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ABSTRACT

A suite of phosphorites ranging from Tertiary to Precambrian in age has been examined for organic content. The average organic carbon value of the phosphorites is intermediate between that of shales and carbonates. They differ from shales by having a larger proportion of organic matter which is soluble in organic solvents, a higher asphalt content, and a more complex saturated hydrocarbon fraction. The n-paraffin distributions indicate that organic matter in phosphorites is primarily algal in origin. The insoluble organic matter (kerogen) isolated from phosphorites is rich in nitrogen, sulphur, and oxygen compared with that from other sediments, and reflects the highly euxinic nature of the phosphorite-forming environment. The composition of the associated kerogens supports the contention that oils with high nitrogen contents are derived from phosphatic source beds. The high proportion of soluble organic matter in unaltered phosphorites suggests that oils derived from phosphatic source beds are capable of migration at an early stage of diagenesis.

INTRODUCTION

Phosphorites are phosphate-rich sedimentary rocks, generally of marine origin. They range in age from Precambrian to Holocene and have a wide geographic distribution. Although phosphorites are comparatively rare, in some sedimentary sequences they form extensive deposits. Because of their geographic proximity to known oil fields and their high content of organic matter, some of these deposits are considered to be the probable source of crude oil (McKelvey, 1959). However, few analyses of the organic material in phosphorites are available to substantiate the nature of the phosphorite-petroleum association.

A genetic association of phosphorites and petroleum has been suggested by Brongersma-Sanders (1948) who considered that abnormally high organic productivity in upwelling areas was responsible for the formation of both. For some time there was doubt that phosphorites are in fact forming at the present day (Kolodny, 1969). Lately, uranium-series dating by Baturin *et al.* (1972) and Veeh *et al.* (1973) has shown that phosphorites are being deposited in regions of upwelling on the continental shelf in the Walvis Bay region off Southwest Africa, and off the Peruvian coast of South America. The continental shelf may not be the only region where phosphorites are forming. Evidence from ancient phosphorites has been taken to indicate that they may also be deposited under estuarine conditions (Bushinski, 1964; Pevear, 1966).

The present study was undertaken in order to clarify the nature of the phosphorite/petroleum association, and the depositional environments in which phosphorites occur.

SAMPLES

Twenty samples (Table 1) were analysed for their organic content; of these, 18 were phosphorites and two (samples 9 and 11) were from phosphatic sequences but were themselves non-phosphatic. The samples were selected to give a wide geographic and chronostratigraphic distribution. There is however, an obvious sampling bias in favour of the Phosphoria Formation, partly because of the author's particular interest in that formation, but also because it is commonly regarded as one of the best examples of a phosphorite source for petroleum. Most samples were collected by the authors in the field, but the Karatau sample was kindly supplied by G.I. Bushinski of the Academy of Sciences of the USSR and two others (Tasmanian Shelf and Algeria) were obtained from the Bureau of Mineral Resources collection. In these three cases field associations are not fully known to us.

Most of the samples are black fine-grained pelletal phosphorites; fossil fragments are abundant in some, particularly in the samples from the Fish Scale Marker Bed of the Phosphoria Formation. Several phosphorites are coarse-grained with nodules up to 20 mm in diameter. One sample (number 20) is a non-pelletal phosphorite. The ages of the various phosphorites are given in Table 1. Although the Florida samples were collected from the Pliocene Bone Valley Formation these nodules are in fact believed to have been derived from the underlying Miocene Hawthorn Formation. Consequently the age of these phosphorites (samples 3 and 4) is given as Miocene. The estimates of a maximum depth of burial of the phosphorites (at any time during their post-depositional history) are based on the authors' evaluation of the sedimentary and tectonic history of the basin in which the phosphorite is located. Such an exercise is fraught with difficulties in a complex structural area such as the Idaho Thrust Belt. The values were arrived at without any foreknowledge of the diagenetic characteristics of the organic fraction. The degree of tectonic disturbance could not reasonably be quantified. 'Undisturbed' implies no significant folding or faulting. Sediments which have been gently folded or subjected to minor faulting are termed 'slightly disturbed'. Sediments from regions which have been severely folded, and overthrust, e.g. those from Idaho-Wyoming and the Lesser Karatau, are termed 'strongly disturbed'. In general the older phosphorites tend to be more tectonically disturbed than the younger ones. A notable exception to this is the Beetle Creek Formation phosphorite of Queensland which, despite its Cambrian age, has been subjected to only minor folding and faulting.

These phosphorites probably did not accumulate in the same depositional environment. They fall into two major groups, commonly termed the geosynclinal or west-coast type and the platform or east-coast type (Delegation of the Soviet Union, 1968; Collette, 1968). The geosynclinal phosphorites, of which the Phosphoria and Karatau deposits are examples, are generally considered to have originated in moderately deep water (depths of hundreds of metres) and are believed to have a clear association with upwelling (Sheldon, 1963). The platform deposits (most of the remaining samples) are regarded as shallower, nearer-shore deposits that formed in some instances in localized basins, embayments, and estuaries (the Moroccan, Algerian, and possibly the Queensland phosphorites) or alternatively in broad shallow intracratonic basins (the Ordovician phosphorites of central Australia). Therefore the samples may be somewhat heterogeneous with respect to their inferred depositional environments although all may reasonably be assumed, because of their fossils and the associated sedimentary assemblage, to have been deposited under varying types of marine conditions ranging from outer shelf to paralic. In lithology they are a homogeneous group (excepting samples 9 and 11) as all are phosphorites in which the dominant rock-forming mineral is collophane (carbonate-fluorapatite).

EXPERIMENTAL

All solvents were distilled through a Podbielniak fractionating column prior to use. The general procedures to avoid contamination during the course of analysis were essentially those outlined by Eglinton et al. (1966). After removal of the outside surface of the rocks with a diamond saw, the samples were crushed in a disc mill to less than 200 mesh (.074 mm) size. The powdered samples were extracted for three days with benzene and methanol (1:1) in Soxhlet apparatus. Evaporation of the solvent yielded the crude extract as a brown gum, this was dissolved in the minimum amount of chloroform and the asphaltenes were then precipitated by adding petroleum ether. The material soluble in petroleum ether was chromatographed on alumina (Grade 1) and eluted successively with petroleum ether (40°-60°C), benzene, and methanol to yield the Saturate, Aromatic, and ONS (oxygen, nitrogen and sulphur compounds) fractions respectively.

Gas chromatography was carried out using a 50 m x 0.25 mm ID capillary column coated with Apiezon L. and nitrogen as a carrier gas. The column was temperature programmed from 100°C to 250°C at 4°C per minute and held at 250°C until all peaks had been eluted. Normal alkanes, pristane, and phytane were identified by co-injection of authentic standards and by comparison of retention times with published data.

Kerogen concentrates were prepared from the solvent-extracted sediments by a combination of chemical and physical methods. The sediments were treated with hydrochloric acid to remove carbonates. Silicates were dissolved by repeated digestion with concentrated hydrofluoric and hydrochloric acid (5:1) mixture. The residue was washed repeatedly with distilled water until neutral. Pyrite was removed by treatment with sodium borohydride as follows: the residue was slurried with ca 50 ml of distilled water and sodium borohydride (0.5 to 1.5 g) was added. The mixture was placed on a steam bath and stirred occasionally until effervescene ceased. On cooling, dilute hydrochloric acid was added to dissolve the reduced sulphide. This procedure was then repeated. This treatment also released pyrite grains within the kerogen matrix; a separation was achieved by slurrying with distilled water and carefully decanting the kerogen in suspension. Microscopic examination of the kerogen concentrates showed that heavy-mineral grains, e.g. rutile and anatase, were commonly present, coated with organic material. In such cases a further separation was attempted by dispersing the concentrate in chloroform, immersing it briefly in an ultrasonic bath, and decanting. A final treatment with sodium borohydride was often required to complete the removal of pyrite.

X-ray diffraction data were obtained as follows. Kerogen (ca 2-3 mg) was spread as a slurry with ethanol on a glass disc and the solvent allowed to evaporate. The instrument used was a Phillips Recording Diffractometer and each sample (not spun) was analysed under the following instrument conditions: CuK & radiation; Ni filter; 40kV/24 mA 1° beam silts; goniometer scan rate 1° 2/min, range 5-32° 2; chart speed 10 mm/min; EHT on flow counter 1680 volts; time constant 4sec; nominal attenuation 4 x 10^2. Elemental analysis of kerogen concentrates was carried out by the CSIRO Microanalytical Service, Melbourne.

After digestion in hydrochloric acid, the organic carbon contents of the sediments (carbonate-free) were determined using an Aminco C-H Analyser. These results were then corrected to obtain the organic carbon content of the whole rock.

Phosphate contents of the sediments were determined colorimetrically by the Australian Mineral Development Laboratories, Adelaide.

RESULTS

Organic carbon

All the phosphorite samples had organic carbon values below 2% (Table 2). In contrast a calcareous mudstone from the Phosphoria Formation (sample 11) containing only 1.7% P_2O_5 had an organic carbon content of 10.7%. The average organic carbon value for the phosphorites is 0.62%. Clearly then the phosphorites examined in this study are not exceptionally rich in organic carbon by comparison with shales which average 0.99% organic carbon or with carbonates (average of 0.33% organic carbon), (Hunt, 1972).

Extractable organic matter

The quantity of soluble organic matter in phosphorites ranges from 22 to 4372 ppm (Table 2) and in several samples forms up to half the total organic carbon. In samples 1 to 6, 17, and 18 (Tasmania, N. Carolina, Algeria, Morocco, Florida, Stairway, and Beetle Creek) the saturated hydrocarbons form less than 5% of the total extract. The remainder of the extract is composed of aromatic and asphaltic substances. The yield of organic extract from the Phosphoria Formation samples (8-16) is erratic, but the proportion of saturated hydrocarbons in the total extract is very high (20-80%). The Karatau and Areyonga samples (19, 20) also have a high proportion of saturated hydrocarbons in the total extract (35%). The yield of saturated hydrocarbons was insufficient to allow separation of the normal alkanes. Gas chromatography of the saturated hydrocarbons shows that they are an extremely complex mixture (Fig. 1). Normal alkane distributions mostly show no odd-over-even predominance (Fig. 2) and the distribution maxima fall in the range n-C_{17} to n-C_{22}. Exceptions are sample 15 from the Phosphoria Formation, in which the n-C_{29} and n-C_{27} alkanes are dominant, and the N. Carolina sample, in which the n-C_{23} alkane is very prominent. A slight predominance of the n-C_{22} alkane occurs in the Moroccan,Phosphoria (samples 9 and 15), Beetle Creek, Stairway, and Areyonga samples. Pristane and phytane peaks occur in many of the chromatograms (Fig. 1) but there is no predominance of pristane over phytane.

Kerogen

It is practically impossible to obtain kerogen concentrates entirely free of ash content (Table 3). The main contaminants in the present samples are heavy minerals such as rutile and anatase which are resistant to treatment with hydrofluoric acid. The sulphur values obtained in this study are very high (up to 16.3%) and the possibility that the sulphur is due to contamination must be considered, but the following reasons suggest that most of the sulphur is indigenous to the kerogen structure.

1. Oxidizing agents, e.g. nitric acid, that might result in the formation of free sulphur were not used.
2. There is no relation between sulphur content and ash content.
3. All kerogen concentrates were monitored by X-ray diffraction, and traces of pyrite were found only in one sample from the Phosphoria (number 13), and in the Stairway and Beetle Creek samples.
4. Organic solvents were used during the final stages of the kerogen isolation procedure so that any free sulphur created during the extraction would be removed.
5. Similar procedures, used in the isolation of kerogens from a suite of Cambrian and Precambrian samples (McKirdy and Powell, 1974), gave lower sulphur values.

Thus high sulphur values seem to be a characteristic feature of the kerogen isolated from phosphorites, with the exception of the Mona Vale sample (No. 7) which has a sulphur content of only 0.8%. The nitrogen values range up to 2.9% and like the sulphur values are considered to be representative of the kerogen. The younger samples tend to have a higher ratio of atomic hydrogen to carbon (1.19 - 1.46) than the older ones (0.51 - 0.78) with the exception of the Beetle Creek sample (1.13). X-ray diffraction analysis of kerogen concentrates shows a tendency for incipient graphite formation in certain of the older samples, namely Phosphoria Formation and Mona Vale (Fig. 3). The younger samples show no such tendency.

DISCUSSION

Diagenetic effects

The organic contents of sediments from widely separated locations are likely to have reached different stages of diagenetic maturation. It is important to assess the effects of these differences in diagenetic history before considering possible variations in the organic matter due to environment of deposition. Organic matter in sediments changes composition in a regular fashion during diagenesis (Philippi, 1965; Tissot et al. 1971). There appears to be an increase in the yield of extractable organic matter per unit weight of organic carbon and an increase in the proportion of saturated hydrocarbons with increasing depth of burial. The major change in the kerogen is a decrease in the ratio of elemental hydrogen to carbon and a decrease in the content of hetero-atoms. The degree of diagenesis is related to depth of burial and geothermal gradient, and to a lesser extent to age.

It can be seen from Table 2 that there is no clear relation between extract yield (in milligrams per gram of organic carbon) and age. However, the younger samples (Tertiary) have a very low proportion of saturated hydrocarbons and higher ratios of atomic hydrogen to carbon (H/C) in the kerogen (Table 3). The older samples have a high proportion of saturated hydrocarbons and low atomic H/C ratios, with the exception of the Beetle Creek sample. A clear diagenetic trend can be seen if the atomic H/C ratio of the kerogen is plotted against the estimated maximum depth of burial of the formations samples (Fig. 4A). The yield of saturated hydrocarbons with depth shows a similar diagenetic sequence (Fig. 4B). The Tertiary and Beetle Creek samples are the least altered, followed by the Stairway and Mona Vale samples. The

Phosphoria, Karatau, and Areyonga samples are the most altered. They have similar atomic H/C ratios but vary in the in yield of saturated hydrocarbons.

The XRD patterns (Fig. 3) show that the decrease in atomic H/C ratio of kerogen is accompanied by progressive graphitization of its structure. From a diffuse peak of low intensity (e.g. Morocco and Beetle Creek) the profile of the d_{002} reflection sharpens in the Mona Vale and Phosphoria samples. The increase in peak sharpness, together with its gradual shift in position to a higher 2θ value, represents an increase in the ordering or crystallinity of the incipient graphite lattice (Landis, 1971).

Comparison with other rock types

The striking feature of phosphorites is not in the abundance of organic carbon but the extremely high proportion of organic matter soluble in organic solvents in those samples which have undergone little diagenesis. Nearly all the soluble material is asphaltic. This is shown in Figure 5A where the total extract is plotted against the proportion of saturated hydrocarbons in the total extract. This trend contrasts sharply with that for shales, in which the proportion of soluble organic matter is considerably lower (Fig. 5B). The precise pathway in phosphorites is not clear. There appears to be a loss of asphaltic materials but no direct corresponding increase in the proportion of saturated hydrocarbons.

As diagenesis proceeds further, both the yield of extract per gram of organic carbon and the proportion of saturated hydrocarbons in the total extract increase. This trend is similar to that in shales. The samples from the Phosphoria Formation show an erratic yield of extract and hydrocarbons. This may be the result of migration of hydrocarbons since the Phosphoria Formation is thought to be the source for certain Wyoming oils (Barbat, 1967; Stone, 1967).

The phosphorites resemble carbonates in the proportion of organic matter which is soluble in organic solvents (Gehman, 1961). This relation is particularly well shown in Table 4 where the yield of organic extract per gram of organic carbon is tabulated against the percentage of acid-insoluble residue in a suite of carbonate rocks. Clearly there is a similarity in the conditions leading to the formation and preservation of organic matter in some carbonates and phosphorites.

Gas chromatography of the saturate fractions (Fig. 1) shows that they are complex and contain a high proportion of naphthenic components. The low yield of saturates and the complexity of the mixtures precluded the separation of normal and branched-cyclic components. Most of the n-alkane distributions (Fig. 2) reach a maximum in the range n-C_{16} to n-C_{22}, which is consistent with a derivation from micro-organisms (Powell and McKirdy, 1973). The absence of a pronounced odd-over-even predominance in the range n-C_{23} to n-C_{30} in most of the n-alkane distributions indicates that the debris of higher plants has not contributed to the parent organic matter. Exceptions are the North Carolina phosphorites, where n-alkanes derived from land plants (range n-C_{23} - n-C_{30} with a pronounced odd-over-even predominance) dominate the distribution, and a single sample from the Phosphoria Formation, where there has also been some contribution from land plants (Fig. 2). Pevear (1966) has suggested that North Carolina phosphorites were deposited in an estuarine environment whereas Gibson (1967) considers that they were deposited in cool temperate waters in a coastal embayment with a water depth of 100-200 metres. Our evidence suggests that the depositional environment was sufficiently close to shore for land-derived plant material to make an important contribution to the organic matter in the North Carolina deposits. A subsidiary maximum at n-C_{23} in the Algerian n-alkane distribution suggests that minor debris of higher plants may have contributed to the source organic matter, but there is no clearly defined odd-over-even predominance.

The n-C_{22} alkane is a prominent constituent in the Moroccan, Phosphoria (samples 9 and 15), Beetle Creek, Stairway, and Areyonga samples. This feature has been reported previously in both ancient (Schenk, 1969; Powell and McKirdy, 1973) and recent sediments (Palacas et al. 1972). The probable source is polyunsaturated C_{22} fatty acids found in modern phytoplankton and zooplankton (Ackman et al., 1968; Lee et al., 1971). Reduction of unsaturated to saturated fatty acids occurs readily in recent sediments (Rhead et al., 1971). Further reduction of the fatty acid to yield the corresponding paraffin is less likely to occur, although Blumer (1965) found that decarboxylation of modern pigments could not always account for the molecular structure of fossil porphyrins and suggested that reduction of carboxyl groups to methyl groups must have occurred. Similarly Welte and Ebhardt (1968) have reported a parallel distribution between the n-alkanes and n-fatty acids in recent sediments in the Persian Gulf, indicating that the paraffins may be formed by reduction of the corresponding acids.

The oxygen, nitrogen, and sulphur values of kerogens in phosphorite tend to be higher than those in other sediments (Figs. 6 and 7). In a plot of normalized C, H, and O values (Fig. 7) the Phosphoria kerogens fall outside the compositional field for kerogens as defined by McIver (1967). The oxygen content was determined by difference after the original C, H, N, and S values had been corrected for the ash content. Whilst this practice may lead to spurious values, particularly in those samples with a high ash content, it does not explain why the Phosphoria samples with a wide range of ash values (2.4% - 20.4%) are consistently high in oxygen. It is considered therefore that the calculated oxygen contents closely resemble the true values and that the compositional field for kerogens must be enlarged (Fig. 7) to incorporate the Phosphoria samples.

Although the nitrogen content decreases with diagenesis it is clear that phosphorite kerogens as a group tend to have higher nitrogen values than other types (Fig. 6). This and the high oxygen content indicate that during the early diagenesis of organic matter in a phosphorite-forming environment, proteins and carbohydrates are not eliminated to the same extent as in other depositional environments. It is of interest that Lindblom and Lupton (1961) reported that live bacteria could be found only within the top 1.5 metres of sediment in a carbonate-forming environment whereas in a deltaic environment live bacteria were found to a depth of 46 metres. Thus in some carbonates decay is effectively halted at an earlier stage of diagenesis than in shales, and this may lead to the retention of proteins and carbohydrates. The carbonate muds also had a high hydrogen sulphide content and an Eh value of -200 mV, which is the same value as has recently been recorded in modern phosphatic sediments forming near Walvis Bay (Romankevich and Baturin, 1972). In contrast, a positive Eh was found to a considerable depth in the deltaic muds investigated by Lindblom and Lupton (1961). A possible cause of the difference in bacterial activity between the two environments is that iron is associated with clays in the deltaic muds and may combine with hydrogen sulphide produced by sulphate-reducing bacteria to form iron sulphides. Carbonates on the other hand, have a relatively low iron content, and consequently free hydrogen sulphide may become the limiting factor to bacterial activity.

Nissenbaum and Kaplan (1972) have recently demonstrated that marine humic acids have consistently higher sulphur contents than humic acids formed on land, and suggested that the activities of sulphate-reducing bacteria may be the cause. It is possible therefore that sulphur derived from hydrogen sulphide may be incorporated into the kerogen matrix in sediments which have a low iron content. The kerogen from the Mona Vale phosphorite is interesting in this respect. The kerogen has a very low sulphur content (0.8%) and the host sediment has a high iron content (40% Fe_2O_3 compared with 1-2% in the other samples). The sediment also has a low sulphate value, which may indicate that the Mona Vale phosphorite was formed in a less saline environment than the other phosphorites. The generally high sulphur content of the phosphorite kerogens implies that they were formed in euxinic environments in which sulphate-reducing bacteria were active, but their high nitrogen and oxygen contents suggests that this activity ceased at an early stage on diagenesis.

On the plot of normalized C, H, and O values (Fig. 7) the phosphorite kerogens fall into two groups. The younger samples and the Beetle Creek kerogen are richer in hydrogen (above 6.75%) than the remainder (below 5%).

McIver (1967) has discussed the possible changes in the composition of kerogens which can occur as a result of diagenesis. The difference in composition between the two groups can be partly explained by the generation of hydrocarbons which depletes the kerogen in hydrogen. The variation in composition within the two groups, however, is largely in their oxygen content and this is more difficult to explain. In the case of the Florida samples weathering may have resulted in a higher oxygen content since these phosphorites are probably derived from older sediments. Other variations between the members of the younger group may be due to differences in source organic material and relative decay rates of the source organic detritus. Loss of carbon dioxide during the later stages of diagenesis may account for differences in composition of the older group of phosphorite kerogens.

Relevance to petroleum genesis

Numerous examples are known in which crude oil composition can be related to source environment(Neumann *et al.*, 1947; Hunt, 1953; Jones and Smith, 1965; Barbat, 1967; Evans *et al.*, 1971; Reed and Henderson, 1972). In general terms heavy oils (naphthenic to asphaltic) with a high sulphur content are associated with carbonate and evaporite sequences,whereas light oils (paraffinic and paraffinic-naphthenic) with a low sulphur content are associated with clastic sequences. Higher plants may be a source of waxy hydrocarbons (Hedberg, 1968; Brooks and Smith, 1969; Powell and McKirdy, 1974), but the wide variation of crude oil quality in marine sediments suggests that the physical, chemical, and biological conditions in the source environment may exert some control on crude oil composition. Barbat (1967) in particular has suggested that phosphorite source beds may give rise to petroleums of naphthenic to asphaltic composition with high nitrogen and sulphur content. The following chemical evidence supports Barbat's contention:

1. Kerogens isolated from phosphorites have high nitrogen and sulphur values compared with kerogens from other sediments
2. The yield of asphaltic substances per gram of organic carbon is higher in phosphorites than shales
3. The saturated hydrocarbons obtained from phosphorites are low in n-alkanes and comprise an extremely complex mixture of naphthenic components.

In a survey of over 2400 crude oil samples Smith (1968) found that 80% had nitrogen values below 0.15%. In this paper, therefore, it is oils with greater than 0.2% nitrogen that are considered to be high-nitrogen crudes. Examples of nitrogen-rich oils and their possible phosphatic source beds are listed in Table 5. Crudes from the Los Angeles Basin, California, are extremely rich in nitrogen. The source sediments of Mohnian age which underlie and occur between the productive zones are highly phosphatic and rich in organic matter (Barbat 1958, 1967).

Compelling geological and chemical evidence has been presented by several authors (e.g. Barbat, 1967; Sheldon, 1967; Stone, 1967) to show that most oils in Palaeozoic rocks in central Wyoming have been derived from the Phosphoria Formation to the west. The nitrogen content of these oils (averaging 0.24%) is lower than those from California (average of 0.43%).

Heavy oils from the BolivarCoast, Maracaibo Basin, in Venezuela also have a high nitrogen content. Although the precise origin of these particular oils is uncertain (Miller at al., 1958) the phosphatic La Luna Formation is known to be a source for petroleum in this area. It may also be a source for oils in Columbia.

The Golden Lane Fields in Mexico (Viniegra and Castillo-Tejero, 1970) also produce high nitrogen oils. No specific source rock has been cited in the literature, but it is significant that the underlying Jurassic sediments are phosphatic to the west of the Golden Lane Fields.

The nitrogen content of an oil is primarily related to the amount of asphalt present (Smith, 1968). Geochemical processes such as maturation, gas-deasphalting, and chromatographic fractionation during migration will tend to remove asphalt and to decrease the nitrogen content. Therefore whilst a high nitrogen content may indicate a phosphatic source, a low value does not eliminate the possibility. Hence phosphatic sediments may also be involved in petroleum generation in Kansas and Alaska (Dickerts, 1972).

Recent geochemical studies have emphasized the depth/temperature dependence of petroleum generation. One of the main objections to this hypothesis has been the lack of an adequate mechanism for primary migration of hydrocarbons from sediments at depths of several thousand metres. In the case of shales this objection has been overcome by demonstrating that the diagenetic transformation of montmorillonite to illite releases considerable volumes of water that may act as a driving force for migration (Burst, 1969; Perry and Hower, 1972). Movement of petroleum from source beds with a low clay content, e.g. carbonates, still constitutes a problem. In the case of carbonates it is thought that primary migration must occur early in their diagenetic history, but the lack of available hydrocarbons has always been a problem for this hypothesis.

Phosphorites and some carbonates differ from shales in that a larger proportion of their organic matter is soluble in organic solvents. At an early stage in the diagenesis of phosphorites the ratio of soluble organic matter to organic carbon is equivalent to the saturations (200 mg per gram of organic carbon) existing at depths of several thousand metres in shaley source rocks: the Algerian sample contains 540 mg per gram of organic carbon.

The clay mineral content of carbonates and phosphorites is generally low so that the absorptive capacity of the mineral matrix is also low compared with shales. There seems to be no barrier therefore to the migration from phosphorites of asphaltic substances and associated hydrocarbons at an early stage of diagenesis to yeild heavy oils of the type found in the Los Angeles Basin, western Wyoming, and elsewhere.

CONCLUSIONS

1. Phosphorites are not abnormally rich in organic matter; the average organic carbon value falls between those of shales and carbonates.
2. In contrast to shales a substantial proportion of the organic matter in phosphorites (and in carbonates) is soluble in organic solvents.
3. The proportion of asphaltic material in the extract is very high in those phosphorites which have undergone little diagenesis.
4. The organic matter of phosphorites, derived primarily from marine algae, accumulated in a euxinic environment. Sulphate-reducing bacteria were initially active but the nitrogen and oxygen values in the phosphorite-associated kerogens rule out extensive microbial decay. Only the North Carolina phosphate deposit was found to contain abundant organic detritus derived from land plants.

5. Analyses of phosphorite organic matter provide supporting evidence for the hypothesis that nitrogen-rich oils are formed from phosphate source beds.

6. The high proportion of extractable organic matter in unaltered phosphorites suggests that migration of heavy oil is possible at an early stage of diagenesis.

7. Several of the world's major oil fields are believed to have phosphatic source rocks.

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Table 1. Location, lithology and geological setting of samples

Sample	Location	Lithology	Age	Formation	Maximum depth of burial (metres)	Degree of Tectonic Disturbance
1	N.W. Tasmanian Shelf, Australia	calcareous phosphorite and phosphatic limestone	Miocene	un-named	10	undisturbed
2	North Carolina USA	pelletal phosphorite	Miocene	Pungo River Fm	100	undisturbed
3	Florida USA	pelletal phosphorite	Miocene	Bone Valley Fm	200	undisturbed
4	Florida USA	nodular phosphorite	Miocene	Bone Valley Fm	200	undisturbed
5	Algeria	pelletal phosphorite	U. Paleocene		200	slightly disturbed
6	Morocco	pelletal phosphorite	U. Cretaceous	Youssoufia deposit	200	slightly disturbed
7	Mona Vale N.S.W. Australia	phosphatic nodules	Triassic	Ashfield Shale	1500	moderately disturbed
8	Idaho USA	fossiliferous phosphorite	Permian	PHOSPHORIA FORMATION Fish Scale Marker Bed	4500	strongly disturbed
9	Idaho	siliceous limestone	"	Rex Chert	"	" "
10	Idaho	fossiliferous phosphorite	"	Fish Scale Marker Bed	"	" "
11	Idaho	calcareous mudstone	"	Meade Peak Member	"	" "
12	Idaho	pelletal phosphorite	"	Meade Peak Member	"	" "
13	Idaho	pelletal phosphorite	"	Meade Peak Member	"	" "
14	W. Wyoming	pelletal phosphorite	"	Meade Peak Member	"	" "
15	W. Wyoming	pelletal phosphorite	"	Meade Peak Member	"	" "
16	W. Wyoming	pelletal phosphorite	"	Meade Peak Member	"	" "
17	Northern Territory, Australia	nodular phosphorite	Ordovician	Stairway Sandstone	2500	moderately disturbed
18	Queensland, Australia	pelletal phosphorite	Cambrian	Beetle Creek Fm	750	slightly disturbed
19	Karatau, USSR	pelletal phosphorite	Cambrian	Phosphorite suite	3000+	strongly disturbed
20	Northern Territory, Australia	laminate phosphorite	Late Precambrian	Areyonga Fm	5750	strongly disturbed

TABLE 2. Organic carbon and extract data for phosphorite and associated samples

ample	P_2O_5 %	Org C %	Total extract ppm	Asphalt ppm	Saturates ppm	Aromatics ppm	ONS ppm	Saturates % of total extract	Extract mg per gram of Org C
1	10.0	0.16	709	614	2	3	78	0.3	443
2	15.7	1.14	1749	1110	2	2	250	0.1	153
3	29.9	0.17	637	477	18	18	126	3.0	374
4	30.4	0.23	1748	1205	34	34	176	2.0	760
5	29.0	0.55	2973	2143	56	15	303	2.0	540
6	26.4	1.98	4372	3193	157	43	432	3.0	220
7	9.9	0.30	75	10	10	9	46	13.0	25
8	33.5	0.31	22	nd	14	7	1	63.0	7
9	0.2	0.25	55	nd	36	10	nd	65.0	22
10	33.5	0.51	1715	112	1324	98	181	77.0	336
11	1.7	10.76	73	nd	39	nd	nd	53.0	1
12	19.6	1.75	514	16	361	58	79	70.0	29
13	32.2	0.73	1160	195	722	101	142	62.0	158
14	26.3	0.50	116	49	25	6	36	21.0	23
15	26.3	1.09	75	nd	23	3	58	30.0	7
16	31.2	0.52	494	59	365	12	58	74.0	95
17	9.6	0.15	842	652	44	6	140	5.0	561
18	16.2	1.32	1756	1420	56	56	224	3.0	133
19	29.4	0.04	67	nd	23	3	41	34.0	167
20	18.4	0.11	63	30	23	14	12	36.0	57

nd = not determined

Differences between total extract and sum of fractions are due to un-eluted material remaining on alumina column.

TABLE 3. Elemental composition of kerogen concentrates

Sample	Ash %	Atomic H/C ratio	Elemental composition, ash free basis				
			C%	H%	N%	S%	O%*
1	not determined						
2	11.3	1.46	55.8	6.8	2.0	16.3	18.9
3	10.9	1.19	60.5	6.0	2.8	7.7	22.9
4	9.4	1.19	62.9	6.3	2.9	7.3	20.6
5	3.7	1.24	66.0	6.9	2.5	11.5	13.0
6	4.1	1.26	66.4	7.0	2.3	12.2	11.9
7	13.6	0.64	80.5	4.3	2.8	0.8	11.6
8	5.8	0.55	66.3	3.1	1.1	10.5	19.6
9	18.1	0.76	77.7	4.1	2.0	3.3	12.9
10	4.9	0.78	67.4	4.5	1.1	9.9	17.1
11	2.4	0.51	80.5	3.4	2.1	9.4	5.5
12	6.4	0.63	63.4	3.4	1.4	7.4	24.5
13	5.5	0.66	65.8	3.6	1.5	6.0	23.0
14	20.4	0.55	64.4	3.0	1.6	10.2	20.7
15	17.2	0.59	62.6	3.1	1.5	10.0	22.8
16	12.8	0.54	68.7	3.1	1.6	9.8	16.8
17	35.6	0.71	72.7	4.3	2.5	4.0	16.6
18	6.5	1.13	80.9	7.7	2.1	3.7	5.5
19	54.1	0.53	84.0	3.8	2.5	8.1	1.5
20	73.1	0.53	86.9	3.8	2.2	5.2	1.8

* Oxygen determined by difference

TABLE 4. Yield of bitumen in calcareous sediments with varying clay mineral content (calculated from data of Uspenskiy and Chernysheva, 1951).

Acid-insol.Residue%	Org C%	Bitumen (mg/g Org C)
4.3	0.049	306
10.2	0.123	170
15.5	0.23	147
24.5	0.39	87
57.9	0.57	80
66.1	0.76	54
72.8	1.93	27
Phosphorites*	0.16-1.98	133-760

* Phosphorites considered to be at an early diagenetic stage (samples 1-6, 17, 18; this paper).

TABLE 5. Crude oils with a high nitrogen content (Data from McKinney and Garton, 1960; McKinney *et al.*, 1966; Smith 1964).

State	Reservoir age	No. of samples	Nitrogen content Range	Av.	Phosphatic source
California-Ventura, Los Angeles Basins	Miocene-Pliocene	59	0.007-0.871	0.43	U. Miocene shales
Wyoming-Big Horn Basin	Palaeozoic	36	0.000-0.426	0.24	Phosphoria
Oklahoma (Sho-Vel-Tum field)	Pennsylvanian	5	0.094-0.482	0.268	?
Mexico-Golden Lane Fields	Cretaceous	42	0.002-0.451	0.24	?La Caja or equivalent
Venezuela-Bolivar Coast	Younger Tertiary	3	0.21-0.37	0.29	La Luna

Fig. 1 Gas chromatograms of saturated hydrocarbons from selected samples

Fig. 2 Normal-alkane distributions of selected phosphorites

Fig. 3 X-ray diffraction traces of selected kerogen concentrates

Fig. 4 Effects of depth of burial on organic content of phosphorite samples

A Atomic hydrogen to carbon ratios of kerogens

B Saturated hydrocarbons as percentage of total extract

Fig. 5 Variation of saturated hydrocarbon content with yield of organic extract in phosphorites, shales, and carbonates.

Fig. 6 Frequency distributions of nitrogen and sulphur contents of kerogens (Data calculated from Forsman and Hunt, 1958; McIver, 1967; Long *et al.*, 1968)

Fig. 7 Composition of phosphorite kerogens: normalized C, H, and O contents.

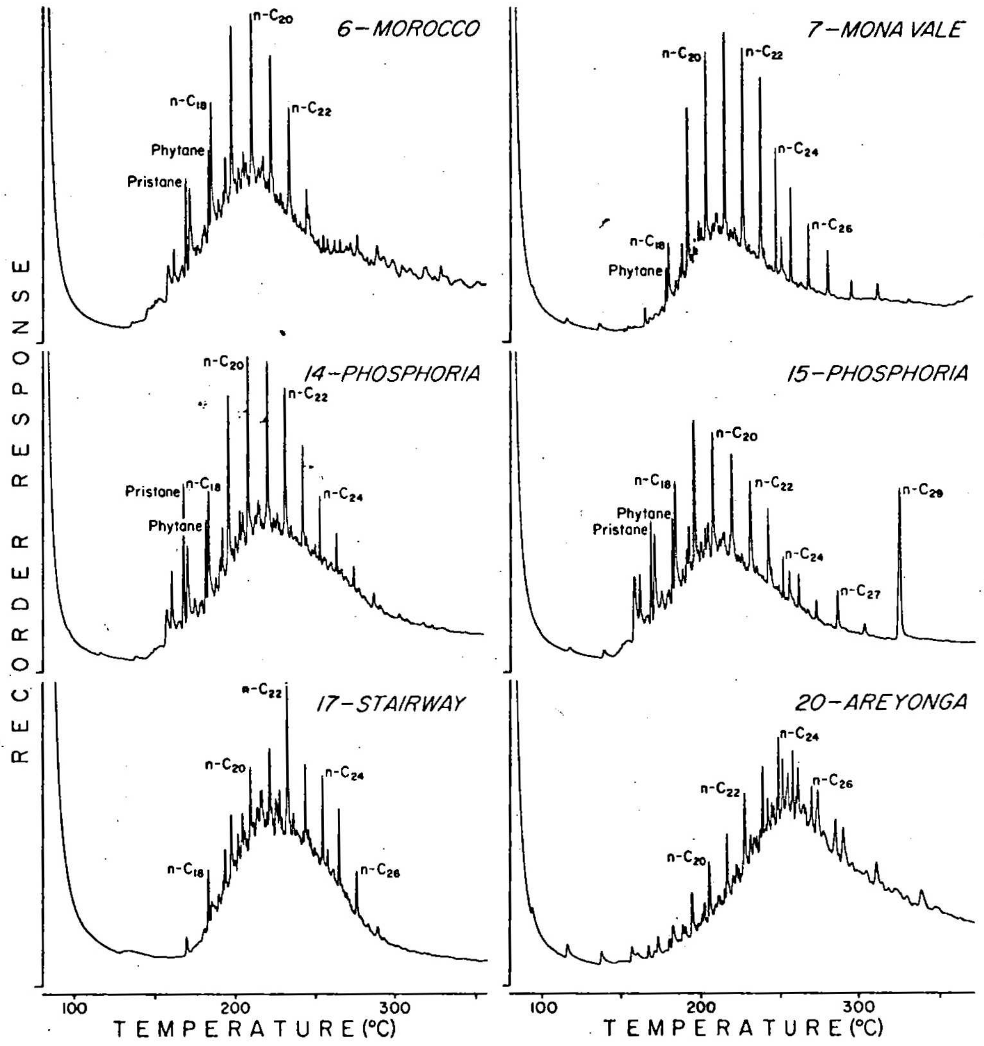


Fig 1

To accompany Record 1974/22

M (G) 417

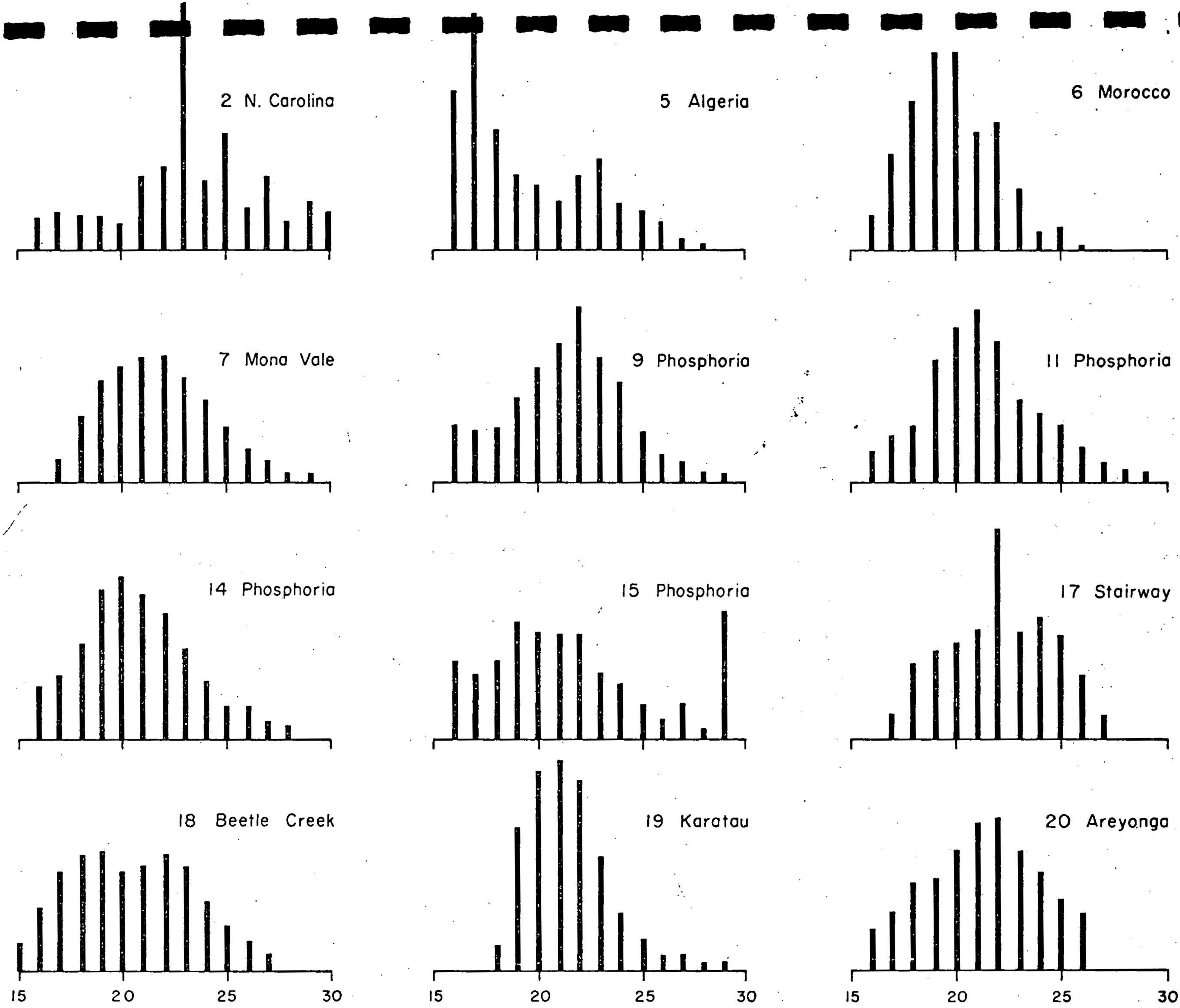


Fig 2

To accompany Record 1974/22

M(G)413

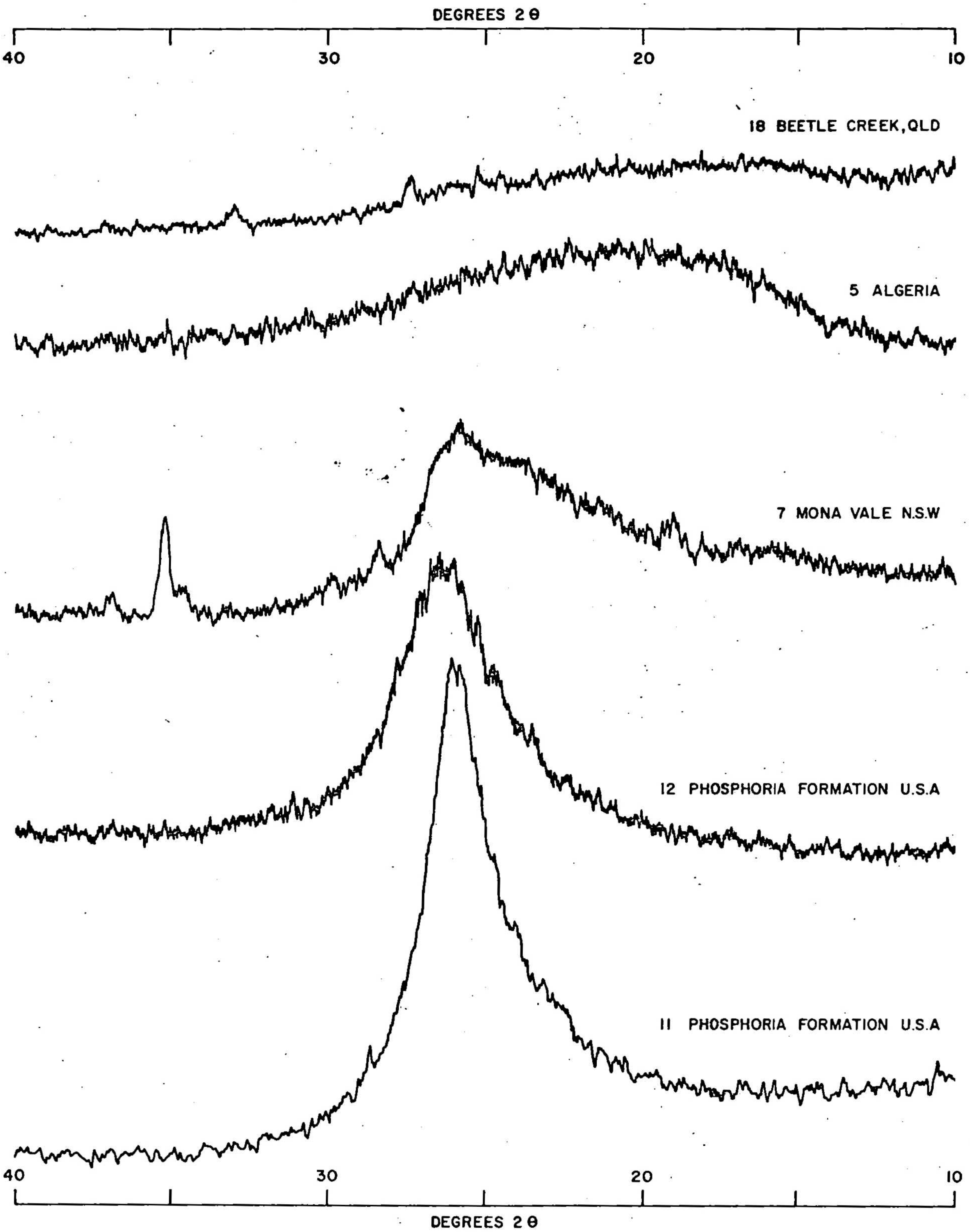


Fig. 3 *To accompany Record 1974/22*

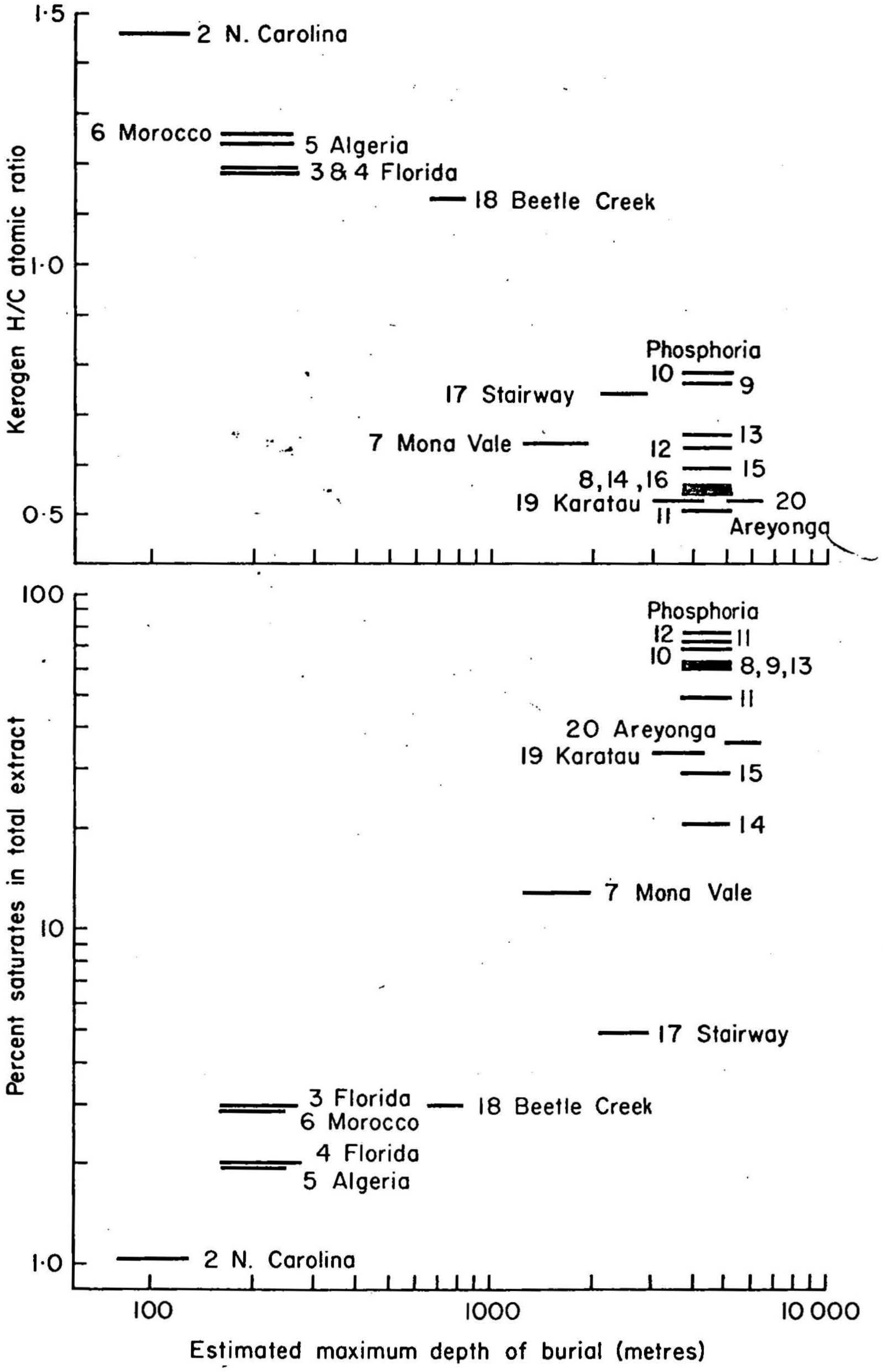


Fig. 4 *To accompany Record 1974/22*

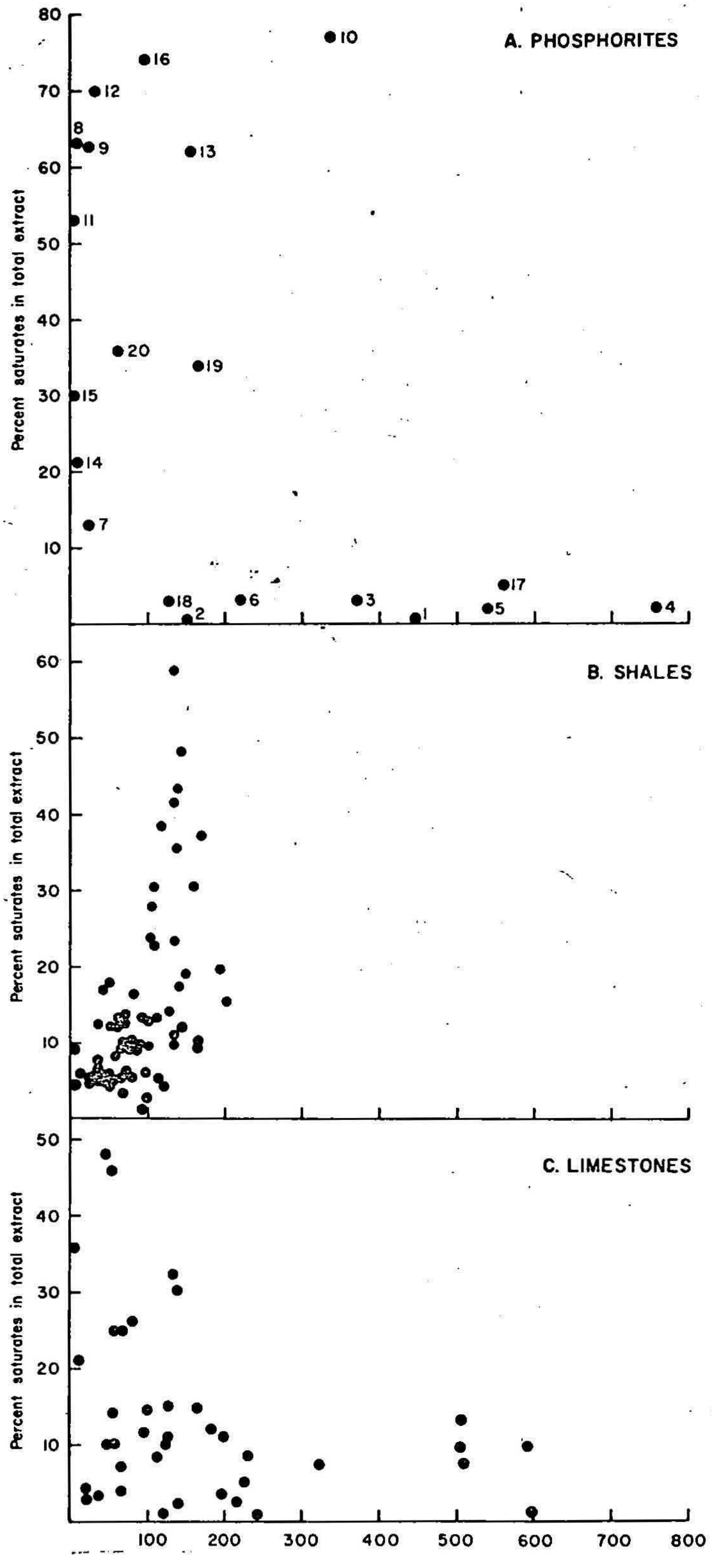
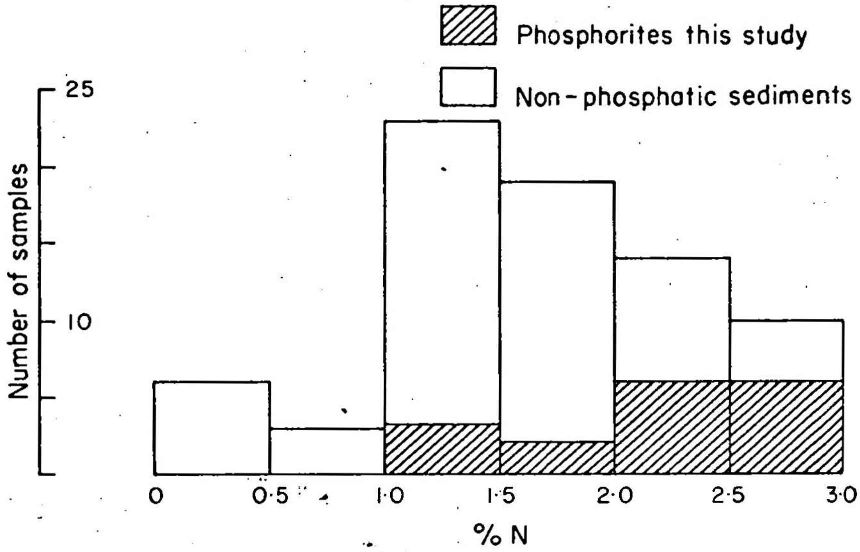


Fig.5

To accompany Record 1974/22

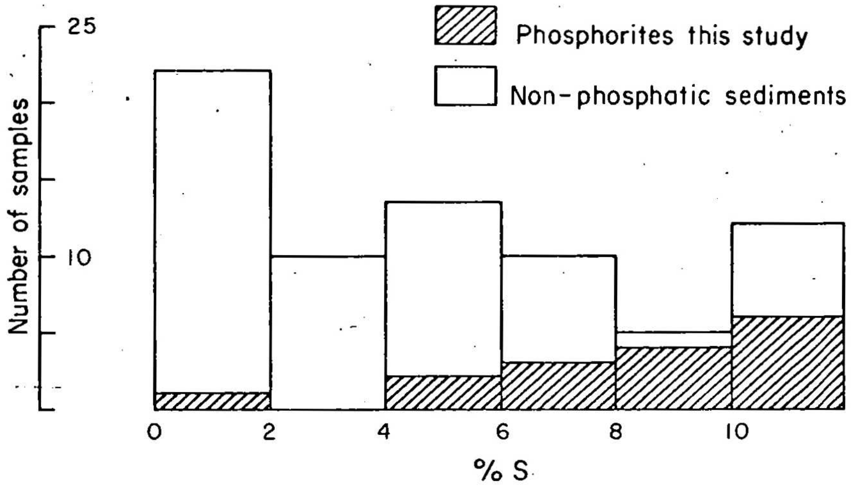
Nitrogen % - 76 samples



Non-phosphorites 21%>2%N

Phosphorites 57%>2%N

Sulphur % - 74 samples



Non-phosphorites 27%>6%S

Phosphorites 72%>6%S

Fig 6

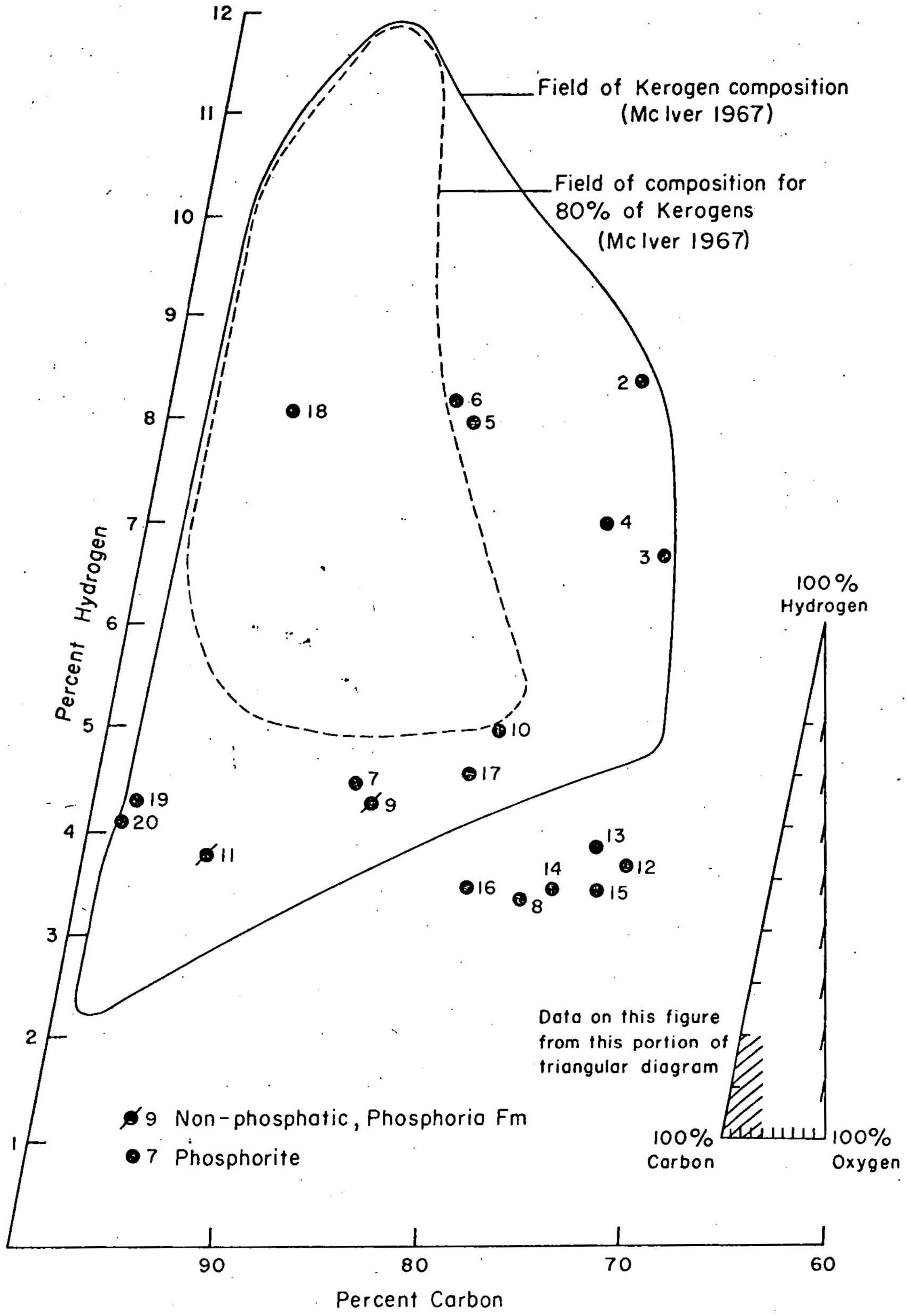


Fig 7

To accompany Record 1974/22

M(G)412