side of the nodule (Plate 1). Organisms growing on the nodules (e.g. solitary corals) indicate which side of the nodule rested on the sea floor.

The geochemistry of these central and marginal areas shows (see Chapter V.2.6.) that the outer margins are richer in P_2O_5 as compared to the inner central areas (14.5% vs 11.5%). Thin sections cut from the marginal and central areas of the same nodule clearly show that mineralogically the central area is characterized by a high micrite and low collophane-francolite content, whereas the reverse is true for the marginal areas.

These colour, geochemical and mineralogical variations are therefore considered to be related to a phosphatizing process operating, from the surface inwards, on the original carbonate rock. Bushinsky

---

+Rock Color Chart, Rock Color Chart Committee (1951).

(1935, p. 87) has described similar phosphatization processes in Russian phosphorites.

Brown goethite-limonite is occasionally present as a true cement, but typically it occurs disseminated in a finely divided form throughout the collophane/micrite cement. The cement has occasionally become glauconized

(c) Textures.

The micro and macrofossil grains generally form a grain supported texture (Plate 2). In places, however, the grains are matrix supported. Using the classification of Dunham (1962) for carbonate rocks, class NI nodules are classified as medium-grained phosphorite packestones. Dunham's prefix "lime" is replaced by the prefix "phosphorite" as the phosphate mineral collophane is the dominant cementing agent.

(d) Secondary Features.

A secondary layer of collophane/micrite carrying variable quantities of glauconite, microfossils and quartz is present as a thin (usually < 1cm) discontinuous surface coating on some of the nodules. Medium sand sized glauconite grains are the dominant grain type present and form 30 - 75% of the secondary layer while medium to fine sand sized microfossil shells and shell fragments and silt sized quartz grains form 5 - 10% of this layer. The glauconite grains may be self supporting, especially in layers where the glauconite content is high (e.g. DR - 57), or the grains may be cement supported. This secondary layer may infill burrows left by boring organisms (e.g. DR - 57).

D. Geographical Distribution.

NI class nodules have been recovered from three principle areas on the Agulhas Bank (see Fig. 3).

(a) The Western Upper Continental Slope Area.

West of Cape Agulhas NI class nodules are found in isolated patches on the upper continental slope at a depth of 300 - 400 metres (e.g. DR - 5, 10 and 14).

(b) The East-Central Continental Shelf and Upper Slope Belt.

This is the richest NI nodule area on the Agulhas Bank and it forms a roughly S.W. - N.E. trending belt below latitude 35° S and between longitude 21° and 23° E. This belt transgresses from the continental shelf proper in the S.W. (ca. 120 - 150 metres) to the shelf break and upper continental slope in the N.E. (ca. 300 metres).

(c) The Eastern Continental Shelf/Shelf Break Area.

East of longitude 24° E NI nodules occur in patches located on the continental shelf and in shelf break areas (100 - 160 metres).

Apart from these three areas, the central Agulhas Bank has produced isolated patches of NI nodules (e.g. DR - 39, 40 and 46).

E. Petrographic Variations.

(a) The Western Upper Continental Slope Area.

In the area west of Cape Agulhas the nodules recovered from Station DR - 5 are distinctly enriched (3 - 5%) in silt sized quartz when compared to DR - 10 and 14 ($<1\%$). DR - 14 is petrographically similar to DR - 5 (especially with respect to its planktonic foraminiferal content) but is distinguished by a higher porosity (± 10%), an increased bryozoan content, and the absence of pyrite, goethite-limonite and glauconite as test infillings.

DR - 10 is unique in that its fossil content is restricted almost entirely to bryozoan fragments set in an otherwise featureless collophane/-micrite cement.

(b) The East-Central Continental Shelf and Upper Slope Belt.

The NI nodules found in this belt are all distinguished by the virtual absence of detrital quartz. They are characteristically composed of minor quantities of thick (i.e. up to 0.5 mm) platy macrofossil fragments, while the dominant components are sand sized thick and thin walled microfossil shells and shell fragments. Sand sized bryozoan fragments are common in some rocks (e.g. DR - 44). The thick walled microfossils predominate over thin walled types. The texture varies from grain supported to matrix supported, and the porosity of these nodules is also variable. Net-work structures are present in the collophane rich areas of the cement, similar structures having been described by Bushinsky (1935) in Russian phosphorites.

The microfossils include the three foraminiferal types (vitreous, porcelanous and agglutinous). Examples of this group are DR - 43, 44 and 125.

DR - 123, also found in this area, is distinctly different from the above group and it is characterized by the presence of occasional intraclasts (composed of material similar to the bulk nodule cement) and for ubiquitous silt sized microfossil fragments. DR - 60 appears to be transitional between DR - 123 and the DR - 43, 44, 125 group.

(c) The Eastern Continental Shelf/Shelf Break Area.

The high concentrations of thin walled planktonic Foraminifera (e.g. Globigerinidea) found in DR - 166 and DR - 183 and the silty quartz content of DR - 183 suggests a lithological connection of this area with NI nodules recovered from DR - 5 and DR - 14 located on the western side of the Agulhas Bank. DR - 57 may belong to this group as well.

III.2.2 : Class NII.

A. Summary.

Class NII nodules are composed of variable quantities of micro and macrofossil grains (50 - 70%) set in a dark brown goethite/micrite/-collophane cement. This cement infills the great majority of intact microfossil shells. Silt sized angular quartz, glauconite grains and glauconite infillings of shell chambers are present in minor quantities in some of the nodules. There are similarities between the fossil contents of NI and NII nodule classes. However, the fundamental characteristic of the latter class is the presence of a dark brown (iron oxide rich) cement.

Cayeaux (1934, p. 112) has described iron rich microfossiliferous nodules from the Agulhas Bank which belong to this class.

B. Morphology.

The nodules assigned to this class are irregular tabloid in shape. The number of burrows is greatly reduced as compared with nodules from other classes (Plate 3). The surface texture is smooth while the surface colour is a vitreous moderate brown (5YR 3/4)+. The interior colour on a freshly broken surface is opaque moderate brown (5YR 4/4)+.

C. General Petrographic Descriptions.

(a) Allogenic Components.

The size of the microfossil grains (or shells) ranges from fine to very coarse sand with the majority in the medium to coarse sand size range. Minor quantities of thick platy macrofossils are present in some nodules (e.g. DR - 84) while silt sized microfossil fragments are occasionally prominent (e.g. DR - 91). The state of preservation of the fossils is variable, some being intact and fresh, while the majority are broken, corroded and algal bored.

The microfossils include Perforata Foraminifera (e.g. Globigerinidea, a plaktonic type) and bryozoan fragments (Plate 4). Thick walled Imperforata types are also fairly common while Arenacea types are present in some nodules (e.g. DR - 91) in minor quantities. Bryozoans are locally plentiful. The majority of thick platy macrofossil fragments are considered to be bi-valve in origin. Some coral and echinoid debris is present.

(b) Authigenic Components.

X-ray diffraction studies show that goethite, collophane (i.e. francolite) and calcite are present in NII nodules. Calcite is associated with microfossils and micrite cement while the goethite and collo-

+Rock Color Chart, Rock Color Chart Committee (1951).

phane are considered to form the main components of the cement. It is impossible to distinguish optically these latter two mineral phases in the dark brown cement. They appear to form an intimate mixture, the strong goethite colour masking the presence of collophane. In some nodules the goethite content decreases locally and the cement becomes similar to that found in NI nodules.

(c) Textures.

In the majority of nodules the test grains are in contact with one another and hence the grains form a self-supporting framework. This class may therefore be classified as a medium to coarse grained ferro-phosphorite packstone.

(d) Secondary Features.

Some of the nodules are porous in places and the interstices have been lined or filled up with sparry calcite.

A secondary layer, similar to that described for NI nodules, is found as a thin discontinuous surface coating on some nodules (e.g. DR - 61). In comparison with NI nodules, this NII surface layer has a decreased glauconite content while carrying scattered very fine pebbles of microfossiliferous NI type phosphorite. Secondary sparry calcite is present infilling and/or lining pores in this surface layer.

D. Geographical Distribution.

The NII nodules recovered are primarily restricted to a N.E. - S.W. trending belt located in the shelf break and continental slope area bordering the south eastern flank of the Agulhas Bank between depths of 200 and 1000 m (see Fig. 3). Isolated examples of NII phosphorite have been recovered from the continental shelf east of latitude 23° E.

West of Cape Agulhas only one dredge station has produced NII phosphorite, i.e. DR - 213, located in 350 m of water.

E. Petrographic Variations.

The south western end of the N.E. - S.W. trending belt is noted for (i) its medium to very coarse sand sized generally thick walled fossil content, (ii) the presence of scattered thick platy macrofossil fragments and (iii) the absence of quartz grains. Foraminifera and Bryozoans are typical fossil types found in the nodules from this area. Examples are DR - 61 and 84.

The middle part of this continental slope belt is characterized by the near absence of macrofossil fragments, the presence of silt sized microfossil fragments and intact fine sand sized thin walled foraminiferal tests. Accessory quantities (< 1%) of silt sized quartz are present. Examples are DR - 91 and 98. DR - 92, a deep water variety from this area carries an opaque mineral rich in manganese (as indicated by a semi-quantitative x-ray fluorescence scan) in an intimate mixture with the goethite/collophane cement.

The north eastern end of this belt is noted firstly for the presence of silt sized quartz (5 - 10%) and secondly the clacite leaching of the bulk of the fine sand sized calcitic foraminiferal test to produce voids (e.g. DR - 164). The only continental shelf example of NII nodules examined in thin section (DR - 186) revealed similar fossil calcite leaching effects as in DR - 164. However the voids have generally been filled up with secondary sparry calcite and goethite. Quartz grains are absent but glauconite is present in accessory quantities.

III.2.3 : NIII Class.

A. Summary.

The nodules belonging to this group are composed of variable quantities of microfossil shells and shell fragments (0 - 40%), minor amounts of macrofossil shell debris (5 - 10%), glauconite grains (5 - 60%) and quartz/felspar grains (5 - 25%) set in a micrite/collophane cement. The characteristic feature of this group of nodules is the presence of glauconite grains (usually > 10%) and the near absence of enclosed microfossiliferous pebbles (c.f. the conglomeratic classes CI and CII).

Murray and Renard (1891, p. 393) and Cayeaux (1934, p. 110 - 111) have described NIII type nodules recovered from the western Agulhas Bank in the Cape Point area.

B. Morphology.

NIII nodules are irregularly oval to tabloid in shape. They range in size from pebbles to cobbles. The nodules may exhibit a rough and pitted surface texture, while others are less irregular. Burrows, due to boring organisms are common.

The interior colour (i.e. on a freshly broken surface) is controlled by the concentrations of glauconite and microfossils present. It is typically olive grey (5Y 3/2)+. (Plate 5).

C. General Petrographic Descriptions.

(a) Allogenic Components.

The fossil content of most of the nodules belonging to this froup ranges from zero to moderate (0 - 20%). Isolated dredges (DR - 248) have however produced NIII nodules composed of up to 40% microfossils. Intact microfossil shells range in size from fine to medium sand, while microfossil fragments fall usually in the silt to very fine sand size range. Thin walled foraminiferal types are common.

Thick (up to 0.5 mm) platy macrofossil fragments are present in minor amounts in some nodules, (e.g. DR - 39, 43). They are bi-valve in origin.

Glauconite grains exhibit a range of sizes (fine to coarse sand), surface features (sutured and unsutured) and concentrations (< 10% to 60%). Pyrite is associated with the glauconite as inclusions within these grains and as blebs and shreds in the surrounding cement.

In most of the NIII nodules the quartz content is present as angular silt to very fine sand grains and forms from 3% to 15% of the nodule. In some of the more quartz rich (15 - 25%) NIII nodules the degree of quartz grain rounding and sorting is unusually variable (Plates 6, 7). For example nodules from DR - 194 and 216 exhibit grain sizes ranging from angular silt through to angular coarse to very coarse sand. In contrast to these angular grains there is a population of perfectly rounded medium quartz sand. Furthermore DR - 194 carries occasional sub-

+Rock Color Chart, Rock Color Chart Committee (1951).

rounded coarse sand to very fine pebble fragments of quartzite rock.

Minor quantities of sub-rounded medium sand sized collophane pellets are present in nodules recovered at dredge station DR - 214. These pellets are optically very similar to the enclosing collophane cement. Furthermore these nodules carry minor amounts ($<$10%) of fine phosphorite pebbles rich in microfossils and angular silty quartz. In distinct contrast to the enclosing cement these pebbles are virtually free of glauconite grains. The proportion of enclosed pebbles is not sufficient to class these nodules as conglomeratic (c.f. conglomeratic classes CI and CII).

Accessory quantities of allogenic zircon, garnet and tourmaline may be present in NIII nodules (e.g. DR - 216).

(b) Authigenic Components.

The cement may be pure collophane (DR - 4) or a mixture of this mineral and micrite (e.g. DR - 43). Disseminated throughout the cement are finely divided blebs and particles of brown iron oxides (goethite?) and organic matter which gives the cement a turbid appearance in plane polarized light in thin section. Sparry calcite is present as a secondary cement lining pores and interstices.

(c) Textures.

The allogenic components in some nodules (DR - 39, 248) are predominantly in contact with one another and a grain supported texture results, while in other nodules (DR - 4, 216, 43) these grains are matrix supported (Plate 7).

This class of nodules may therefore be classified as glauconitic phosphorite wackestones and packstones after Dunham (1962).

D. Geographical Distribution.

NIII nodules have been recovered from three main areas on the Agulhas Bank (Fig. 3) :

(a) The Cape Point Area.

This area is located west and south-west of Cape Point in the region of latitude 34° 30' S and longitude 18 E, on the continental shelf and upper continental slope in water depths ranging from 200 - 500 metres. South-east of this area an isolated patch (DR - 211 and 209) is found on the continental slope.

(b) The East Central Agulhas Bank Area.

This second area is located south east of Cape Agulhas in the east-central region of the Agulhas Bank around latitude 35° 50' S and longitude 21° E on the continental shelf in 100 - 200 metres of water. Directly north of this area an isolated patch of nodules (DR - 39, 40) is present.

(c) The Eastern Agulhas Bank Area.

Patches of NIII nodules have been found in 100 - 200 metres of water on the continental shelf south of Cape Seal and south and south-east of Cape St. Francis.

E. Petrographic Variations.

(a) The Cape Point Area.

The NIII nodules from this area generally display a matrix supported texture. They are characterized, when compared to the east-central Agulhas Bank area, by their low microfossil concentrations and their coarser (medium to coarse sand vs fine sand) and sometimes sutured (DR - 216) glauconite grains. DR - 216 also carries ubiquitous intact and fragmented macrofossils.

Within the Cape Point area nodules from dredge stations DR - 4 and DR - 214 contain angular quartz silt to fine quartz sand while DR - 216 located near the Cape Peninsula coast has produced a poorly sorted NIII nodule rich in angular coarse to very coarse quartz sand while containing a finer (and also angular) quartz grain fraction similar to that found in DR - 4 and DR - 214. This has produced in the DR - 216 nodule a seriate texture with respect to the quartz grain content (Plate 7). The presence of tourmaline, garnet and ubiquitous zircon is also a feature of this nodule. This apparent coastward increase (i.e. DR - 216) in clastic components suggests that the coastal Cape Granite is the source rock for these components. Cape Granite forms the basement to the Cape Peninsula and carries zircon, garnet and tourmaline as accessory minerals. DR - 216 and DR - 194 (eastern Agulhas Bank area) are remarkably similar with respect to their matrix supported, and poorly sorted angular quartz contents.

(b) The East-Central Agulhas Bank Area.

DR - 39 and DR - 123 both exhibit grain supported textures and are furthermore very similar with respect to their well sorted (c.f. DR - 4, 216) very fine to fine sand sized quartz, glauconite and microfossil contents. These three components are present in similar concentrations and together form ±60% of the bulk of the nodule. DR - 39 is however depleted in glauconite but enriched in quartz with respect to DR - 123 (and vice versa). The increased fine quartz sand concentration of DR - 39 is possibly due to its location nearer possible source rocks on the coastline.

Silt sized quartz is present in these two nodules but its concentration is sharply reduced in comparison with nodules recovered from the Cape Point area.

Thick (up to 0.7 mm), platy bi-valve macrofossil fragments are present in minor quantities in both DR - 39 and DR - 123. They may be up to 3 cm long.

In contrast with the nodules from the previous two dredges, DR - 43 is matrix supported and exhibits sharply reduced concentrations of fine to very fine glauconite and quartz sand, while being enriched in microfossils. Macrofossil fragments are present as in DR - 39 and DR - 123.

Secondary sparry calcite and glauconitic micrite fill voids and burrows in the nodules from this area.

(c) The Eastern Agulhas Bank Area.

(c) The Eastern Agulhas Bank Area.

Two distinctly different NIII nodules were found in this area. The first (DR - 248) is a well sorted fine to medium (sand) grained microfossiliferous (± 40%) and glauconitic (10 - 20%) phosphorite packstone. The cementing material is a micrite/collophane mixture. The second nodule (DR - 194) is a micrite/collophane cemented poorly sorted (silt to very coarse sand) quartz rich (30 - 40%), microfossiliferous (± 3%) and glauconite poor (± 5%) phosphorite wackestone. Occasional quartzite rock fragments (as large as very fine pebbles) are present. The degree of rounding of the grains is variable; the material finer than medium grained usually being sub-angular to angular while most of the coarser material (including rock fragments) is sub-rounded. Irregular bedding planes are present on a microscopic scale and are associated with isolated grain supported textures. The above textural and sedimentological features exhibited by DR - 194 suggest an interesting mode of origin for this nodule.

That this particular nodule (i.e. DR - 194, see Plate 6) has had a most unusual depositional history is further underlined by the presence of <u>intact</u> thin walled planktonic Foraminifera (e.g. Globigerinidea) in the collophane/micrite matrix in close association with coarse quartz sand grains. The genetic implications of the above features will be discussed in Chapter VI.

Zircon is present as an accessory allogenic mineral, while sparry calcite is also present as a secondary mineral.

As noted previously this nodule is very similar to the NIII nodules recovered from dredge station DR - 216 in the Cape Point area.

Conglomeratic Group.

III.2.4 : Class CI.

A. Summary.

The characteristic feature of this class of nodules is their conglomeratic texture produced by the presence of abundant enclosed irregularly shaped and variably phosphatized microfossiliferous limestone pebbles (Plate 9, 10). These pebbles are set in a usually grain supported matrix composed of variable quantities of glauconite, microfossils, quartz and pelletal sand. The prime matrix cement is collophane.

B. Morphology.

The nodules assigned to this class exhibit various shapes, sizes and surface textures. They may be either tabloid, oval or irregular to very irregular in shape. They range in size from pebbles to boulders, the mean size falling in the cobble range. Surface textures vary from smooth to rough, knobbly and pitted (Plate 8). In some nodules which have insufficient matrix material, an irregular, open stockwork texture results, with the pebbles being merely cemented together at their points of contact with each other.

Surface colours are confused by marine growths, the nett effect being a mottled pale grey brown. In some nodules the surface coating is distinctly dark grey-black (N3)+.

The nodules are penetrated and permeated by burrows (boring organisms) and cavities which often reach the centre of even the largest nodules.

C. General Petrographic Characteristics.

(a) Matrix.

(i) Allogenic Components.

Glauconite : This mineral is the dominant matrix grain in the majority of CI nodules. The size of the grains ranges from fine to coarse (occasionally very coarse) sand, the modal size being medium sand (Plates 10, 11, 12). The grains are generally unsutured and well rounded. The majority of glauconite grains seen in thin section are considered to be the "black glauconite" variety found in the unconsolidated glauconite rich sediments of the Agulhas Bank (Birch, in prep.).

Microfossils : Class CI nodules contain variable quantities of microfossil calcite grains. They seldom form more than 20% of the matrix grains. Where plentiful they are dominated by foraminiferal types (e.g.

+Rock Color Chart, Rock Color Chart Committee (1951).

vitreous, porcelanous and agglutinous). The microfossils may be intact or broken and fragmented. Intact varieties fall in the medium sand range while the broken and fragmented grains range down to silt sized material. The majority of intact shells are infilled by collophane which is optically similar to the enclosing cement. Occasionally the infilling material is a collophane/goethite mixture. In certain nodules (e.g. DR - 10, 14) a pellicle of isotropic collophane is found surrounding some of the microfossil grains. These grains are considered to be incipient oolites. Macrofossil fragments are generally absent in CI nodules, although some examples are noted for the minor amounts (ca. 5%) found enclosed.

Quartz : The quartz grain content of the matrix of class CI nodules is generally less than 10%, while the size range of this component varies from silt to very coarse sand. The coarser grained material may be rounded or angular, while the finer material is angular.

In certain CI nodules (e.g. DR - 248) subrounded quartzite rock fragments of up to very fine pebble size are present.

Pellets : Occasional nodules (e.g. DR - 10, 14) carry minor quantities of sand sized collophane pellets. They are similar to the pellets already described in NIII nodules.

Garnet and Zircon : Accessory quantities of these minerals may be present.

(ii) Authigenic Components.

Collophane is the primary nodule cement. It is very similar to the cement described for the NIII class of nodules. Like the NIII nodules this is intermixed with a variable amount of micrite.

(iii) Matrix Texture.

The allogenic components may be cement supported (e.g. DR - 4, 10, 14) or they may support each other, producing a grain supported texture (e.g. DR - 219, 58, 121 and 248) (Plates 10, 11, 12). This latter texture is the most common and is associated with nodules recovered from the continental shelf while the former is found in continental slope nodules.

(iv) Secondary Matrix Features.

Secondary sparry calcite and goethite may be present lining or filling pores and interstices. Another secondary feature especially common in grain supported areas is the encrustation of glauconite, quartz and microfossil grains by a thin (ca. 0.005 mm) rind of an anisotropic, uniaxial negative, colourless and weakly birefringent apatite-like mineral (Plates 11, 12). This rind is similar optically and in its mode of occurrence to the secondary phosphate mineral dahllite described by Rogers and Kerr (1942, p. 225). Bushinsky (1935, p. 86) and Summerhayes (1970) have described similar grain encrusting rinds found in Russian and N.W. African phosphorites respectively. As the correct identification of dahllite, as opposed to the optically similar phosphate mineral francolite, is dependant on the F content of these two minerals (cf. Deer, Howie and Zussman, 1962) the term "dahllite" (cf. Rogers and Kerr, 1942) will be used in this work to describe these rinds. This "dahllite" encrusting rind is not to be confused with the nearly isotropic collophane pellicle found coating microfossil grains. DR - 109 carries pellicled microfossil grains that have been encrusted by an outer "dahllite" rind, indicating the order of occurrence of these two minerals. A further point of interest is the similarity, in plane polarized light, of these dahllite rinds to the fibrous calcite encrustations found enveloping microfossil and quartz grains in certain South African coastal limestones as described by Siesser, (1970, p. 55).

(b) Enclosed Pebbles.

The enclosed silty quartz/microfossiliferous limestone fragments, in various states of phosphatization, range in size from sand to cobble grades, the modal value being in the pebble range (Plates 9, 10, 11). They are usually sub-rounded to sub-angular while their shape ranges from equant to highly irregular. Re-entrant angles (or surfaces) are common in very irregular enclosed pebbles (Plate 9).

The pebbles are primarily composed of variable quantities of angular silty quartz (0 - 40%) and intact and fragmented foraminiferal tests (0 - 60%) set in a collophane/micrite/goethite cement. In certain pebbles medium sand sized glauconite grains are present in minor quantities ($<$ 10%), in addition to quartz and microfossil grains. Those pebbles rich in goethite are pale brown in colour while the goethite poor or free pebbles are pale grey in colour. Foraminiferal tests are often preferentially infilled by goethite. Colour variations similar to those found in NI class nodules are present in these enclosed pebbles (Plate 9), suggesting that they have been phosphatized either before or after their incorporation in the present nodules. The pebbles may be sub-divided into two groups, the first being quartz silt rich and the second quartz silt poor (Plates 10, 11). The quartz rich varieties tend to be depleted in microfossils (usually fragmented) while the quartz poor varieties are dominated by intact microfossils (especially planktonic Foraminifera, e.g. Globigerinidea). The majority of pebbles exhibit a grain supported texture, the microfossils and quartz grains forming a close packed structure. These enclosed pebbles may be classified as fine to medium (sand) grained phosphorite packstones (after Dunham, 1962); i.e. very similar texturally (and compositionally) to the NI phosphorite class.

The Textural Relationship of the Pebbles to the Matrix : The enclosed pebbles may be either self-supporting or matrix supported. The self-supported pebble texture is the most common and in these nodules the pebbles constitute greater than 50% of the total bulk of the rock.

(c) Internal Structures - Bedding.

Certain nodules exhibit distinct macro-scale (i.e.> 1 cm) bedding planes which separate the rock into two conglomeratic layers that exhibit differences in the glauconite content and in the average size of the enclosed pebbles (Plate 9). The orientation of these bedding planes is parallel to the a/b plane (Pettijohn, 1957, p. 55) of the tabloid nodules in which they usually occur.

Micro-scale bedding planes, often separating different matrix textures (i.e. grain supported vs cement supported), are present in some thin sections (DR - 109, 58, 60; Plate 13). These micro-scale planes are delineated and characterized by the presence of increased concentrations of finely divided iron oxides and organic matter.

Micro-scale erosional surfaces, free of iron oxides and organic matter are also present in association with bedding surfaces. These erosional surfaces cleanly truncate glauconite and microfossil grains, and older bedding planes (e.g. DR - 60).

The last phase in the formation of these nodules is marked by the introduction of a white micrite infilling into cavities and bore tubes (burrows). This infilling carries scattered glauconite and microfossil grains.

D. Geographical Distribution.

By far the greatest number of nodules recovered from the Agulhas Bank belong to the CI class. They are found in three main areas : one west of Cape Agulhas and two east of Cape Agulhas (see Fig. 3).

(a) West of Cape Agulhas.

The Cape Point Area : This CI area is located within the NIII Cape Point area, already described, i.e. in the region of latitude 34° 30' S and longitude 18° E. This CI area is however generally limited to the upper continental slope and shelf-break areas (between depths of 300 and 400 metres) and does not spread across the continental shelf as does the NIII area.

South east of this area isolated dredge hauls on the continental slope have recovered CI nodules (i.e. DR - 10, 14).

(b) East of Cape Agulhas.

(i) The East-Central Agulhas Bank Area.

This area is located around latitude 35° 40' S and longitude 21° 35' E on the continental shelf in depths of 100 to 200 metres of water. This area is situated between an NI/NIII area immediately to the west and an NI/NII/CII area immediately to the east.

(ii) The Eastern Agulhas Bank Area.

This widespread and productive area covers a large part of the eastern Agulhas Bank continental shelf (east of longitude 22° 20' E). The majority of CI dredges from this area were recovered in 100 - 200 metres of water. This eastern Agulhas Bank area may be further sub-divided into a far eastern area, south of Cape St. Francis, and a western area to the south of Mossel Bay.

E. Regional Petrographic Variations.

The CI nodules recovered from the continental shelf and upper continental slope west of Cape Agulhas may be differentiated from the CI nodules recovered to the east of Cape Agulhas (i.e. primarily on the continental shelf) by the following features :

The western nodules are noted for the similarity of the enclosed pebbles to the surrounding matrix, as seen in hand specimen and in thin section. The pebble boundaries in these nodules are often vague and indistinct (e.g. DR - 4, 10). The CI nodules from the east of Cape Agulhas, on the other hand, are noted for the dissimilarity of the pebbles as compared to the matrix, and this results in well defined pebble boundaries.

The matrix grains are usually cement supported in the western nodules, especially in those nodules recovered from the upper continental slope (e.g. DR - 4, 10 and 14), while in the east the matrix grains are usually self supporting.

Furthermore, in western CI nodules, collophane pellets and incipient oolitic microfossil grains are relatively common (5 - 10%), while east of Cape Agulhas they are only occasionally present.

In contrast to the above regional differences, CI nodules from DR - 219 (located west of Cape Point) exhibit similar quartz rich grain supported matrixes as compared with the CI nodules from the continental shelf in the far eastern Agulhas Bank area (e.g. DR - 248, see below). It may be noted that DR - 219 is on the continental shelf, as opposed to DR - 4, 10 and 14, which are on the continental slope.

The genetic significance of the matrix textures exhibited by these western continental slope phosphorites, as compared to the matrix textures of the nodules from the eastern continental shelf area, will be discussed in Chapter VI.

F. Localized Petrographic Variations.

(a) The Area West of Cape Agulhas.

This region includes the Cape Point area and the nodules recovered to the south west, i.e. DR - 10, 14.

An important variation within this region is the north-westward increase in the glauconite sand content of the matrix, while a similar increase is noted in the quartz silt content of both the matrix and the enclosed pebbles.

The north-westward increase in the matrix glauconite content parallels a similar glauconite enrichment trend found in the unconsolidated sediments in this area (Birch, in prep.).

Within the Cape Point area itself there is a similar north-westward increase in the concentration and coarseness of the quartz sands found in the matrix (e.g. DR - 219 vs DR - 4). DR - 219 is however anomalous in that, while being north of DR - 4, it contains much lower concentrations of quartz silt in both its matrix and pebbles, as compared to DR - 4. A further characteristic of DR - 219 is that the matrix is grain supported, while the majority of CI nodules recovered from this region (i.e. DR - 4, 10 and 14 to the south east) are cement supported. The third unusual feature of DR - 219 is that the originally high microfossil calcite content of the enclosed pebbles has been reduced to zero by a calcite leaching process that has removed the microfossil calcite and left behind empty voids or moulds. Similar leaching effects are present in some of the enclosed pebbles in DR - 4, while others are rich in microfossil calcite. The matrix microfossil content of DR - 4 has not been leached out, implying that in the case of this DR - 4 nodule, the leaching process took place prior to the incorporation of the pebbles in the nodule matrix.

The enclosed pebble content of the nodules from this region include quartz rich and quartz poor varieties. They are usually glauconite free, although some pebbles carry minor, medium sand sized, quantities of this component (e.g. DR - 219, 4). Intraclastic pebbles (very similar in composition and texture to the surrounding matrix) are present in some nodules (e.g. DR - 10). They are noted for their very indistinct boundaries. The enclosed pebbles usually form less than 50% of the total bulk of the nodule and they are generally matrix supported.

(b) The East Central Agulhas Bank Area.

This region is noted for its grain supported matrix textures, in contrast to the area west of Cape Agulhas. Medium sand sized glauconite is the dominant matrix grain and forms 40 - 60% of the matrix. The interesting feature of this area is the presence of micro-scale bedding (Plate 13) and erosional surfaces in some of the nodules (i.e. DR - 58, 60).

The enclosed pebble content of the nodules from this area is relatively uniform (50 - 60% of the rock), and both types of pebbles (i.e. quartz rich vs quartz poor) are found in the majority of nodules.

(c) The Eastern Agulhas Bank Area.

The matrix texture and composition of the nodules from this rich CI area are similar to those described for the CI nodules from the east-central Agulhas Bank area.

In this area the matrix is however locally enriched in sand sized microfossils, at the expense of glauconite, e.g, DR - 109. DR - 109 is also noted for the presence of both macro- and micro-scale bedding features.

The characteristics of the enclosed pebble content of the nodules recovered from this area are generally similar to those described for the nodules from the east-central area. Important petrographic variations are however exhibited by nodules recovered from the far eastern part of this eastern Agulhas Bank area. These nodules (e.g. DR - 165, 248) are enriched in detrital quartz (10 - 15%) as compared to the middle and western parts of this eastern area (5%). This is especially noticeable with regard to increases in the size and concentration of the sand sized quartz fraction, for example DR - 248 carries rounded coarse to very coarse quartz sand grains as well as sub-rounded coarse sand sized quartzite rock fragments. There is a similar eastward increase in the maximum size of the glauconite sand grains present (e.g. DR - 248).

A further feature of the CI nodules from this far eastern area is that the enclosed pebbles often carry minor amounts of glauconite sand grains (e.g. DR - 248).

The following points are of interest :

(i) The non-conglomeratic NIII nodules recovered from this far eastern area are, like the CI nodules from this area, enriched in coarser quartz and glauconite sands (e.g. DR - 194).

(ii) The NIII and CI nodules from the Cape Point area (e.g. DR - 219, 216) are similar, with respect to matrix grain composition and size, to the NIII and CI nodules from this far eastern area.

(iii) Glauconite sand grains are present in minor amounts in some of the enclosed pebbles found in CI nodules recovered from both the Cape Point area (e.g. DR - 219) and this far eastern Agulhas Bank area (e.g. DR - 248).

(iv) The continental shelf in both the Cape Point area and the far eastern Agulhas Bank area is relatively narrow (see Fig. 1).

III.2.5 : Class CII.

A. Summary.

Nodules assigned to this class are characterized by an inhomogeneous conglomeratic texture produced by the presence of enclosed microfossiliferous pebbles (often internal casts of macrofossils), macrofossil shell fragments and fossil bone debris (Plate 14) set in a grain to cement supported matrix composed of variable amounts of glauconite, microfossil and quartz grains. The cementing material is a collophane/micrite/goethite mixture.

CII nodules may be distinguished from CI nodules by the following features :

(i) The presence of pebble sized microfossiliferous internal casts of macrofossils (Plate 15).

(ii) The generally lower glauconite content and higher microfossil content (up to 40%) of the matrix.

(iii) Increased iron oxide (i.e. goethite) concentrations.

(iv) Increased concentrations of macrofossil shell fragments and bone debris.

All of the above features are not necessarily exhibited by every CII nodule.

B. Morphology.

The morphology of the CII class of nodules is similar to that described for CI nodules.

C. General Petrographic Characteristics.

(a) Matrix.

(i) Allogenic Components.

Glauconite : The glauconite grain content of the matrix varies from less than 5% in some nodules, to greater than 40% in others. The grains fall in the medium sand range and they are generally rounded and spheroidal to elongate in shape. Sutures are relatively uncommon. Pyrite is often associated with the grains as included blebs and shreds. The glauconite grains are provisionally identified as the "black glauconite" variety (i.e. the same as for CI nodules) described from local unconsolidated sediments by Birch (in prep.).

Microfossils : These calcite grains are the dominant (ca. 30 - 40%) matrix component of some CII nodules while in others they are present in minor amounts (ca. 5%). There is an inverse relationship between the matrix glauconite and microfossil grain concentrations. The microfossil grains occur most commonly in the medium sand sized fraction. They are predominantly Foraminifera (including vitreous, porcelanous and agglutinous types). The test interiors are sometimes sparry calcite or goethite rich, but normally the infilling is a collophane/micrite mixture similar to the matrix cement.

As in CI nodules the microfossil grains may be incipient oolitic in places. Other microfossils include occasional fish teeth, echinoid plates and bryozoans.

Macrofossils : Macrofossil calcite fragments are present in many CII nodules. They are typically bi-valve in origin, although gastropod, coral and bone material is also present.

Quartz : This detrital component of the matrix ranges from zero to 5 - 10%. As with CI nodules the size distribution of the grains (in the quartz rich nodules) tends to follow a bimodal pattern, with an angular silt sized fraction contrasting with an angular to sub-rounded fine to medium sand fraction.

Accessory quantities of collophane pellets and zircon (in quartz rich nodules) are present.

(ii) Authigenic Components.

The primary nodule cement is a collophane/micrite (and in places goethite) mixture similar to that already described for NIII and CI nodules.

Secondary authigenic features include "dahllite" rinds around glauconite, quartz and microfossil grains while secondary sparry calcite and goethite line and fill interstices and voids. In restricted areas secondary sparry calcite may become the dominant cementing agent. These secondary features are similar to those already described for CI nodules.

In many CII nodules dark brown goethite/limonite colloform (i.e. not to be confused with collophane) layers are present as surface coatings and within the body of the nodule. Relative to CI nodules, CII nodules are enriched in goethite/limonite.

(iii) Matrix Textures.

The matrix texture of CII nodules varies from distinctly cement supported to distinctly grain supported. The majority of nodules exhibit both textural forms, often within the space of a single thin section. This small scale textural variability may be associated with micro-scale bedding planes that separate one texture from another (e.g. DR - 62). In some nodules however the texture is more uniformly grain supported (e.g. DR - 155).

(b) Enclosed Pebbles.

The enclosed pebble content of CII nodules is generally less than in CI nodules and forms 20 - 50% of the total volume of the rock. The pebbles are usually matrix supported. They range in size from 1 - 2 mm (i.e. very coarse sand) to 5 - 6 cm (very coarse pebbles).

The pebbles are typically composed of variable quantities of microfossil shells (intact and fragmented) and silt sized quartz set in a collophane/goethite/micrite cement mixture. Glauconite grains are usually absent, although there are exceptions. A distinctive feature of CII nodules is that a proportion of the enclosed pebbles indicate by their shape that they are internal casts of fossil shells (Plates 15, 16), especially molluscs, brachiopods and corals. Some of these pebble casts still preserve the outer and originally enclosing calcite shell layer while the majority do not. Irregular pebbles not obviously related to internal casts are present and these are often similar (i.e. quartz poor/microfossiliferous rich and vice versa) to the enclosed pebble types found in CI nodules. Occasional "irregular" and "internal cast" pebbles are very similar in composition to the matrix material, indicating an intraformational origin.

(c) Internal Structures - Bedding.

Micro-scale bedding planes are present in CII nodules and are associated (as already noted) with changes in the matrix texture. They are similar to the bedding planes described for CI nodules. Erosional surfaces were not found however (cf. CI nodules). Some nodules exhibit brown, glazed, macro-scale bedding planes along which the nodule tends to split (e.g. DR - 62).

D. Geographical Distribution.

Areas from which class CII nodules have been recovered are restricted to two distinct regions west of Cape Agulhas on the Agulhas Bank (see Fig. 3).

(a) The South Eastern Shelf Break Area.

This area forms a N.E. - S.W. trending belt roughly parallel to the shelf break on the south eastern margins of the Agulhas Bank. This belt has produced samples from both the continental shelf proper (e.g. DR - 87, 89) and from the upper continental slope (e.g. DR - 91, 104).

(b) The Eastern Continental Shelf Area.

This important CII area is found on the continental shelf between Mossel Bay in the west and Port Elizabeth in the east. The nodules generally come from relatively shallow water (75 - 150 m) as compared to the south eastern shelf break area (150 - 300 m).

E. Petrographic Variations.

(a) The South Eastern Shelf Break Area.

The CII nodules from this area typically exhibit mixed matrix textures (i.e. cement supported and grain supported), low matrix glauconite contents ($<$ 20%), moderate matrix microfossil contents (20 - 40%), macrofossil shell and bone debris, micro- and macro-scale bedding surfaces, and variable quantities of enclosed pebbles. The proportion of "internal cast" pebbles is however not as high in these nodules as compared to the eastern continental shelf area.

Some nodules are noted for their well developed colloform limonite layers (e.g. DR - 87). The nodules recovered from DR - 62 and DR - 83/791 provide good examples of the association of bedding planes with changes in matrix texture; for example in these nodules grain supported textures are often separated from overlying cement supported textures by bedding surfaces.

The detrital quartz content of the nodules from this area is usually negligible, although angular silt sized quartz grains are present in accessory amounts in the matrix of DR - 89.

(b) The Eastern Continental Shelf Area.

A higher proportion of "internal cast" pebbles and a richer matrix glauconite (30 - 40%) and quartz (up to 5%) content characterise the CII nodules from this area (e.g. Plate 15), as compared to the previous area.

The matrix of certain nodules (DR - 112, 155) exhibit grain supported textures while the majority exhibit both grain and cement supported textures.

A similar quartz enrichment trend, as compared to CI and NIII nodules, is noted in the CII nodules recovered from the 'far' eastern continental shelf area (e.g. DR - 246, 248). Apart from this absolute increase, the quartz grains follow a bimodal size pattern, a silt sized angular fraction contrasting with a medium sand sized sub-rounded fraction.

The goethite/limonite content of the CII nodules recovered from the eastern continental shelf area is higher than the CI and NIII nodules from this area.

III.2.6 : Interrelationships Between Classes.

Where CI, CII and NIII nodules are found together the following points are noted with regard to their matrix composition :

(i) Geographical quartz enrichment and depletion trends are similar in these three classes.

(ii) Quartz enrichment is associated with the introduction of coarser quartz and glauconite grain fractions. As a result poorly sorted textures are produced by the presence of medium to very coarse quartz sand fractions (often rounded) in sharp contrast to angular quartz silt fractions.

Similar examples of these compositional and textural trends and associations are noted in the Cape Point area (e.g. DR - 219, 216) and the far eastern Agulhas Bank area (e.g. DR - 248, 246, 194). These similarities are further underlined by the relatively narrow continental shelf found in these two areas. There are exceptions; DR - 248 has produced, apart from quartz rich CI and CII nodules, a geographically atypical NIII nodule which is depleted in quartz (cf. the nearby quartz rich NIII nodule found at DR - 194).

(iii) Some of the NI and NII nodules are noted for their thin (< 1cm) surface coatings of CI/NIII type phosphorite. These coatings suggest that the phosphate mineralization of the NI and NII groups was penecontemporaneous with, or as a result of, the phosphatization regime responsible for the formation of CI and NIII nodules.

(iv) The enclosed quartz-silty/microfossiliferous pebbles found in CI and CII conglomerate nodules are correlated with similar NI nodules, suggesting a distinct change in the low energy (i.e. quiet 'deep' water) environments represented by these NI nodules to the higher energy environments associated with conglomerate formation.

Apart from these interrelationships between CI, CII and NIII nodules, there is also a strong areal correlation of NI and NIII nodules in the east-central Agulhas Bank area (e.g. 39, 40, 43, 44 and 123).

III.3 : Petrographic Comparisons of Phosphorites and Phosphatic Rocks from other Localities.

III.3.1 : The North West African Continental Shelf Phosphorite Deposits.

A. Introduction.

The phosphatic rocks and phosphorites found on the N.W. African continental shelf and described by Summerhayes (1970) have been divided into three basic varieties : The first being a glauconitic conglomeratic type, the second a moderately conglomeratic pelletal type while phosphatic limestones comprise the third type.

B. The Glauconitic Conglomeratic Type.

This conglomeratic type is similar in many respects to the Agulhas Bank CI conglomeratic class of phosphorites : Like the Agulhas Bank CI class these N.W. African rocks are composed of angular to sub-angular variably phosphatised foraminiferal limestone pebbles set in a poorly sorted matrix composed of variable quantities of sand sized glauconite, silt sized quartz, and Foraminifera, cemented by a turbid micrite/collophane mixture. Finely divided inclusions of iron oxides and organic matter found in these geographically widely separated matrix cements results in a similar turbid appearance. Grain supported areas in both rock types are noted for the presence of clear colourless "dahllite" rims around grains of glauconite, quartz and microfossils.

The matrix texture of the N.W. African variety is variable and ranges from matrix (i.e. cement) supported to grain supported within the space of single thin section. Similar textural variations are found in some of the Agulhas Bank CI nodules, but they are more often either dominantly cement supported or dominantly grain supported. Irregular erosional surfaces found in these two groups of nodules is a further point of similarity.

C. Pelletal Types (Moderately Conglomeratic).

The matrix of this N.W. African variety is characterized by the absence of glauconite grains and the presence of phosphate pellets, Foraminifera and silt sized quartz. A relatively (with respect to A) decreased enclosed pebble content is a further feature. Most of the enclosed pebbles appear to be intraformational in origin. The matrix cement is similar to that found in the glauconitic conglomeratic variety.

This N.W. African variety finds no ready correlation with the Agulhas Bank groups, but certain similarities are noted with the glauconite poor, moderately pelletal, and conglomeratic CI nodules recovered from the western continental slope areas of the Agulhas Bank at dredge stations DR - 10 and DR - 14. In support of this correlation some of the enclosed pebbles found in DR - 10 and DR - 14 also appear to be intraformational in origin.

D. Phosphatic Limestones.

The descriptions of this group of N.W. African phosphatic rocks are not suitable for making a direct comparison with the phosphatized limestones found on the Agulhas Bank, (i.e. the NI class). Nevertheless it is tentatively suggested that these two phosphatized limestone groups be correlated.

Surface to centre phosphatization gradations and associated colour variations, found in some of the phosphatized limestone nodules from the Agulhas Bank, do not appear to be present in the N.W. African phosphatic limestones.

III.3.2 : The Southern Californian Off-Shore Deposits.

The phosphorite nodules recovered from the rich seafloor deposits off southern California have been described by Dietz, Emery and Shepard (1942) and Emery (1960) :
The shapes and surface textures of these Californian submarine nodules are often highly irregular, while some nodules are distinctly tabloid. The primary phosphate mineral present is collophane-francolite. Structurally many of the nodules are conglomeratic, while irregular bedding layers, separated by a thin film of brown collophane, are also common.

The Californian nodules carry a wide variety of enclosed material. Phosphate oolites are present in minor quantities while Foraminiferal microfossils are also present and in some rocks may be "extremely abundant" while the original microfossil calcite has usually been converted to "francolite" (Dietz et al., 1942). Clastic grains such as quartz and felspar are present in both rounded and angular forms, while rounded glauconite grains are plentiful in most nodules.

The conglomeratic varieties found in this Californian off-shore area are particularly interesting (cf. the conglomeratic N.W. African and Agulhas Bank phosphorite nodules). These nodules carry enclosed pebbles of "phosphorite" and rock fragments such as andesite and chlorite schist (Dietz et al., 1942).

The above features are remarkably similar to the features described for the CI and NIII Agulhas Bank nodule classes. The Californian conglomeratic and non-conglomeratic (i.e. enclosed pebble free) types are therefore equated with the Agulhas Bank CI and NIII classes respectively.

Point of dissimilarity are as follows :

(i) The microfossil calcite content of Californian nodules has usually been converted to or replaced by phosphate minerals (i.e. francolite), while in the Agulhas Bank nodules this is rare. Petrographic and x-ray diffraction studies by Dietz et al., (1942) have shown that in the Californian nodules calcite is absent or at best only present in accessory quantities. In comparison calcite is a major mineral component of most of the Agulhas Bank phosphorites. It may however be noted that certain CI class nodules found on the continental slopes of the western Agulhas Bank exhibit calcite leaching effects and appear to be free of this mineral (e.g. DR - 219). The original microfossil shells in these nodules are now represented by empty moulds which could easily be infilled by collophane-francolite to produce a similar effect as that found in the Californian nodules.

(ii) The Californian conglomeratic varieties are not noted (Dietz et al., 1942) for the presence of enclosed quartz silty/microfossiliferous limestone pebble fragments, while in the conglomeratic CI class of nodules from the Agulhas Bank they are the dominant enclosed pebble type.

III.3.3 : Unconsolidated Pelletal Phosphorite Deposits.

Phosphorite deposits in this category have been found on the seafloor off Baja, California, Mexico, (D'anglejan, 1967), onland in Beaufort County, North Carolina, U.S.A. (Brown, 1958; Rooney and Kerr, 1967) and onland near Saldanha Bay, South Africa, (Smith, 1971).

The pelletal phosphorite grains found in these deposits typically fall in the sand-sized range and may be sub-rounded to rounded (e.g. Saldanha Bay and Beaufort County deposits) or sub-angular (Baja deposit). The primary pelletal phosphate mineral in these deposits is collophane-francolite and in all three areas the pellets may carry isolated angular silt sized quartz grains as detrital inclusions.

The optical studies presented by these workers show that these pelletal grains from widely separated localities are mineralogically very similar to each other and to the pelletal grains found in minor quantities in some CI (e.g. DR - 10, 14) and NIII (e.g. DR - 214) Agulhas Bank nodules.

A very interesting feature of these pelletal grains is their similarity, in thin section, to the collophane matrix of CI, CII and NIII Agulhas Bank nodules, especially with respect to the large number of finely divided inclusions which give both pellets and matrix a turbid appearance.

X-ray diffraction data presented by Rooney and Kerr (1967) and in this work clearly shows that the primary phosphate mineral present in the Beaufort County pelletal grains and in the Agulhas Bank nodules is structurally identical (see Chapter IV).

III.3.4 : The Lithified Pelletal Phosphorites of the Phosphoria Formation, Central U.S.A.

The Agulhas Bank phosphorite deposits do not have many features in common with the extensive stratified rocks of Permian age in the Central U.S.A., i.e. the Phosphoria Formation.

These bedded phosphorites are typically composed of well rounded and well sorted medium sand sized phosphate pellets and oolites, while in some areas phosphate "nodules" are present (Sheldon, 1963). In the Meade Peak Phosphatic Shale Member of the Phosphoria Formation the dominant pelletal and oolitic strata are under and overlain by relatively thin bio-clastic horizons. The Phosphoria phosphorites are intimately associated with mudstones, cherts and carbonaceous rocks.

Apart from sharing a similar primary phosphate mineralogy (i.e. carbonite fluorapatite) the Phosphoria and Agulhas Bank phosphorite deposits are linked by two features :

(i) The presence of minor quantities of phosphate pellets and incipient phosphate oolites found in the CI class of Agulhas Bank nodules.

(ii) The presence in rocks from both deposits of phosphatized internal shell casts and bioclastic material.

PLATES 1 - 16

Note:- All the photomicrographs, except Plate 12B, were taken using plane polarized light. Plate 12B was taken with the nicols crossed.

Plate 1: N I nodule (DR-43) - This phosphatized limestone exhibits colour graduations considered to be related to a surface to centre inward phosphatization process.

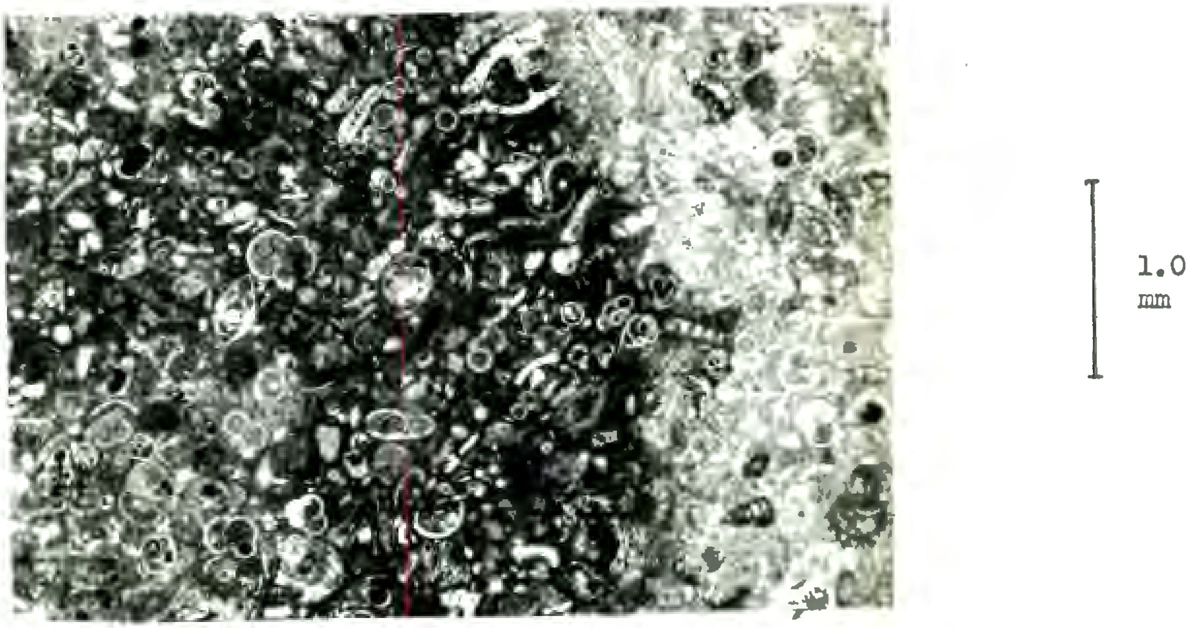


Plate 2: N I nodule (DR-183). Intact end fragmented foraminiferal microfossils form a grain supported packstone texture. The cement is a dark collophane/micrite/goethite mixture in the centre which grades abruptly into a light collophane/micrite cement to the right, and more gradationally to the left.

Plate 3: N11 nodule (DR-61) exhibiting a smooth brown black surface glaze.

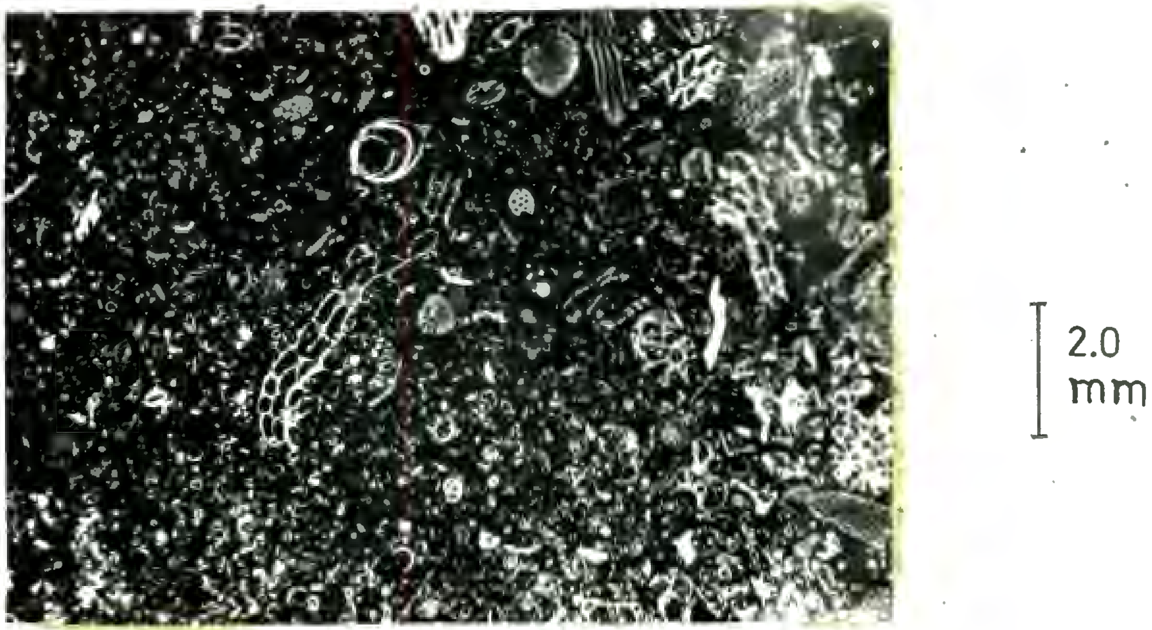


Plate 4: N11 nodule (DR-61). Intact and fragmented microfossils form a grain supported packstone texture. The microfossils include Bryozoa and Foraminifera, while the cement is a highly ferruginous goethite/micrite/collophane mixture.

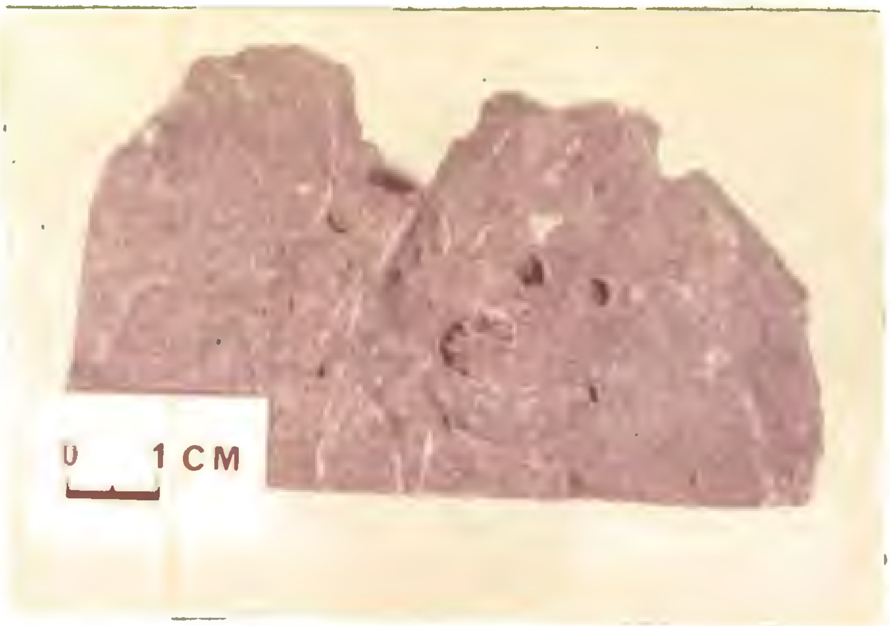


Plate 5: N 111 nodule (DR-44) exhibiting a grey internal colour. Note the enclosed platy microfossils and a coral internal cast. (The bottom of the nodule is flat as a result of thin sectioning).

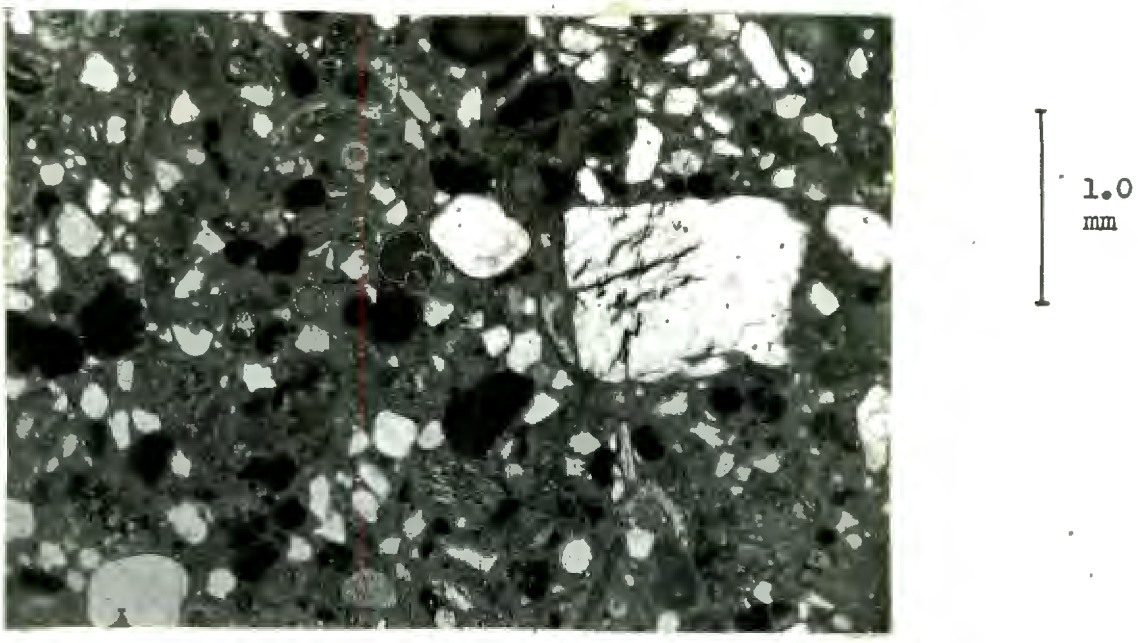


Plate 6: N 111 nodule (DR-194) exhibiting a poorly sorted and cement supported assemblage of "dark" glauconite and "light" quartz grains, as well as intact and fragmented microfossils. The intergranular cement is a turbid micrite/collophane mixture.

Note:- (i) variations in the size and degree of rounding of the quartz grains, and (ii) the perfectly preserved "thin" walled foraminiferal microfossil (centre) and the fragmented "thick" walled microfossil (bottom right).

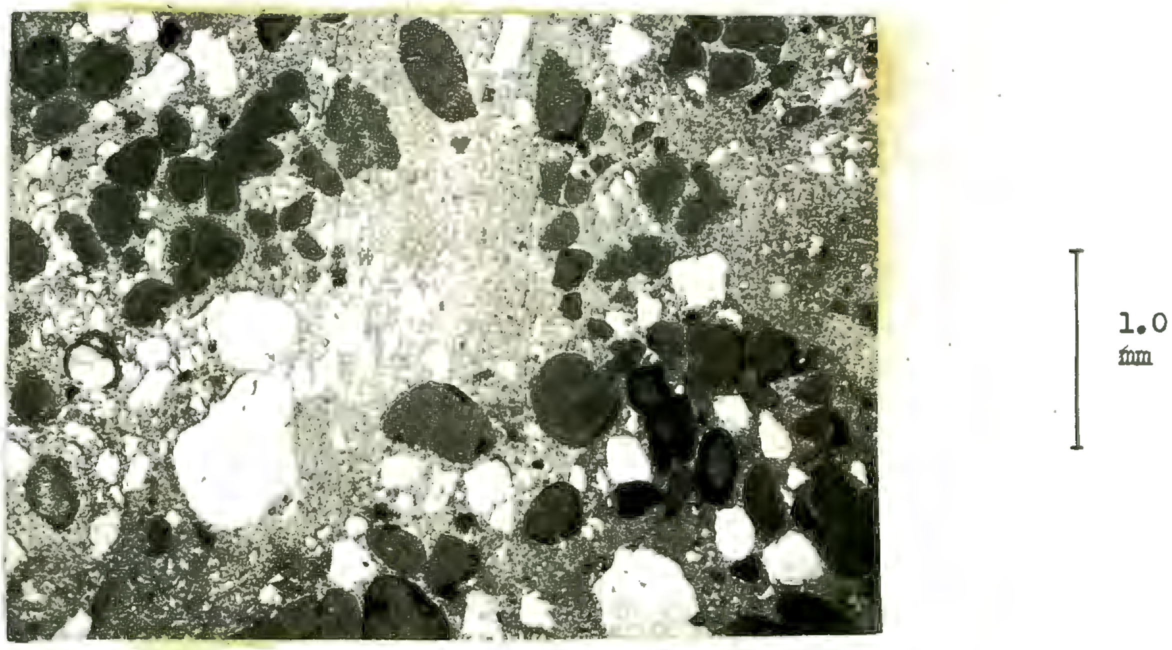


Plate 7: N 111 nodule (DR-216). This western Agulhas Bank nodule is very similar to DR-194 (Plate 6) from the eastern Agulhas Bank. Note the poorly sorted and cement supported quartz and glauconite grains. A corroded microfossil is present (middle left). The cement is a turbid micrite/collophane mixture.

Plate 8: C 1 nodule (DR-109) exhibiting a highly irregular burrowed surface texture.

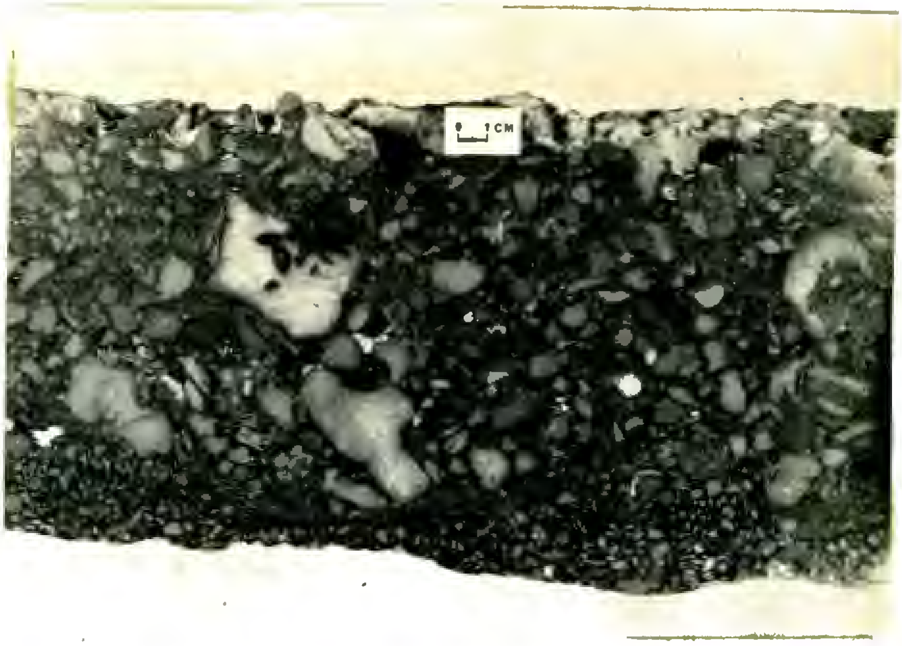


Plate 9: Tabloid conglomeratic C 1 nodule (DR-109).
Note:- (i) the highly irregular shape and surface-to-centre colour graduations of some of the enclosed pebbles, and (ii) the irregular bedding plane associated with a change in the size of the enclosed pebbles.

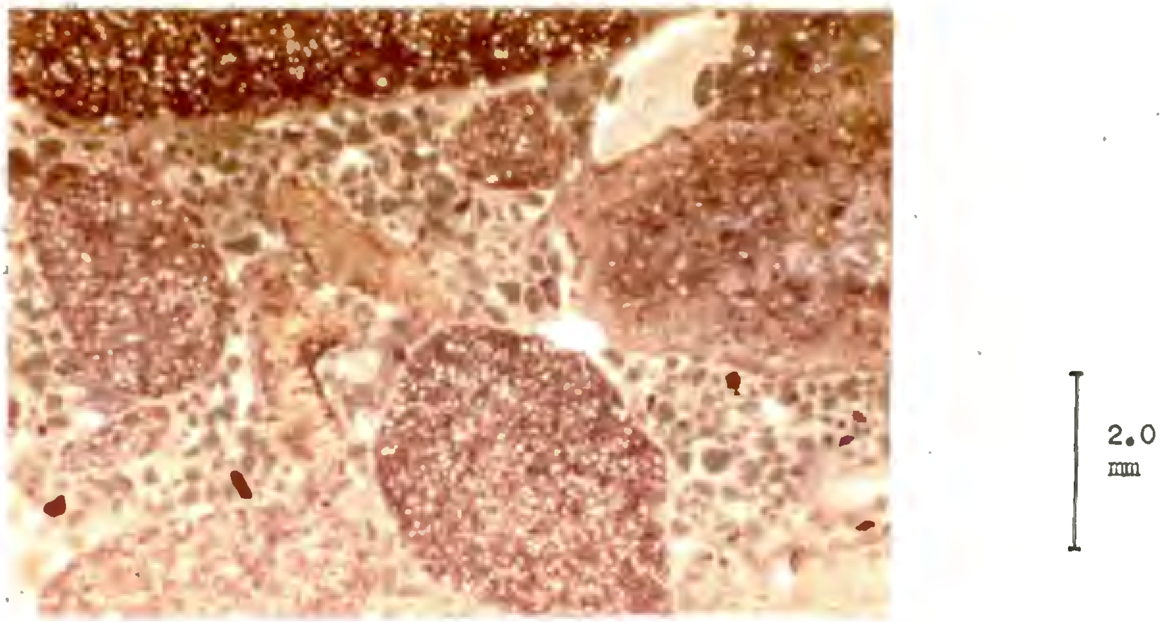


Plate 10: C 1 nodule (DR-121) exhibiting enclosed pebbles which may be (i) microfossil rich/quartz silt poor (right) or (ii) quartz silt rich/ microfossil poor (left). The sand sized matrix grains (dominantly glauconite) display a typically grain supported texture. The intergranular cement is a turbid, yellow, collophane/micrite mixture.

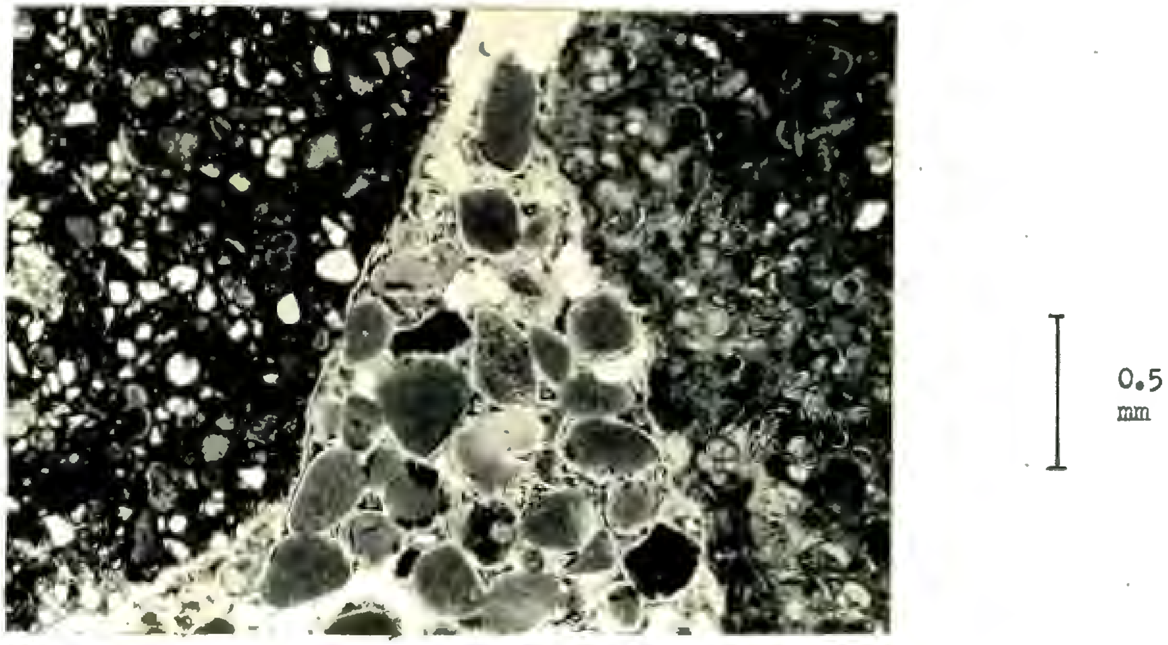


Plate 11: C 1 nodule (DR-121) exhibiting a close packed porous matrix of glauconite grains separating a quartzose ferruginous pebble (left), from a microfossiliferous quartz ~~free~~ poor pebble (right.) The matrix grains are rimmed by a colourless "dahllite" rind.

Plate 12A: C 1 nodule (DR-121). Colourless "dahllite" rind encrusting glauconite grains. Note intergranular pore spaces.(plane polarized light).

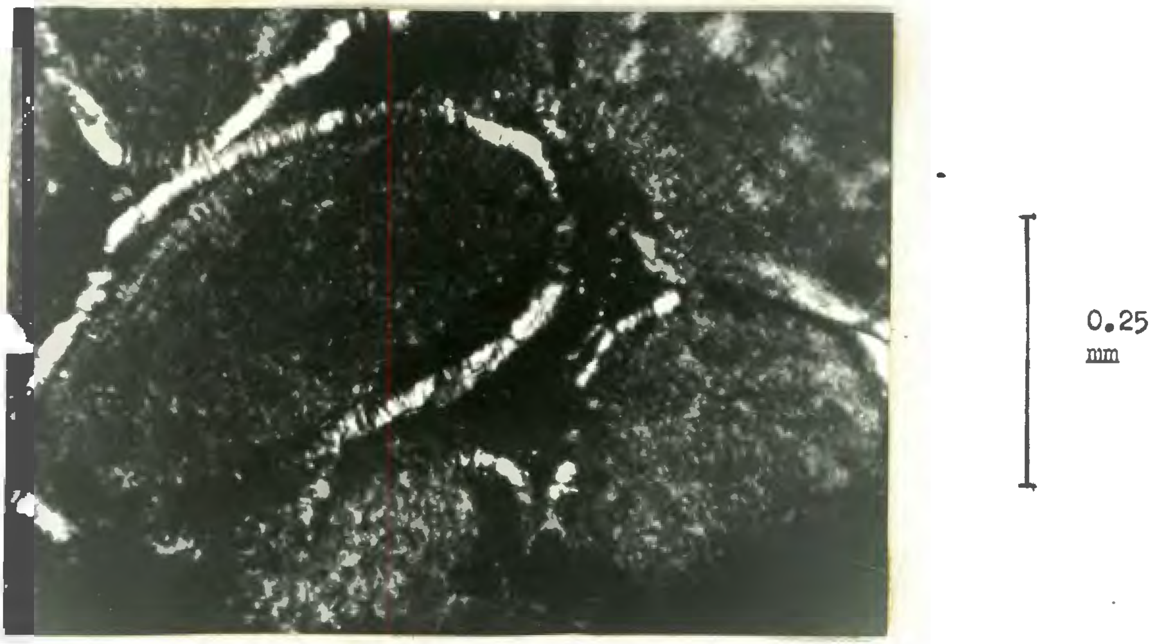


Plate 12B: C 1 nodule (DR-121). "Dahllite" rinds encrusting glauconite. (crossed nicols).

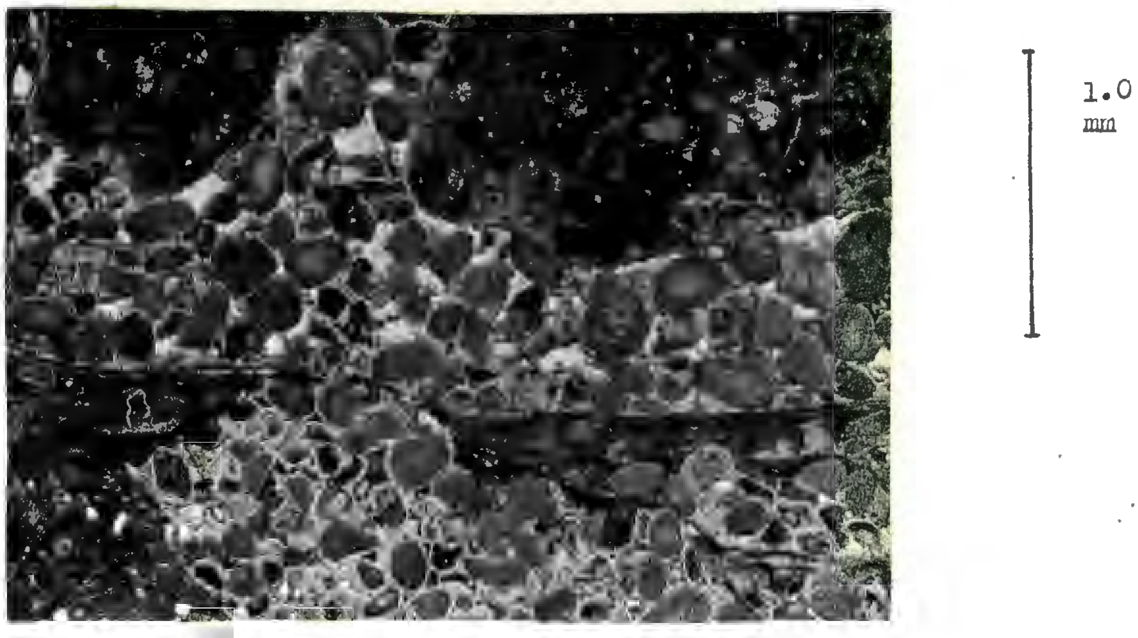


Plate 13: C1 nodule (DR-58). Microscale bedding planes delineated by iron oxides. Note enclosed pebbles set in a matrix of "dahllite" encrusted glauconite grains.

Plate 14: Tabloid C 11 nodule (DR-87). Note enclosed glauconite free macrofossil internal casts (lower left and upper centre - right) and the scattered glauconite grains in the surrounding matrix. White infilling of voids represents secondary deposition of micrite.

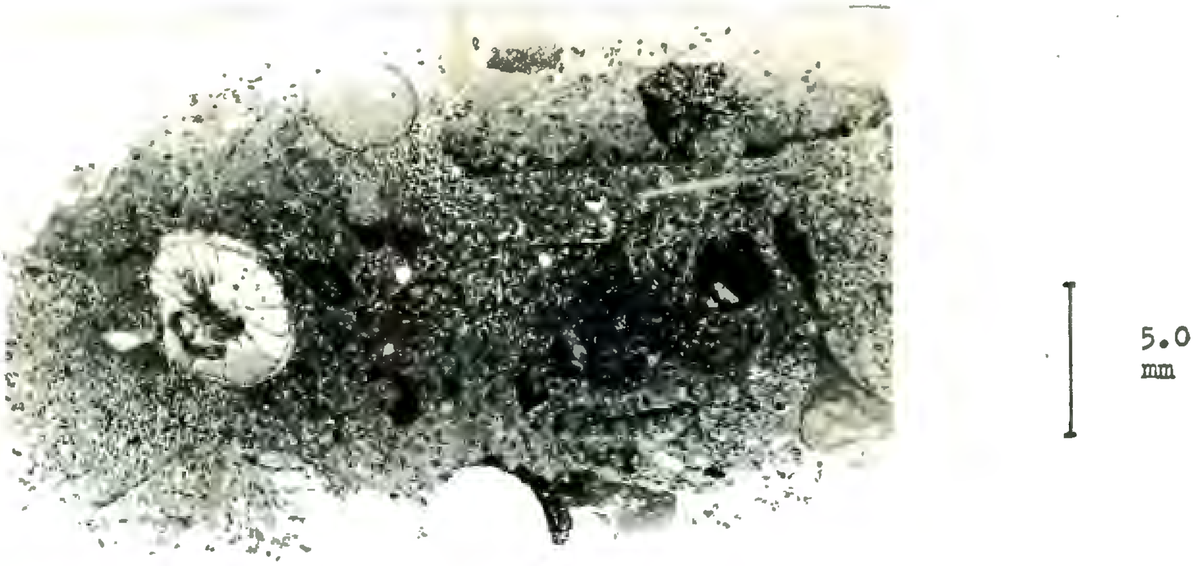


Plate 15: C 11 nodule (DR-112). Note enclosed internal cast of macrofossil (upper right) as well as a heterogeneous assortment of enclosed pebbles and biogenic debris set in a grain supported glauconite matrix.

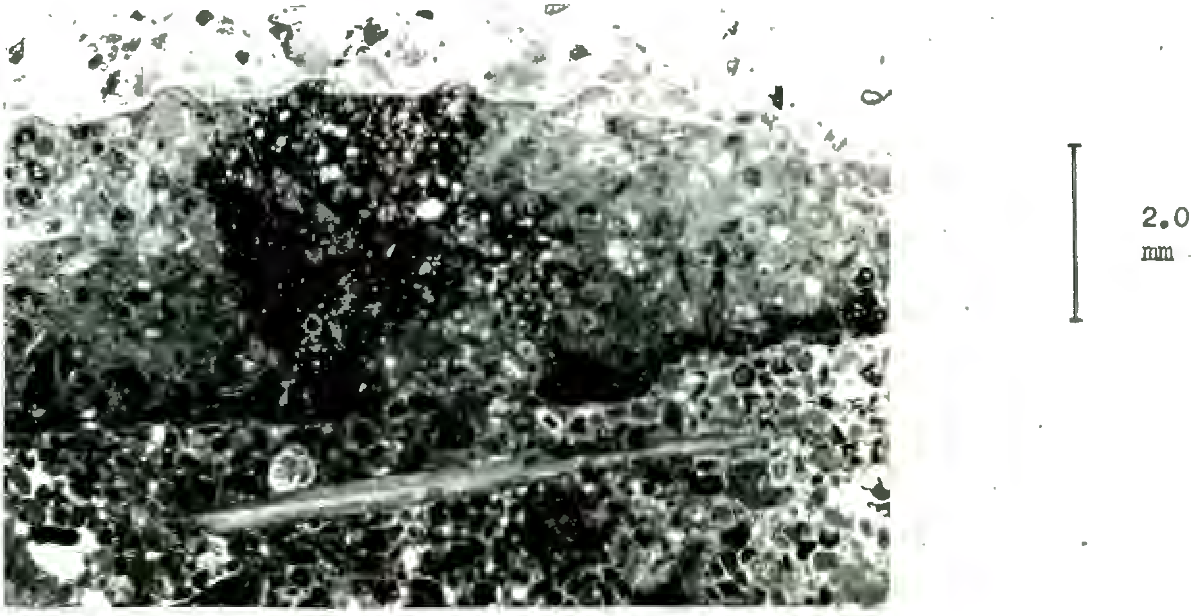


Plate 16: C 11 nodule (DR-112). Microfossiliferous internal cast of a macrofossil shell set in an enclosing glauconite matrix. Note:- (i) the absence of the originally enclosing macrofossil shell walls, (ii) the introduction of an iron rich and glauconitic sediment into a central "breached" area of the internal cast, and (iii) the presence of a macrofossil calcite fragment, below the internal cast, which was possibly part of the original macrofossil shell.

CHAPTER IV.

X-RAY DIFFRACTION (X.R.D.) STUDIES.

IV.1 : Introduction.

X-ray diffraction studies were carried out on a large number of samples from each of the five phosphorite classes. The objects of this were firstly to determine the mineralogical nature of the phosphate phase, and secondly to determine the CO_2 content of the carbonate-fluorapatite phase present in these bulk geochemical samples by the peak-pair method described by Gulbrandsen (1970).

IV.2 : Methods.

IV.2.1 : Sample Selection and Preparation.

In the first part of this X.R.D. study samples were selected as far as possible from thin sectioned areas of nodules so that a comparison could be made between the X.R.D. patterns and the mineralogy observed in thin section. These samples were powdered to - 120 mesh and then hand pressed into a standard Philips aluminium cavity mount.

In determining the CO_2 content of the carbonate-apatite phase present in the bulk geochemical samples, the whole rock pellets prepared for the Na and S analyses (see Appendix A) were used.

IV.2.2 : Instrumental Variables.

These X.R.D. studies were carried out on a Philips x-ray diffractometer using Ni-filtered CuK_α radiation and a proportional counter with pulse height selection. In the first part of this study (i.e. the determination of the phosphate mineral phase) various scanning speeds and instrumental settings were used. In the determination of the CO_2 content of the carbonate-fluorapatite phase the instrumental conditions were kept constant and a slow scan ($1/2^\circ$ 2θ /min.) was made between 50.5° and 53.5° (cf. Gulbrandsen, 1970).

IV.3 : Results and Discussion.

The primary phosphate mineral phase was identified on X.R.D.

patterns as francolite, a variety of carbonate-fluorapatite (Gruner and McConnell, 1937; McConnel, 1938, 1960; Rooney and Kerr, 1967). Altschuler, Clarke and Young (1958) propose the chemical formula for carbonate-fluorapatite found in phosphorites to be approximately $Ca_{10}\ (PO_4,CO_3)_6\ F_{2-3}$.

X.R.D. patterns from the NI, NIII, CI and CII class phosphorite samples all show well defined diffraction lines while the patterns from the NII class samples are broadened and rather poorly resolved suggesting that the apatite in the NII class is not so well crystalized.

A typical Agulhas Bank X.R.D. pattern (of a CII class nodule (DR - 112)) is shown in Figure 4 and its equivalent d-spacings are listed in Table I along with the d-spacings presented by Rooney and Kerr (1967) for the pelletal phosphorite francolite from North Carolina, U.S.A. The X.R.D. pattern for this Agulhas Bank phosphorite sample (Figure 4) shows sharp well defined diffraction lines in contrast to those presented by Rooney and Kerr (1967) suggesting a higher degree of crystallinity for the Agulhas Bank francolite as compared to the North Carolina francolite.

In thin section the phosphate mineral is identified as collophane on its optical characteristic (yellow colour in plane polarized light and isotropism under crossed nichols; (Rogers and Kerr, 1942)+. As noted above collophane is a "sack" name for a variety of microcrystalline marine apatites including francolite (Deer, Howie and Zussman, 1962). The microcrystalline nature of collophane is considered to be responsible for its isotropism.

The other major mineral components of the phosphorites such as quartz, glauconite and calcite were easily identified in thin section and by X.R.D. patterns. Clay minerals other than glauconite (i.e. illite) were not detected by these techniques.

The carbonate content of marine apatites is of some considerable interest . According to McConnell (1938) francolite is described as an apatite mineral containing "appreciable" carbonate and more than 1% F. The structural relationship of the carbonate radical in the apatite mineral phase has been the subject of much debate. McConnell (1952, 1960) considers that the carbonate radical (CO_3^{-2}) is present primarily as a substitute for the phosphate (PO_4^{-3}), radical and that it is an integral

+See also Kerr, 1959.

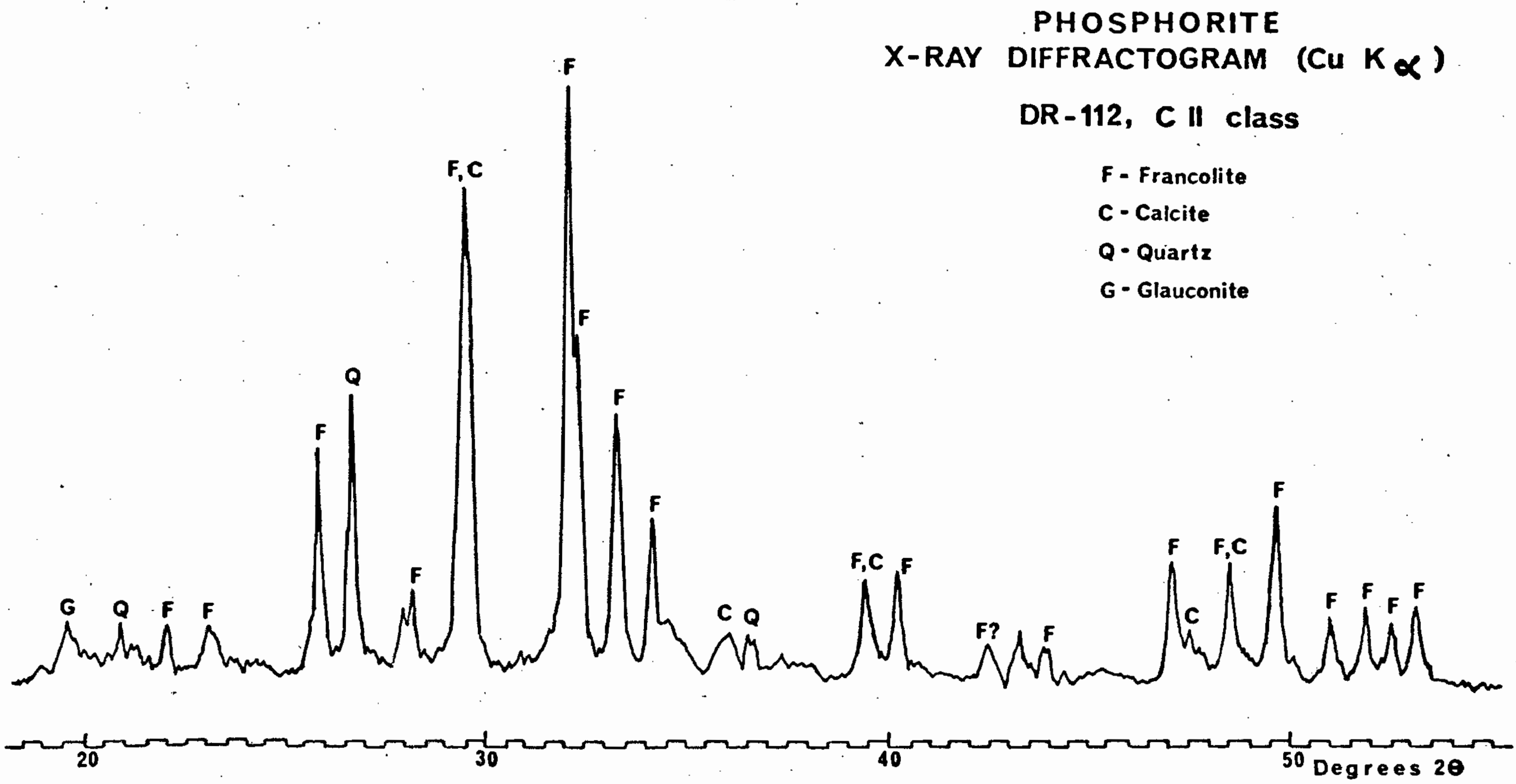

PHOSPHORITE
X-RAY DIFFRACTOGRAM (Cu Kα)
DR-112, C II class
F - Francolite
C - Calcite
Q - Quartz
G - Glauconite
G
Q
F
F
F
Q
F
F,C
F
F
F
F
C
Q
F,C
F
F?
F
F
C
F,C
F
F
F
F
F
20
30
40
50
Degrees 2Θ

FIGURE 4

TABLE I.

APATITE X-RAY DIFFRACTION DATA.

	Agulhas Bank Phosphorite[+1]		North Carolina Phosphate Pellets[+2]		Francolite, Piles Peak[+2]		Fluorapatite, Durango[+2]	
hkl[+3]	d.(Å)	I/Io	d.(Å)	I/Io	d.(Å)	I/Io	d.(Å)	I/Io
200	4.04	10			4.04	25	4.06	15
111	3.85	10			3.86	15	3.86	15
002	3.45	30	3.45	50	3.44	25	3.43	95
102	3.17	10	3.16	15	3.16	15	3.16	30
120	[+4]		3.06	20	3.06	50	3.07	35
121	2.79	100	2.79	100	2.79	90	2.80	100
112	2.77	50	2.78	85	2.77	35	2.78	75
300	2.69	40	2.70	45	2.70	100	2.71	85
202	2.62	25	2.62	30	2.62	20	2.63	50
301					2.51	10	2.51	15
122	2.28	15	2.29	10	2.29	10	2.29	15
130	2.24	15	2.24	25	2.25	65	2.25	30
131	2.12	10	2.13	10	2.13	10	2.14	10
113	2.06	10	2.06	10	2.06	10	2.06	10
203			1.996	10			2.000	10
222	1.930	20	1.932	20	1.934	20	1.939	50
132	1.877	20	1.875	15	1.883	15	1.883	20
123	1.836	25	1.835	30	1.836	20	1.836	40
231	1.788	10	1.789	15	1.792	20	1.799	20
140	1.762	15	1.763	15	1.770	40	1.773	20
402	1.743	10	1.738	15	1.745	15	1.750	25
004	1.725	15	1.723	20	1.720	10	1.717	15

+1 This work, CII class phosphorite, DR - 112 (see Fig. 5).

+2 After Rooney and Kerr (1967).

+3 Orthohexagonal indexes, after Rooney and Kerr (1967).

+4 Calcite Peak interference.

part of the apatite structure, as opposed to its possible presence in discrete calcite particles (Carlström, 1955) or absorbed on apatite crystallite surfaces (Neuman and Neuman, 1953).

Evidence from infrared spectral analysis and differential thermal analysis (Rooney and Kerr, 1967) favours the structural incorporation of the CO_3^{-2} radical within the apatite mineral phase. This is also supported by other workers such as Altschuler, Cisney and Barlow (1953), Ames (1959), McClellan and Lehr (1969).

The CO_2 values listed in Table III A, B and C for the bulk geochemical samples are dominated by the contribution from skeletal calcite and this smothers and CO_2 contributed by carbonates associated with the apatite phase. However the work of McClellan and Lehr (1969) has shown that variations in the cell dimensions of marine apatites may be explained in terms of CO_3^{-2} substitution and that there is an empirical relationship between the amount of this substitution and the cell dimensions. The work of Gulbrandsen, (1970) (based on that of McClellan and Lehr, 1969) has provided a semi-quantitative X.R.D. peak-pair method for determining the amount of carbonate substituted in the apatite phase. Carbon dioxide determinations based on this method have been made for 18 of the 21 bulk geochemical samples and the results are presented in Table II along with the francolite $2\theta_{(004)-(410)}$ values (in degrees) required to make these determinations (cf. Gulbrandsen, 1970). The three NII class bulk geochemical samples were not determined as the poorly defined apatite X.R.D. peaks produced by these samples were not suitable for making the peak-pair measurements.

The average CO_2 value determined in the apatite phase of the Agulhas Bank phosphorites was 5.5%. There do not appear to be any significant differences between the phosphorite classes nor are there any regional trends in evidence. What differences there are, are will within the instrumental error of the method (cf. Gulbrandsen, 1970).

Compared to the Phosphoria Formation the Agulhas Bank phosphorite apatites are enriched in CO_2, the average Agulhas Bank value (5.5% CO_2) being more than three times the average value for the Phosphoria apatites (1.8% CO_2). Furthermore, regional trends in the CO_2 content, as noted by Gulbrandsen (1970) for the Phosphoria formation, are character-

TABLE II.

X.R.D. Peak-Pair Determination of CO_2 in the Apatite Phase

Class	DR - No	$2\theta_{(004)-(410)}$ (in degrees)	% CO_2
NI	5	1.25	5.3
NI	43	1.20	5.9
NI	183	1.20	5.9
NIII	216	1.20	5.9
NIII	4	1.25	5.3
NIII	43	1.23	5.6
CI	4	1.25	5.3
CI	10	1.23	5.6
CI	14	1.25	5.3
CI	58	1.22	5.5
CI	60	1.25	5.3
CI	94	1.22	5.5
CI	122	1.20	5.9
CI	248	1.25	5.3
CII	89	1.22	5.5
CII	154	1.22	5.5
CII	155	1.20	5.9
CII	246	1.25	5.3
		Average	5.5

istically absent in the Agulhas Bank phosphorites. Gulbrandsen (1970) associates the regional increase in the CO_2 content of these Phosphoria apatites with a regional increase in the water temperature of the original environment and hence the high CO_2 values determined for the Agulhas Bank phosphorites may imply that these apatites formed in waters that were warmer than those in which Phosphoria apatites were formed.

However this supposition is not in keeping with the data presented by Shannon (1966) which shows that the present day bottom water temperature on both the west and east Agulhas Bank is relatively uniform and low at 9 - 11° C (notwithstanding the surface water temperature differences associated with the two ocean currents found in the Agulhas Bank area, see above, Chapter II). These temperatures are not typical of the "evaporate" conditions suggested by Gulbrandsen (1970) as being favourable for the formation of phosphorite apatite enriched in CO_2. It is acknowledged that the water temperature regime on the Agulhas Bank may however have been considerably different at the time of phosphorite formation in comparison to that prevailing today.

The uniform present day bottom water temperature of both the eastern and western Agulhas Bank does however correlate with the uniform (albeit high) CO_2 content of the apatite found in the phosphorite from either the eastern or western regions of the Agulhas Bank (cf. Gulbrandsen, 1970).

Apart from the above, the possible interrelationship between the high "apatite" CO_2 content and the high F/P_2O_5 ratio determined for Agulhas Bank phosphorite will be discussed in Chapter V.2.2.

CHAPTER V.

THE MAJOR ELEMENT GEOCHEMISTRY OF THE AGULHAS BANK PHOSPHORITE NODULES.

V.1 : Introduction.

The literature on phosphorites includes detailed geochemical studies of stratified onland phosphorite deposits such as those found in the Phosphoria Formation in the central United States of America (Gulbrandsen, 1966) and in Russia (Bushinsky, 1935). There are however few comprehensive studies on the bulk geochemistry of present day sea floor phosphorite nodules as such. This paucity of geochemical data represents a gap in our knowledge of these rocks, a gap that is made all the more significant by the distinct possibility that the submarine phosphorite nodules on the Agulhas Bank (and elsewhere, i.e. the Californian submarine nodules, described by Dietz et al., 1942) have been deposited in situ.

The aim of the geochemical work undertaken was therefore to determine the average major element composition of a representative selection of Agulhas Bank phosphorite; and at the same time determine the average composition of the five phosphorite groups described in Chapter III.

Twenty-three samples were selected for chemical analysis from 19 dredge stations on the Agulhas Bank (see Figure 5). The samples were selected from the different phosphorite groups in the following proportions : three each from groups NI, NII and NIII, eight from group CI and four from group CII. A further two samples were selected from a single NI nodules, in order to study chemical variations within that nodule. Sample selection from the different groups was based on the following points :

(i) The number of samples selected from a given group should reflect the frequency with which this group occurs; i.e. the bulk of the Agulhas Bank phosphorite recovered belongs to the conglomeratic groups CI and CII and hence this is reflected in the number of samples taken for analysis from these two groups.

(ii) In order to minimise variations due to inhomogeneity in the

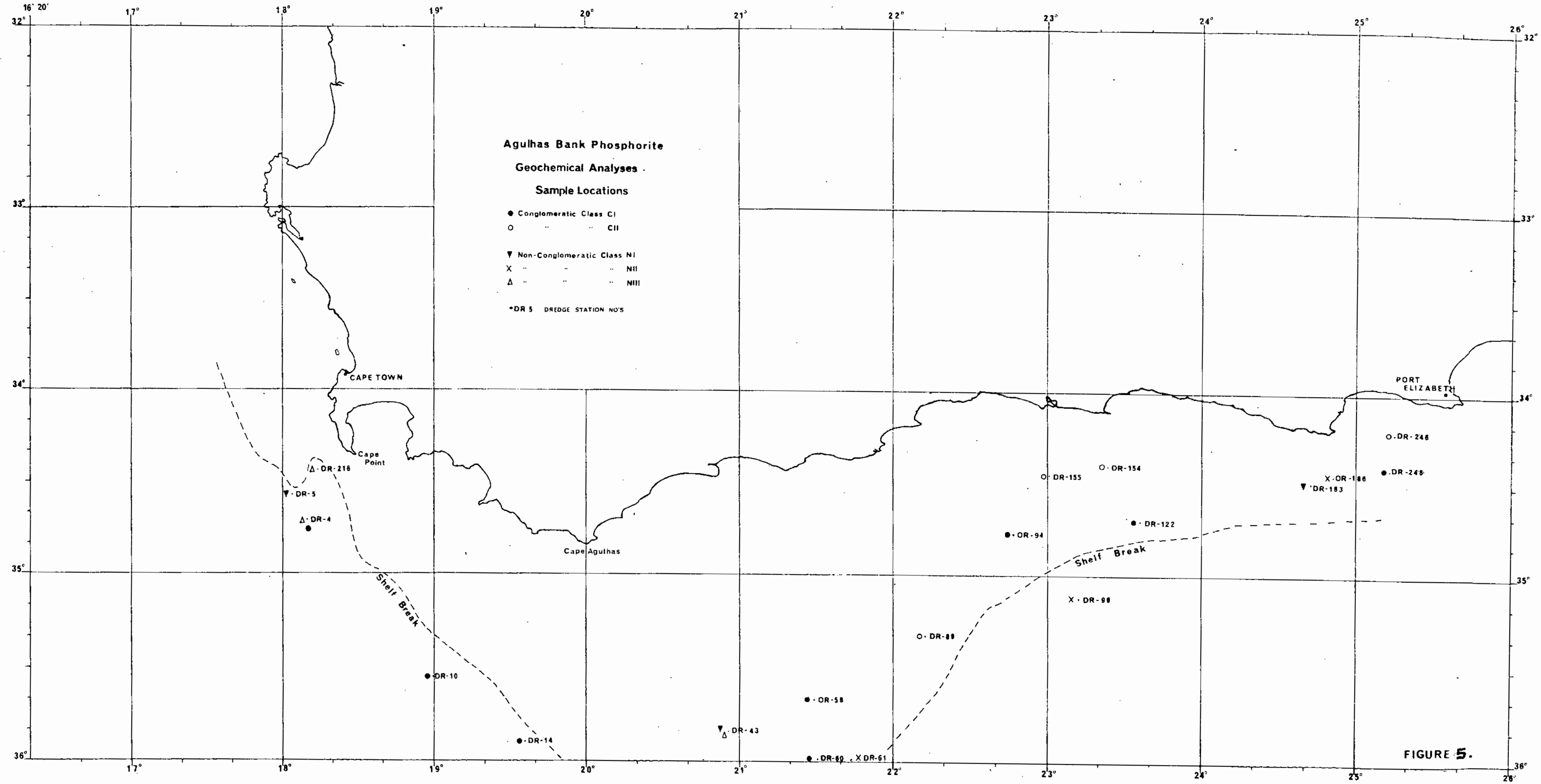
Agulhas Bank Phosphorite
Geochemical Analyses -
Sample Locations
● Conglomeratic Class CI
○ " " CII
▼ Non-Conglomeratic Class NI
X " " " NII
Δ " " " NIII
•DR 5 DREDGE STATION NO'S
16° 20′
17°
18°
19°
20°
21°
22°
23°
24°
25°
26°
32°
33°
34°
35°
36°
CAPE TOWN
Cape Point
Cape Agulhas
PORT ELIZABETH
Shelf Break
Shelf Break
Δ · DR-218
▼ · DR-5
Δ · DR-4
● DR-10
● · DR-14
▼Δ · DR-43
● · OR-58
● · DR-60
X DR-61
○ · DR-89
● · OR-94
○ · DR-155
○ · DR-154
● · DR-122
X · DR-98
▼ ·DR-183
X · OR-186
● ·DR-248
○ · DR-246

FIGURE 5.

conglomeratic groups at least 5 kg of sample should be available for crushing. Whenever possible a single nodule was selected, but in certain cases 5 kg of sample was only achieved by combining several small nodules. This was considered to be acceptable because only similar nodules from the same dredge station were combined. In the case of the non-conglomeratic variety it was considered that $\frac{1}{2}$ - 1 kg of sample was sufficient for crushing.

(iii) The samples selected should represent as wide a geographical and bathymetrical coverage of the Agulhas Bank as possible.

The following major elements were determined by x-ray fluorescence spectrometry (X.R.F.) : Si, Ti, Al, total Fe (expressed as Fe_2O_3), Mn, Mg, Ca, Na, K, P and S. Wet chemical methods were used to determine CO_2, FeO, and F while weight loss methods were used to determine H_2O^- (at 120° C), and the loss on fusion (with lithium borate flux at 1000° C). The results are presented in Table III, while Appendix A describes the analytical methods used to obtain these data.

V.2 : Results and Discussion.

V.2.1 : Introduction.

The average major element composition of the 21 phosphorite samples analysed is listed in Table III C. The unique and characteristic geochemical feature of these rocks is their unusual P_2O_5 content (average : 16%). It is this feature that is responsible for their economic and geochemical importance. The major element geochemistry of the Agulhas Bank phosphorites is a reflection of the dominant authigenic and allogenic minerals found in these rocks. Thus the SiO_2 content is equated with quartz and glauconite, Fe_2O_3 with glauconite and goethite, P_2O_5 with collophane-francolite, CaO with collophane-francolite and calcite, etc. The variability shown by the analyses on the 21 samples is due to variations in the sedimentological, and physico-chemical factors responsible for the supply of the allogenic and authigenic minerals.

V.2.2 : Composition of Collophane-Francolite.

X-ray diffraction studies showed (see Chapter IV) that the prime phosphate mineral present in the Agulhas Bank nodules is francolite, a

Table III A: Agulhas Bank Phosphorite : Major Element Geochemistry

Class	NI			Average	NII			Average	NIII			Average
DR-No	5	43	183		61	98	186		216	4	43	
SiO_2	11.99	2.30	4.32	6.20	1.73	5.86	2.76	3.45	27.40	23.47	12.28	21.05
TiO_2	.09	.04	.05	.06	.02	.06	.05	.04	.20	.14	.15	.16
Al_2O_3	1.55	.93	.90	1.13	.63	1.27	.85	.92	2.49	2.53	2.05	2.36
* Fe_2O_3	1.93	.75	1.53	1.40	16.82	10.42	50.16	25.80	6.52	6.72	4.23	5.83
MnO	.01	.01	.01	.01	.09	.05	.03	.06	.01	.01	.01	.01
MgO	.99	.96	.96	.97	1.67	1.05	1.76	1.49	1.50	1.74	1.26	1.50
CaO	42.32	50.21	48.53	47.02	41.04	41.48	17.73	33.42	29.02	30.46	39.88	33.14
Na_2O	.62	.62	.62	.62	.19	.52	.30	.34	.80	.63	.65	.69
K_2O	.63	.30	.36	.43	.25	.55	.36	.39	2.19	2.58	1.30	2.02
P_2O_5	14.24	14.75	15.46	14.82	7.74	15.63	7.42	10.26	16.59	18.90	18.67	18.05
S	.30	.32	.32	.31	.16	.29	.17	.21	.54	.41	.38	.44
F	1.91	2.15	2.28	2.12	1.17	2.10	.99	1.42	2.08	2.21	2.42	2.24
L.O.F.	22.78	28.03	25.74	25.52	29.85	22.31	17.57	23.24	10.77	10.47	16.87	12.70
Total	99.36	101.37	101.08	100.61	101.37	101.58	100.15	101.04	100.11	100.26	100.17	100.19
Less O	.80	.90	.96	.89	.49	.88	.42	.60	.87	.93	1.04	.94
Total	98.56	100.47	100.12	99.72	100.88	100.70	99.73	100.44	99.24	99.33	99.13	99.25
FeO	.20	.13	.20	.18	.05	.10	.18	.11	.70	.84	.33	.62
CO_2	16.1	22.4	18.5	19.0	22.5	15.0	6.7	14.7	4.4	3.5	10.9	6.1
H_2O^-	1.6	1.0	.5	1.0	.7	1.2	1.0	1.0	1.6	1.6	1.0	1.4
F/P_2O_5	.134	.146	.147	.143	.151	.134	.133	.138	.125	.111	.129	.124

* Fe_2O_3 = total iron

Table III B: Agulhas Bank Phosphorite : Major Element Geochemistry

Class DR-No	CI 4	 10	 14	 58	 60	 94	 122	 248	Average
SiO_2	24.89	13.84	7.81	12.25	11.45	13.75	18.20	20.17	15.30
TiO_2	.20	.12	.07	.06	.05	.10	.13	.09	.10
Al_2O_3	3.18	2.17	1.40	2.02	1.59	2.21	2.45	2.10	2.14
* Fe_2O_3	4.32	2.14	2.25	5.99	7.67	5.38	6.34	10.52	5.58
MnO	.01	.01	.01	.01	.01	.01	.01	.02	.01
MgO	1.19	.88	.91	1.51	1.49	1.32	1.44	2.00	1.34
CaO	31.81	40.25	43.94	38.41	38.53	37.93	34.87	30.48	37.04
Na_2O	.95	.90	.91	.69	.75	.72	.77	.58	.78
K_2O	1.70	.81	.80	1.93	1.67	1.42	1.66	2.53	1.57
P_2O_5	18.79	20.94	21.47	16.65	16.65	17.21	16.31	15.10	17.89
S	.58	.65	.54	.40	.40	.41	.39	.34	.46
F	2.05	2.74	2.88	2.00	2.18	2.04	1.94	1.82	2.21
L.O.F.	11.04	14.84	18.42	17.89	18.98	17.50	15.97	14.53	16.15
Total	100.71	100.28	101.99	99.83	101.43	100.00	100.50	100.29	100.56
Less O	.86	1.15	1.21	.84	.92	.86	.82	.77	.93
Total	99.85	99.13	100.28	98.99	100.51	99.14	99.68	99.52	99.63
FeO	.62	.34	.33	.47	.46	.36	.45	.58	.45
CO_2	4.3	8.5	10.7	11.9	12.4	11.1	9.9	7.3	9.5
H_2O^-	2.0	1.7	1.6	1.5	1.4	1.4	1.3	1.9	1.6
F/P_2O_5	.109	.131	.134	.120	.131	.118	.119	.121	.124

* Fe_2O_3 = total iron

Table III C: Agulhas Bank Phosphorite : Major Element Geochemistry

Class			CII		Ave-rage	Grand Average (21 Analyses)
DR-No	89	155	154	246		
SiO_2	8.10	15.09	13.85	18.11	13.79	12.84
TiO_2	.07	.11	.12	.12	.11	.12
Al_2O_3	1.50	2.44	2.47	2.08	2.12	1.85
* Fe_2O_3	8.24	6.90	6.51	7.71	7.34	8.24
MnO	.04	.01	.01	.02	.02	.02
MgO	1.38	1.43	1.38	1.61	1.45	1.35
CaO	40.04	35.71	36.62	33.77	36.54	37.29
Na_2O	.62	.79	.76	.73	.73	.67
K_2O	.96	1.78	1.72	1.59	1.51	1.29
P_2O_5	17.13	17.50	17.19	15.45	16.82	16.18
S	.35	.44	.56	.43	.45	.40
F	2.24	2.00	2.00	1.91	2.04	2.10
L.O.F.	19.73	14.96	16.66	16.27	16.89	18.15
Total	100.32	99.16	99.87	99.79	99.81	100.50
Less O	.94	.84	.84	.80	.86	.88
Total	99.38	98.32	99.03	98.99	98.95	99.62
FeO	.23	.49	.41	.35	.37	.37
CO_2	12.8	9.8	10.0	9.8	10.6	11.3
H_2O^-	1.6	1.5	1.5	1.3	1.5	1.4
F/P_2O_5	.131	.114	.116	.124	.121	.130

* Fe_2O_3 = total iron

carbonate fluorapatite. As noted above this mineral has been identified on optical grounds as collophane.

Due to the presence of detrital minerals, the data presented in Table III is not suitable for determining the major element composition of this Agulhas Bank collophane-francolite. Only the F/P_2O_5 ratio is of any significance as these two elements are associated primarily with francolite. The average value determined for this ratio is 0.130 (Table III C) which is significantly higher than the average ratios reported by Dietz, Emery and Shepard (1942) for the Californian offshore phosphorite nodules and Rooney and Kerr (1967) for the Beaufort County (U.S.A.) phosphate pellets, as well as being higher than the ratios calculated from the data presented by Bushinsky (1935) for the Russian phosphorites and by Gulbrandsen (1966) for the Phosphoria Formation (U.S.A.) phosphorites . (Average ratios:- 0.109, 0.112, 0.114 and 0.102 respectively. See also Table V). The ideal F/P_2O_5 ratio characteristic of non-carbonate fluorapatite is 0.089 (Rooney and Kerr, 1967) and the ratios reported above for phosphorite apatite, especially the Agulhas Bank ratios, indicates that F is present in excess of the structural requirement (for non-carbonate fluorapatites). This has been explained by some workers in terms of the compensation of the charge imbalance resulting from the substitution of CO_3^{2-} for PO_4^{3-} (in carbonate fluorapatites) by the extra introduction of F^- (Gulbrandsen, Kramer, Beatty and Mays, 1966). The enrichment in the Agulhas Bank phosphorites of CO_2 in the apatite phase (see above, Chapter IV) and of F, as compared to the lower "apatite" CO_2 and F/P_2O_5 levels reported for the Phosphoria Formation phosphorites (Gulbrandsen, 1966, 1970), clearly lends support to this "charge imbalance/F enrichment" hypothesis. When reading the above, it should however be borne in mind that the accuracy of the F analytical method used for the Agulhas Bank phosphorites is not entirely beyond suspicion; see Appendix A(h).

Substitution in marine apatites (e.g. CO_3^{2-} and SO_3^{2-} for PO_4^{3-} , Na^+ for Ca^{2+} and Si^{4+} for P^{5+}) is well documented (Tooms, Summerhayes and Cronan, 1969). Apart from the inter-relationship between Na and S substitutions discussed below, these effects are hidden in the Agulhas Bank francolite by the presence of detrital minerals having elements in common with the francolite substitutions.

V.2.3: The FeO/Fe_2O_3 Content

The FeO values listed in Table III closely follow the listed K_2O values, indicating that the 'detrital' mineral glauconite is the primary source of Fe^{+2}. However, some of this ferrous iron must reside in the minor quantities of authigenic pyrite identified optically in group N III, C I and C II nodules.

Ferric iron is correlated with authigenic goethite which is found as an intimate mixture with collophane-francolite in all the phosphorite groups (especially NII). Ferric iron is also present in glauconite where it may form up to 20% of this mineral.

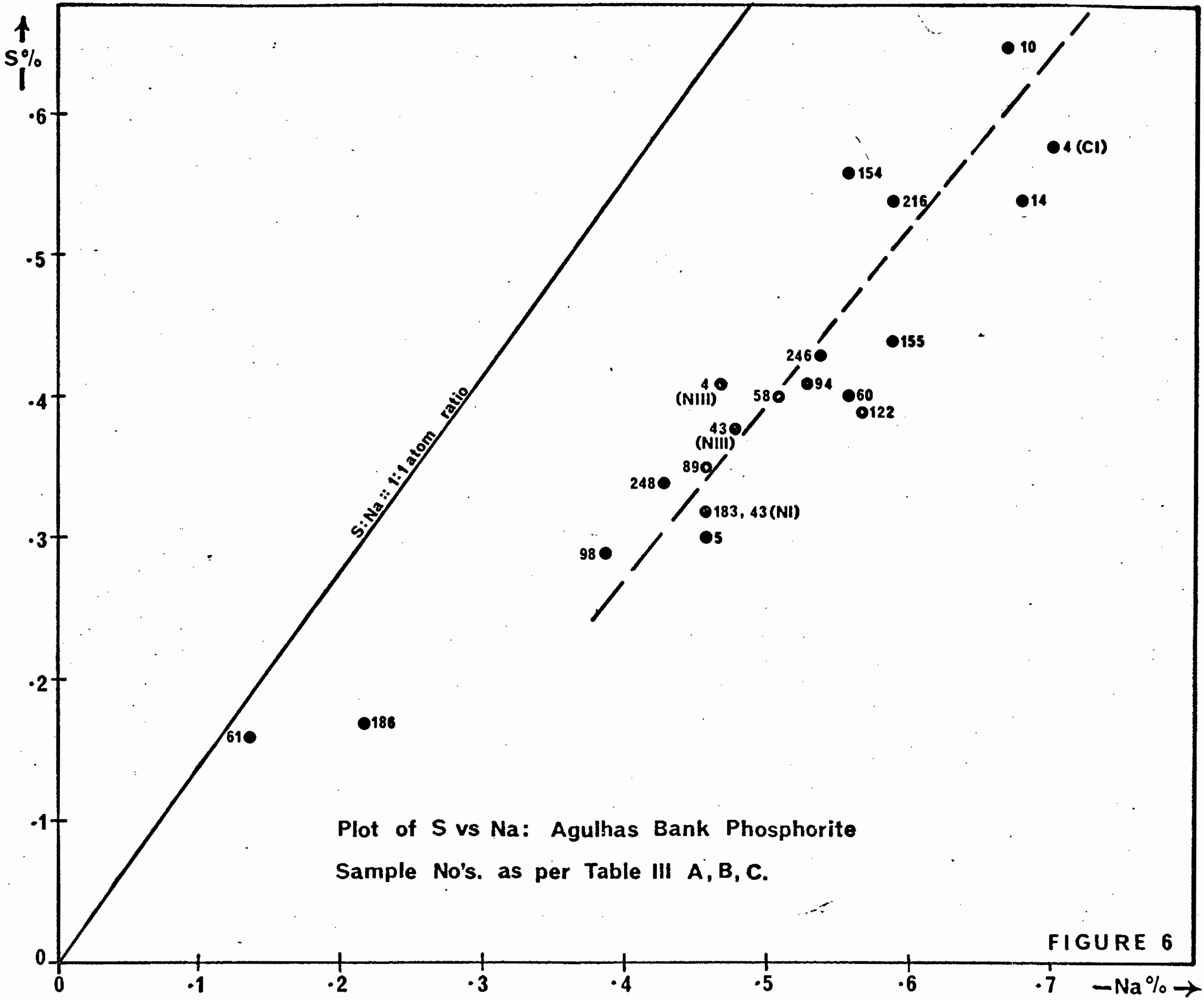
V.2.4 : The S/Na Ratio.

Figure 6 shows a plot of percentage sulphur against percentage sodium for the 21 analyses of the Agulhas Bank phosphorites. It is clear that there is a strong sympathetic relationship between the two elements. Gulbrandsen (1966) has shown there is an approximately 1 : 1 relationship between the atomic ratio of S to Na in the Phosphoria phosphorites. He has interpreted this as reflecting a coupled substitution in the phosphate mineral of Na^+ and S^{6+} for Ca^{2+} and P^{5+} (i.e. the overall charge balance is preserved). The unbroken line drawn in Figure 6 represents the locus of points which have an Na : S atomic ration of 1 : 1. While the dashed line drawn (by visual inspection) through the Agulhas Bank Na/S analyses (excluding the iron rich DR - 186 (NII) and DR - 61 (NII) samples) is roughly parallel to the 1 : 1 :: Na : S atomic ratio, it is clear that there is a considerable enrichment of Na over S with respect to this 1 : 1 atom ratio. Samples DR - 186 and DR - 61 were excluded because of their anomalously high iron contents, and low P_2O_5 contents (see Table IIIA).

The extra Na may represent the presence of detrital Na felspar grains and/or glauconite grains. Alternatively it may represent the substitution of CO_3^{2-} (instead of SO_4^{2-}) for PO_4^{3-} (cf. Tooms, Summerhayes and Cronan, 1969) thus resulting in the observed enrichment of Na with respect to S. This would be compatible with the high CO_2 content determined for the apatite phase in these Agulhas Bank phosphorites (see above, Chapter IV), as compared to the lower CO_2 content found in the Phosphoria apatites (Gulbrandsen, 1970), which also do not exhibit a "Na over S" enrichment trend (Gulbrandsen, 1966).

V.3.5 : The Major Element Geochemistry of the Five Agulhas Bank Phosphorite Classes.

The chemical compositions of the analysed samples will be used in this sub-section to characterise the five phosphorite classes with respect to their bulk geochemistry, to relate this geochemistry to the observed



Plot of S vs Na: Agulhas Bank Phosphorite

Sample No's. as per Table III A, B, C.

FIGURE 6

mineralogy and to correlate chemical variations between nodules from the same class with the geographical distribution of these nodules. Initial inspection of Table III shows that the bulk geochemistry of nodules within a class is with the exception of class NII, similar. Furthermore, classes CI and CII display similar average compositions and geochemically these two classes are considered to be the same. The symbol C will be used to refer to these latter two classes. Distinct differences are however noted between the average compositions of the NI, NII, NIII and C classes.

In order to relate the bulk geochemistry of each sample to its dominant mineralogy, representative sub-splits of the nodules selected for geochemical analysis were thin sectioned for petrographic examination. In the descriptions of the different classes that follow below, the percentage value quoted for a given element is the average value for that group, unless otherwise stated. The average analyses for the first three classes suffer in that they are based on only three individual analyses per class. The position is improved for the conglomerate class (see above for sample selection criteria).

Class NI.

This class is primarily characterised by relatively high CaO (47.0%) values, moderate P_2O_5 (14.8%) values and relatively low SiO_2 (6.2%) and Fe_2O_3 (1.4%) values. These chemical values fit the dominant mineralogy of the group, i.e. calcite and collophane-francolite.

Geographically it is noted that the central-southern area of the Agulhas Bank, represented by DR - 43 is low in SiO_2 (i.e. quartz) but highest in CaO (i.e. calcite) while samples from the area south-west of the Cape Peninsula (DR - 5) are highest in SiO_2. The eastern area of the Bank (DR - 183) is noted for a slightly increased P_2O_5 value.

Class NII.

This group is primarily noted for its relatively high Fe_2O_3 (25.8%) value. Low SiO_2 (3.5%) and moderate P_2O_5 (10.3%) values are a feature. The MnO value (.06%) for this class is three to six times the average values determined for the other classes. This Mn enrichment probably reflects the "scavenger" action of authigenic goethite (iron oxide) found as a major mineral component in the nodules from this class. DR - 186 is exceptional in that its Fe_2O_3 is extremely high (i.e. 50.16%).

The bulk geochemistry fits the bulk mineralogy, the dominant minerals being goethite, calcite and collophane-francolite. Geographical trends are not evident.

Class NIII.

This class is characterised by relatively high SiO_2 (21.1%), TiO_2 (0.16%), Al_2O_3 (2.36%), K_2O (2.02%), FeO (0.62%), S (0.44%), and P_2O_5 (18.05%) values. The Fe_2O_3 (5.83%) content is similar to the C class. The predominant minerals present are quartz, calcite, collophane-francolite and glauconite. The relatively high Fe^{2+}, K, TiO_2 and Al_2O_3 values are correlated with a relatively high glauconite concentration observed in thin section. Some of the Al_2O_3 must also reside in the minor quantities of felspar present as noted in thin section. Detrital rutile may also be responsible for the observed TiO_2 enrichment, but this mineral was not identified in thin section. Geographically the nodules from the area southwest of the Cape Peninsula (DR - 216 and DR - 4) are enriched, with respect to the south central Bank area (DR - 43), in SiO_2, K_2O, Fe_2O_3 and FeO. This enrichment is correlated with a high quartz and glauconite content. DR - 43 is enriched in CaO and CO_2 with respect to the area off the Cape Peninsula and this is linked to the higher calcite content, observed in thin section.

Class C.

This important class is characterised by having intermediate values, when compared with the other classes, for the elements etc. determined. The P_2O_5 (17.4%) value is high relative to the groups NI and NII and approaches the value for the NIII group. The bulk geochemistry is comparable with the observed mineralogy, i.e. quartz, glauconite, calcite, collophane-francolite and goethite. Interesting geographical variations are present in this class. The most obvious feature is the increase in SiO_2 values for samples recovered from the western and eastern margins of the Bank, relative to those samples recovered from the central Bank area. Inversely related to the SiO_2 content are the CaO and P_2O_5 values, these elements being concentrated in samples recovered from the central Bank area, as opposed to the eastern and western margins of the Bank. These chemical variations are linked to variations in the supply of detrital quartz, which acts as a diluent in the nodules, especially in those recovered from the marginal areas, such as south and south-west of Cape Point in the west and south of Cape St. Francis in the east.

V.2.6 : Phosphatization of NI Class Nodules.

In order to study possible geochemical variations associated with the colour gradations observed in some NI nodules, two 4g samples were selected for major element analysis from a single NI nodule which displayed distinct surface to centre colour variations (see petrographic descriptions above). The first sample (DR - 43 (S)) was taken from the outermost part of the nodule, while the second (DR - 43 (C)) was located at the centre of the nodule. The results of the analyses are presented in Table IV, as well as the same results recalculated on a silica free basis. The recalculation to a silica free basis was made in order to remove the effects of diluent quartz on the observed concentrations. It is apparent that the central nodule area is depleted in P_2O_5 with respect to the surface areas by approximately one quarter (silica free basis). The L.O.F. (mainly CO_2) value for the central area is also significantly increased.

These geochemical trends, in association with related petrographic information (see petrographic section above) are interpreted as indicating an inward (i.e. surface to centre) phosphatization process operating on the original limestone rock. This process has produced a P_2O_5 enriched surface area, while the central area is carbonate enriched. It is suggested that the observed colour gradations are therefore a response to variations in the surface to centre apatite content of these rocks.

V.2.7 : Comparisons of Agulhas Bank Phosphorites With Phosphorites From Other Localities.

The major element geochemistry of phosphorites from the sea floor off California, N.W. Africa and South Africa will be discussed in this section, as well as onland deposits from Russia and from the Phosphoria Formation in the central U.S.A., and from Russia. Table V lists the average major element geochemistry of the various phosphorite deposits considered and the source for these data. This table shows that the

Table IV: Surface to Centre Geochemical Variations, NI Phosphorite Nodule

DR-No	43(s)	43(c)	Silica Free 43(s)	Silica Free 43(c)
SiO_2	3.88	1.77	-	-
TiO_2	.06	.06	.06	.06
Al_2O_3	1.34	.82	1.39	.83
* Fe_2O_3	.93	.54	.97	.55
MnO	.01	.01	.01	.01
MgO	.89	1.09	.93	1.11
CaO	49.53	51.33	51.50	52.25
Na_2O	.53	.38	.55	.39
K_2O	.40	.28	.42	.29
P_2O_5	13.93	11.32	14.50	11.52
L.O.F.	26.69	30.90	27.77	31.46
Total	98.09	98.49	98.10	98.47

s = surface; c = centre

* Fe_2O_3 = total iron

Californian phosphorite is relative to the Agulhas Bank phosphorite, enriched in P_2O_5, CaO, and F, but depleted in Fe_2O_3 and Al_2O_3 (grouped as R_2O_3 by Dietz et al., 1942) and CO_2. If the values listed by Dietz et al., (1942) for "Insoluble in HCL" may be equated with Si bearing minerals like quartz and felspar then the Californian phosphorite is also depleted in SiO_2 as compared with Agulhas Bank nodules. In the above comparison it should be noted that the Californian average may not be representative as it is based on only six analyses.

The Phosphoria phosphorite is similarly enriched in P_2O_5, CaO and F and depleted in CO_2 and Fe_2O_3 when compared with the Agulhas Bank phosphorite. The more comprehensive data presented by Gulbrandsen (1966) shows that the Phosphoria phosphorites are also depleted relative to the Agulhas Bank nodules, in K_2O and MgO, while the SiO_2, Al_2O_3, TiO_2 and Na_2O values are similar.

The data for the N.W. African phosphorites shows that on average these rocks are, in comparison to the Agulhas Bank deposits, enriched in MgO (associated with dolomite) and marginally in P_2O_5, while being depleted in SiO_2, CaO, Fe_2O_3 and K_2O.

The quantitative geochemical and mineralogical data presented by Bushinsky (1935) for the Russian onland phosphorite deposits shows that, in comparison to the S. African offshore deposits these Russian phosphorites are enriched in SiO_2, which is linked to a higher detrital quartz content, and marginally enriched in P_2O_5 and S. They are however depleted in Fe_2O_3, MgO, CaO, K_2O and CO_2 which is a reflection of their distinctly lower glauconite and calcite contents when compared to Agulhas Bank phosphorites. The aluminium content is also marginally depleted in Russian phosphorites, this being associated with a decrease in aluminium silicates (e.g. felspars and glauconite), in comparison to the Agulhas Bank phosphorites. The similarities of the Na_2O and S contents of Russian and Agulhas Bank phosphorites suggests similar phosphate mineral substitutions (see above).

Examination of the individual analyses presented by Dietz et al., (1942), Bushinsky (1935), Gulbrandsen (1966), Summerhayes (1970), and in this work, shows that there is an inverse relationship between the (SiO_2 (or "Insoluble in HCL") + CO_2) contents and the (P_2O_5 + CaO) contents. This relationship is primarily explained in terms of variations in the

Table V: Average Major Element Geochemistry of Phosphorites from Different Localities

Region	Agulhas Bank[*1]	N.W.Africa[*2]	California[*3]	Phosphoria[*4]	Russia[*5]
No. of Analyses	21	11	6	60	9/10
SiO_2	12.84	6.73		11.9	38.54
TiO_2	.12	.08		.1	.08
Al_2O_3	1.85		1.47[*9]	1.7	1.38
Fe_2O_3	8.24[*6]	4.30		1.1	2.54
MnO	.02	.06		$<$.01	.03
MgO	1.35	3.29		.3	.40
CaO	37.29	31.16[*7]	44.91	44.0	27.94
Na_2O	.67			.6	.66
K_2O	1.29	.73		.5	.45
P_2O_5	16.18	16.96	28.15	30.5	17.84
F	2.10		3.08	3.1	2.04
CO_2	11.3		4.38	2.2	3.65
S	.40			.72	.48
Insoluble in HCl[*8]			6.22		
F/P_2O_5	.130		.109	.102	.114

[*1] This work

[*2] Summerhayes, 1970

[*3] Dietz, Emery and Shepard, 1942

[*4] Gulbrandsen, 1966

[*5] Bushinsky, 1935

[*6] Total iron

[*7] Recalculated CaO value, C.P.Summerhayes, Pers.Com.

[*8] Equated with quartz, amorphous silica, felspar, glauconite and carbonaceous material, Dietz, Emery and Shepard, 1942.

[*9] R_2O_3

concentration of diluent minerals such as quartz, felspar and with Phosphoria phosphorites excepted, glauconite. Bushinsky (1935), Dietz et al. (1942), and Gulbrandsen (1966) report negligible amounts of calcite in their phosphorites whereas it is present as a major mineral component in the Agulhas Bank and North West African phosphorites. This would explain the low average value for CO_2 and higher average values for P_2O_5 reported for the Californian and Phosphoria phosphorites. The similarity of the P_2O_5 content of the calcite free Russian phosphorites to the Agulhas Bank and N.W. African phosphorites is due to the increased concentrations in these Russian phosphorites of detrital quartz acting as the diluting material, instead of clacite.

The Fe enrichment found in the Agulhas Bank and North West African nodules is due to the presence of "detrital" glauconite and/or iron oxides (e.g. goethite), these minerals being absent, or present in very minor quantities in the Phosphoria phosphorites, while the Californian and Russian phosphorites carry only moderate amounts of glauconite and negligible iron oxides (Dietz et al., 1942; Bushinsky, 1935).

CHAPTER VI.

THE GENESIS OF THE AGULHAS BANK PHOSPHORITES.

VI.1 : Introduction.

It is clear from the petrographic studies that the formation of the Agulhas Bank phosphorite nodules is firstly a result of sedimentary processes (such as the transportation and deposition of the various sedimentary components) and secondly the result of chemical processes (such as the formation of the various cements, i.e. collophane-francolite, calcite and goethite, during diagenesis).

Apart from the influence of provenance and dispersal, the composition and texture of a sedimentary rock are responses to a particular depositional environment (Pettijohn, 1957). Furthermore it is possible that the chemical factors (such as pH and Eh) responsible for the *in situ* lithification and phosphate mineralization of the proto-phosphorite sediments may be dependant on the depositional environment itself (Krumbein and Garrels, 1952).

The purpose of this section is therefore to deduce as far as possible, from compositional and textural characteristics, the environmental conditions responsible for the formation of these rocks. The section will be divided into two parts, the first being concerned with establishing the depositional factors responsible for the accumulation of the proto-phosphorite sediments and the second will be concerned with the diagenetic processes responsible for the lithification and phosphate mineralization of these sediments.

VI.2 : Depositional Environments.

VI.2.1 : NI and NII Nodule Classes.

The nodules from these two classes are texturally and compositionally similar with respect to microfossil grains, and are only separated by their distinctly different cement/matrix iron contents. Some transitional nodule types show gradations from NI to iron rich NII type areas within the space of a thin section.

These nodules are primarily composed of close packed planktonic foraminiferal tests and they are identical texturally and compositionally to the pelagic foraminiferal lime packstone facies described by Siesser (in prep.) in his work on the limestone rocks recovered from the Agulhas Bank. Siesser (in prep.) considers that the sediments belonging to this facies accumulated in a moderately deep water open ocean environment such as the continental shelf and slope.

NI and NII nodules are therefore considered to have been formed by the accumulation of bioclastic grains (sand sized shell material and clay sized micrite) in an "open ocean, moderately deep (continental shelf and upper slope), quiet water" environment and were subjected to normal carbonate rock lithification processes. In some nodules these processes may have included the introduction of ferrous iron. At this point the depositional environment changed considerably, as indicated by the deposition of compositionally and texturally different NIII and CI type phosphorite surface layers on the limestone rock. It is proposed that this environmental change is associated with the development of a major phosphate mineralization regime which was responsible for the conversion of the micritic carbonate matrix of these limestone rocks to a collophane-francolite matrix, thus producing the NI/NII variety of nodules. These diagenetic replacement processes will be discussed below (Chapter VI.3).

VI.2.2 : NIII, CI and CII Nodule Classes.

A. Introduction.

The petrographic studies have indicated a number of features in the nodules from these classes which are sedimentologically incompatible with each other under normal hydrodynamic conditions. For example the fine quartz silt and clay sized micrite content are usually not found in association with coarse sand and gravel grades, as they are in these rocks. Furthermore the high energy environments normally required to erode, transport and deposit objects the size of the enclosed pebbles found in CI nodules is in contradiction to the textural features exhibited by these pebbles, namely a low degree of rounding and often highly irregular shapes which indicates non-existant or at least negligible mechanical abration. In support of this "high energy environment vs low mechanical abrasion" contradiction is the presence of delicate and well preserved foraminiferal tests in the matrix of pebble rich CI nodules, as well as in NIII nodules carrying coarse to very coarse quartz sand grains. Apart from these contradictions the following features must also be accounted for by any environment responsible for the deposition of these nodules: The marked compositional differences between the enclosed microfossiliferous pebbles and the surrounding glauconite rich matrix indicate that the deposition of the pebbles and the matrix took place in distinctly different environments and that in order to admix these two components to form the conglomerates some mixing and/or transporting mechanism must be sought. The general presence of grain supported textures in those nodules recovered from the eastern Agulhas Bank area, while nodules from the Western Agulhas Bank area predominantly exhibit cement supported matrix textures also requires explanation. In addition interstitial areas in grain supported textures often carry cement supported silt sized quartz. Furthermore the presence in some nodules of macrofossil fragments, microfossiliferous internal casts of macrofossils (CII class), bedding planes and erosional surfaces must also be explained.

The unusual textural features exhibited by these nodules closely resembles the textural features found in diamictites, as described by Flint, Sanders and Rodgers, 1960; Pantin, 1967, and poorly sorted mudflow conglomerates as described by Pettijohn, (1957) and Dzulynski, Ksiazkiewicz and Kuenen, (1959). It has been proposed by these workers that these poorly sorted rocks originated through turbidity currents and /or mudflows and it is here suggested that such erosional, transporting and depositional mechanisms, along with tidal and storm wave currents associated with and accentuated by a eustatic shallowing of the sea, account for the deposition of the texturally and compositionally heterogeneous proto-phosphorite sediments. It is postulated that these transporting agencies were unable to produce effective abrasion of the transported components due to the low energy levels involved and/or the mechanical buffering capacity of the associated muds.

A key assumption is implicit in the above hypothesis, namely that the proto-phosphorite sediments were originally rich in mud. It is further postulated that this mud was "lime mud" which subsequently gave rise to the micrite and collophane cement, observed today in the nodules, as a result of diagenetic processes which will be discussed in detail in the diagenetic sub-section (see below, Chapter VI.3).

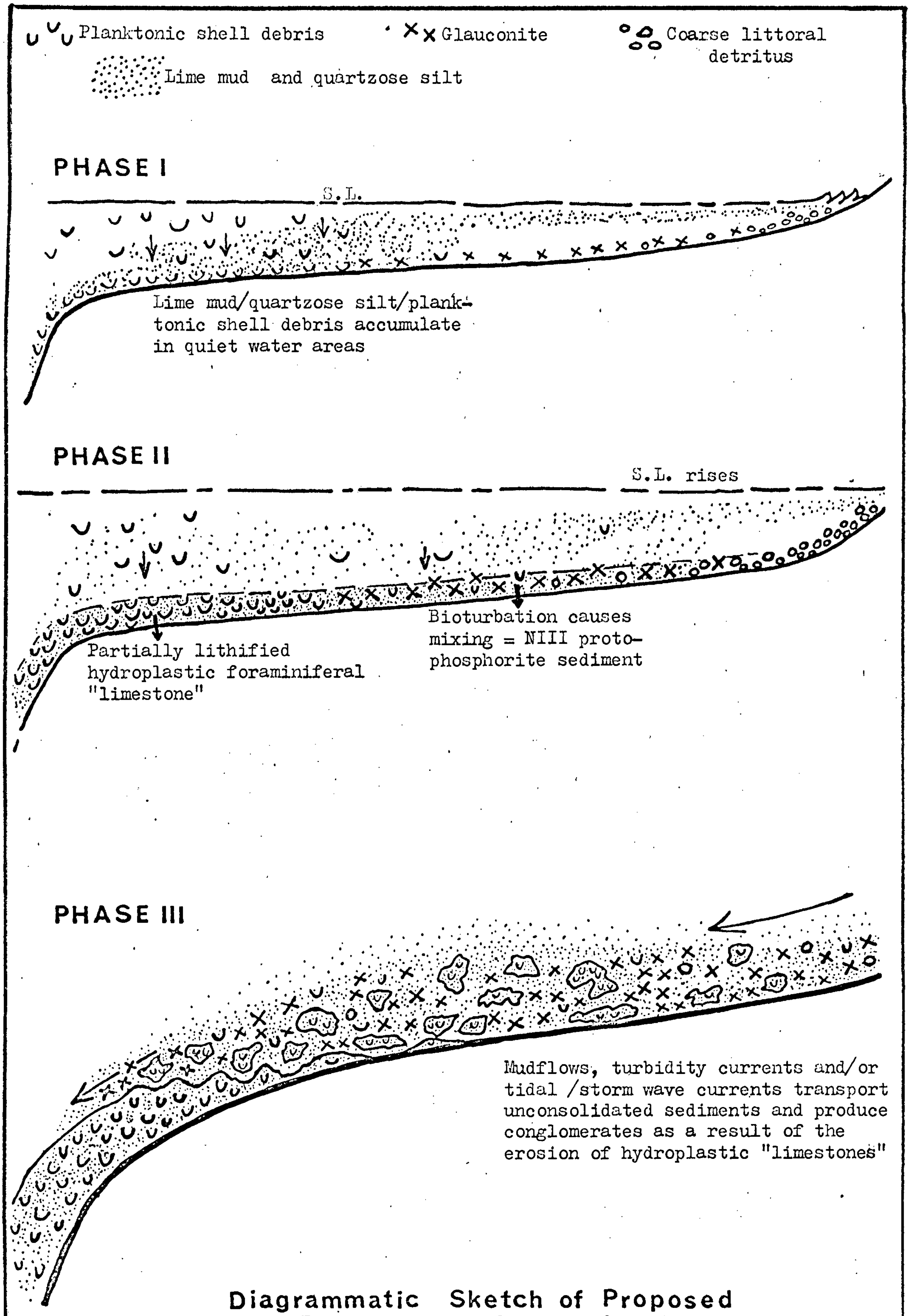
B. Postulated Depositional Sequence.

The sedimentological features and hypothesis discussed in the previous section will now be used to develop a hypothetical sequence of events responsible for the deposition of the proto-phosphorite sediments. It is acknowledged that the creditability of this proposed sequence of events rests in large part on the validity of the hypotheses outlined above.

(a) Phase I (Figure 7.A).

Wave action in the surf zone of a stationary or slowly rising sea level was responsible for the generation of terrigenous detrital materials which were then carried seawards by inshore currents, where they mixed with glauconitic sands located on the inner and middle continental shelf. (The origins of the glauconite sands on the Agulhas Bank are discussed by Birch, in prep.). Further out in quiet water conditions found in outer shelf and upper slope areas planktonic foraminifera test accumulated along with lime mud generated by the breakdown of biogenic calcite by (i) mechanical attrition in the surf zone and (ii) biological activity, such as algal borings. Variable amounts of silt sized quartz were also deposited along with the micrite and tests. This quartz silt may be fluvial or aeolian, or it may have originated along with the coarser quartz detritus in the coastal surf zone.

The above sedimentological sub-division of the continental shelf is compatible with the sedimentological data presented by Rogers (1971) for the phosphorite-productive continental shelf west and south-west of Cape Point (western Agulhas Bank). The depth of the major portion of the continental shelf in this area (150 - 400 metres) precludes the widespread emergence of the shelf during eustatic sea level lows, at least since Tertiary times (Guilcher, 1969). If it is accepted that the phosphorite is of late Tertiary or early Pleistocene age (see Chapter II) then the present day sediment patterns in this area probably reflect the sediment distributions on the shelf at the time of the phosphorite formation. On the other hand the sediments in the shallower (< 150 metres) and phosphorite productive eastern Agulhas Bank area do not fit the proposed sub-division nearly so well, due to the sediments in this area being dominated by "relict" sediment patterns associated with Pleistocene regressive and transgressive coastlines (Rogers, 1971). The present day sediment patterns in this



Lime mud/quartzose silt/planktonic shell debris accumulate in quiet water areas

Partially lithified hydroplastic foraminiferal "limestone"

Bioturbation causes mixing = NIII protophosphorite sediment

Mudflows, turbidity currents and/or tidal /storm wave currents transport unconsolidated sediments and produce conglomerates as a result of the erosion of hydroplastic "limestones"

Diagrammatic Sketch of Proposed Phosphorite Depositional Sequence

FIGURE 7

eastern area therefore are not considered to accurately represent the sediment distributions at the time of the phosphorite formation.

(b) Phase II (Figure 7.).

The sea-level then rose, leaving behind a mantle of sand sized detrital sediments grading in a seaward direction into glauconite sediments. In response to this sea-level rise the micrite, quartz silt and microfossil depositional zone migrated across the shelf and these fine sediments were then deposited on top of the coarser glauconite and quartz sediments.

Bioturbation (Rhoads, 1967, and Winston and Anderson, 1971) was then responsible for the thorough mixing of these coarse and fine grades and provided sufficient lime mud was admixed the original sediment texture will change from grain supported to mud supported. Minor quantities of planktonic foraminiferal tests also accumulate and are "gently" mixed in alongside the coarse grains by bioturbation. The result of this sequence of events is the production of a bioturbated proto-NIII-phosphorite sediment. Using the classification of Pantin (1967) for unsorted sediments these proto-phosphorites would be classified as B-Diamictons. The microfossil/quartz silt sediment formed in phase one continues to accumulate and the lower portions of this sediment acquire a certain degree of coherence in response to initial lithification processes.

At this point a phosphate mineralization regime may result in the lithification of the sediment to produce a non-conglomeratic NIII class phosphorite rock. (The mechanisms of the phosphate lithification processes will be discussed in more detail below). The presence of enclosed bivalve macrofossil shells and shell fragments found in NIII class nodules is in keeping with the assumption that bioturbation took place; but without the positive identification of macrofossil shells belonging to burrowing organisms, this mixing process is still hypothetical. The development of the phosphate pellets found in NIII class nodules is associated with this phosphatizing regime, although the mode of origin remains obscure. This phosphatizing regime may also phosphatize the microfossiliferous/quartz silt sediment concurrently with normal diagenetic processes, thus producing NI phosphorites.

Should the NIII proto-phosphorite sediment not become lithified, then the micrite component may continue to accumulate and become admixed by bioturbation.

(c) Phase III (Figure 7.).

Excessive admixture of micrite to the sediment would render it susceptible to transporting mechanisms such as mudflows and turbidity, tidal and storm wave currents. At this point a genetic distinction will be made between the origins of the phosphorite nodules recovered from east and west of Cape Agulhas.

(i) The Western Agulhas Bank.

It is suggested that mudflows and turbidity currents were active on the relatively steep gradients present on the continental shelf in this region (especially south-west of Cape Point where the shelf gradient varies between 1 in 50 and 1 in 100, see Figure 2) and that these agents transported the poorly sorted lime mud rich sediments into the microfossil/quartz silt "limestone" accumulation area, whereupon the current or flow broke up the very soft hydroplastic, microfossiliferous "limestone-sediment" into pebble sized fragments, often of the most peculiar shapes, which then became incorporated into the turbidity current or mudflow. These lime-mud rich sediments were then deposited in their present position in shelf break/upper continental slope areas. Because of the excess amounts of lime-mud present, the resulting matrix texture was usually mud supported.

A phosphatizing regime is then considered to have converted these unconsolidated "diamicton" sediments into conglomeratic CI class phosphorite nodule "diamictites". According to Pantin's (1967) classification these phosphorites would be P- or M- diamicities depending on whether the depositing agent was a turbidity current (P-diamictite) or a mudflow (M-diamictite).

In support of the above hypothesis it may be noted that recent dredging operations carried out to the north of Cape Town have recovered conglomeratic phosphorite nodules from the Cape Canyon, i.e. in a classical turbidity current environment.

(ii) The Eastern Agulhas Bank.

The much lower seaward gradients of continental shelf in the eastern Agulhas Bank (ca. 1 in 1000 to 1 in 10,000) in comparison to the Cape Point area on the western Agulhas Bank (see Figure 2) does not favour the development of mudflows and turbidity currents. The following mechanisms are therefore suggested for the generation of transporting agencies on the eastern Agulhas Bank.

The flatness and uniform depth (100 - 140 metres) of thousands of square kilometers of phosphorite productive seafloor in the eastern Agulhas Bank area would provide ideal conditions, in association with a eustatically lowering sea-level, for the development of tidal and/or storm wave surges and currents, especially if the sea-level approached to within 20 - 30 metres of the seafloor. The regular development of gale force winds in this area (as is the case today) would be another mechanism for generating currents in these postulated shallow but wide-spread seas.

Currents generated by the above mechanisms are considered to have been responsible for the movement of the muddy glauconitic sediments (see Phase II) to areas of microfossil limestone accumulation. As in the western Agulhas Bank area these soft, hydroplastic microfossil "rocks" were then broken up by these currents and mixed in along with the muddy glauconitic sediments to form a conglomeratic CI class proto-phosphorite sediment. The energy levels involved were low enough to preserve the peculiar shapes of the highly plastic "microfossil" pebbles, as well as preserving the thin walled planktonic forams found in the matrix. The lime mud content of the sediments may originally have been high, but winnowing effects during transportation and deposition are indicated by the dominantly grain supported textures exhibited by the sand sized quartz, microfossil and glauconite matrix grains. The interstitial areas are generally occupied by cement, and cement supported silt sized quartz grains, thus indicating that not all the original lime mud was removed (on the assumption that the cement was originally lime-mud). Other areas (often within the same thin section) clearly show that the original lime mud was removed completely, the intervening space now being filled by secondary minerals (see diagenesis section below).

The presence of erosional surfaces in isolated nodules from this eastern area indicates the development of temporary high energy phases while micro-scale bedding planes indicate quiet water non-depositional phases possibly associated with fair weather periods.

The origin of the CII class of nodules (found only on the eastern Agulhas Bank) possibly occurred in the following manner :

Surface biological activity in an unconsolidated microfossiliferous/quartz silty sediment resulted in the production of "macro" shells which became infilled (after the death of the organisms) by the surrounding microfossiliferous sediment. Later reworking of these unconsolidated sediments by glauconite transporting currents (associated with the formation of CI nodules) resulted in a microfossiliferous and glauconitic sediment. The microfossiliferous infilling of the fossil shells remained undisturbed and hence glauconite free. The net result was a proto-CII-sediment which subsequently became lithified by phosphatization processes. The generally higher microfossil and lower glauconite contents of the matrix of CII nodules, in comparison to CI nodules, is in keeping with their postulated mode of origin.

It is possible that the unconsolidated "microfossiliferous/quartz silty" sediment referred to in the preceeding paragraph may be the surficial unconsolidated equivalent of underlying semi-plastic material destined to become the enclosed pebbles found in CI nodules. This supposition is supported by the frequent recovery of both CI and CII nodules from the same dredge station. It would also explain the presence of varieties transitional between CI and CII classes.

The association of phosphorite deposits and stratigraphic erosional surfaces or unconformities (see Pettijohn, 1957, p. 474, and Dunbar and Rodgers, 1957, p. 126, for discussions on this topic) is compatible with the "shallowing sea/regressive coastline" environment postulated for the formation of conglomeratic phosphorites found east of Cape Agulhas.

It is suggested that the above theories, developed to explain the sedimentological aspects of the formation of conglomeratic phosphorites found east and west of Cape Agulhas, may have some application to the genesis of petrographically similar sea floor phosphorites from other localities, such as those found in the Californian and N.W. African offshore areas.

VI.3 : Diagenetic Processes.

VI.3.1 : Introduction.

The petrographic and geochemical studies have revealed in the phosphorite nodules a number of mineralogical and geochemical features which require explanation in terms of diagenetic processes : The first of these is the intimate mixing of collophane with micrite in the nodule matrix. Associated with this inter-mixing are gradational colour changes in NI nodules shown to be related to changes in the proportions of micrite and collophane present. The typical development in grain supported matrix areas of secondary "dahllite" rims around glauconite, quartz and microfossil grains needs to be accounted for. Variations in the Eh implied by the presence of glauconite, pyrite and goethite are of diagenetic interest, as is the presence of microfossil leaching effects and the presence of sparry calcite found as a secondary mineral in interstices in grain supported areas. The sparry calcite crystals are later than the "dahllite" rims.

Apart from the above features, a key diagenetic assumption was made in the preceding depositional environment section, namely that the collophane cement was originally lime mud. If this assumption is valid then some diagenetic mechanism must be sought whereby the original lime mud may be converted to the present day collophane cement.

Before the above features and assumptions are discussed in terms of the diagenetic processes responsible for the lithification and phosphatization of the various phosphorite nodule classes, the literature on the formation of phosphate minerals in the marine environment will be briefly reviewed.

VI.3.2 : The Formation of Phosphate Minerals in the Marine Environment.

Two basic theories or mechanisms have been developed, by various workers, to account for the genesis of marine apatites :

The first theory postulates the direct inorganic precipitation of the apatite phase from phosphate saturated seawater as proposed by Kazakov (1937); Dietz, Emery and Shepard (1942); McKelvy, Swanson and Sheldon (1953); Kramer (1966) and others. The second theory invokes inorganic replacement mechanisms whereby pre-existing calcite grains are converted to carbonate fluorapatite by reaction with phosphate rich interstitial solutions as was suggested by Murray and Renard (1891) and more recently by Hamilton (1956); Ames (1959); Simpson (1964); Pevear (1966, 1967) and Summerhayes (1967, 1970). The above workers have provided field, experimental and theoretical evidence in favour of both theories, suggesting that phosphorite genesis cannot be ascribed entirely to either one or the other mechanism. Gulbrandsen (1969) has presented theoretical data in support of both theories, although his calculations are based on the assumption that the apatite formed is fluorapatite ($Ca_5 (PO_4)_3F$), instead of carbonate fluorapatite (approximate formula = $Ca_{10}(PO_4, CO_3)_6F_{2-3}$, Altschuler, Clarke and Young, 1958).

Degradation of organisms in biologically productive areas is considered to be a prime source for the phosphate required for either the direct precipitation or replacement theories (Murray and Renard, 1891; Bushinsky, 1964 and D'anglejan, 1967). The high organic productivity required is frequently linked to nutrient enriched waters such as are found in regions of upwelling (Brongersma-Sanders, 1957) and in river estuaries (Bushinsky, 1964; Pevear, 1966, 1967).

Baturin (1969) has presented convincing evidence for present day authigenic phosphorite formation in diatomaceous, organic matter rich, calcite poor, hydrogen sulfide bearing (i.e. reducing conditions) mud recovered from a region of pronounced upwelling on the inner continental shelf off the coast of South West Africa. His evidence indicates that the phosphatization has taken place through the action of phosphate rich interstitial solutions operating below the sediment-water interface. The actual phosphatization mechanism (i.e. replacement vs precipitation) is however not clearly delineated.

Tooms, Summerhayes and Cronan (1969) in their review article note that evidence has been presented for the formation of phosphorites in both oxidizing and reducing environments, while the pH range suitable for marine apatite formation lies between Ph = 7.0 to 7.8 (see also Krumbein and Garrels, 1952). The diagenesis of the various Agulhas Bank phosphorite classes will now be discussed.

VI.3.3 : The Diagenesis of NI and NII Nodules.

The progressive decrease in the collophane concentration (coupled with an increase in the micrite content) from the surface to the centre of some NI nodules suggests that the phosphate mineralization of the petrographically similar NI and NII nodules was the result of micrite-to-collophane replacement processes, produced by phosphate rich interstitial solutions working their way inwards from the surface of nodules already partially lithified by normal carbonate rock diagenetic processes (i.e. dehydration and the conversion of lime mud to micrite (Folk, 1965)). This partial lithification would have hindered the movement of the interstitial solutions thereby inhibiting the completion of the phosphatization process, the net result being the colour, mineralogical and geochemical gradients observed today in these nodules.

The interpretation of the phosphatization of these nodules as being the result of micrite-to-collophane conversion processes is in keeping with the inorganic replacement theory referred to in the preceding section. Bushinsky (1935) has ascribed the formation of certain Russian phosphorites to similar inward phosphatizing mechanisms operating on carbonate rocks.

It is not clear at what point in their history the NII nodules acquired their high cement iron content. The association in these nodules of iron oxides, carbonates and phosphates warrants further investigation.

VI.3.4 : The Diagenesis of NIII, CI and CII Nodules.

While it is impossible to present irrefutable evidence that the present day collophane-francolite found in NIII, CI and CII nodules was originally lime mud at the time of the deposition of the proto-phosphorite sediment, it is nevertheless proposed that the collophane-francolite cement originated through replacement processes brought about by the reaction of phosphate rich interstitial waters (i.e. below the sediment - water interface) with finely divided calcite (i.e. lime mud) (cf. Summerhayes, 1970).

This hypothesis is in keeping with the inorganic replacement theory discussed above and furthermore it is entirely compatible with the collophane-francolite replacement of micrite demonstrated for the phosphatized limestone NI nodules. The finely divided silt sized calcite grains disseminated throughout the cement can easily be explained, on this hypothesis, as the remnants of the original micrite/lime mud. The petrographic evidence, while supporting the above hypotheses, does not provide any evidence (except perhaps for the very minor quantities of "dahllite", see below) for large scale inorganic precipitation of marine apatite from seawater.

The colour gradations observed both in hand specimen and in thin section for the enclosed microfossiliferous pebbles found in the conglomeratic nodules suggests lithification and phosphatization processes, similar to those described for NI and NII nodules, operated on these enclosed pebbles. The characteristically untruncated surface to centre gradations found in these enclosed pebbles clearly indicate that the phosphatization took place after the formation of the pebbles, as truncated gradations would have been expected if the reverse was true. The formation of these pebbles is considered to be intimately linked to their incorporation within the unconsolidated proto-phosphorite sediment (see above) and it is reasonable to suppose that the subsequent phosphatization (and lithification) of this sediment was also responsible for the phosphatization of the enclosed microfossiliferous pebbles.

In nodules recovered from the Agulhas Bank, of whatever class, the enclosed skeletal calcite has usually not been phosphatized and this is considered to be due to surface area effects : The porous extremely finely divided nature (and therefore large surface area) of lime mud is considered to be much more susceptible to penetration by phosphate rich liquids and subsequent chemical reaction, than the large massive skeletal calcite fragments.

The "dahllite" rims found encrusting quartz, glauconite and microfossil grains in porous, grain supported matrix areas free of interstitial collophane-francolite cement possibly formed as the result of inorganic apatite precipitations from the same phosphate rich interstitial waters considered to have been responsible for the micrite-to-collophane replacement process. This encrusting rim warrants further investigation in as much as well crystallized marine apatite precipitates are rare. The petrographic similarity of these encrusting "dahllite" rims to the fibrous calcite encrustations found enveloping quartz and microfossils in certain Agulhas Bank and South African coastal limestones (Siesser, 1970) suggest however that these "dahllite" rims may have originated through replacement processes operating on pre-existing fibrous calcite.

Upwelling (as noted in Chapter II) occurs in the phosphorite productive western and eastern Agulhas Bank areas and this therefore supports the nutrient rich waters/high biological activity/phosphorite association discussed above (Chapter VI.3.2).

The ubiquitous presence of finely divided iron oxides disseminated throughout the cement indicates that the replacement of micrite by collophane took place under oxidizing conditions. The occasional presence of pyrite is considered to indicate the development of reducing environments in restricted areas within the nodule, subsequent to the formation of the nodule.

The enclosed glauconite grains are considered to be allogenic in origin (w.r.t. the phosphorite nodules) and the conditions for the formation of these grains are not considered to reflect the conditions under which the phosphorite originated.

Calcite leaching effects observed in certain rare instances suggest that the pH of the solutions associated with these particular rocks were acidic at some point in their history (cf. Friedman, 1964). The circumstances of this low pH are obscure. Sub-aerial exposure could have been responsible (Friedman, 1964) but the depths of recovery on the continental shelf and upper continental slope, in the Cape Point area, of the nodules which exhibit this feature are 305 metres (DR - 219) and 440 metres (DR - 4) considered to be too deep for Pleistocene and Tertiary sea-level lowerings (Guilcher, 1969). Another possibility is that these leaching effects represent low pH conditions developed in interstitial solutions operating below the sediment - sea water interface.

After lithification of the nodules, subsequent low sea levels (especially during the Pleistocene, cf. Guilcher, 1969) sub-aerially exposed large areas of the shallow phosphorite rich eastern Agulhas Bank with the resulting formation of secondary sparry calcite infillings in porous interstitial areas (cf. Friedman, 1964). The absence of interstitial sparry calcite in the nodules recovered from west of Cape Agulhas indicates that these nodules have not been sub-aerially exposed, a feature that is compatible with the location of the majority of these western nodules in water depths below the maximum Pleistocene sea-level lowering, assuming that tectonic influences have not affected the bathymetry significantly, in Quaternary times at least.

CHAPTER VII.

CONCLUSIONS.

VII.1 : Summary.

The aerial extent of a widespread and economically important *in situ* phosphorite nodule deposit of possible upper Tertiary Age has been delineated on the Agulhas Bank as a result of a systematic dredging programme carried out in this area. The phosphorite nodules recovered have been classified into five classes according to petrographic criteria and it has been shown that these classes are genetically interrelated. The five classes include two conglomeratic and three non-conglomeratic types.

The first non-conglomeratic variety, NI, is a silty quartz microfossiliferous limestone in various stages of phosphatization. Geochemical and petrographic data has shown that in certain of these nodules phosphatization has taken place from the periphery to the centre and it is considered that the prime mechanism involved is a micrite-to-collophane/francolite conversion process. The second non-conglomeratic variety, NII, is a brown ferrugenous microfossiliferous limestone which has been cemented by a micrite/collophane-francolite/goethite mixture. Inward phsophatization has also been indicated in some NII nodules. The third subtype, NIII, is composed of variable quantities of sand sized quartz, glauconite, and microfossil grains and macrofossil fragments cemented together by a collophane-francolite/micrite matrix carrying minor amounts of quartz silt.

Texturally, NI class nodules are classified as medium grained packstones, NII class nodules as medium to coarse grained packstones while NIII class nodules include both fine grained packstones and coarse grained wackestones.

The first conglomeratic class, CI, is composed of sub-rounded to angular, and often highly irregularly shaped, pebbles of NI phosphorite cemented together by a usually grain supported matrix which is similar in composition to NIII class nodules. Some of the enclosed NI pebbles are moderately ferruginous, suggesting a transition to NII class enclosed pebbles. The second conglomeratic variety, CII, is composed of often regularly shaped microfossiliferous pebbles which originated through the infilling of macrofossil shells by a quartz silty microfossiliferous sediment prior to the incorporation of these shell cast "pebbles" within the original proto-CII-phosphorite matrix, this matrix being similar in composition to NIII class nodules. The matrix is however usually poorer in glauconite and richer in microfossils as compared to the CI matrix.

The matrix textures of CI and CII nodules may be either grain or cement supported.

The large number of widely distributed phosphorite samples collected from the Agulhas Bank has enabled regional petrographic trends within the different classes to be described. A coastward increase in the quartz content is a notable trend, while variations in the matrix texture are also important : The matrix of NIII and CI nodules found in the shallower areas east of Cape Agulhas are usually grain supported, while the matrix of CII nodules, only found east of Cape Agulhas may be grain or cement supported. The NIII and CI nodules found in deeper water west of Cape Agulhas on the other hand normally exhibit cement supported matrix textures.

The conglomeratic varieties, CI and CII are the most plentiful and they constitute the bulk of the rich phosphorite belt found on the continental shelf in the eastern and south-eastern areas of the Agulhas Bank. The CI class is also prominent, along with NIII type nodules, in the shelf break and upper continental slope areas south-west and west of Cape Point. The NI class is most plentiful on the continental shelf in the east-central region of the Agulhas Bank, while the NII variety is normally found on the south-eastern flank of the Agulhas Bank in the shelf break and upper continental slope area.

In comparison with subsea phosphorite deposits from other parts of the world, remarkable similarities have been noted between the CI class Agulhas Bank phosphorites and the glauconite conglomerates found off the N.W. African coast. Furthermore, the CI class displays affinities to the conglomeratic phosphorites found off the Californian coast.

X-ray diffraction studies have identified the prime phosphate mineral present as being francolite, a carbonate fluorapatite. These studies have also shown that iron oxides such as goethite are intimately associated with the phosphorites found on the Agulhas Bank, thus indicating that these rocks formed under oxidizing conditions, in contrast to the normally accepted reducing environment considered to be favourable for phosphorite formation. An x-ray diffraction peak-pair method for the determination of CO_2 in apatites has shown that the Agulhas Bank phosphorites contain on average 5.5% CO_2 within the apatite structure.

Major element analyses carried out on 21 representative samples selected from amongst the five classes have shown that the major element geochemistry is a reflection of the dominant mineralogy found in these rocks. The average P_2O_5 content of the Agulhas Bank phosphorites is 16.2% and hence the majority of the nodules are not true phosphorites, as they contain less than 18% P_2O_5 (= 50% Apatite). The F/P_2O_5 ratio (average = 0.130) for Agulhas Bank phosphorites is significantly higher than the ratios reported for Californian subsea phosphorites, and ~~to~~ the ratios reported for the Phosphoria (U.S.A.) and Russian phosphorites.

With regard to the origins of the Agulhas Bank phosphorites, the petrographic studies have revealed a number of sedimentologically incompatible features in the NIII, CI and CII nodules, indicating a complex depositional history. Unusual associations such as intact thin walled foraminiferal tests adjacent to very coarse angular quartz grains, poor sorting (i.e. from silts to gravels), and the often highly irregular shapes of the enclosed pebbles and cobbles (in the conglomeratic classes) suggest contradictions in the energy levels of the environment responsible for the transportation of the various nodule components.

In order to explain the above features it has been postulated that initially three depositional environments prevailed on the Agulhas Bank :

(i) An outer shelf/upper continental slope, quiet water zone where planktonic foraminiferal tests and quartz silty lime mud (micrite) accumulated,

(ii) a midshelf area rich in authigenic glauconite sands which grade into

(iii) an inshore region noted for the production of coarse detrital terrigenous material as well as comminuted clay sized skeletal calcite.

A eustatic rise in the sea level is then considered to have caused the landward migration of the depositional zones thereby allowing lime mud (and some foraminiferal tests) to accumulate on top of coarser glauconite and terrigenous material. It is suggested that "gentle" bioturbation mixing of these coarse and fine grades and occasional foraminifera tests produced NIII class proto-phosphorite sediments.

Conglomerate formation is considered to have resulted from submarine transporting (and depositional) agencies moving the glauconitic lime muds downslope to erode and incorporate fragments of weakly lithified hydro-plastic foraminiferal "limestone" accumulate. West of Cape Agulhas the location of the great majority of the conglomerate nodules in relatively deep water on the "steep" upper continental slope suggests that mud-flows and/or turbidity currents were the prime transporting and depositing agents. East of Cape Agulhas the majority of the conglomeratic nodules are located on the relatively shallow, wide and flat continental shelf, i.e. in areas unfavourable to the development of mudflows and turbidity currents. It is however postulated that abnormally strong currents due to tides and storm waves acting in a shallowing body of water associated with a regressive shoreline were responsible for the formation of the CI and CII nodules found in this area. The conglomeratic textures from either area are not considered to reflect high energy surf zone conditions. Diagenetic phosphatization of the lime mud is postulated as the primary lithifying process.

The formation of NI and NII nodules is considered to have been the result of the accumulation of planktonic foraminiferal skeletal material and lime mud, the latter component subsequently becoming phosphatized in response to the same phosphate mineralization regime indicated for the lithification of NIII, CI and CII nodules. The origin of the high iron content of NII nodules remains obscure.

The Agulhas Bank phosphorites are oceanographically linked to areas associated with the upwelling of nutrient rich and therefore biologically productive waters.

The average P_2O_5 content (ca. 16%) of the nodules, successful pot plant fertilizer tests, the relative shallowness of most of the rich phosphorite areas and their proximity to ports and agricultural areas indicate clearly that this widespread ore body is potentially of great economic importance.

VII.2 : Recommendations for Future Work.

With regard to future work on the Agulhas Bank phosphorites, the following fields of research are suggested :

(i) The trace element composition of the nodules is an important aspect of their geochemistry and warrants further investigation. The separation of the pure carbonate fluorapatite phase from the nodules (possibly by selective leaching processes) and a study on the major and trace element composition of this phase would lead to a clearer understanding of the possible substitutions present in the apatite structure. Furthermore a comparison of the trace element distributions found in this pure apatite phase with those found in micritic limestones from the Agulhas Bank may throw some light on the creditability of the micrite-to-collophane (i.e. apatite) replacement process, suggested in this work, as the prime phosphate mineralization mechanism for the Agulhas Bank phosphorites.

(ii) Quantitative geochemical studies (using x-ray fluorescence microprobe techniques) on the thin "dahllite" rims found encrusting glauconite, quartz and microfossil grains may prove rewarding, as these "rims" possibly represent true inorganic precipitation of marine apatite.

(iii) The association of iron oxides and phosphates in many of the nodules (especially NII class nodules) warrants further investigation in as much as the environmental conditions responsible for the formation of these minerals may be interrelated.

(iv) Accurate age dating of the phosphorite nodules by a study of their micro- and macrofossil fauna (as has been successfully accomplished for the N.W. African and Californian offshore phosphorites) is a field of study that certainly requires attention.

(v) The quantitative evaluation of the Agulhas Bank phosphorite ore reserves is an important pre-requisite to the economic recovery of the nodules.

(vi) The phosphorite nodules recovered on the continental shelf to the north of Cape Town, i.e. outside the thesis area, require petrographic and geochemical investigation. The study of the conglomeratic nodules recovered from the Cape Canyon, an ideal area for the development of turbidity currents and/or mud flows, should more clearly delineate the postulated relationship between these submarine transporting agencies and conglomeratic phosphorite formation.

(vii) In the Saldanha Bay area the possible genetic relationship of the onland pelletal/skeletal phosphate deposits to the phosphorites found offshore should prove to be a rewarding avenue of research.

APPENDIX A.

GEOCHEMICAL ANALYTICAL METHODS.

This appendix describes the analytical techniques used to obtain the geochemical data presented in Chapter V :

(a) Sample Preparation.

The phosphorite nodules selected for analysis were converted into powder samples by the following procedure :

(i) The nodules were scrubbed with a wire brush in cold tap water to remove loose sediment and soft organic growth. The samples were then dried at room temperature.

(ii) Organic calcium carbonate contamination was removed from the nodule surface.

(iii) A suitable weight of rock (see above) was then put through a rock splitter. If more than 5 kg (conglomerate group) or 1 kg (non-conglomeratic group) of rock was available for crushing, then a representative fraction was set aside for reference purposes.

(iv) The rock fragments were then put through a hardened steel jaw crusher twice to produce rock fragments with an average diameter of 0.5 cm.

(v) The crushed rock was then successively split until a 500g sample remained. This material was then crushed for 10 minutes in a vibratory carbon steel ball mill to give a powder of ± -40 mesh.

This air-dried powder then served as the basis for the following analyses :

(b) H_2O-

The H_2O- determination was made by measuring, in duplicate the weight loss of the air dried powder samples at 120°C in a silica crucible. The samples were kept at this temperature for eight hours.

An attempt was made to determine the loss on ignition value for the samples at 1,000°C. This proved unsuccessful as the silica crucibles used were attacked by the sample, invalidating any measured weight loss. The attack by the sample powder on the silica crucibles was possibly due to the presence of fluorine in francolite (a carbonate-fluorapatite), this mineral being the primary phosphate bearing mineral in the Agulhas Bank phosphorites. The fluorine, combining with any structurally bound water present, would form HF, a potent gas capable of attacking the silica in the crucibles to produce SiF_4.

Considerations of the time factor and the short supply of platinum crucibles precluded the determination of the loss of ignition in platinum crucibles. It was therefore decided to determine the loss on fusion (with lithium borate flux at 1000°C) during the preparation of the glass discs used for the x-ray fluorescence analyses described in the next section.

(c) Si, Ti, Al, Fe (total), Mn, Mg, Ca, K, P and the Loss on Fusion.

These elements were determined by x-ray fluorescence (X.R.F.) spectrometry on glass discs prepared by the fusion of sample powder with lithium borate flux, after the method described by Norrish and Hutton (1969).

In the preparation of the glass discs, a loss on fusion (L.O.F.) value was determined by measuring the weight loss, after fusion for ten minutes at 1,000°C, of the sample powder/flux mixture. These values were then blank corrected by subtracting the weight loss after fusion of pure flux, as described by Norrish and Hutton (1969, p. 445). The L.O.F. values are needed in the application of matrix corrections to the measured x-ray count rate (see Norrish and Hutton, 1969, p. 445).

Table 6 lists the seven rock standards (six natural and one artificial) and the two artificial blanks that were used to set up working curves, as well as the major element composition of each standard and blank and the source of this data. The glass fusion discs were prepared in duplicate for the unknown samples, standards and blanks. Each disc was then analysed in duplicate using a Philips PW 1212 automatic x-ray fluorexcence spectrometer. Table 7 lists the instrumental settings for each element analysed.

The x-ray intensity data from the analyses were then processed in two stages with the help of a computer program devised for this purpose by Mr. J.P. Willis, Department of Geochemistry, University of Cape Town. The first part of this program normalized the x-ray intensity data for the standards and blanks and then computed (from this normalized data) the slope of the working curve for each element. The data from these standards and blanks were normalized with respect to :

(i) dead time corrections
(ii) machine drift
(iii) blank corrections and
(iv) matrix effects.

The normalization of the data with respect to matrix effects was achieved by the method described by Norrish and Hutton (1969). The second stage of this program then used the working curve "slope" data to convert normalized x-ray intensities for the unknown samples into element oxide percentages, after the method described by Norrish and Hutton (1969). The x-ray intensities for these unknown samples were normalized w.r.t. the same factors as described for the standards and blanks.

For any given unknown sample the results of the duplicate analyses on the first disc were averaged and sililarly an average result was calculated for the duplicate analyses on the second disc. The results for these two separate discs (prepared from the same unknown sample) were then averaged to produce a final analysis.

Precision and Accuracy.

Norrish and Hutton (1969, p. 447), have shown that when a sample has been prepared and analysed by their method, then the coefficient of variation of the results is less than 1% for any element present in a concentration greater than 1%. Norrish and Hutton (1969) note that it is important to allow sufficient counting times for the different elements in order to achieve this precision. The counting times listed in Table 7 are sufficient and the precision of the method is therefore considered to be good. The accuracy of the method is primarily limited by the accuracy with which the composition of the standard samples is known. The data for standards BR, GH, S1 and U.S.B.S. 1a is considered to be reliable, while the data for standards E2 and U.S.B.S. 56b are not so well documented. The artificial standard A-Si was prepared from "Specpure" reagents.

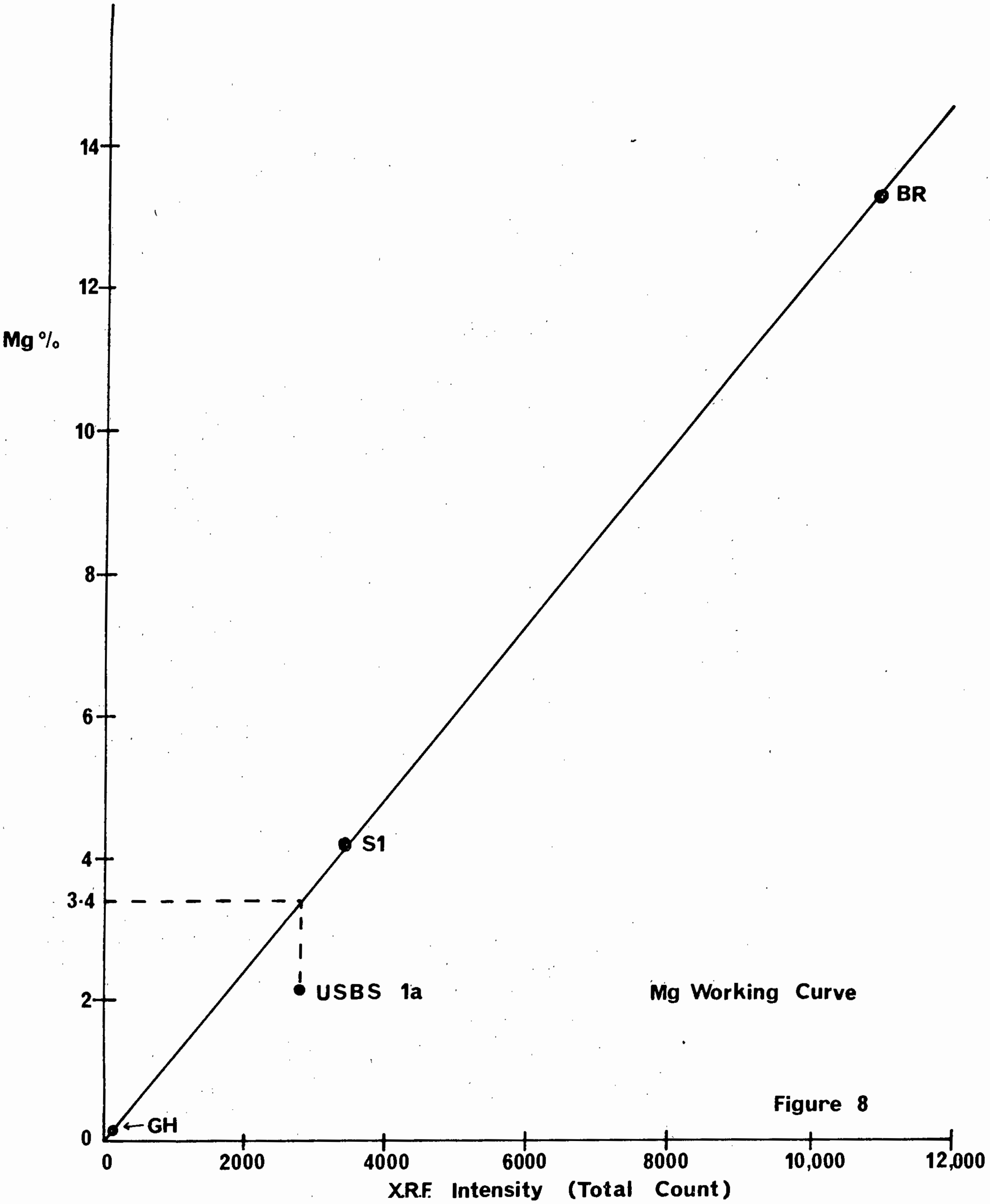
The accuracy of the method is also controlled by factors such as dead time, machine drift and matrix effect corrections. If corrections for these factors have been applied, as in this work, then Norrish and Hutton (1969, p. 449) conclude that the "accuracy of the results may be taken as comparable to their precision".

The Mg Working Curve.

The MgO concentration of the rock standards BR, S1 and GH when plotted against the normalized count rate for these standards, defined a reasonably good straight line working 'curve', (see Fig. 8). However, when the normalized X.R.F. count for Mg in rock standard U.S.B.S. 1a was plotted against the listed MgO percentage, it was found that the plot did not fit the working 'curve' at all (see Fig. 8). This gave some cause for concern as this argillaceous limestone rock standard was in some ways similar to the expected average major element composition of the phosphorite samples, especially with respect to its CaO content.

It was accepted that the MgO value (2:19%) listed in the U.S.B.S. data sheet, accompanying this standard was correct and that therefore the anomalously high X.R.F. count rate (=3.4% MgO) given by Mg in this standard must be due to an error inherent in the analytical method used.

It was considered that this error was due to the excitation of P in the A.D.P. analysing crystal of the spectrometer by the high concentrations of Ca (41.32% CaO) found in this standard. The CaK_α radiation is on the short wavelength side of the P absorption edge and therefore would cause P to fluoresce. The flow counter pulse distributions for PK_α and Mg K_α radiation are close enough to overlap, thus causing an anomalously high Mg count rate. Even though the discriminator window on the x-ray spectrometer was set (see Table 7) so as to minimize this interference, the MgO concentration determined for the Ca rich U.S.B.S. 1a standard was still too high with respect to the Mg working curve (see Fig. 8). It was therefore decided to use the working curve derived from the standards GH, BR and S1 (i.e. excluding U.S.B.S. 1a) and then apply a correction factor to the MgO results for the unknown samples, such that when applied to U.S.B.S. 1a, this standard would fall on the working curve. As the anomalously high X.R.F. count rate for Mg in U.S.B.S. 1a was considered to be related to the high CaO content of this standard, it was decided to make the correction



Mg Working Curve

Figure 8

factor proportional to CaO contents of the unknown samples, i.e.

$$\text{Corrected MgO\%} = \text{Observed MgO\%} - \Delta\text{MgO\%} \cdot \frac{x}{y}$$

where Δ MgO% = difference between the literature value for MgO in U.S.B.S. 1a and the X.R.F. value determined in this work. (Δ MgO% = 1.21%)

x = CaO% of the unknown sample. y = CaO% of standard U.S.B.S. 1a (= 41.32% CaO).

(d) Na.

This element was determined by x-ray fluorescence spectrometry on a whole rock pellet, as described by Norrish and Hutton (1969). The Na determination was not made on the fusion discs (see above), as the count rate for Na in these 'diluted' fusion discs is too low, and furthermore $NaNO_3$ had been added as part of the flux mixture. The pellet was prepared by grinding 4g of -40 mesh rock powder in an automatic agate grinder for 40 minutes to produce a ± - 120 mesh powder, which was then briquetted under 15 tons pressure with a backing of bakelite powder/boric acid. These analyses were carried out in a Philips PW 1220 spectrometer, and the instrumental settings used are listed in Table 7.

The following standards G1, W.1 and OK272, prepared as whole rock pellets, were analysed along with the unknown samples. The data from the standards were used to calibrate the unknown sample intensities in terms of oxide percentages. The Na_2O composition of these sodium standards, as well as the sources for these data, are listed in Table 6.

The precision of this method is ca.2% while the accuracy is ca 10% (J.P. Willis, Dept. of Geochemistry, U.C.T., personal communication).

(e) S.

Sulphur was determined by x-ray fluorescence spectrometry on the whole rock pellets prepared for the Na analyses. The instrumental settings used on the Philips PW 1220 spectrometer are listed in Table 7. The background and dead time corrected nett peak intensity was corrected for secondary absorption by applying a mass absorption coefficient correction factor calculated from the previously determined major element composition data for each sample and the mass absorption coefficient data of Birks (1963).

A working curve was determined for S by the analysis of a depart-

TABLE VI: Adopted Major Element Composition of the Geochemical Standards used in this Work.

STANDARDS.								BLANKS.	
	BR	GH	SI	Ia	56b	E2	A.Si	Fe/Ca/Si Blank	Fe/Na Blank
SiO_2	38.20	75.00	59.57	14.11	10.10	-	21.25	21.16	0.0
TiO_2	2.62	.09	.48	.16	-	-	0.0	0.0	0.0
Al_2O_3	10.20	12.50	9.30	4.16	-	-	0.0	0.0	0.0
Fe_2O_3	12.93	1.33	8.21	1.63	-	41.59	38.96	38.80	39.29
MnO	.21	.05	.40	.04	-	-	0.0	0.0	0.0
MgO	13.28	.03	4.19	2.19	-	-	0.0	0.0	0.0
CaO	13.74	.65	10.10	41.32	44.06	20.01	38.96	37.56	0.0
Na_2O	3.05	3.80	3.37	.39	-	-	0.0	0.0	43.93
K_2O	1.40	4.78	2.63	.71	-	1.37	0.0	0.0	0.0
P_2O_5	1.04	.01	.22	.15	31.55	-	0.0	0.0	0.0
F					3.4				
+LOSS	2.83	.70	.55	35.80	9.53	19.11	0.83	2.48	16.79

	G.I.	W.I.	OK 272
Na_2O	3.32	2.15	5.29

+LOSS = Loss on fusion with lithium borate flux, as determined in this work (see Appendix A, (c)).

SOURCE OF DATA:

BR:	After Roubault et al. (1968).
GH:	After Roubault et al. (1968).
SI:	After Sine et al. (1969).
Ia:	U.S.B.S. Analysis certificate.
56b:	U.S.B.S. Analysis certificate.
E2:	Data as supplied with the standard.
A - Si:	Prepared from "Specpure" reagents.
Fe/Ca/Si Blank:	Prepared from "Specpure" reagents.
Fe/Na Blank:	Prepared from "Specpure" reagents.
G.I.:	After Fleischer (1969).
W.I.:	After Fleischer (1969).
OK 272:	Departmental Standard, Department of Geochemistry, U.C.T.

TABLE VII.

INSTRUMENTAL SETTINGS.

Philips P.W. 1212 X-Ray Fluorescence Spectrometer.

Element	Tube	Kv	mA	Detector	Counting time (sec)	Crystal	Collimator μm
Fe	Au	60	24	$F^+ + S^+$	10	LiF_{220}	160
Mn	Au	60	32	F + S	100	LiF_{220}	160
Ti	Cr	60	32	F	10	LiF_{200}	480
Ca	Cr	40	16	F	10	LiF_{200}	160
K	Cr	60	32	F	10	LiF_{200}	480
Si	Cr	60	32	F	20	P.E.T.	480
Al	Cr	60	32	F	40	P.E.T.	480
P	Cr	60	32	F	40	Ge	480
Mg	Cr	60	32	F	200	A.D.P.	480

K_α lines and vacuum were used for all elements. The pulse height selector was used in the external mode for all elements except Mg, for which a lower level of 250 and a window width of 375 was set in order to minimise background interference arising from P fluorescence in the A.D.P. crystal.

Philips P.W. 1220 X-Ray Fluorescence Spectrometer.

Element	Tube	Kv	mA	Detector	Counting time (sec)	Crystal	Collimator μm
Na	Cr	50	32	F^+	240	Gypsum	480
S	Cr	50	32	F	40	Ge	480

K_α lines and vacuum were used for both elements. The pulse height selector was used in the external mode for Na while a lower level of 320 and a window width of 380 was set for S. The background was counted on either side of the SK_α peak (background 2θ positions = 105.90° and 115.90°) for half the S peak counting time. The Na background was counted once only at 2θ = 96.40°, also for half the Na peak counting time.

[+] F = Flow Proportional, S = Scintillation.

mental standard containing 0.20% S (Department of Geochemistry, U.C.T.). The slope of this working curve was then used to convert the corrected x-ray intensity data, for the unknowns, into percentage S. The precision of this method is considered to be 2 - 3% while the accuracy is approximately 10% (J.P. Willis, Dept. of Geochemistry, U.C.T., personal communication).

(f) FeO Determinations.

FeO was determined titrimetrically using the method of Shapiro and Brannock (1962). Each unknown sample was analysed in duplicate and the results averaged. In order to estimate the precision of the method, sample DR - 248 was analysed eight times. Calculations based on the data from the precision run show that the standard deviation of the results was 0.028% while the coefficient of variation was 4.85%. These values are acceptable.

The accuracy of the method was not checked due to the lack of a suitable standard of similar chemical and mineralogical composition. The magnitude of the results are however compatible with the observed mineralogy.

(g) CO_2 Determinations.

Carbon Dioxide was determined volumetrically by the method described by Hülseman (1966). Each sample was analysed twice and the results averaged. DR - 60 was analysed eight times, in order to estimate the precision of the method. The standard deviation of the results from the precision run was 0.47%, while the coefficient of variation was 3.80%.

The accuracy of the method was tested by analysing U.S.B.S. rock standards 88a and 1b. The results are presented in Table 8, along with the literature values. The observed results agree well with the literature values.

(h) F Determinations.

Fluorine analyses were carried out by the Phosphate Development Corporation using a fluoride specific ion electrode technique. The instrument used was an Orion Research Ionalyzer Model 801/Digital, standardized against sodium fluoride.

The majority of the samples were analysed once only, while DR - 43 (NI), DR - 4 (NIII) and DR - 10 (CI) were analysed in duplicate. DR - 4 (CI) was analysed six times in order to estimate the precision of the method. The standard deviation calculated from this precision run was 0.035% while the coefficient of variation was 2.0%. The accuracy of the method was checked by the inclusion of two samples of U.S.B.S. rock standard 56b (recommended value = 3.4% F). The F value determined for this standard was 2.9% F (i.e. distinctly low). It was considered that while the precision of the method was reasonable, the accuracy was at fault and therefore all data were recalculated so as to give a 3.4% F value for U.S.B.S. 56b.

A phosphorite powder sample DR - 4 (CI) was fused with lithium borate flux (as per (c) above), the resulting mixture was then analysed for F and the results showed that no F had been lost during the fusion process. The L.O.F. values presented in Table III are therefore considered to exclude fluorine. The totals presented in Table III therefore include F as a separate species, in contrast to the CO_2 values which form the main part of fusion "loss".

TABLE VIII.

CO_2 ANALYSIS OF U.S.B.S. ROCK STANDARDS 1b and 88A.

1b.

Recommended Value = 40.4% CO_2

This Work : (i) 40.5% CO_2

(ii) 40.9% CO_2

88A.

Recommended Value = 46.6% CO_2

This Work : (i) 46.8% CO_2

(ii) 46.0% CO_2

APPENDIX B.

PHOSPHORITE DREDGE HAULS.

Listed below are the dredge stations from which phosphorite nodules have been recovered, along with their latitude and longitude, the depth of recovery and the class(es) assigned to the nodules from each station. The listings also indicate whether nodules from a given class have been thin sectioned and/or geochemically analysed.

1. SANCOR Samples.

Dredge No's.	Depth.	Class.	Kg.	Thin Section.	Analyses.	Lat.S.	Long.S.
DR - 4	440	NIII; CI	100	NIII; CI	NIII; CI	34°43'	18°10'
5	333	NI, NIII; CI	22	NI	NI	34 35	18 05
6	1035	NIII	1			34 26	17 38
10	315	NI; CI	27	NI; CI	CI	35 30	19 00
14	293	NI; CI	11	NI; CI	CI	35 53	19 37
39	73	NI, III	1	NIII		35 03	20 51
40	80	NI, III	1			35 10	20 54
42	84	NI	1			35 40	20 56
43	120	NI, III	93	NI, III	NI, III	35 50	20 56
44	128	NI, III	16	NI, III		35 56	20 57
45	135	NI, III	3			35 56	20 10
46	93	NI	1			35 11	21 14
57	128	NI; CI	64	NI; CI		35 32	21 30
58	140	NI; CI	66	CI	CI	35 40	21 30
59	160	CI	1			35 48	21 31
60	170	NI; CI	10	NI; CI	CI	35 59	21 31
61	198	NII; CI	61	NII	NII	35 59	21 44
62	179	NI, II; CI, II	13	NII; CII		35 49	21 45
63	127	CI	1			35 12	21 46
64	116	NI	1			35 02	21 47
78	80	CI	32			34 17	22 50
80	100	CII	1			34 36	22 39
81	111	CI	8			34 46	22 38
83/ 791	197	NI; CII	12	CII		35 45	21 57

Dredge No's.	Depth.	Class.	Kg.	Thin Section.	Analyses.	Lat.S.	Long.S.
DR - 83/ 792	230	NII	1			35°51'	22°00'
84	210	NI, II; CII	14	NI, II		35 54	22 00
85	202	NI, II; CII	2			35 38	22 13
86	140	NI	9	NI		35 25	22 14
87	140	CII	32	CII		35 15	22 15
88	120	CI	1	CI		35 07	22 15
89	125	CII	33	CII	CII	35 19	22 13
90	170	CII	11			35 26	22 22
91	230	NII; CII	25	NII		35 37	22 22
92	1070	NII	24	NII		34 57	22 23
93	90	CI	1			34 22	22 48
94	113	NI; CI	100	CI	CI	34 46	22 47
95	115	CI	47			34 53	22 49
96	190	CI	12			35 04	22 54
97	265	NI; CI, II	19			35 12	22 48
98	370 - 470	NII; CI	100	NII; CI	NII	35 07	23 13
100	110	CI	2			34 42	22 30
102	130	CI	8			34 04	22 37
104	320	NII; CI, II	4			35 20	22 39
105	790	NII	5			35 30	22 36
109	112	CI	71	CI		34 52	23 03
110	645 - 728	NII	1			35 16	23 03
111	122	CI; NII	1			34 43	23 23
112	109	CII	32	CII		34 23	23 12
113	108	CI	1	CI		34 34	23 13
114	102	CI, II	8	CI		34 28	23 35
119	110	CI	1			34 22	23 47
120	108	CI	5	CI		34 32	23 48
121	139	CI	2	CI		34 44	23 37
122	120	CI	38	CI	CI	34 42	23 37
123	120	NI, III	4	NI, III		35 51	21 01
125	113	NI	16	NI		35 51	20 54
147	88	CI, II	30			34 15	22 49
148	89	CII	1			34 20	22 48

Dredge No's.	Depth.	Class.	Kg.	Thin Section.	Analyses.	Lat.S.	Long.S.
DR - 150	82	NIII	1			34°21'	22°24'
153	104	NIII; CII	1			34 19	23 25
154	112	CII	18	CII	CII	34 24	23 24
155	108	CII	18	CII	CII	34 27	23 00
156	110	CI	18			34 35	22 47
158	108	CI, II	95			34 30	22 57
160	122	CI	1			34 27	24 00
161	117	CI	73	CI		34 35	23 57
163	435	NII; CI	1	CI		34 56	23 59
164	355	NII; CI	9	NII; CI		34 55	23 11
165	128	NI; CI	1	CI		34 44	24 19
166	130	NI; CI	14	NI		34 30	24 22
167	118	CI	3			34 24	24 12
168	168	NIII; CI	1			34 14	24 12
171	122	CI	14			34 27	24 19
172	116	CI	10			34 34	24 12
175	112 - 130	CI	34			34 32	24 30
176	123	CI	36			34 27	24 24
177	120	CI	2			34 20	24 30
183	120	NI; CI, II	31	NI	NI	34 29	24 42
184	122	CI	1			34 38	24 42
186	120	NI,II,III; CI	26	NII	NII	34 27	24 51
194	115	NIII	16	NIII		34 16	25 09
195	75	NII	1			34 08	25 10
198	101	CII	1			34 12	23 31
199	99	NIII	1			34 16	23 21
202	119	CI	0.5			34 24	24 57
203	120	CI	6			34 38	24 08
206	134	CI	15			34 50	22 58
207	148	CI	6			34 52	22 54
209	340	CI; NIII	1			35 18	18 49
210	280	CI	0.2			35 06	18 43
211	720	NIII	1			35 10	18 34
213	335	NII, III	9			34 36	18 22
214	345	NIII; CI	100	NIII; CI		34 38	18 06
215	310	NIII; CI	9			34 32	18 10

Dredge No's.	Depth.	Class.	Kg.	Thin Section.	Analyses.	Lat.S.	Long.S.
DR - 216	293	NIII	14	NIII	NIII	34 27	18 13
217	120	NIII	1			34 19	18 18
218	260	NIII	1			34 20	18 07
219	305	CI	59	CI		34 21	17 59
220	310	NIII	1			34 18	17 53
222	240	NIII	1			34 08	17 57
225	127	CI	1			34 42	23 57
226	112	CI	44			34 31	24 02
227	118	CII	43			34 23	24 02
230	130	NIII; CI	5			34 39	24 15
231	116	CI	75			34 37	24 15
232	119	NIII; CI	20			34 36	24 14
233	122	CI, II	27			34 28	24 15
234	122	CII	4			34 23	24 14
235	118	CI, II	38			34 20	24 13
239	105	NIII	1			34 30	24 38
240	127	CII	1			34 27	24 39
241	109	NIII; CI, II	6			34 25	24 38
242	120	CII	14			34 17	24 50
243	118	NIII; CII	7			34 26	24 51
244	119	NIII	5			34 30	24 51
246	110	CII	30	CII	CII	34 12	25 15
247	120	CII	4			34 17	25 15
248	125	NIII; CI, II	65	NIII; CI, II	CI	34 24	25 14
250	420	CI, II	5			34 34	25 15

2. Gilchrist Samples.

GIL - 332	110	CI	1			34 15	25 51
674	187	NIII; CI	1			34 26	18 21
675	366	NIII; CI	7			34 13	17 46

3. Fisheries Samples.

A - 4034	128	NI	1			35 48	21 23
4027	135	NI, III	4			35 55	21 21

Dredge No's.	Depth.	Class.	Kg.	Thin Section.	Analyses	Lat.S.	Long.S.
A - 4099	154	NI, III	4			35°46'	20°12'
4100	165	NI	2			35 46	20 01
4103	238	NI	1			35 37	19 28

ACKNOWLEDGEMENTS.

This project was funded by the SANCOR Marine Geology Programme in the Department of Geology, U.C.T. I am grateful to Professor E.S.W. Simpson for providing the opportunity to undertake this study, and for his overall encouragement and support.

My supervisors, Dr. A.O. Fuller and Mr. J.P. Willis provided much essential guidance, and in particular I wish to thank the latter for his help in the geochemical studies undertaken and for the use of various computer programmes. During the absence of Dr. A.O. Fuller on sabbatical leave, Dr. C.P. Summerhayes, acting as an "unofficial supervisor" provided timely guidance and no small measure of both inspiration and constructive criticism in the preparation of the manuscript.

The Phosphate Development Corporation, Phalaborwa very kindly made available to me the analytical facilities in their chemical laboratories, including the x-ray fluorescence spectrometer used for the bulk of the analyses undertaken. They also very kindly paid for my travelling expenses to Phalaborwa, and allowed me to stay in their guest house while making the analyses. My thanks are also due to this corporation for undertaking the fluorine analyses for me.

Fruitful discussions were held at various times with Dr. R.V. Dingle and Messrs. R.A. Slater, R.I. Gentle, J. Rogers, G.F. Birch and W.G. Siesser, all of the Marine Geology Research Group, U.C.T.

I wish to thank Professor L.H. Ahrens for the use of various analytical facilities in the Department of Geochemistry, U.C.T. I also wish to acknowledge the time and help given to me by Drs. M.J. Orren and R.V. Danchin and Messrs. E.J.D. Kable, P.K. Hofmeyr and T.S. McCarthy with regard to various geochemical and mineralogical aspects of this study.

Messrs. N.D. Bang and P. Zoutendyk provided me with relevant oceanographis data and the latter helped me as well with the photographic aspects of this study. My thanks are also due to Mr. A.M. Shipley who helped me in the writing of a number of computer programmes.

I wish to thank the officers and crew of the R.V. Thomas B. Davie for their co-operation and goodwill, which played an important part in the success of the sample collection programme.

My thanks are due to Miss I. Milligan who drew many of the diagrams and maps, and finally I am indebted to Mrs. Frost and Mrs. G. Pomplun who so willingly gave of their time to type the manuscript.

REFERENCES.

Altschuler, Z.S., Cisney, E.A., and Barlow, I.H., 1953. X-ray evidence of the nature of carbonate apatite. Am. Miner., 38, 328 (abstract).

Altschuler, Z.S., Clarke, R.S., and Young, E.J., 1958. Geochemistry of uranium in apatite and phosphorite. U.S. Geol. Survey Prof. Paper 314-D, 45 - 90.

Ames, L.L., 1959. The genesis of carbonate apatites. Econ. Geol., 54, 829 - 841.

Bang, N.D., 1970. Dynamic interpretations of a detailed surface temperature chart of the Agulhas Current retroflexion and fragmentation area. S. Afr. Geogr. Jour., 52, 67 - 76.

Bang, N.D., 1971. The southern Benguela Current region in February, 1966 : : Part II. Bathythermography and air-sea interactions. Deep-Sea Research, 1971, 18, 209 - 224.

Baturin, G.N., 1969. Authigenic phosphate concretions in recent sediments of the Southwest Africa shelf. Doklady Akad. Nauk SSSR, 189, 227 - 230.

Birch, G.F., (in prep.). The nature and distribution of glauconite on the Agulhas Bank, South Africa. M.Sc. thesis, in preparation, Univ. of Cape Town.

Birks, L.S., 1963. Electron Probe Microanalysis. Interscience.

Brongersma-Sanders, M., 1957. Mass mortality in the sea. In Hedgpeth, J.W. (Ed.), Treatise on Marine Ecology and Palaeoecology, Vol. 1, Ecology. Geol. Soc. Am. Mem. 67, 941 - 1010.

Brown, P.M., 1958. The relation of phosphorites to ground water in Beaufort County, North Carolina. Econ. Geol. 53, 85 - 101.

Bushinsky, G.I., 1935. Structure and origin of the phosphorites of the U.S.S.R. J. Sediment. Pet., 5, 81 - 92.

Bushinsky, G.I., 1964. On shallow water origin of phosphorite sediments. In van Straaten, L., (Edit.), Deltaic and Shallow Marine Deposits, Developments in Sedimentology, Vol. 1. Elsevier Amsterdam. 62 - 70.

Bushinsky, G.I., 1969. Old phosphorites of Asia and their genesis. Isr. Progr. Sci. Trans. Jerusalem. 266 pp.

Carlström, D., 1955. X-ray crystallographic studies on apatites and calcified strustures. Acta Radiol., Supplement 121, 59 pp.

Cayeaux, L., 1934. The phosphatic nodules of the Agulhas Bank : Ann. S. Afr. Mus., 31, 105 - 136.

Collet, L.W., 1905. Les concrétions phosphatées de l'Agulhas-Bank. Proc. Roy. Soc. Edin., 25, 862 - 893.

D'anglejan, B.F., 1967. Origin of marine phosphorites off Baja, California, Mexico. Marine Geol., 5, 15 - 44.

Deer, W.A., Howie, R.A., and Zussman, J., 1962. Rock-forming Minerals, V.5. London, Longmans, Green, and Co., Ltd., 371 pp.

Dietz, R.S., Emery, K.O. and Shepard, F.P., 1942. Phosphorite deposits on the sea floor off southern California : Geol. Soc. Amer. Bull., 53, 815 - 848.

Dingle, R.V., SANCOR 1970. Bathymetry. In, SANCOR Marine Geology Programme, Technical Report No. 2, Department of Geology, Univ. of Cape Town.

Dingle, R.V., 1970. Preliminary geological map of part of the eastern Agulhas Bank, South African continental margin. Proc. geol. Soc. Lond., 1663, 137 - 142.

Dingle, R.V., Gerrard, I., Gentle, R.I., and Simpson, E.S.W., (in press). The continental shelf between Cape Town and Cape Agulhas. Proc. SCOR/IUGS Symposium, Cambridge, 1970. H. M. S. O.

Dunbar, C.O., and Rodgers, J., 1957. Principles of Stratigraphy. John Wiley and Sons, New York.

Dunham, R.J., 1962. Classification of carbonate rocks according to depositional texture. In Ham, W.E. (Ed.), Classification of Carbonate rocks. Amer. Assoc. Petrol. Geol. Mem. 1., 108 - 121.

Dzulynski, S., Ksiazkiewicz, M., and Kuenen, Ph. H., 1959. Turbidites in flysch of the Polish Carpathian Mountains. Bull. Geol. Soc. Am. 70, 1089 - 118.

Emery, K.O., 1960. The sea off southern California. Wiley, New York, N.Y., 366 pp.

Fleischer, M., 1969. U.S. Geol. Survey Standards-I additional data on rocks G-1 and W-1, 1965 - 1967. Geochim. et Cosmochim. Acta., 33, 65 - 79.

Flint, R.F., Sanders, J.E., and Rodgers, J., 1960. Diamictite : a substitute term symmictite. Bull. Geol. Soc. Am., 71, 1809.

Folk, R.L., 1951. A comparison chart for visual percentage estimation. J. Sediment. Pet., 21, 32 - 33.

Folk, R.L., 1962. Spectral subdivision of limestone types. In Ham, W.E. (Ed.), Classification of Carbonate Rocks. Amer. Ass. Petrol. Geol. Mem. 1, 62 - 84.

Folk, R.L., 1965. Some aspects of recrystallization in ancient limestones. In Dolomitization and Limestone Diagenesis. Soc. Econ. Paleont. and Miner. Spec. Pub. 13, 14 - 48.

Friedman, G.M., 1964. Early diagenesis and lithification in carbonate sediments. J. Sediment. Petrol., 34, 777 - 813.

Gruner, J.W. and McConnell, D., 1937. The problem of carbonate-apatites : The structure of francolite. Zietschr. Kristallographie, 97, 208 - 215.

Guilcher, A., 1969. Pleistocene and Holocene sea level changes. Earth-Science Revs., 5, 69 - 97.

Gulbrandsen, R.A., 1966. Chemical composition of phosphorites of the Phosphoria Formation. Geochim. et Cosmochim. Acta., 30, 769 - 778.

Gulbrandsen, R.A., 1969. Physical and chemical factors in the formation of marine apatite : Econ. Geol., 64, 4, 365 - 382.

Gulbrandsen, R.A., 1970. Relation of carbon dioxide content of apatite of the Phosphoria Formation to regional facies. U.S. Geol. Survey Prof. Paper 700-B, B9 - B13.

Gulbrandsen, R.A., Kramer, J.R., Beatty, L.B., and Mays, R.E., 1966. Carbonate bearing apatite from Faraday Township, Ontario, Canada. Am. Miner., 51, 819 - 824.

Hamilton, E.L., 1956. Sunken Islands of the Mid-Pacific Mountains. Mem. geol. Soc. Am., 64, 97 pp.

Haughton, S.H., 1956. Phosphatic-glauconitic deposits off the West Coast of South Africa. Ann. S. Afr. Mus., 42, 329 - 334.

Hülseman, J., 1966. On the routine analysis of carbonates in unconsolidated sediments. J. Sediment Petrol., 36, 622 - 625.

Kazakov, A.V., 1937. The phosphorite facies and the genesis of phosphorites. In Geological investigations of agricultural ores. Leningrad, Sci. Inst. Fertilizers and Insecto-Fungicides Trans., 142, 95 - 113.

Kerr, P.F., 1959. Optical mineralogy. 3rd Edit. McGraw-Hill, New York, 442 pp.

Kolodny, Y., and Kaplan, I.R., 1970. Uranium isotopes in sea-floor phosphorites. Geochim. Cosmochim. Acta., 34, 3 - 24.

Kramer, J.R., 1966. Phosphorites : mineralogy, seawater chemistry and mineral formation. Abstracts, 2nd Int. Oceanogr. Congress, Moscow, 205.

Krumbein, W.C., and Garrels, R.M., 1952. Origin and classification of chemical sediments in terms of pH and oxidation-reduction potentials. J. Geol., 60, 1 - 33.

McClellan, G.H., and Lehr, J.R., 1969. Crystal-chemical investigation of natural apatites. Am. Miner., 54, 1374 - 1391.

McConnell, D., 1938. A structural investigation of the isomorphism of the apatite group. Am. Miner., 23, 1 - 19.

McConnell, D., 1952. The problem of the carbonate apatites. IV. Structural substitutions involving CO_3 and OH. Bull. Soc. Franc. Mineralogie Crist., 75, 428 - 445.

McConnell, D., 1960. The crystal chemistry of dahllite. Am. Miner., 45, 209 - 216.

McKelvey, V.E., Swanson, R.W., and Sheldon, R.P., 1953. The Permian phosphorite deposits of western United States. 19th Internat. Geol. Cong., Algiers, 1952, Comptes Rendus. sec.11, pt 11, 45 - 64.

Murray, J., and Renard, A.F., 1891. Deep-sea Deposits. Rep. Sci. Res. HMS Challenger, 1873 - 1876, H.M.S.O. London. 525 pp.

Neuman, W.F., and Neuman, M.W., 1953. The nature of the mineral phase of bone. Chem. Revs., 53, 1 - 45.

Norrish, K., and Hutton, J.T., 1969. An accurate x-ray spectrographic method for the analysis of a wide range of geological samples. Geochim. et Cosmochim. Acta, 33, 431 - 453.

Pantin, H.M., 1967. The origin of water-borne diamictons and their relation to turbidites. N.Z. J. Mar. Freshwat. Res., 1., 118 - 38.

Pettijohn, F.J., 1957. Sedimentary Rocks (2nd Edit.). Harper and Row. New York.

Pevear, D.R., 1966. The estuarine formation of United States Atlantic Coastal Plain phosphorite. Econ. Geol., 61, 251 - 256.

Pevear, D.R., 1967. Shallow water phosphorites. Econ. Geol., 62, 562 - 567.

Rhoads, D.C., 1967. Biogenic reworking of intertidal and subtidal sediments in Barnstable Harbour and Buzzards Bay, Massachusetts. J. Geol., 75, 461 - 466.

Rock Color Chart Committee, 1951. E.N. Goddard, Chairman, Rock Color Chart. National Research Council, Washington, D.C.

Rogers, A.F., and Kerr, P.F., 1942. Optical Mineralogy. 2nd Edit., McGraw-Hill, New York, 390 pp.

Rogers, J., 1971. Sedimentology of Quaternary Deposits on the Agulhas Bank. Unpubl. M.Sc. thesis, Univ. of Cape Town.

Rooney, T.P., and Kerr, P.F., 1967. Mineralogic nature and origin of phosphorite, Beaufort County, North Carolina. Geol. Soc. Am. Bull., 78, 731 - 748.

Roubault, M., De La Roche, H., and Govindaraju, K., 1968. Report 1966 - 1968 on geochemical standards GR, GA, GH, BR, Fe-Mica, and Mg-Mica. Sci. de la Terre, 8, 379 - 404.

Shannon, L.V., 1966. Hydrology of the south and west coasts of South Africa. Investl. Rep. Div. Sea Fish. S. Afr., 58, 1 - 62.

Shapiro, L., and Brannock, W.W., 1962. Rapid analysis of silicate, carbonate and phosphate rocks. Bull. U.S. Geol. Survey, 1144-A, A1 - A56.

Sheldon, R.P., 1963. Physical stratigraphy and mineral resources of Permian rocks in western Wyoming. U.S. Geol. Surv. Prof. Paper 313-B, 1 - 273.

Siesser, W.G., 1970. Carbonate components and Mineralogy of the South African coastal limestones and limestones of the Agulhas Bank. Trans. Geol. Soc. S. Afr., 73, 49 - 63.

Siesser, W.G. (in prep.). Petrology of South African coastal and offshore carbonate rocks and sediments. Ph.D. thesis, in preparation, Univ. of Cape Town.

Simpson, D.R., 1964. The nature of alkali carbonate apatite. Am. Miner., 49, 363 - 376.

Sine, N.M., Taylor, W.O., Webber, G.R., and Lewis, C.L., 1969. Third report of analytical data for CAAS sulphide ore and syenite rock standards. Geochim. et Cosmochim. Acta, 33, 121 - 131.

Smith, P.J.R., 1971. Langebaan phosphate deposits. Unpubl. B.Sc. (Hons.) thesis, Univ. of Cape Town.

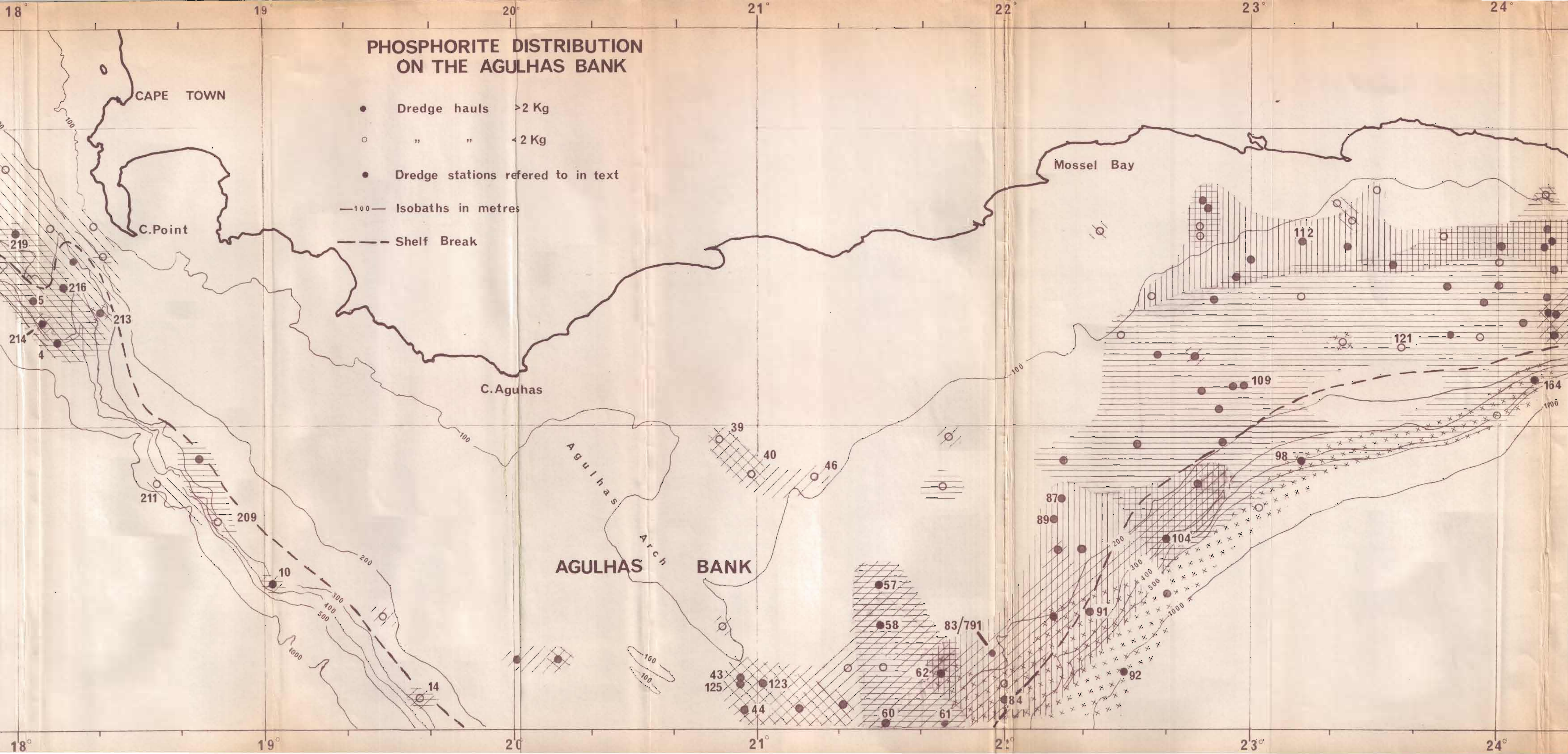
Summerhayes, C.P., 1967. Marine environments of economic mineral deposition around New Zealand : A review. N.Z. J. Mar. Freshwat. Res., 1, 267 - 282.

Summerhayes, C.P., 1970. Phosphatic deposits on the North West African continental shelf and slope. Unpubl. Ph.D. thesis, Univ. of London.

Tooms, J.S., Summerhayes, C.P., and Cronan, D.S., 1969. Geochemistry of marine phosphate and manganese deposits. Oceanogr. Mar. Biol. Ann. Rev., 7, 49 - 100.

Winston, J.E., and Anderson, F.F., 1971. Bioturbation of sediments in a northern temperate estuary. Mar. Geol., 10, 39 - 49.

Zoutendyk, P., 1970. Zooplankton density in the south western Indian Ocean. In Symposium on Oceanography in South Africa, 1970. C.S.I.R. South Africa.



PHOSPHORITE DISTRIBUTION ON THE AGULHAS BANK