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BUREAU OF MINERAL RESOURCES, GEOLOGY AND GEOPHYSICS

Record 1973/99

ORGANIC GEOCHEMISTRY IN PRECAMBRIAN RESEARCH

by

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Record No. 1973/99.

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SUMMARY

Cherts, shales, and carbonates containing small amounts of organic matter occur throughout the Precambrian sedimentary record. The oldest known organic-rich sediments have been dated at > 3,000 million years. Knowledge of the composition, origin, and fate of the organic content of these rocks relates to many facets of Precambrian earth history. Apart from its primary palaeobiological significance, organic geochemical research is also concerned with problems in atmospheric and hydrospheric evolution, sedimentation, diagenesis, metamorphism, and ore genesis.

Precambrian organic geochemistry to date has rested on the premise that ancient life processes can be profitably studied at a chemical level, as well as by examination of the morphological fossils of conventional palaeontology. A decade of intensive research on selected Precambrian carbonaceous and bituminous sediments has been made possible by the refinement of analytical techniques (notably gas chromatography and mass spectrometry) which are now capable of detecting and characterizing the minute quantities of complex organic mixtures found in geological materials. It has resulted in the development of criteria which allow discrimination between indigenous and adventitious organic matter. A diverse array of stable organic compounds has been isolated from Precambrian sedimentary rocks. The compounds, termed chemical fossils, are thought to be derived from ancestral microorganisms and as such have contributed to the formulation of the biological marker concept. Despite reports of possible abiotic occurrences, a biological origin for most of the organic matter preserved in Precambrian rocks (whether sedimentary or metamorphic) now appears likely.

The possibility of secondary emplacement from migrating formation fluids means that an indigenous chemical fossil need not have been syngenetic with the deposition of its host sediment. No conclusive test of Precambrian age as yet exists for these compounds. The bulk of the organic material (kerogen) in Precambrian rocks is insoluble in organic and aqueous solvents. For this reason, kerogen is almost certainly both

indigenous and syngenetic, but clarification of its chemical structure must await the development of new analytical procedures. The nature and extent of the modification that the soluble and insoluble organic fractions have undergone during late diagenesis and incipient metamorphism is still virtually unknown. Correlation of chemical fossils with specific biogenic precursor compounds, or a particular type of primitive organism, therefore remains equivocal. So also comparison of the organic geochemical facies of one sediment with that of another may be complicated by differences in their thermal history and mineralogy.

Recent interest in the possible involvement of living and decayed microorganisms in the genesis of certain Precambrian Fe, U, Au, Cu, Pb, and Zn metal deposits signals the beginning of an important new phase in organic geochemical studies.

INTRODUCTION

The application of organic geochemical methods (Breger, 1963; Eglinton and Murphy, 1969; Maxwell et al., 1971) to sedimentary rocks of Precambrian age over the last ten years or so has generated an extensive literature which has been reviewed in part by Hoering (1967b), Cloud (1969), Calvin (1969), Schopf (1969, 1970), Echlin (1970), Sylvester-Bradley (1971) and Kvenvolden (1972). The primary aim of this research has been to isolate and identify stable organic compounds which, by virtue of their characteristic molecular configuration or isotopic composition, are indicative of a biological source. The occurrence of such chemical fossils in an otherwise barren sediment implies the operation of life processes at the time of its deposition. Chemical fossils may also provide a basis for locating in geological time specific stages in the development of the biosphere, e.g. the transition from chemical to biochemical evolution, the first use of photosynthesis by the primordial biota,and the emergence from procaryotic stocks (organisms having non-mitosing cells without a nuclear membrane e.g. bacteria, blue-green algae) of eucaryotic cellular organization (mitotic cell division and membrane-bound organelles). Preoccupation with the geochemical implications of such phenomena probably accounts for the primary interest of nearly all the Precambrian organic geochemical studies so far undertaken.

A feature of the search for chemical evidence of ancient biological activity has been the tendency to evaluate the organic content of the oldest known sediments purely in terms of an abiological versus biological origin. The impact of post-depositional processes on its present composition has often been minimized, and sometimes completely ignored. By confining their attention to the ultimate source of particular organic compounds, without sufficient regard for the total geological history of the host rock, chemists risk oversimplifying the problem. Geologists, on the other hand, have been slow to realize that the organic matter commonly preserved within Precambrian (and younger) sediments may hold valuable clues to the depositional, diagenetic, and metamorphic conditions these sediments have experienced (Moore et al., 1969; Taylor, 1971; J.D. Brooks, 1971). Naturally-occurring organic matter in various forms can influence mineral phase equilibria in not only sedimentary (Evans, 1964; Suess, 1970) but also metamorphic (Robinson, 1971) and magmatic-hydrothermal (Kranz, 1969) environments. Berner (1970) has shown that sedimentary pyrite formation depends largely on the availability of organic matter for assimilation by sulphate-reducing bacteria. Of considerable interest, therefore, is the finely-divided carbonaceous matter dispersed throughout the sulphide-bearing sediments of many Proterozoic stratiform base-metal deposits (Trudinger et al., 1972). The intimate association of uraninite with thucolite, an enigmatic carbonaceous substance, in certain early Precambrian conglomerates (Schidlowski, 1969) is a further example of the frequent occurrence of organic matter in economically-significant mineralization. In few cases, if at all, are the genetic implications of this association fully understood.

The present review summarizes the more important findings of Precambrian organic geochemistry. The limitations of organic geochemistry as a tool for investigating the origin and early development of life on earth are discussed. Increasing recognition of the role of organic matter in sedimentary, diagenetic, and metamorphic processes has brought to light other problems in Precambrian geology which may be amenable to organic geochemical study.

HISTORICAL PERSPECTIVE

P.H. Abelson was the first to predict that studies of an organic geochemical nature could throw light on the problems of Precambrian evolution and palaeoecology (Woodring, 1954; Abelson, 1956). The discovery of a spectacular assemblage of fossil microorganisms preserved in black cherts of the Gunflint Iron Formation (Tyler and Barghoorn, 1954) provided the necessary stimulus for a renewed and more systematic search of the Precambrian geological record by palaeontologists for evidence of ancient life. A subsequent study (Oró et al., 1965) of fossiliferous chert from this 1,900 million year (m.y.) old formation was among the first to demonstrate how organic geochemistry could complement conventional techniques in Precambrian palaeontological investigations.

Meanwhile, the need to find new geochemical means of identifying ancient biological events, particularly those which had occurred before the beginning of the Palaeozoic, became increasingly apparent (Cloud and Abelson, 1961). Already, hydrocarbons and trace amounts of carbohydrates had been isolated from the Precambrian of Minnesota (Swain et al., 1958). These compounds were considered by the authors to be of biological origin, and indigenous to the rocks, but others (e.g. Abelson, 1963) remained sceptical. Preliminary accounts of unusually rigorous and sophisticated chemical analyses of the organic content of the Nonesuch Shale (Eglinton et al., 1964; Meinschein et al., 1964) and Soudan Shale (Meinschein, 1965; Belsky et al., 1965) appeared in quick succession. These formations have been dated at approximately 1,075 m.y. and 2,700 m.y., respectively. The organic geochemical data obtained from both were consistent with the existence of biological activity at the time of their deposition.

Since 1964, studies of Precambrian carbonaceous and bituminous sediments have contributed significantly to the overall development of organic geochemistry. The prospect of examining geological samples from the surface of the moon and more remote bodies of the solar system for possible traces of extraterrestrial life, past or present, highlighted the need for sensitive techniques capable of detecting and analysing small amounts of complex mixtures of organic compounds. Precambrian sediments, and carbonaceous meteorites (Hayes, 1967; Nagy, 1968) were obvious choices as appropriate materials on which to test these new methods. The refinement of analytical techniques for the isolation (gas chromatography) and characterization (mass spectrometry) of nannomole quantities of individual organic compounds, the idea of a biological marker, and the development of criteria for distinguishing indigenous from adventitious organic matter are all largely the result of investigations of Precambrian rocks.

ASPECTS OF PRECAMBRIAN GEOLOGY

Sediments and Metamorphism

Crystalline (igneous and metamorphic) rocks tell us much about Precambrian orogeny and tectonism, but it is to sediments of this age that we must look for clues on the atmospheric, climatic, and biological evolution of the primitive earth (Cloud, 1972)(Fig.1). Sidorenko (1969) has pointed out the fundamental similarity between the sedimentary processes of the Precambrian and those of the Phanerozoic, and emphasized the major contribution that sedimentary rocks make to the structure of the Precambrian shields.

The oldest recognizable sediments are found in Archaean greenstone (metabasalt) belts which comprise arcuate synclinal troughs of volcanic-sedimentary rocks dated in the range 3,400-2,400 m.y. (Glikson, 1971). Greenstone belts form an essential part of the stable cratonic regions of the continental crust. Although they are tightly folded, one of their most significant features from an organic geochemical viewpoint is an unexpectedly low grade of metamorphism. Low-pressure, middle greenschist facies regional metamorphism is typical and explains the preservation of original volcanic and sedimentary structures (Anhaeusser et al., 1969) in addition to primary chemical features, both inorganic (Glikson, 1971) and organic (Kvenvolden, 1972).

Detailed examination of the often complex stratigraphy and structural relations of greenstone belts on the African, West Australian and Canadian Shields (Goodwin, 1968; Anhaeusser et al.,1969; Viljoen and Viljoen, 1969c; Glikson, 1970) has clarified the distinctive geotectonic framework within which these early sediments originated. For detailed discussions of the evolution of Archaean greenstone belts the reader is referred to Glikson (1971, 1972) and Anhaeusser (1972). The basal part of the greenstone succession usually comprises an assemblage of calc-alkaline volcanics with subordinate interbedded greywacke, conglomerate, quartzite, carbonaceous shale and chert, banded iron formation, and some carbonate, and is exemplified by the Onverwacht Group of the Barberton region, South Africa, and the Coolgardie Ophiolites and lower Mungari Beds in the Eastern Goldfields, Western Australia. Its sediments are characteristic of low energy dispersal (Glikson, 1970). Sedimentary structures (e.g. rill marks, cross-bedding) in some chert beds indicate a probable shallow-water environment (Viljoen and Viljoen, 1969b; Viljoen and Viljoen, 1969). Certain other cherts are black and carbonaceous and contain the oldest known (> 3,200 m.y.) structurally preserved microfossils (Engel et al., 1968; Nagy and Nagy, 1969a,b).

Higher in the sequence pelitic intercalations increase, marking the decline of volcanic activity and ushering in a period of deeper-water turbidite deposition represented by greywacke, shale, argillaceous sandstone, interbedded banded iron formation, and chert, with subordinate volcanics. In the Barberton greenstone belt this argillaceous sedimentary unit is the Fig Tree Group. Reclassification of the Swartkoppie Formation (Viljoen and Viljoen, 1969a; Viljoen and Viljoen, 1969) means that the majority of the primitive micro-organisms previously described from Fig Tree black chert (Barghoorn and Schopf, 1966; Schopf and Barghoorn, 1967) are now regarded as uppermost Onverwacht in age. Finally, a return to shallow-water conditions saw the accumulation of a molasse-like sequence of quartzite , conglomerate , and arenaceous shale (e.g. Moodies Group, South Africa; Kurrawang Beds, Western Australia).

According to Glikson (1971, 1972) subsidence of these vast volcanic-sedimentary piles into warmer levels of the crust between granitic island batholiths led to their folding and low-pressure isochemical metamorphism. By the time isostatic equilibrium was achieved, and the deformed, metamorphosed greenstone belts had cooled, the granitic nuclei were effectively welded together into shields. Thus, the numerous organic-rich sediments of great potential significance to organic geochemistry (c.f. Oehler et al., 1972; Kvenvolden, 1972) became insulated from further metamorphic overprint, whereas the boundaries of the shields abutting the surrounding oceanic crust subsequently developed into younger mobile belts i.e. linear zones of high-grade (amphibolite and granulite facies) metamorphism and complex folding.

The major part of the Precambrian sedimentary record, however, is preserved in younger intracratonic basins, or basins marginal to the shields. This is especially true of Australia where over twenty such basins, geosynclines, and platforms are recognized (Brown et al., 1968; Compston and Arriens, 1968). All are known to contain sequences of Proterozoic sediments, for the most part unaffected by severe regional metamorphism.

The recognition that little-altered sediments, some of them sufficiently rich in organic matter to be identified as carbonaceous or bituminous (Fig. 1), form a significant part of the Precambrian geological record is a recent development. In many places Precambrian sediments contain just as much organic carbon as younger rocks of equivalent lithofacies (Nanz, 1953; Sidorenko and Sidorenko, 1968; Shaw et al., 1967). However, the number of different organic-rich formations from the Precambrian which have been the subject of any organic geochemical study remains very small (Table I).

Possible indirect evidence for the original presence of disseminated organic carbon in sediments as old as 3,000 m.y. is provided by the stable sulphur isotopic composition of various minerals in Precambrian strata. Chukhrov et al. (1970) have noticed that the degree of fractionation between the ^{34}S and ^{32}S isotopes in sulphur-containing minerals (relative to that in meteoritic sulphur) is greatest when graphite, presumed to be a product of the metamorphism of biogenic matter, is also found in the Precambrian host rock. The most common and effective mechanism of sulphur isotope fractionation in nature is dissimilatory bacterial sulphate reduction (Kaplan and Rittenberg, 1964; Kemp and Thode, 1968). As assimilable organic matter is necessary for the growth of the bacteria, the detection of isotopic fractionation in sulphates and sulphides was considered a good indication of the prior existence of such organic matter. The degree of fractionation accompanying microbiological sulphate-reduction, however, is variable (Rees ,1970; Trudinger and Chambers, in press), so that caution is necessary in interpreting the geochemical history of sulphides (and sulphates) on the basis of their sulphur isotopic composition alone (Trudinger et al., 1972). Sulphide ore minerals with $\delta^{34}S$ values[1] which deviate more than 7 per mil from zero have commonly been regarded as biogenic or sedimentary in origin (e.g. Jensen, 1967), but Ohmoto (1972) has recently shown that similar values could also result from hydrothermal systems depending on the temperature, oxygen fugacity, and pH of the ore-forming fluids. On the other hand, the very occurrence of authigenic pyrite in a sediment means that suitable organic matter must have been available as a carbon source for the bacterial sulphate-reducers which play a key role in sedimentary pyrite formation (Berner, 1970).

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[1] $$\delta^{34}S \text{ per mil} = \left[\frac{^{34}S/^{32}S \text{ sample}}{^{34}S/^{32}S \text{ standard}} - 1 \right] . 1000$$

The observed overall continuity of similar sedimentary facies and their lithological expressions into the Phanerozoic provides little evidence of sudden sedimentological or geochemical change accompanying, or immediately preceding, the onset of Cambrian sedimentation. It has been noted that sedimentary rocks found in the Precambrian are lithologically comparable with those of Cambrian age and younger (Murray, 1965; Sidorenko, 1969). From time to time, various environmental changes have been postulated to account for the "eruptive" proliferation of a diversified metazoan invertebrate fauna early in the Cambrian, in contrast to the sparse and more limited biota of the Precambrian. Such postulations have invariably been found wanting (Glaessner, 1962, 1972). Current thinking in palaeobiology favours an explanation for the rapid emergence of the Cambrian fossil fauna based on the timing of the first appearance of aerobic, eucaryotic organisms in the record (Cloud, 1968a; Glaessner 1972; Schopf et al., 1973).

Despite the general similarity of Precambrian and younger sedimentary rock types, there is some evidence that their relative proportions, particularly those of the siliceous and carbonate "chemical" sediments, change with decreasing age (Cloud, 1968a, 1969; Ronov, 1972; Veizer, 1973). Although carbonates are rare amongst early Precambrian (or Archaean) sediments (Pettijohn, 1943; Anhaeusser et al. 1969; Cameron and Baumann, 1972), they become abundant from the middle Precambrian (2,500-1,700 m.y.) onwards. The oldest thick, extensive carbonate rocks are cratonal and date from ca. 2,000 m.y. (Cloud, 1972). Abelson (in Margulis, 1970a) ascribed the lack of early Precambrian carbonates to the relatively late appearance of carbon dioxide as a significant component of the earth's primitive atmosphere (see next section), whereas Cameron and Baumann (1972) considered the crucial factor to be the absence of "extensive stable shelf or miogeosynclinal environments" on a thin Archaean crust. The particular importance of carbonates to the organic geochemistry of the Precambrian lies in the fact that, broadly speaking, their development coincides both chronologically and geographically with the opening up of the surface waters of the shelf and platform to habitation by planktonic photosynthesizers (Fig. 1). According to Berkner and Marshall (1965a,b, 1972), this ecological expansion finds a ready explanation in the gradual accession of oxygen to the Precambrian atmosphere (see next section). They point out that at oxygen concentrations of ca. 1% present atmospheric level (P.A.L.), penetration of surface waters by lethal ultraviolet radiation diminishes to a few centimetres. Previously, Precambrian communities had been confined to shielded environments e.g. algal mats (Cloud, 1968b), crevices or re-entrants in erosion surfaces (Cloud and Licari, 1972) and anaerobic bottom sediments (Cloud, 1968a cf. Fenchel and Riedl, 1970) which afforded some degree of protection from such irradiation. Accordingly, their organic detritus (where preserved) is found in rocks characteristic of those rather specialized Precambrian sedimentary regimes - stromatolitic carbonate (e.g. Schopf et al., 1971), stromatolitic chert (e.g. Walter, 1972a), and carbonaceous siltstone or shale (e.g. Engel et al., 1968), respectively.

With the advent of extensive limestone deposition, then, we can reasonably expect to find organic geochemical evidence of the first marine planktonic ecosystem(s) (Tappan, 1968, 1971). Early lithification of fine-grained carbonate rocks under submarine conditions is a well known phenomenon (Zankl, 1969; Bathurst, 1971). Hence, syndepositional organic matter will tend to be retained. Furthermore, as carbonate minerals have appreciably less catalytic effect than clays on the maturation of organic matter, the chemical structure and composition of the latter are less likely to alter than if it were trapped in an argillaceous matrix (Hunt, 1967).

Data compiled by Ronov and Migdisov (1971) reveal broad evolutionary trends in the accumulation of organic matter in sediments from the Russian platform (Table II). These authors drew attention to the marked increase in average organic carbon content of Palaeozoic sediments over those of Proterozoic age and ascribed it to "the qualitative and quantitative leap in the development and amount of living matter which occurred at the very beginning of the Palaeozoic era" (op. cit., p. 176). Of greater interest to the present discussion is the six-fold enrichment of organic carbon in late Proterozoic carbonates, as compared to their older equivalents, which is entirely consistent with the expansion of phytoplankton into previously unoccupied marine shelf environments at about this time. Tectonic activity may also play a role in controlling levels of disseminated organic matter in sediments (Strakhov, 1970). A general increase in the organic carbon content of sediments in a basin can just as easily be due to a reduced influx of barren detrital material from the hinterland during a period of tectonic calm, as to a larger or more productive biomass.

Atmosphere and climate

The same advance of scientific inquiry which gave rise to Precambrian organic geochemistry also led to a renewed interest in the wider problems of the nature and origin of organic matter in the early solar system. Hayes (1967) critically evaluated all reported occurrences of organic matter in meteorites which had been published before December 1966. It has since been demonstrated (Hayatsu et al., 1968; Studier et al., 1972; Levy et al., 1973) that most of the organic compounds found in carbonaceous chondrites (and likely to be indigenous) could form by "Fischer-Tropsch-type" reactions of CO_2, H_2, and NH_3 on meteoritic dust surfaces in the solar nebula. Much of the prebiotic organic matter on the primitive earth may have arisen in like manner.

Of crucial importance to any consideration of the origin of organic matter on this planet, the "primordial soup" (or "oil slick": Lasaga et al., 1971) from which life arose by processes of biopoesis (Pirie, 1957) or chemical evolution (Calvin, 1969), is the composition of the early atmosphere. The pertinent conclusions of the debate that this problem has generated are summarized by Cloud (1968a). The earth's primitive atmosphere (and hydrosphere) is now generally accepted as having resulted from volcanic outgassing and may be regarded as secondary in the sense that it was not directly inherited from the hydrogen-rich solar nebula (Sylvester-Bradley, 1971). The main constituents of an atmosphere so produced are likely to have been CO, CO_2, N_2, H_2, and H_2O. Free oxygen was not present. The geological evidence and chemical equilibria on which this anoxygenic composition is based are outlined by Abelson (1966). Miller (in Margulis, 1970a) argued that initially some CH_4 and NH_3 were also present.

The generation of molecular oxygen and its rate of accession to the atmosphere has far-reaching implications for the development of terrestrial life and the geochemistry, both organic and inorganic, of Precambrian sediments (Fig. 1). The first free oxygen was almost certainly derived from the photodissociation of water vapour by solar ultraviolet radiation, assuming that the resultant hydrogen then escaped from the photochemically active region of the atmosphere and the nascent oxygen combined to form the molecular species. For reasons proposed by Urey (1959), and elaborated by Berkner and Marshall (1966), this process was widely understood to be self-limiting and capable of producing no more oxygen than 0.1% P.A.L., although this has recently been disputed (Brinkmann, 1969; Van Valen, 1971).

The appearance of oxygen-releasing photosynthetic organisms early in the Precambrian (Schopf, 1970) was assumed to be the means by which the "Urey level" was eventually exceeded. Cloud (1968a,b, 1972) advocated an initial link between these microorganisms and the deposition of abundant haematitic banded ironformations during the early Precambrian. He suggested that a fluctuating balance between biological oxygen generation and inorganic oxidation of ferrous iron could be expected to persist until effective oxygen-mediating and peroxide-mediating enzymes had evolved, freeing the photosynthesizers from their close physical dependence on mineralogical oxygen acceptors. This and other methods of oxygen *toleration* (e.g. bioluminescence) probably preceded oxygen *utilization* mechanisms such as respiration in the evolution of the photoautotrophs (Margulis, 1970b).

Carbon isotopic evidence indicates that organic activity may have played an important part in the genesis of the vast Brockman Iron Formation (2,200-2,000 m.y.) in the Hamersley Basin, Western Australia (Becker and Clayton, 1972). An otherwise anoxygenic aqueous environment would seem to be necessary to account for the transport of ferrous iron to its eventual site of oxidation and deposition, in sufficient quantity to form iron formations of this type and regional extent. The general lack of red bed sequences, and the local abundance of readily oxidized, supposedly detrital pyrite and uraninite, in sediments older than 1,800-1,900 m.y. (Holland, 1962, Rutten, 1969, 1971; Cloud,1968a,b, 1972) are also consistent with an atmosphere containing less than 1% P.A.L. of oxygen, despite an exponentially expanding biomass. Rutten (1969) made the novel suggestion that the level of free oxygen may have remained at 1% P.A.L. for ca. 1,000 m.y. before this date under the regulating influence of microbial facultative aerobes. It is at oxygen concentrations of about 1% P.A.L. (the "Pasteur level") that modern facultative anaerobes change their metabolism from fermentation to respiration. Also at this oxygen concentration (or possibly lower: Ratner and Walker, 1972) ozone would begin to accumulate in the evolving atmosphere close to the earth's surface and progressively screen out biologically-damaging ultra-violet radiation (Berkner and Marshall, 1965, 1972). The way would be opened for phytoplankton to colonize the open sea, in all likelihood causing a dramatic rise in dissolved and atmospheric oxygen. This in turn would eventually provide sufficient oxygen (about 3% P.A.L. according to Berkner and Marshall, as quoted by Cloud , 1968a, p. 19) to support a metazoan grade of evolution (see Glaessner, 1972 for a recent discussion of the problem.) The significance of this for the organic geochemist becomes apparent when the nature and age range of the known Precambrian biota are considered.

Certainly, then, there is a body of geological evidence which would seem to support the existence of an atmosphere strongly deficient in oxygen until somewhat less than 2,000 m.y. ago. So too, the current theories of the origin of life (Miller and Horowitz, 1966; Ponnamperuma and Gabel, 1968; Calvin, 1969; Lemmon, 1970; Margulis, 1970a), based on an impressive volume of data from primitive atmosphere experiments, invariably assume more or less anoxygenic conditions.

A major initial limitation on the concentration of free oxygen in the atmosphere was the formation of lithospheric oxides from reduced minerals exposed at the earth's surface and highly reactive ozone (a product of the ultraviolet photodissociation of molecular oxygen). As Marshall explains: "Not until the net rate of production of oxygen, primarily by photosynthesis, exceeds the net rate of O_2 dissociation, and its consequent loss as an active oxidant, can equilibrium values of oxygen exceed the levels in the primitive atmosphere and building of a stable oxygenic atmosphere begin" (Berkner and Marshall, 1972, p. 854).

The inexorable growth of photosynthesizing communities in size, efficiency, and number was eventually sufficient to raise the free-oxygen content of the atmosphere above the "Pasteur level". Thereafter, its increase is thought to have continued more or less unchecked until the P.A.L. was reached (and perhaps even exceeded) during the mid-Palaeozoic when continental floras appeared. Meanwhile, recurrent episodes of widespread volcanism may have released oxygen-deficient gases and reduced mineral matter into the environment, leading to minor fluctuations in oxygen level.

Cloud (1972) stressed the gradual nature of oxygen accession to the atmosphere. By referring to the reversible nature of the photosynthetic reaction he made the further point that not only do all the contemporary oxygen sinks have to be filled but also "a chemically equivalent mass of carbon" has to be sequestered before oxygen can accumulate (cf. Van Valen, 1971).

He cites the shungites (metacoals) of U.S.S.R. (Vologdin, 1970) dated at 1,900-1,800 m.y. and other more extensive carbonaceous sediments of similar age as the "carbon counterpart" of a Proterozoic oxygen build-up. Cheney (1971) suggested that the absence of coelomate burrowing organisms 700 m.y. ago (cf. P.F. Hoffmann quoted by Margulis, 1970b, p. 138-141; Glaessner, 1972), as evidenced by the widespread occurrence of nonbioturbated laminated Precambrian pelites, may have enhanced the preservation of organic matter in such sediments and aided the accumulation of atmospheric oxygen.

Probably the only unequivocal Precambrian climatic event was the widespread late Precambrian glaciation (Mawson, 1949; Harland, 1964; Dunn et al., 1971). The reduction in temperature which triggered this ice age may have resulted from a significant decrease in atmospheric CO_2 (via the "greenhouse effect"), brought about by a concomitant increase in oxygen partial pressure following the large-scale invasion of Precambrian seas by phytoplankton (Cloud, 1968a). In a subsequent paper, Cloud (1972, p. 547) postulated a link between the suggested late Precambrian oxygen influx and the fact that "the fine clastics associated with tillites and dropstone breccias of this age are often relatively carbonaceous". However, the Proterozoic glaciations are probably not synchronous (Crawford and Daily, 1971), in which case the "atmospheric trigger" hypothesis becomes untenable. The explanation for the increased volume of carbonaceous sediments in the late Precambrian record may simply lie in the characteristic features of the emerging global ecosystem, notably high productivity compared to community respiration and biomass, short food chains, and relative lack of deposit feeders (Tappan, 1971). In other words, the extensive accumulations of disseminated organic matter in these sediments appear directly attributable to a high net community production before the development of the consumer trophic level.

Recent developments in the study of stable carbon isotopic fractionation in modern organisms and sedimentary organic matter, as well as carbonate rocks and fossils, offer some hope of improving our ability to detect more subtle variations in palaeoenvironment. Weber (1967) presented evidence of a small but real increase in the deficiency of the ^{13}C isotope in marine limestones of decreasing age from Precambrian to Silurian. He interpreted this as a possible indication of (cyclic) changes in the isotopic composition of the oceanic and atmospheric carbon reservoir which, according to Tappan (1968) and Broecker (1970), may in turn reflect variations in the amount of biological activity over geologic time. Similarly, organic carbon in Phanerozoic sediments tends to exhibit a decrease in ^{13}C content with increasing age (Degens, 1969), a trend which although not marked continues into the Precambrian reaching a maximum in sediments ca. 2,100 m.y. old (Oehler et al., 1972) (Fig.2). Degens (1969) has summarized the results of recent experiments with marine phytoplankton which suggest that the major controls of carbon isotopic fractionation in organic matter are pH, water temperature, concentration of dissolved CO_2, and growth rate of the organisms. Sackett et al. (1965) were able to demonstrate marked differences in stable carbon isotopic fractionation between warm and cold-water marine plankton (Fig.2). What is most encouraging is that $\delta^{13}C$[1] measurements on finely disseminated organic matter which has survived microbiological attack (kerogen) and coals, indicate that diagenesis and even metamorphism does not significantly alter the original inherited isotope pattern (Degens, 1969; Oehler et al., 1972).

The distinctly lighter isotopic composition noticed for pre-Devonian crude oils and Precambrian to Lower Palaeozoic kerogens, by comparison with equivalent materials of younger age (Fig.2), may mean that, in general, the marine environment of that time was characterized by a higher molecular CO_2 content

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[1] $$\delta^{13}C \text{ per mil} = \left[\frac{^{13}C/^{12}C \text{ sample}}{^{13}C/^{12}C \text{ standard}} - 1 \right] .1000$$

The PDB carbonate (a belemnite from the Peedee Formation, South Carolina) is a commonly used standard.

of the sea, and therefore a slightly lower pH or temperature (Degens, 1969). Similar variations in the same environmental parameters would also explain the isotopic data on pre-Devonian marine limestones reported by Weber (1967), although it is worth noting here that Perry and Tan (1972) and Becker and Clayton (1972) have questioned the validity of interpreting the carbon isotopic composition of Precambrian marine carbonates in terms of the oxygen content of the atmosphere (cf. Broecker, 1970). Furthermore, Degens et al. (1967b) have observed that changes in water temperature, pH, and salinity significantly alter the amino acid composition of the shell protein matrix of molluscs, which first appeared early in the Cambrian. It is also of interest to note that Martin et al. (1963) were able to speculate as to the nature of the Lower Palaeozoic climate on the basis of the unusual normal alkane composition of several crude oils of that age.

Stable sulphur isotope data on sulphides, sulphates, and elemental sulphur fall within the ambit of organic geochemistry mainly insofar as they have been used to infer the operation, or absence, of bacterial sulphate reduction (e.g. Jensen, 1967; Chukhrov et al., 1970; Smith et al., 1970). It should be emphasized, however, that the controls upon biogenic sulphur isotope fractionation are complex and $\delta^{34}S$ values difficult to predict. Rees (1970, p. 366) stated: "The ratio of rates of reduction for ^{32}S and ^{34}S may vary widely depending on temperature, sulphate concentration, availability of metabolites, etc........ and the fractionation produced also varies between wide limits depending on whether the reduction takes place in muds in contact with ocean sulphate or in muds which are buried, where there is no mixing between the ocean reservoir and the trapped sulphates". It is perhaps not surprising then that sulphur isotope studies on sedimentary rocks have so far provided little unambiguous information on the Precambrian environment. A possible exception is the work of Perry et al. (1971) in which they interpret the small enrichment of ^{34}S in sedimentary barite (relative to contemporaneous pyrite) from the Swaziland System as indicating an early Precambrian sulphur cycle "grossly different" from the present one.

In particular, they proposed (p. 1016) a much smaller reservoir of oceanic sulphate and a less oxidizing atmosphere: "oxidation occurred in an oxidizing photosynthetic zone near the ocean surface in which .... primitive organisms may have used electron doncr reactions such as $Fe(OH)_2 + OH^- \longrightarrow Fe(OH)_3 + e^-$ instead of reactions involving free oxygen. Under these conditions, green or purple sulphur bacteria could oxidize H_2S or S^{2-} to SO_4^{2-} in the photosynthetic layer ..... (producing) little isotopic fractionation".

Thus most problems of Precambrian organic geochemistry are intimately linked with the nature of the atmosphere, the hydrosphere, and the climate of the time. Consideration of the types of organisms which first populated the face of the earth, and what is known, or can be deduced, about their palaeobiochemistry bears this out.

MORPHOLOGICAL AND MOLECULAR PALAEONTOLOGY

It is now well known that fossils occur in strata of Precambrian age. Details of their preservation, morphology, and affinities with extant taxa are contained in an extensive literature which has been tabulated in the comprehensive bibliographies of reviews by Murray (1965), Glaessner (1962, 1966a), Cloud (1968a), and Schopf (1969, 1970). Schopf, in particular, stressed the complementary nature of the roles played by palaeontology and organic geochemistry in Precambrian studies. Both approaches seek to elucidate the nature of biological activity and its influence on the geological environments of the time, although organic geochemistry as such is not necessarily confined to biogenic organic matter. The types of primitive organisms for which fossil evidence is known from the Precambrian, and their time ranges, impose limits on the possible sources of chemical fossils isolated from Precambrian rocks.

During Precambrian time at least three major events in the evolutionary history of the biosphere took place: the first living system(s) originated, biological photosynthesis evolved, and eucaryotic organisms first appeared. Each could reasonably be expected to leave its imprint on the geological record, in both a palaeobiochemical and a morphological sense. However, because of the considerable limitations of the fossil record, the location of these events in time is difficult to specify, as are the exact environmental conditions under which they occurred (Glaessner, 1966b).

The presence of microscopic bacterium-like rods and organic spheroids resembling unicellular coccoid blue-green algae in black shales and cherts of the lower Swaziland System, South Africa (> 3,000 m.y. old) constitutes the oldest currently known occurrence of fossil organisms. While their simple morphology does not permit an unequivocal assignment of physiological mode, these microfossils have been interpreted (Schopf and Barghoorn, 1967; Schopf, 1969) as probable remnants of a primitive photosynthetic biota. If correct, this interpretation has profound implications. It would mean that a significant period of biochemical evolution had occurred before 3,200 m.y. ago, the apparent minimum age of the Onverwacht Series (Engel et al., 1968). This in turn would probably place the origin of terrestrial life somewhat earlier than the oldest sedimentary rocks for which reliable dates are available. Consequently, the possibility of finding geochemical evidence of the transition from chemical to biochemical evolution appears to be remote. Nevertheless, Calvin (1969) speculated that the distinctive gas chromatogram of a saturated hydrocarbon (alkane) extract of a sample of Onverwacht argillaceous chert may represent a mixture of abiogenic and biogenic compounds (see Figure 3A). Meinschein (1967) similarly admitted the possibility of random abiotic processes accounting for some of the younger (minimum age 3,100 m.y.: Schopf and Barghoorn, 1967) Fig Tree alkanes (Fig. 3B), although he pointed out that their unusual complexity could also have arisen from the geochemical alteration of ancient biolipids. An abiotic source for part of the Onverwacht organic matter would be by no means unlikely if Cloud's suggested 3,400 - 3,700 m.y. age (quoted by Han and Calvin, 1969) for the host rocks proves to be correct and may even explain new carbon isotopic data on lower Onverwacht cherts (Oehler et al., 1972)

The proposed photosynthetic autotrophic physiology of the Fig Tree and Onverwacht spheroids[1] is supported by other geological evidence, most of which has been summarized by Schopf (1969) and Kvenvolden (1972). It includes the following organic geochemical data:

(i) Beds of carbonaceous chert and shale are known from both the Fig Tree and Onverwacht Series. With a view to gaining some idea of its likely origin, several attempts have been made to characterize the structure of the somewhat intractable polymeric organic matter (kerogen) of these sediments. Bitz et al. (1967) and Nagy and Nagy (1969a) used a relatively mild ozonolysis procedure on solvent-extracted rock powder. Hoering (1967a,b), Simmonds et al. (1969), and Scott et al. (1970) used various pyrolysis techniques on powdered whole-rock samples. The low-temperature pyrolysis data obtained by Hoering for the Fig Tree shale was interpreted by him as implying a highly aromatized kerogen. At the same time, however, he noted the apparent inconsistency of this conclusion with the high molecular weight alkanes shown in Figure 3B. On the other hand, both the ozonolysis method, and the high temperature pyrolysis experiments of Scott and coworkers showed the Fig Tree kerogen to be quite significantly aliphatic, in contrast to the Onverwacht which appears to consist of condensed aromatic nuclei linked by short aliphatic chains. An algal (or bacterial) precursor, of the type suggested by the microfossils, would readily account for an aliphatic Fig Tree kerogen. A direct explanation for the aromatic Onverwacht kerogen is harder to find. Polymeric aromatic organic substances found in much younger rocks can be related to the lignin of vascular green plant detritus. One possible source of aromatic[2]

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[1] The microbiota of the Swaziland System possibly included both heterotrophs and bacterial (but not necessarily algal) autotrophs (Kvenvolden, 1972).

[2] Brooks and Shaw (1971) argued that sporopollenin derived largely from a carotenoid ester (as opposed to a free carotenoid) will be of an aliphatic type.

kerogen in early Precambrian sediments is sporopollenin (Brooks and Shaw, 1968, 1970, 1971, 1972) found in algal and fungal spore exines. Another is the polymerization of unsaturated fatty acids (Abelson, 1967) of blue-green algae (Parker and Leo, 1965; Parker et al., 1967; Holton et al., 1968; Margulis, 1969; Schneider et al., 1970; Kenyon and Stanier, 1970) during diagenesis of the organic-rich sediment, with subsequent metamorphism leading to increased aromatization of the resultant polymer. In fact, until the relative metamorphic rank of the samples studied can be ascertained, the above speculation is likely to remain inconclusive.

(ii) The isoprenoid alkanes norpristane ($C_{18}H_{38}$), pristane ($C_{19}H_{40}$) and phytane ($C_{20}H_{42}$) have been identified in the solvent extracts of both Fig Tree (Oró and Nooner, 1970) and Onverwacht (MacLeod, 1968; Han and Calvin, 1969) sediments; the C_{14}, C_{15} and C_{16} homologues were also reported by Han and Calvin. The regular isoprenoid skeleton occurs widely in modern organisms. Photosynthetic systems, including primitive anaerobic bacterial photosynthesis, always involve isoprenoid compounds (Margulis, 1969). Precambrian isoprenoid hydrocarbons are generally considered to be degradation products of the branched alkyl (usually C_{20} phytyl) side-chain of algal and bacterial chlorophylls (Eglinton et al., 1966; McCarthy and Calvin, 1967), although other isoprenoid-containing lipids may contribute (Kates et al., 1965; Eglinton and Calvin, 1967).

(iii) Kvenvolden and Hodgson (1969) have presented detailed evidence for the presence of small concentrations of indigenous metal-chelated porphyrins in samples of Fig Tree shale and Overwacht chert. Although the excitation and emission spectral characteristics of these porphyrins differ from those of porphyrins typically found in younger geological materials, it is still likely that they are structural remnants of ancient biological pigments (e.g. chlorophylls, cytochromes) (Schopf, 1970).

(iv) Various other classes of organic compounds, structurally similar to present-day biochemicals, have been detected in Swaziland System rocks. These include C_{12}-C_{29} normal alkanes (Hoering, 1967a,b; Oró and Nooner, 1970), C_{16}, C_{18}, C_{20} and C_{22} normal alkenes (Oró and Nooner, 1970), and amino acids (Schopf et al., 1968; Pflug et al., 1969) from the Fig Tree; and C_{12}-C_{31} normal alkanes (MacLeod, 1968; Han and Calvin, 1969), and C_{14}, C_{15}, C_{16} and C_{18} normal alkanoic acids (Han and Calvin, 1969) from the Onverwacht.

(v) The stable carbon isotopic composition of the Fig Tree and Onverwacht organic matter (Hoering, 1967a,b; Oehler et al., 1972) is similar to that of more recent organic material of photosynthetic origin (Fig. 2).

The possibility that at least part of the soluble organic matter found in Swaziland System rocks may represent contamination from geologically younger sources (Meinschein, 1967; Hoering, 1967a,b; MacLeod, 1968; Abelson and Hare, 1969; Nagy, 1970; Sanyal et al., 1971; Kvenvolden, 1972) cannot be ignored. Nevertheless, the organic geochemical information, in conjunction with the microfossil evidence, appears to indicate that photosynthesis antedated the earliest Swaziland sedimentation.

Recent advances in molecular biology have led to the conclusion that the basic dichotomy of the modern biosphere is not, as traditionally thought, between plants and animals, but rather between procaryotes (bacteria, blue-green algae, phycomycetous fungi) and eucaryotes (green plants, animals, protozoans, "higher" algae and fungi) (Whittaker, 1969; Margulis, 1969, 1970b). One of the more important features which distinguishes these two major groups of organisms is the absence of organelle membranes in procaryotes, and their presence in eucaryotes. This fact is regarded (Bloch, 1965) as a morphological expression of the apparent lack of sterols (Levin and Bloch, 1964) in procaryotes (but see below) and their ubiquitous distribution in eucaryotic organisms. Sterols are considered to function as strengthening components of cytoplasmic and intracellular membranes, a role for which their rigid planar molecular configuration and hydrophobic nature would undoubtedly suit them.

Polyunsaturated fatty acids, like sterols, are also more characteristic of eucaryotes than procaryotes (Margulis, 1969, 1970b). The biosynthesis of sterols involves molecular oxygen (Bloch, 1965); and polyunsaturated fatty acids have been thought to participate in oxygen production during "green plant" photosynthesis (Erwin and Bloch, 1963), although their exact function is not yet understood (Holton et al., 1968). The appearance of the eucaryotic cell "with its potentialities for mitosis, meiosis, and genetic exchange via sexuality" (Schopf, 1969, p. 162) also presupposes an established ozone layer in the atmosphere to screen out lethal ultra-violet radiation and permit the gradual expansion of the biosphere into less protected, more freely planktonic habitats to commence (Cloud, 1968a). The eucaryotic cell, having its genetic material carried on a number of chromosomes and confined within a membrane-bound nucleus, is more subject to radiation damage, leading to disadvantageous mutations or death, than are procaryotes (Witkin, 1966; Werbin and Rupert, 1968). Thus a close genetic relationship between the evolution of nucleated organisms, the exploitation of the biosynthetic routes to sterols and polyunsaturated fatty acids, and the advent of widespread oxidative respiration is strongly suggested. The ability of blue-green algae to respire aerobically in the dark at the expense of photosynthetically-produced carbohydrates probably represents a later stage in their evolution which coincided with the transition from a reducing to an oxidizing atmosphere (Margulis, 1970b). The first biochemical synthesis of polyunsaturated fatty acids may have accompanied this transition.

Small amounts of polyunsaturated fatty acids (Parker et al., 1967; Holton et al., 1968; Kenyon and Stanier, 1970) and sterols (De Souza and Nes, 1968; Reitz and Hamilton, 1968) have now been found in certain species of extant blue-green algae. Nevertheless, the accumulation of detectable quantities of these compounds in the geological record would seem to be likely only after the evolution, diversification, and proliferation of aerobic eucaryotic organisms.

The oldest presently known fossil evidence of nucleated organisms has been found in primary cherts of the late Precambrian Bitter Springs Formation of the Northern Territory (Schopf, 1968; Schopf and Blacic, 1971). The estimated age of this unit is 900 m.y. Other microfossils of presumable eucaryotic organization from somewhat older rocks have been described by Pflug (1965), Cloud et al. (1969) and Croxford et al. (in press). Schopf et al. (1973) postulated that the first eucaryotic cell probably appeared between 1,700 and 1,300 m.y. ago. (Fig. 1). On this basis, the report of biogenic steranes in the 2,700 m.y. old Soudan shale (Burlingame et al., 1965) is open to question (Margulis, 1969). On the other hand, sterane-type alkanes in the younger (1,075 m.y. old) Nonesuch Shale (Barghoorn et al., 1965) are consistent with the fossil record. Normally, polyunsaturated fatty acids would not persist intact from Precambrian sedimentary environments. Hydrogenation of the double bonds and loss of the carboxylic acid functional group by decarboxylation or reduction could be expected to have occurred during diagenesis (Blumer, 1965). Alternatively, these unsaturated fatty acids may have been incorporated into a heterogeneous polymeric kerogen precursor soon after burial (Abelson, 1967); in which case, late Precambrian kerogens may yet prove to be a fruitful source of information on the nature and fate of this most important biochemical fraction of the first eucaryotic biota (Hoering, 1967b).

The diverse microbiota which populated late Precambrian seas is exemplified by the Bitter Springs assemblage of blue-green algae, green algae, colonial bacteria, fungus-like filaments, and possible dinoflagellates, some fifty species in all (Schopf, 1968; Schopf and Blacic, 1971). Towards the close of the Precambrian, soft-bodies metazoans also appeared. The

Ediacara fauna of South Australia consists of at least twenty-five species which include coelenterates and annelids, as well as others of unknown affinity (Glaessner and Wade, 1966; Wade, 1972). By this time the marine biomass had increased to a point where it was able to provide organic source material sufficient to give rise to the commercial quantities of hydrocarbons found today in certain "unmetamorphosed" Precambrian strata (Murray, 1965; Vassoyevich et al., 1971; Tappan, 1971).

The transition from Precambrian to Cambrian is marked by the first appearance in the fossil record of invertebrate animals with mineralized skeletons and hence readily preservable hard parts although this in itself does not constitute a precise definition of the base of the Cambrian (Glaessner, 1963, 1972; Daily, 1972). The difficulty of producing collagen under oxygen-poor conditions (Towe, 1970), and the problems inherent in secreting and maintaining calcareous tests in dysaerobic (containing <1 ml. dissolved O_2 per l.) water (Rhoads and Morse, 1971) are among the reasons recently advanced to explain why "shelly faunas" did not evolve until the dawn of the Palaeozoic Era. Comparison of the amino acid content of shell protein in living examples of primitive and more advanced molluscs led Degens et al. (1967a) to conclude that the explanation for the sudden change from soft (uncalcified) to hard (calcified) tissue in invertebrates probably lies in the sensitivity of the protein secretion process to water temperature, pH and salinity. Changes in these variables alter the amino acid pattern and the degree of cross-linking in the resultant proteinaceous matrix, which in turn control the number of sites available for carbonate (or phosphate) nucleation.

In his pioneering work on palaeobiochemistry, Abelson (1954, 1956, 1959a, 1963) demonstrated that certain amino acids had sufficient inherent stability to persist intact in favourable environments for geologically significant periods of time. Thus arose the possibility that direct analysis of fossil shells or permineralized microfossils would reveal free amino acids, perhaps even intact peptide residues. The mineral phase (carbonate, phosphate, or silica) provides a natural protective barrier against oxidation, leaching, and bacterial degradation (Abelson, 1959b). Recent experimental work by Hare and Mitterer (1969) has, however, indicated that the actual inorganic shell material actually catalyses amino acid breakdown during diagenesis. Similarly Abelson and Hare (1969) concluded that the siliceous matrix of Precambrian fossiliferous cherts was unlikely to have stabilized syngenetic amino acids. Nevertheless, in exceptional cases remnants of the shell organic matrix may survive. The finding of chitin preserved in a Cambrian pogonophore (Carlisle, 1964) is an interesting example. The remarkable organic preservation of the Bitter Springs microbiota in black laminated chert suggests that geochemical analysis of hydrofluoric acid macerates of such sediments may reveal valuable information on the composition of fossil cell walls.

Where the vagaries of fossil preservation, in particular recrystallization and replacement, are critical enough to have effected the removal or destruction of all organic matter, it may still be possible to ascertain clues to the palaeobiochemistry of the original organism by examining close living relatives. Such was the approach adopted by Gelpi et al. (1970) and Schneider et al. (1970) in their study of lipids in selected contemporary algae. If the fossil organism lived in a geochemically stressed environment (e.g. high salinity or metal ion concentration) its biosynthetic pathways and metabolite composition may have become drastically altered (Bubela, 1970; Pugh, 1971). This would need to be taken into account in any attempted biochemical correlation with modern equivalents.

CHEMICAL FOSSILS AND THE BIOLOGICAL MARKER CONCEPT

Since the discovery of porphyrins in crude oils and shales by Treibs in 1936, the notion that ancient life processes can be profitably studied on a molecular level, as well as in terms of the morphological fossils of conventional palaeontology, has gained wide acceptance. It was not until some five years ago, however, when literature reports of various organic compounds of probable biological origin in ancient rocks had become sufficiently numerous and comprehensive in their coverage of the geological record, that one could discern the emergence of a loosely defined sub-discipline which Calvin (1969) has called molecular palaeontology.

The subject matter of molecular palaeontology is chemical fossils: organic compounds which have survived entombment in the lithosphere with their molecular structure intact, or little altered from the time they were once part of a living organism (Eglinton and Calvin, 1967). Table III illustrates the distribution of chemical and morphological fossil evidence of biological activity in the Precambrian record. Depending on their original molecular configuration, and the extent to which they have been modified during diagenesis and early metamorphism, chemical fossils may or may not be useful as "biological markers". Johns et al. (1966, p. 1191-2) stated:"'biological markers' are compounds which show reasonable chemical stability to diagenesis and possess a marked specificity of structure understandable in terms of known biosynthetic sequences and whose formation is of low probability by abiological synthesis". The notion of biological marker compounds has been central to the search for chemical traces of early life in Precambrian rocks (Fig. 4). Its practical value has diminished somewhat following recent experimental work which showed that geologically younger biogenic materials may (and probably did) invade Precambrian sediments as impermeable as chert (see next section). But whereas this undoubtedly highlights the need to develop means of establishing the contemporaneity of the marker compounds, or their precursors, with the deposition of the host rock, it does not necessarily invalidate the concept of a biological marker as defined by Johns et al.. Neither does the abiological synthesis of certain amino acids (Ponnamperuma and Gabel, 1968), porphyrins (Hodgson and Ponnamperuma, 1968; Hayatsu et al., 1972) and deuterated equivalents of short-chain ($< C_{14}$) acyclic isoprenoid alkanes

(Studier et al., 1972) in the laboratory. Such "prebiotic biological markers" are unlikely to have been preserved in any but the very oldest sediments (dating from pre-Fig Tree time), partly because primitive anaerobic heterotrophs would have used much of this abiotic organic material as food. In any case, methods (eg. stereochemical analysis of isoprenoid geolipids; carbon isotopic analysis of individual alkanes) are available for distinguishing abiogenic from biogenic compounds (McCarthy and Calvin, 1967; Eglinton, 1969; Maxwell et al., 1971), although technical difficulties have so far prevented their application to Precambrian sediments. Despite occasional claims to the contrary (Robinson, 1963; Rudakov, 1967), the evidence of a biogenic origin for the bulk of organic matter preserved in sediments (those of Precambrian age included) is nevertheless almost overwhelming. Thucolites (Spence, 1930; Davidson and Bowie, 1951; Schidlowski, 1969; J.D. Brooks, 1971) are of rather less certain derivation, and bituminous and carbonaceous matter in hydrothermal, alkaline, and ultrabasic igneous rocks (Zezin and Sokolova, 1967; Petersilie et al., 1968; Petersilie and Sorensen, 1970; J.D. Brooks, 1971; Mueller, 1972) may be of inorganic origin.

The anaerobic conditions usually required for the preservation of sedimentary organic matter effect what Eglinton (1969) terms a "data reduction step" on its original biochemical molecular structure. Reactive sites, such as double bonds and heteroatomic functional groups, tend to be lost, leaving the basic carbon skeleton in a more or less fully hydrogenated form. Thermal cracking experiments on hydrocarbons demonstrate the considerable strength of carbon-carbon bonds. It has been estimated that such compounds, in the absence of catalysts, should be stable for 10^{12} years at 100°C (McCarthy and Calvin, 1967). Of all the major "building blocks" of life, the nucleic acids undoubtedly have the highest biological information content. Not unexpectedly, however, their chemical stability as biopolymers is insufficient to permit their survival under geological conditions, although their constituent purine and pyrimidine bases can persist for appreciable periods (Degens, 1967). The polypeptides of structural and enzymatic proteins have similar limitations as potential biological markers. Peptide linkages are prone to hydrolysis, and the released amino acids to deamination and decarboxylation. While amino acids (Fig. 4) have been isolated from several Precambrian rocks (Prashnowsky and Schidlowski, 1967; Schopf et al., 1968; Oberlies and Prashnowsky, 1968) (Table III), they are considered by Schopf (1970, p. 324) to be "in part of secondary and relatively recent origin" on the basis of their general lack of geochemical stability (see also next section). Likewise, doubt as to the long-term stability of carbohydrates (Vallentyne, 1963) reduces the signficance of reports of Precambrian sugars (Prashnowsky and Schidlowski, 1967; Oberlies and Prashnowsky, 1968; Swain et al., 1970). Although severe restraints are thereby placed on our ability to discern the palaeobiochemical information encoded in ancient nucleic acids and enzymes, much can be learned from the smaller and less complex metabolites, the lipids, in that their stereospecific synthesis is enzymatically controlled.

The lipids of modern organisms (biolipids) are known to include various long-chain hydrocarbons, fatty acids, alcohols, and esters. The same solvents used to extract geolipids (lipids found in geological materials) from rocks will also remove the porphyrin pigments. The undoubted geochemical stability of both lipids and porphyrins, and their consequent widespread occurrence in sediments of all ages, probably accounts for the fact that their particular study has dominated organic geochemistry since its inception. It also explains why porphyrins, isoprenoid alkanes and steranes are among the most reliable chemical fossils in the Precambrian (Schopf, 1970) (Fig. 4).

The general lack of gross structural complexity displayed by the geolipids (steranes and triterpanes possibly excepted) is no indication of their potential usefulness as biological markers.

The geolipids, in fact, exemplify the "carbon skeleton" approach to the study of chemical fossils and biological markers (Fig. 4). This usually involves isolating the geolipid fraction, identifying in it specific groups (often homologies: Johns et al., 1966) of compounds, and inferring from their structure and molecular weight distribution, possible biolipid precursors.

The kind of biological information which may be retained in geolipids varies according to compound type. In the straight-chain and branched-chain alkanes (plus fatty acids and alcohols when preserved), for instance, we find good presumptive evidence for the operation of a palaeobiosynthetic scheme analogous to the contemporary "polyacetate" (or acetate/malonate) biogenetic pathway. Hence the predominance of straight-chain fatty acids with an even number of carbon atoms in many rock geolipid fractions finds a ready explanation in terms of an enzymatically controlled addition of C_2 acetate units to a C_2 malonyl starter. The normal alkanes synthesized in modern biological systems (Douglas and Eglinton, 1966; Clark, 1966; Gelpi et al., 1970) are often of odd carbon-numbered chain length, probably being formed by decarboxylation of the equivalent acid (or an intermediate). Alcohol biogenesis is believed to involve reduction of the carboxylic acid function of a fatty acid, which would account for their similar even carbon-numbered chain length. Eglinton (1969) refers to the various means by which methyl branching is introduced into biolipid alkyl chains.

Fatty alcohols are virtually unknown in ancient sediments, except as components of intact esters in low rank coals (Brooks and Smith, 1969). Fossil fatty acids (normal, isoprenoid, and branched) have been widely reported from the sedimentary record (cf. reviews by Kvenvolden, 1967; and Parker 1969), including the Precambrian (Hoering and Abelson, 1964; Roblot et al., 1966; Van Hoeven et al., 1969; Han and Calvin, 1969; Smith et al., 1970; Pedersen and Lam, 1970). The saturated straight-chain C_{14}, C_{16}, and C_{18} homologues dominate these fatty acid patterns which therefore resemble those of contemporary microscopic algae (Holton et al., 1968; Schneider et al., 1970). The isoprenoid acids are not present as such in living algae, and when found in ancient sediments are probably products of the diagenesis of algal and bacterial chlorophylls. Unsaturated fatty acids, although major components of modern algae, normally would not be expected to escape reduction to the equivalent saturated acid during diagenesis (Rhead et al., 1971). The unsaturated acids extracted from three Precambrian cherts were interpreted as recent contaminants (Smith et al., 1970). Mineral-bound acids (eg. as calcium salts: Berner, 1968; Burlingame and Simoneit, 1968; Suess, 1970) are more likely to be indigenous than are their free (or interstitially trapped) counterparts, however. Any evaluation of the significance of fatty acids as biological indicators must rest heavily on the other chemical fossils preserved in association with them. Iso and anteiso fatty acids (or their derivatives) may be indicative of a bacterial contribution to sedimented organic matter (Cooper and Blumer, 1968).

In general, the value of the n-alkanes as biological markers lies not in the presence (or absence) of any particular homologue, but in certain characteristics of their overall pattern of distribution with respect to carbon number: its range, concentration maximum (or maxima), and the degree of preference for odd over even carbon-numbered chain lengths. An inherited marked odd carbon number preference is characteristic of the n-alkane patterns in many recent sediments (Bray and Evans, 1961), especially those to which land plant detritus has contributed (cf. Mazliak, 1969). It is commonly preserved in Phanerozoic sediments (Powell and McKirdy, 1973), but its occurrence in Precambrian rocks (Van Hoeven et al., 1969; Smith et al., 1970) is surprising. The straight-chain hydrocarbon distributions of marine bacteria and algae, ancestral forms of which comprised the bulk of the Precambrian biomass, usually display no odd-even predominance (Stransky et al., 1967; Oró et al., 1967; Clark and Blumer, 1967; Han et al., 1968; Winters et al., 1969). Moreover, such predominance, where originally present, diminishes rapidly during burial diagenesis (Brooks and Smith, 1967). The n-C_{17} alkane, the major constituent of many Precambrian hydrocarbon patterns, has been attributed (Gelpi et al., 1970) to the blue-green algae, but its relative concentration may again be a function of diagenesis (McKirdy and Powell, in preparation) or even extraction procedure. The isomeric 7-methyl and 8- methyl heptadecanes are also potential blue-green algal markers (Han et al., 1968; Han and Calvin, 1970; Sever and Parker, 1970). The higher molecular weight ($> C_{21}$) straight-chain alkanes (and alkanoic acids) found in sediment extracts of Devonian age and younger can be related to the hydrocarbons and esters of higher plant waxes and cuticles (Eglinton and Hamilton, 1967; Brooks and Smith, 1967, 1969). Needless to say, these precursors cannot be invoked for Precambrian geolipids. On the other hand, the finding of C_{14} to C_{37} n-alkanes of predominantly odd carbon number in fungal spores (Oró et al., 1966), C_{25} to C_{35} n-alkanes in a sulphate-reducing bacterium (Davis, 1968), and long-chain alkanes and alkenes in certain geologically significant species of algae (Gelpi et al., 1970) may be extremely relevant to the origin of similar hydrocarbons extracted from Precambrian sediments.

The geochemically important isoprenoids arise in living systems from the regular "head to tail" condensation of a reactive C_5 unit (isopentenyl pyrophosphate) under the directive influence of enzyme and cofactors, to form the terpene (C_{10}), sesquiterpene (C_{15}), and diterpene (C_{20}) compounds. Further "tail to tail" coupling of two C_{15} or C_{20} units leads to the larger triterpenoids (C_{30}) and tetraterpenoids (C_{40}), respectively. The steroids (C_{27}-C_{29}) are degraded and alkylated tetracyclic triterpenoids. When present in uncontaminated ancient sediments, usually as fully reduced (or, if cyclic, possibly aromatic) derivatives, compounds with isoprenoid carbon skeletons are excellent biological markers in their own right (Fig. 4). This is particularly true of steranes and triterpanes (Hills et al., 1970). However, only one reliable determination of sterane-type compounds in a Precambrian rock has been made (Barghoorn et al., 1965). Steranes found in the Soudan Shale (Burlingame et al., 1965; Johns et al., 1966) do not appear to be syngenetic (Hoering, 1967a; Schopf, 1970). The experimental difficulties in satisfactorily characterizing such large alkane molecules, especially when present as minor constituents of already very complex geolipid mixtures, are almost insurmountable. The prospect of obtaining corroborative geochemical evidence for the first appearance of nucleated cells is therefore not bright.

Significant concentrations of specific isoprenoid alkanes, notably phytane (C_{20}) and pristane (C_{19}), occur in nearly all the Precambrian sediments so far examined. Together with porphyrins and carbon isotopic data, they supposedly constitute evidence for the operation of photosynthesis from the time of the oldest sediments in the record. Whereas contemporary isoprenoid biosynthesis is stereospecific, non-biogenic acyclic isoprenoid alkanes are likely to comprise a random mixture of all possible stereoisomers (McCarthy and Calvin, 1967). Theoretically, stereochemical analysis of such isoprenoid hydrocarbons affords a means of distinguishing abiogenic occurrences. Methods based on high-resolution gas chromatography with special stationary phases have recently permitted the determination of the absolute stereochemistries of isoprenoid acids (possible intermediates in the diagenetic formation of isoprenoid alkanes) in the Eocene Green River shale (Maxwell et al., 1973). The absolute configuration of pristane from this formation had previously been ascertained by the same group of workers and shown to be compatible with a derivation from chlorophyll (Maxwell et al., 1972). It is to be hoped that the successful application of these techniques to isoprenoid geolipids recovered from Precambrian sediments will soon be reported.

Metal-chelated porphyrins (Fig.4) have been found, usually only in trace amounts, in several rocks of Precambrian age (Barghoorn et al., 1965; Hodgson et al., 1968; Kvenvolden and Hodgson, 1969) (Table III, Suggested biochemical precursors include the various bacteriochlorophylls; the iron-containing coenzymes (cytochromes, catalase, peroxidase) of microbial photosynthesizers; vitamin B_{12} (cobalamine) present in anaerobic methane bacteria; and the algal photosynthetic pigment, chlorophyll a (Margulis, 1969, 1970b; Schopf, 1970). The stability of the distinctive aromatic tetrapyrrole nucleus of porphyrins enhances their ability to survive sedimentation and burial. At the same time, the sensitivity of their peripheral functional groups to changes in geochemical environment provides a useful indication of their diagenetic history (Baker, 1969; Blumer and Rudrum, 1970). Finally, porphyrin abiogenesis, although possible (Hodgson and Ponnamperuma, 1969; Hayatsu et al., 1972), is unlikely to account for more than a negligible proportion of the porphyrins trapped in the earliest Precambrian sediments.

The stable isotopes of carbon, ^{13}C and ^{12}C, are known to undergo kinetic and metabolic fractionation during green-plant photosynthesis, resulting in the overall depletion of the heavier isotope in the organism relative to its carbon source, molecular CO_2 (Degens, 1969). Thus, photosynthetically-produced organic matter is stamped with an isotopic biological marker which is not erased by the processes of post-burial maturation (Gavelin, 1957; Degens, 1969). While the δ^{13} values of insoluble organic matter isolated from Precambrian sediments (Hoering, 1967a,b; Oehler et al., 1972) are similar to those of fossil organic matter generally, they are often significantly lower than the average value, $\delta^{13}C_{PDB}$ = -26 per mil, cited by Degens (1969) (Fig. 2). According to Degens, these low values are explicable in terms of the higher partial pressures of CO_2 which are thought to have existed during the Precambrian. In the presence of high concentrations of dissolved CO_2, fractionation between the cellular carbon of marine plankton and the bicarbonate of sea water may be as great as -28 per mil (Deuser et al., 1968). An experimental study by Calder and Parker (1973) of carbon isotopic fractionation effects in laboratory cultures and Recent mats of blue-green algae confirmed that the degree of fractionation was dependent on the CO_2 content of the feed gas, and showed that variations in pH (7-8) and temperature (30-39°C) had no measurable effect. However, even the highest CO_2 concentration tested (ca. 100 P.A.L.) failed to produce $\delta^{13}C$ values as low as those of organic matter in Precambrian sediments. Nevertheless, as Calder and Parker themselves point out (p. 139), it is still conceivable "that some combination of environmental variables could result in greater enrichments of C^{12}" in modern blue-green algal carbon.

The lipids of modern organisms are isotopically very much lighter than other biochemical fractions (Abelson and Hoering, 1961; Degens et al., 1968). Alternatively, therefore, the kerogen of Precambrian sediments may have arisen mainly by way of polymerization of unsaturated lipids, eg. fatty acids (Abelson, 1967), although it is difficult to see why this should not also be true of Phanerozoic kerogens. One possibility is that unsaturated lipids comprised a higher percentage of the dry weight of the Precambrian biota (algae, bacteria, fungi) than they did in the higher organisms which later evolved. Unsaturated fatty acids are important components of the total fatty acid spectrum extant of blue-green algae (Parker et al., 1967; Schneider et al., 1970), particularly the filamentous forms (Kenyon and Stanier 1970), and green algae (Schneider et al., 1970) in the range C_{14} to C_{18}. However, carbon isotopic measurements on lipids isolated from six species of contemporary blue-green algae suggest that "lipid enrichment alone" is unlikely to explain the observed isotopic composition of Precambrian organic matter (Calder and Parker, 1973). A group of British workers is of the opinion that Precambrian kerogens are chemically identical with sporopollenin, an oxidative polymer of carotenoids and carotenoid esters found in pollen and spore exines

(Brooks and Shaw, 1968, 1970, 1971, 1972; J. Brooks, 1971). Their case would be considerably strengthened if carbon isotopic measurements on modern and fossil algal spores (acritarchs?) were to indicate a similar depletion in the heavier isotope.

The accumulated isotopic data on organic matter in sediments of all ages (Degens, 1969; Smith et al., 1970; Oehler et al., 1972) appears to show that there has been a gradual increase in the $^{13}C/^{12}C$ ratio of organic carbon since ca, 2,100 m.y. ago. This trend may provide the basis for a much needed test of age for Precambrian organic matter (Schopf, 1970). The $\delta^{13}C$ values obtained by Oehler et al. on cherts from the Theespruit Formation of the Onverwacht Group reveal a marked isotopic discontinuity between lower Onverwacht and younger Precambrian cherts. The carbon isotopic composition of the Theespruit cherts ($\delta^{13}C_{PDB} = 14.3$ to $- 18.9$ per mil) is, in fact, similar to that of non-carbonate carbon in certain carbonaceous chondrites (Fig.2) and may indicate a contribution from abiogenic organic matter. Such a conclusion, although necessarily tentative, is consistent with Calvin's interpretation of the total alkane pattern in another sample of Onverwacht chert. It also accords with the aromatic nature of Onverwacht kerogen (Scott et al., 1970).

Schopf (1970) has presented an up-to-date assessment of the contribution organic geochemistry has made to Precambrian evolutionary studies. In it he develops a rationale which subordinates chemical fossils (or more precisely biological markers) to morphological microfossils, the former only to be accepted as contemporaneous with the lithification of the sediment if consistent with the micro (and macro) fossil content of the rock. However, although he relegates the chemical fossil data from the Soudan Iron Formation to the "uncertain" category on the basis of discrepancy between the $\delta^{13}C$ values of the soluble and insoluble organic fractions (Hoering, 1967a), and mineralogic evidence of an elevated thermal history (Cloud et al., 1965), he is prepared to accept even older sediments as containing "probable" chemical fossil assemblages, for want of such evidence. The point to be made here is that no critical examination or systematic assessment of the degree of metamorphic alteration sustained by the Precambrian sediments in question has yet been undertaken. In fact, there is considerable evidence that these and other very old sediments cannot have escaped such alteration. A method of accurately comparing the relative metamorphic grade of ancient organic-rich sediments is obviously needed. But before examining more closely the question of the metamorphism of organic matter, some consideration must be given to the problem of contamination in organic geochemical studies.

CONTAMINATION

Contamination, from whatever source, is a problem which is encountered in every organic geochemical investigation regardless of the nature of the material under study, its age, or its state of preservation. The solvent extraction procedure involved in most geolipid studies effectively divides the organic matter in a rock into two fractions. The insoluble portion (kerogen), being chemically almost inert, is exceedingly difficult to investigate. However, unlike the solvent - soluble fraction, it is immobile and therefore probably syngenetic with the host rock (Hoering, 1967a). Although the soluble geolipids are more amenable to isolation, separation,and identification, they are also readily contaminated by lipids (and other organic compounds) of more recent origin. As a general rule, the lower the extractable organic content of the geological sample (fossil, rock, or unconsolidated sediment), the more serious is the threat of contamination to the validity and therefore correct interpretation of the analytical data. Furthermore, the older the rock, the lower its concentration of extractable material tends to be, owing mainly to the inevitable thermal degradation of its original sedimentary organic matter during burial and,later, regional metamorphism. For these reasons, rocks of Precambrian age are susceptible to gross organic contamination. Neither is the problem obviated satisfactorily by confining one's attention to highly bituminous Precambrian sediments (as suggested by Hoering, 1967a), since relatively few such rocks are known (cf. Table I). The analytical methods presently available have reached a sufficient level of sophistication to enable the isolation and characterization of very low concentrations of geolipids (Murphy, 1969). Nevertheless, if Precambrian organic geochemistry is to continue as a viable field of study, effective means of distinguishing truly indigenous (ie. syngenetic) organic matter from adventitious contaminants must be found. To this end considerable effort has been expended on investigating the nature and origin of contamination in "natural product chemistry" as it applies to geological materials. A detailed discussion of contamination in organic geochemistry is beyond the scope of this review. Instead comment will be confined to the various methods which have been employed to determine whether or not the organic compounds identified in Precambrian rocks are as old as the rock themselves.

A simple approach to the problem of contamination was to study only those rocks which displayed well-indurated or crystalline primary textures, with consequent minimal porosity and permeability. Studies of this type included those of bituminous substances trapped as fluid inclusions in igneous rocks (Petersilie and Sörensen, 1970; Mueller, 1972); and the somewhat more promising organic matter occluded in black fossiliferous cherts (Oró et al., 1965; Schopf et al., 1968; Van Hoeven et al., 1969). In fact, until recently primary cherts were regarded as ideal sediments for organic geochemical investigation. The alleged biogenicity of the amino acids, hydrocarbons, and fatty acids detected was considered to be firmly supported by the fact that each chert sample examined contained microfossils. Furthermore, similar compounds were known as biochemical components (or geochemical derivatives) of present-day organisms.

Subsequent studies (Abelson and Hare, 1969; Nagy, 1970; Smith et al., 1970; Sanyal et al., 1971) of the same and other black cherts have all shown that these apparently impermeable sediments possess sufficient porosity and permeability to admit comparable quantities of recent "biological markers", even over quite short periods of geological time. Abelson and Hare also found that the chert siliceous matrix had no significant stabilizing effect on several of the more thermally labile amino acids (e.g. serine, threonine) detected by Schopf et al., which in turn is good evidence that they are much younger than the sediment itself. In the absence of such stabilization, amino acids indigenous to Precambrian sediments would be expected to be racemic mixtures of the L- and D- forms. Thus the discovery that amino acids recovered from samples of Gunflint and Fig Tree chert comprised only the L-isomers (Abelson and Hare, 1969; Kvenvolden et al., 1969; Oró et al., 1971) is strongly indicative of their relatively recent origin.

Given their finite porosity and permeability, and their tendency to contain only very low concentrations of extractable organic matter, it seems valid to conclude that black cherts may not be as well suited to organic geochemical study as at first thought. And so we return to Hoering's (1967a) original suggestion that only Precambrian rocks with an extractable organic content greater than 100 ppm are likely to yield analytical data free of the misleading influence of contamination. As Table I indicates, such rocks are inevitably shales. In short, argillaceous sediments appear to have a greater capacity to trap and retain bituminous organic matter than do cherts. Moreover, most of the organic-rich Precambrian shales studied by McKirdy (1971) had permeabilities less than those reported by Smith et al. (1970) for ancient cherts.

In addition to the above somewhat general considerations, other more specific criteria for the recognition of organic contaminants in rocks have been proposed. Indigenous bitumen is coeval with the kerogen of a sedimentary rock (cf. Abelson, 1967). According to Hoering (1967a), a discrepancy of greater than 2 per mil in their $\delta^{13}C$ values indicates that the soluble fraction (or part thereof) represents contamination which has migrated into the rock since its lithification. Calvin (1969) disagrees with this interpretation, on the grounds that the thermal cracking processes involved in diagenesis and incipient metamorphism are subject to an isotope effect (Brodskii et al., 1959) which would lead to a significant ^{13}C isotopic enrichment in the insoluble fraction. Whether such an isotope effect is really sufficient to account for the large differences in the carbon isotopic composition of the two organic fractions in many of the rocks examined by Hoering (1967a,b) remains to be seen (cf. next section).

Another method, widely applicable to the problem of distinguishing contamination from truly indigenous organic matter, involves studying the effect of progressive rock particle size reduction on the solvent extract yield and composition. Using this technique on Precambrian black cherts, Smith et al. (1970) found that the highest concentrations of alkanes and fatty acids (saturated and unsaturated) were recovered from the surfaces of the larger-size fractions; only minute amounts were occluded within the actual rock silica. Hence their conclusion that only trace amounts (a few parts per billion, or less) of the extracted geolipids were actually indigenous to the chert. Oró et al., (1965), on the other hand, maintained that less than 1% of the alkanes recovered from the Gunflint chert were attributable to surface contamination. Schopf (1970) rationalized these apparently conflicting results in terms of possible variations in the level of contamination and/or quality of preservation within the same formation. Whatever the explanation, the pitfalls and difficulties of comparative Precambrian organic geochemistry are illustrated. A similar serial size reduction and extraction procedure was employed by Meinschein (1965) in his study of the alkane content of "carbon-rich silicate" and carbonaceous lenses from the Soudan shale. Again most of the extractables were obtained from the surfaces of the intact rock specimens. Nevertheless, on the basis of the different distributional patterns of the normal paraffins and the non-linear alkanes in the various parts of the formation sampled, Meinschein argued that the hydrocarbons were indigenous.

Finally, it should be emphasized that, at present, no specific chemical tests for organic compounds of Precambrian age are available (Smith et al., 1970). Organic carbon of such great age is beyond the scope of ^{14}C dating, which has a maximum range of 70,000 years (De Vries, 1959). Hence, even where it can be shown that the constituents of a rock extract are not the result of contamination from laboratory reagents and procedures, it is still extremely difficult (if not impossible) to prove that they or their geochemical precursors were deposited with the original sediment which eventually gave rise to the rock under investigation (Schopf, 1970). A feature possibly unique to older Precambrian microbiology is the novel finding by Han and Calvin (1969) that the C_{15} and C_{16} isoprenoid alkanes were present in excess of the C_{19} and C_{20} homologues in an Onverwacht rock sample. However, this observation may be little more than a manifestation of a rather advanced state of incipient metamorphism (cf. Robinson et al., 1965; Albrecht and Ourisson, 1969).

INCIPIENT METAMORPHISM OF ORGANIC MATTER

In comparing the "organic geochemical facies" of different ancient sediments (Eglinton 1965), one would normally expect to find similarities or differences according to the types of source organisms living at the time (cf. Bradley, 1970). Since chemical fossils are all susceptible to thermal alteration and degradation, such comparisons are unlikely to be very instructive in the absence of prior knowledge of the relative metamorphic grades of the host rocks, the stability of the presumed biological precursors, and the structure of their likely geochemical derivatives. If, as Degens (1967) suggests, most organic matter in sediments and sedimentary rocks has acquired its present molecular framework during diagenesis, these considerations become even more important. The slow thermal maturation which organic detritus undergoes after burial continues through late diagenesis into low-grade metamorphism. According to Hoering (1967b), by the time a sediment has been metamorphosed to the chlorite stage, the original chemical structure of its organic content is beyond recognition. Surprisingly, however, most major organic geochemical studies of Precambrian sediments have been marked by a lack of metamorphic control. There has been a tendency to assume that, because a rock displays no obvious metamorphic features, its organic matter has escaped serious alteration. This assumption is highly questionable.

Working on coals, Karweil (1956) was able to demonstrate a correlation between burial temperature, duration of heating, and coal rank. He showed that although the maximum temperature to which an organic deposit is exposed may remain low (say 80°C), given sufficient time it will attain a much higher rank or degree of maturation than it presently displays. His findings suggest that the syngenetic organic content of a Precambrian sediment, by virtue of its age, is likely to have undergone extensive alteration, irrespective of whether or not it has had a low temperature history (Cooper and Murchison, 1969). The Precambrian black cherts examined by Smith et al. (1970) contained no petrographic or micropalaeontological evidence of alteration. And yet, in view of the low extraction yields obtained, the authors were forced to conclude that nearly all the original geolipids may have been converted to low molecular weight gases and insoluble polymer (kerogen) during diagenesis. The "nonmetamorphosed" sample of Onverwacht chert analysed by Nagy and Nagy (1969b) has since been found to have been heated to about 200°C (J. Brooks, 1971; Brooks and Shaw, 1972), well above the threshold temperature at which thermal reconstitution of organic matter in sediments commences.

A good correlation between "sharpness" of the basal X-ray diffraction reflection of the clay mineral illite (expressed as the ratio, peak height at 10 Å to that at 10.5 Å) and degree of metamorphism in low-grade Palaeozoic sedimentary rocks of the Ouchita System was discovered by Weaver (1961). Extensive use of a slightly modified version of Weaver's technique by French geologists (Kubler, 1968; Dunoyer de Segonzac et al., 1968) has subsequently shown that illite is a sensitive reliable index of advanced diagenesis and incipient metamorphism in clay-bearing sediments. Increased sharpness of the 10 Å peak indicates gradual closure of the illite layer lattice and growth in crystallite size, ie. improved crystallinity. Illite crystallinity becomes independent of the lithofacies of the host rock during late diagenesis and is completely so during the transition from diagenesis to metamorphism. Dunoyer de Segonzac (1970) has named this transition zone the <u>anchizone</u> after Harrassowitz's (1927) term "anchimetamorphism" (<u>anchi</u> = close to). By plotting illite crystallinity (10Å peak width at half peak height, ie. Kubler index) against the ratio of the 5Å and 10Å peak intensities according to the method of Esquevin (1969), McKirdy and Powell (in preparation) found that a suite of apparently unmetamorphosed organic-rich shales and carbonates from the Cambrian and Precambrian of Australia straddled the anchizone (Fig. 5). In most Precambrian samples the illites had developed into true micas characteristic of the metamorphic <u>epizone</u> (<u>epi</u> = at or upon). For sediments of the anchizone and epizone , the original 10Å peak sharpness ratio of Weaver provides a more sensitive measure of their relative metamorphic grade than does Kubler's crystallinity index (cf. Kubler, 1968; fig. 3). As illite is of widespread occurrence in Precambrian sediments, the Weaver index would seem to be a useful mineralogical indicator of the extent of their incipient metamorphic alteration. Illite has been identified in samples of Fig Tree and Onverwacht chert (Brooks and Shaw, 1971), which suggests that even certain organic-rich cherts could be ranked on a common basis with shales and carbonates.

Chemically, the comminuted insoluble organic matter (kerogen) which is dispersed throughout many Precambrian strata resembles medium to high rank coal (Saxby, 1970) and may be expected to have responded to diagenesis in much the same way (J.D. Brooks, 1971). Griffin (1967) studied the X-ray diffraction patterns of a collection of mineral-free humic coals of varying rank. A progressive decrease, from 3.8-4.6Å in lignite to 3.35Å in meta-anthracite, was observed for the (002) repeat distance of the graphite-like layers. The coals analysed were assumed to represent different stages in the metamorphism of a common progenitor, but this assumption was acknowledged to be beyond verification. However, in view of the limited range of available precursor organisms (algae, bacteria, and perhaps fungi), the technique would seem to be quite valid when used to measure the degree of alteration of Precambrian kerogens. Coals (see e.g. Tyler, et al., 1957; Pedersen and Lam, 1968, 1970; Vologdin, 1970) are insufficiently common in the Precambrian sedimentary record to be practical rank indicators. Diffraction maxima of acid-insoluble carbonaceous residues from a slate marker bed enabled French (1964) to detect a progressive increase in the metamorphic grade of the middle Precambrian Biwabik Iron Formation along strike towards an intrusive gabbro complex. Similarly, McKirdy and Powell (in preparation) reported a decrease in the d_{002} spacing of the incipient graphite lattice down an anchimetamorphic series of Cambrian and Precambrian kerogens. A corresponding regular decrease in the hydrogen to carbon atomic ratio indicates that the elemental composition of ancient kerogens is strongly controlled by incipient metamorphism. The changes in chemical structure and composition accompanying kerogen metamorphism or degradation (of which the end product is graphite) can be correlated with release of liquid and gaseous hydrocarbons, CO_2 and H_2O (McIver, 1967; Long et al 1968), and understood in terms of reactions analogous to those believed to occur during coalification (e.g. dehydration, decarboxylation, cracking of alkyl side chains, dehydrogenation, and aromatic ring condensation).

Interpretation of the origin of carbonaceous matter in Precambrian sediments is based largely on the results of various types of chemical analysis: determination of elemental composition (Brooks and Shaw, 1968; Cooper and Murchison, 1969; Saxby, 1970; J. Brooks, 1971; J.D. Brooks, 1971; McKirdy and Powell, in preparation); infra-red spectroscopy (Saxby, 1970; Brooks and Shaw, 1971; McKirdy and Powell, in preparation); and gas chromatography or mass spectrometry of the products of pyrolysis (Hoering, 1967a,b; Simmonds et al., 1969; Scott et al., 1970; Brooks and Shaw, 1971), oxidation (Hoering, 1967b; Nagy and Nagy, 1969a,b; Brooks and Shaw, 1971) and alkali fusion (Brooks and Shaw, 1971). The more severely metamorphosed the kerogen, the less the analytical data reflect the composition and structure of the original source material. Of the known organic-rich Precambrian formations, the Bitter Springs (Schopf, 1968; Walter, 1972 b; McKirdy and Powell, in preparation), the Nonesuch (Barghoorn et al., 1965; Moore et al., 1969), and the McMinn (Hoering, 1967a,b; McKirdy and Powell, in preparation) appear to be among the least altered. Hopefully, further work on their residual carbonaceous matter will yield the information necessary to resolve the present uncertainty (Cooper and Murchison, 1969; Brooks and Shaw, 1970; Saxby, 1970) as to the ultimate derivation of Precambrian kerogens.

The extractable organic fraction of rocks also behaves in a recognizable and predictable way during incipient metamorphism. The absolute hydrocarbon yield and the ratio of total hydrocarbons to organic carbon decreases, while the ratio of saturated to aromatic hydrocarbons increases, with advancing metamorphism of shales (Baker and Claypool, 1970). The same is true for carbonates, except that alkanes and aromatic hydrocarbons are destroyed at approximately the same rate whereas, in shales, the aromatics are lost more rapidly (McKirdy and Powell, in preparation). Late diagenesis and early metamorphism of shales appears to result in the preferential generation of branched and cyclic alkanes, and that of carbonates, n-alkanes.

According to McKirdy and Powell, catalytic cracking has occurred in the shales as opposed to thermal cracking in the carbonates (cf. Eisma and Jurg, 1969). In general, the biological information content of alkane distribution patterns steadily diminishes with increasing age and/or depth of burial of the host rock. Thermal maturation results in progressive loss of any inherited odd carbon number preference in n-alkanes (Brooks and Smith, 1967); increased concentration of lower molecular weight alkanes at the expense of the higher homologues (Albrecht and Ourisson, 1969); and a marked increase in the number of isomers present (Henderson et al., 1968). The bimodal alkane patterns (Fig. 6) consistently found in Archaean shales and metasediments from the West Australian Shield (Stevenson and Polgar, 1966; J.D. Brooks, 1971; McKirdy and Powell, in preparation) indicate that under certain circumstances, chain-lengthening reactions (Jurg and Eisma, 1964; Shimoyama and Johns, 1972) may also occur. Similar n-alkane distributions were obtained by J.D. Brooks (1971) from artificial diagenesis experiments on various strains of bacteria.

Welte's (1969) technique for measuring the $^{13}C/^{12}C$ ratios of individual n-alkanes holds promise as a means of distinguishing those hydrocarbons which represent biological markers from those which have been appreciably modified to the extent of being better regarded as products of diagenesis and anchimetamorphism. An isotope fractionation effect (viz. preferential breakage of $^{12}C-^{12}C$ over $^{13}C-^{12}C$ bonds) is inherent in the thermal rupture of carbon- carbon bonds (Stevenson et al., 1948; Brodskii et al., 1959). In any given n-alkane distribution, then, the homologue(s) with the lowest $^{13}C/^{12}C$ ratio will be the least thermally altered, ie. its carbon skeleton will most closely match that of its original biochemical parent. In such a manner it may be possible to determine whether the long-chain ($>C_{21}$) n-alkanes found in Precambrian rocks are derived from similar long-chain biolipids, or are the result of maturational chain-extension processes.

As noted in the previous section it is possible that the discrepancies between the $\delta^{13}C$ values of the soluble and insoluble organic fractions of some ancient sediments may be due to thermal cracking during incipient metamorphism. Baker and Claypool (1970) made $\delta^{13}C$ measurements on both the hydrocarbon extracts (saturated and aromatic fractions) and the total organic carbon (in effect, kerogen) of most of their shales. Examination of their data on "metamorphosed" samples reveals that the saturated hydrocarbons (the dominant fraction of the extract) are, on the average, 4 per mil lighter than the kerogen (with this difference being as great as 13 and 19.4 per mil in two highly metamorphosed samples). This would appear to support Calvin's (1969) hypothesis (see p.000). Baker and Claypool concluded that metamorphism led to increased $\delta^{13}C$ values for kerogen in sedimentary rocks. They were unable to recognize any consistent pattern of alteration in the isotopic composition of the hydrocarbons. Earlier studies (summarized by Degens, 1969) had shown that increasing metamorphism has little or no effect on the isotopic composition of residual carbonaceous matter in metasediments. Its impact on coexistent bitumen has not been specifically investigated. Abelson and Hoering (1961) discovered that the carboxyl groups of amino acids are enriched in ^{13}C relative to the rest of the molecule during photosynthesis. Loss of such functional groups during incipient metamorphism would result in a decreased $\delta^{13}C$ value for the residual reduced material. Conversely, the isotope effect alluded to by Calvin (1969), and which is presumably operative during cracking of methane (and other low molecular weight hydrocarbons) from the kerogen, would tend to leave the latter enriched in ^{13}C (as observed by Baker and Claypool, 1970). Thus the amount of fractionation would appear to depend on the relative amounts of both CO_2 and CH_4 released during kerogen maturation. Such isotopically selective processes are suggested by Meinschein (1965) to explain the discrepancy between the $\delta^{13}C$ values of the soluble and insoluble organic fractions of the Soudan shale. On the other hand, as pointed out by

Degens (1967), the kerogen of a petroleum source rock is invariably almost identical to the generated petroleum. Perhaps the $\delta^{13}C$ values of the soluble and insoluble organic fractions of a sediment only become significantly different in the later stages of incipient metamorphism as the kerogen approaches a graphitic structure and composition.

ORGANIC MATTER IN METAL DEPOSITS

Organic compounds and residual carbonaceous material of apparent biological origin are associated with copper, lead, zinc, iron, gold, and uranium mineralization in the Precambrian metal deposits listed in Table I. Except for the Woodcutters prospect, all are stratiform; and most represent ore accumulations of major economic importance.

Thucolite, an unusual "hydrocarbon mineral", has been recognized in many early Precambrian uranium deposits and its occurrence in the gold-uranium reefs of the Witwatersrand area, South Africa, has been extensively studied (eg. Davidson and Bowie, 1951; Leibenberg, 1955; Ramdohr, 1958; Schidlowski, 1969). Carbonaceous matter in base metal ores at Mount Isa, Queensland, and McArthur River, Northern Territory, contributes to their adverse metallurgical behaviour (Croxford, 1968; Croxford and Jephcott, 1972). Otherwise, the association of organic matter and metallic mineralization in Precambrian rocks has excited remarkably little interest. Recent work, however, suggests that such organic matter may contain valuable information on the genesis and post-accumulation history of an ore (Taylor, 1971).

As is evident from Table IV, carbonaceous matter and anomalous metal concentrations coexist in a variety of lithofacies, although the host rocks of the more organic-rich ores are usually argillaceous. The organic fraction is mostly finely-divided sub-microscopic kerogen. In shales and argillites it is intimately mixed with the layer-lattice silicates of the clay fraction. In ferruginous cherts, such as those of the Biwabik, Gunflint, and Brockman Iron Formations, black carbonaceous material may delineate microstructures of algal and bacterial affinities (Cloud, 1965; LaBerge, 1967). Morphologically recognizable remains of progenitor organisms are rarely preserved in lithofacies other than chert. The remarkable fungal ecosystem in the cupriferous Nonesuch Shale described by Moore et al. (1969) is an exception, as are the sporomorph acritarchs found in diagenetic pyrite at Mount Isa (Love, 1965) and in mineralized shale from the McArthur River lead-zinc deposit (Hamilton and Muir, in press). The petrographic resemblance of thucolite in Witwatersrand conglomerates to algal structures common in torbanite (Snyman, 1965) has been shown to be fortuitous and of doubtful genetic significance (Schidlowski, 1969). On the other hand, stromatolites are stratigraphically related to ore-bearing sequences in the Zambian Copperbelt, McArthur River, Alligator River, and Gunflint deposits where they constitute indirect evidence of an algal (and bacterial) source for much of the carbonaceous matter associated with the economic mineralization. The results of various organic geochemical analyses of this material also indicate a biological origin.

Table IV summarizes the types of organic compounds which have been extracted from Precambrian ores and their host rocks. As in unmineralized sediments, hydrocarbons occur widely with the isoprenoid alkanes usually being represented. For example, pristane and phytane have now been identified in the Nonesuch Shale (Barghoorn et al., 1965; Eglinton et al., 1966), the Urquhart and H.Y.C. Pyritic Shales (McKirdy and Powell, in preparation), the Gunflint Iron Formation (Oró et al., 1965; Van Hoeven et al., 1969; Smith et al., 1970), and the Soudan Iron Formation (Johns et al., 1966; Oró and Nooner, 1970). Of particular interest is the recent identification (Schidlowski, 1971) of these two isoprenoids among the pyrolysis products of a sample of Witwatersrand thucolite. The presence in thucolite of pristane and phytane, porphyrins (Hodgson et al., 1968), amino acids and carbohydrates (Prashnowsky and Schidlowski, 1967), and its stable carbon isotopic composition (Hoering, 1967b; Hoefs and Schidlowski, 1967) strongly suggests a photosynthetic origin for its precursor organic material. The n-alkanes isolated from a West Australian thucolite of Archaean age (J.D. Brooks, 1971) are exceptional in that they display a marked preference for homologues of even carbon number in the C_{20}-C_{26} range. A similar even preference was noticed in hydrocarbons from several ultrabasic rocks. Apart from speculating that the hydrocarbons could be in part abiotic, no explanation for this unusual phenomenon was offered. Supposedly inorganic hydrocarbons have been reported from Precambrian igneous rocks in Russia (Petersilie et al., 1968), Greenland (Petersilie and Sörensen, 1970), and South Africa (Mueller, 1972). Gas chromatographic analyses have been carried out in the last case only. Kvenvolden and Roedder (1970) identified isoprenoids, usually indicative of a biological source, in the hydrocarbons recovered from fluid inclusions in quartz crystals from South-West Africa. Similarly, Calvin (1969) noted the presence of two peaks of similar retention index to pristane and phytane in a capillary gas chromatogram of hydrocarbons extracted from an allegedly abiogenic thucolite located in a pegmatite dyke near Henvey, Ontario (Spence, 1930).

The actual mode of emplacement of thucolite in the Witwatersrand conglomerates and its age relative to the uranium oxide have been the subject of much debate. According to Koen (1961) the uranium was fixed and concentrated by carbonaceous matter already in place. In this regard it is interesting to note that gold-uranium reefs of the carbon seam type on the Kaapvaal Craton are generally confined to low-energy environments (Viljoen et al., 1970) which might be expected to favour algal growth. Schidlowski (1969) advocates an allochthonous origin for the thucolite, involving migration of biogenic hydrocarbons into host conglomerates where they are exposed to α-and β-radiation from detrital uraninite, undergo condensation and polymerization reactions, and finally solidify as carbonaceous material around individual uraninite grains. Some doubt is cast on this latter hypothesis, however, by a recent investigation of Precambrian thucolite occurrences in Australia (G.H. Taylor, personal communication, 1972), which showed that the substance does not have the expected properties of a radiolytic polymer.

Whatever its actual derivation, thucolite illustrates how knowledge of the origin of associated organic matter may be crucial in understanding the history of an ore. It is well known that several processes can contribute to the concentration of trace elements by organic matter (Brongersma-Sanders, 1970). These include direct incorporation of metals into the cells of living organisms, notably bacteria (Koval'skii et al., 1965; Baas Becking Geobiological Laboratory, 1971) and algae (Vinogradov, 1953), and sorption of metallic ions from solution by decaying organic detritus during and after its sedimentation (Szalay and Szilagyi, 1969). In addition, inorganic by-products of life processes, eg. oxygen and hydrogen sulphide, may precipitate metals from solution. Oxygen-releasing photosynthetic algae appear to have played a key role in the deposition of Precambrian banded iron formations (Cloud, 1968a,b; Becker and Clayton, 1972). Similarly, the generation of hydrogen sulphide by sulphate-reducing bacteria can lead to the formation of heavy-metal sulphide in sedimentary environments, possibly on a scale large enough to account for such stratiform deposits as Mount Isa and McArthur River (Trudinger et al., 1972). The operation of sulphate-reducers implies an adequate supply of dead organisms (mainly algae?) as a carbon source for the bacteria (Berner, 1970).

Biological activity has been invoked as one of the processes which facilitated the concentration of gold into the present economic Witwatersrand deposits (Viljoen et al., 1970). D.A. Pretorius (cited by Nagy, 1971) reported the association of finely divided gold and organic matter in Swaziland rocks and concluded that the gold may have been concentrated by algae or trapped in algal mats. The occurrence of copper, iron, and nickel in the walls of alga-like fossils from the Fig Tree Series has been interpreted by Pflug (1967) as indicating that such microorganisms were capable of precipitating metal salts from solution.

Copper mineralization in the Nonesuch Shale at the White Pine Mine is epigenetic (White and Wright, 1966). Degraded organic material (Moore et al., 1969) in the host sediments evidently caused the precipitation of metal cations from percolating copper-bearing solutions during the pre-compaction stage of diagenesis (Ensign et al., 1968). The uranium deposits at Rum Jungle and Alligator River, Northern Territory, are further examples of the apparent localization of ore mineralization by carbonaceous matter (Taylor, 1971). Conversely, metals can react with organic matter to form soluble organo-metallic complexes (Saxby, 1969), thereby preventing the precipitation of metals (Fraser, 1961). This may have been the case in the Woodcutters lead-zinc deposit where the ore minerals occur in veins which transgress the bedding. Roberts (1973) argued that metals in the interstitial solutions of unconsolidated dolomitic sediments may have complexed with algal degradation products. The metals are thought to have precipitated as sulphides only after the onset of post-lithification folding when fractures developed and the organic complexes become unstable. Recent experimental work (Lambert, in press) has shown that metal sulphides, particularly those in replacement textures in sedimentary ores, may form as a result of the diagenetic breakdown of sulphur-bearing organic compounds (eg. cysteine) or metal-organic sulphur complexes. The ability of naturally-occurring organic compounds, particularly amino acids and adenosine triphosphate , to dissolve and reprecipitate ore and other minerals has been demonstrated by Evans (1964) and Kranz (1969). Amino acids are known to be associated with Precambrian uranium (Prashnowsky and Schidlowski, 1967) and asbestos (Harington, 1962) mineralization in South Africa.

Finally, graphite and less well ordered carbonaceous matter may influence the deformation of an ore deposit. It can act as a shearing lubricant (Taylor, 1971), as well as participating directly in metamorphic reactions (Yui, 1968). The presence of organic carbon in carbonates inhibits their recrystallization under contact metamorphic conditions (Robinson, 1971).

Likewise, the organic material which often forms a matrix within pyrite framboids (Love and Amstutz, 1966) can prevent the constituent granules from coalescing into single euhedral crystals. The relation of carbonaceous matter in the Urquhart Shale at Mount Isa to the origin of its first-generation pyrite has been discussed by Love (1965).

CONCLUSIONS

Given the vast span of earth history represented by the Precambrian sedimentary record, the number of different Precambrian formations sampled for organic geochemical analysis is still exceedingly small. There is an urgent need for systematic analysis of many more well-preserved fine-grained sediments containing dispersed organic matter and generally recognizable in the field by their dark colour. In earlier reviews of the organic geochemistry of Precambrian sediments both Hoering (1967b) and Cloud (1969) advocated a careful search for organic-rich rocks which have had a relatively mild thermal history. This search has so far met with only limited success (see Table I). Further examples of little-altered rocks will have to be found and examined, microscopically (Moore et al., 1969; Brooks and Muir, 1971) as well as geochemically, if a comprehensive picture of the nature, distribution, origin, and significance of organic matter in Precambrian sediments is to emerge. Certain key organic geochemical parameters should be determined. These include: organic carbon content; geolipid extraction yield; $\delta^{13}C$ (soluble and insoluble organic matter, coexisting carbonate); ratio of saturated (alkane) to aromatic hydrocarbons; alkane and fatty acid distribution patterns; amino acid composition and isomeric configuration (ie. whether L- or D,L-); porphyrin type and molecular weight distribution; and kerogen d(002) spacing , elemental composition,and pyrolysis products. Such information would not only reveal the kind of organic matter present but also permit assessment of its degree of late diagenetic/incipient metamorphic thermal alteration and the extent to which it comprises epigenetic or recent contamination.

Hopefully, detailed investigations of this kind, in conjunction with studies of recent euxinic environments (eg. Richards, 1970; Fenchel and Riedl, 1970; Deuser, 1971; Rhoads and Morse, 1971; Nissenbaum et al., 1972; Brown et al., 1972) will also lead to more informed estimates of the size and rate of expansion of the aquatic biomass during the Precambrian. A recent "feasibility study" of Precambrian (and other) biogenic sulphide ores (Trudinger et al., 1972) is a step in this direction.

Carbonaceous sediments containing less than 100 ppm extractable geolipids - Hoering's empirical lower limit for suitability - should not necessarily be excluded from consideration simply on the grounds that any contamination they may have sustained will probably represent a significant proportion of their soluble organic matter. On the contrary, such rocks may be expected to form the basis of new attempts to decipher the complex effects of diagenesis and incipient metamorphism on organic detritus originally buried in sediments on the Precambrian earth and now preserved as bituminous and carbonaceous residues in fine-grained rocks of that age. If, in fact, the relevant compositional variables of the soluble organic fraction coincide with those predicted in view of the rank and lithofacies of the host sediment (Baker and Claypool, 1970; McKirdy and Powell, in preparation), then one has good reason for accepting it as essentially free of post-lithification contamination.

The classes of organic compound most likely to survive lithification and prolonged burial are those with the greatest thermal stability. Hence, it is the hydrocarbons (normal alkanes, isoprenoid alkanes, steranes etc) and, to a lesser extent, porphyrins, fatty acids, and amino acids that have most frequently been sought and identified. Whether future research will succeed in isolating other compounds characteristic of different stages of chemical and biochemical evolution (cf. Margulis, 1969, 1970b) remains to be seen. The chemotaxonomic potential of the lipids in contemporary bacteria, blue-green algae, green algae, fungi, and protozoa should be explored further with a view to identifying compounds characteristic of particular groups of microorganisms whose first representatives appeared during Precambrian time. The progress already reported, viz. 7-methyl and 8- methyl heptadecanes in blue-green algae (Han and Calvin, 1970; Sever and Parker, 1970), iso and anteiso fatty acids in bacteria (Kaneda, 1967; Cooper and Blumer, 1968; Blumer, 1970), isoprenoid acids in zooplankton (Blumer, 1970) and C_{27}, C_{29}, and C_{31} n-alkanes in fungal spores (Weete, 1972) is encouraging, but supplementary experiments involving the simulated diagenesis of such microbiota (cf. J.D. Brooks, 1971) are necessary if the geolipid derivatives of these "taxonomic indicators" are to be recognized, if and when they occur in ancient sediments. Experiments of this type are also likely to provide clues to the ultimate source of problematic chemical fossils such as the C_{21} isoprenoid alkane found in the Soudan shale and the Nonesuch seep oil, and the unusual n-alkylcyclohexanes isolated from the latter (Johns et al., 1966).

In looking for chemical fossils which qualify as biological markers, most workers have concentrated on the soluble organic matter obtained by solvent extraction procedures. Quite apart from its susceptibility to contamination by organic compounds from more recent sources, the extractable fraction comprises only a very small proportion (usually $<1\%$) of the total organic content of a rock. The bulk of the indigenous organic matter, kerogen, is relatively unreactive and its complex chemical structure exceedingly difficult to unravel. The need expressed by Hoering (1967b) to develop methods of selectively degrading kerogen is still a pressing one. The last five years has seen little significant progress in this area. Currently, the techniques of cathodoluminescence (Muir and Grant, 1971) and pyrolysis gas chromatography (Giraud, 1970; J. Brooks, 1971) appear to have the greatest potential as analytical tools for kerogenous substances.

During the last three years or so progress in Precambrian organic geochemistry has slowed appreciably because of the practical difficulties encountered in kerogen analysis, detection of optical activity in rock extracts, determination of absolute stereochemistry in individual geolipids, and discrimination between endemic and adventitious organic compounds. Most of these problems still await breakthroughs. Meanwhile there exists in Precambrian geology a host of topics which can be tackled using the organic geochemical techniques presently available. Cloud (1969) has mentioned the opportunities for research that lie in sedimentary phosphate and sulphate deposits and unmetamorphosed pyritic sediments with which organic matter is typically associated. It is doubtful, however, if sulphur isotope studies of the sulphides and sulphates will appreciably extend our knowledge of the Precambrian environment. The carbon isotopic

fractionation between organic matter and marine bicarbonate decreases with increasing temperature over the range 0-30°C in marine phytoplankton (Sackett et al., 1965), suggesting that carbon isotopic measurements on organic and inorganic (carbonate) carbon in stratigraphic intervals over which palaeotemperature changes are known to have occurred (eg. the transition from periglacial Tindelpina Shale to interglacial Brighton Limestone in the late Precambrian Umberatana Group, Adelaide Geosyncline: Preiss, 1973) may be worthwhile.

Knowledge is lacking of the extent to which microbiological activity and residual organic matter has influenced such factors as pH, redox potential, cementation, and recrystallization in Precambrian carbonates during early diagenesis. By analogy with Recent stromatolites from the Persian Gulf (Golubic, 1973), the relative rates of algal production and bacterial decomposition of organic matter in Precambrian stromatolitic algal communities could well have influenced the gross morphology of the resultant stromatolite. Except those preserved in the Bulawayan Group, Rhodesia (Hoering, 1967b; Oberlies and Prashnowsky, 1968; Schopf et al., 1971), stromatolitic carbonates have received less attention than they deserve from organic geochemists. Comparative organic geochemical investigations of carbonates, cherts, and shales should be undertaken to assess the possibility of facies control on Precambrian ecosystems. If, for example, significant discrepancies were found between the suites of chemical fossils isolated from synchronous carbonate and shale in the same depositional basin, and provided these differences could not be reasonably attributed to the distinctive response of each lithofacies to diagenesis (McKirdy and Powell, in preparation), then the likelihood of palaeoecologic constraints on the extant biota would be considerably enhanced.

While problems such as these remain, the place of organic geochemistry in interdisciplinary Precambrian research seems assured.

ACKNOWLEDGEMENTS

This paper is published with the permission of the Director, Bureau of Mineral Resources, Geology and Geophysics, Canberra. The author is indebted to Professor M.F. Glaessner, Dr T.G. Powell, Dr P.D. Trudinger, Dr P.J. Cook, and Dr M.R. Walter for critically reviewing the manuscript. The original version of the paper formed part of an M.Sc. thesis submitted to the Department of Geology and Mineralogy, University of Adelaide, December 1971. It was supported by a University Research Grant post-graduate scholarship from the University of Adelaide and a grant from the American Chemical Society Petroleum Research Fund to Professor M.F. Glaessner.

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TABLE I

Precambrian sedimentary rocks containing $\geqslant 100$ ppm solvent-extractable organic matter.

Rock	Location	Age (10^9 yr.)	Organic carbon (%)	Extract (ppm)	References
Carbonaceous shale, Brachina Formation, Wilpena Group	South Australia	0.6-0.7	1.51	167	McKirdy and Powell (in preparation)
Shale, Cardup Group	Western Australia	0.6 - 0.7	0.95	100	McKirdy and Powell (in preparation)
Shale, Pertatataka Formation	Northern Territory, Australia	0.7	0.89	236	Esso Exploration, Aust. (1965)
Tindelpina Shale Member, Tapley Hill Formation, Umberatana Group	South Australia	0.7	0.51	395	McKirdy and Powell (in preparation)
Shale, Bitter Springs Formation	Northern Territory, Australia	0.8 - 0.9	0.66	117	Esso Exploration, Aust. (1965)
Upper Shale Member, Nonesuch Shale	Michigan, U.S.A.	1.1	0.4	298	Eglinton et al. (1966) Johns et al. (1966)
Shale, Muhos Formation, Jotnian Series	Finland	1.3	0.41*	304*	Hoering (1967a)
Calcareous shale, McMinn Formation, Roper Group	Northern Territory, Australia	1.4	1.04*	1500*	Hoering (1967a)
H.Y.C. Pyritic Shale Member, Barney Creek Formation, McArthur Group	Northern Territory, Australia	1.6	1.85	248	McKirdy and Powell (in preparation)
Carbonaceous, dolomitic shale, Golden Dyke Formation, Goodparla Group	Northern Territory	1.8 - 2.0	2.25	240	McKirdy and Powell (in preparation)

TABLE I continued.

Carbonaceous lens, Roy Hill Shale Member, Jeerinah Formation, Fortescue Group	Western Australia	2.2	80.5*	250*	Hoering (1967a)
Carbonaceous shale, Soudan Iron Formation	Minnesota, U.S.A.	2.7	3.2	477	Johns et al. (1966)

* Computed on carbonate-free rock basis

TABLE II

Percentage organic carbon in sediments and metasediments of the Russian Platform (after Ronov and Migdisov, 1971).

Age	Sandstone Quartzite	Shale Phyllite Schist Paragneiss	Carbonate	Average Rock[1]
Mesozoic - Cainozoic (< 225 m.y.)	0.36	0.94	0.47	0.64
Palaeozoic (600 - 225 m.y.)	0.23	0.70	0.26	0.34
Late Proterozoic (1,400 - 600 m.y.)	0.08	0.35	0.06	0.18
Early & middle Proterozoic (2,700 - 1,400 m.y.)	0.02	0.33	0.01	0.21

1. Computed from values for all sedimentary rock types weighted according to their relative abundance in the geological record

TABLE III

Fossil evidence of biological activity in the Precambrian sedimentary record (modified after Schopf, 1970 and Kvenvolden, 1972)

Age	Rock unit	Morphological fossils		Chemical fossils								
10^9yr.		Stromat-olites	Micro-fossils	n-Alkanes	Isoprenoid alkanes	Steranes	Fatty acids	Porphyrins	Amino acids	Carbo-hydrates	Kerogen degradation products	$\delta^{13}C$
0.6	Brioverian chert	+	+	+		?						+
0.8-0.9	Bitter Springs Formation	+	+	+	+		?		?			+
1.0	Skillogalee Dolomite	+	+	+	+							+
1.1	Nonesuch Shale		+	+	+	+		+			+	+
0.9-1.4	Belt Supergroup	+	+							?		+
1.3	Beck Spring Dolomite	+	+									+
1.3	Muhos Formation		+	+	+						+	+
1.4	McMinn Formation		+	+	+						+	+
1.5	Paradise Creek Formation	+	+	?	?		?					+
1.5	Urquhart Shale		+	+	+							
1.6	McArthur Group	+	+	+	+							
1.7-2.0	Vallen Group	+	+	+	+		?					+
1.8-2.0	Koolpin Formation	+										+

TABLE III continued

1.7-2.2	Gunflint Iron Formation	+	+	+	+		?		?			+
2.0	Brockman Iron Formation		?									+
2.2	Transvaal Supergroup	+	+	?				+	?			+
2.7	Witwatersrand Supergroup	+	+	+				+	?	?	+	+
2.7	Soudan Iron Formation		+	?	?	?	?			?	+	+
3.0	Bulawayan Group	+	+						?		+	+
3.2	Fig Tree Group-Sheba Formation		+	+	+			+	?		+	+
3.4	Onverwacht Group-Swartkoppie Formation		+	+	+				?			+
	Kromberg Formation		+	+	+		?	+	?		+	+
	Theespruit Formation							+	?		+	+

\+ Reliable occurrence ? Questionable occurrence

TABLE IV

Organic matter in Precambrian metal deposits

Deposit	Stratigraphic Interval	Age (10^9 yr)	Organic-rich Lithofacies	Organic Carbon (%)	Geochemistry	Fossils	References
Zambian Copperbelt Cu(Co,U)	Ore Formation, Lower Roan Group, Mine Series (Katangan)	0.8-1.3	Carbonaceous sericitic quartzite	0.04-0.72	-	Stromatolites	Mendelsohn (1961) Malan (1964) Garlick (1964)
White Pine, Michigan Cu	Nonesuch Shale (Keweenawan)	1.1	Thinly interlaminated grey siltstone and black shale	0.4 0.5 0.66	Alkanes (incl. isoprenoids and steranes) Porphyrins Kerogen Optical activity $\delta^{13}C$	Bacteria Fungi Acritarchs	Barghoorn et al. (1965 Eglinton et al. (1966) Ensign et al. (1968) Moore et al. (1969) J. Brooks (1971) Brooks and Shaw (1971)
Mount Isa, Qld. Pb. Zn (Ag)	Urquhart Shale, Mount Isa Group (Carpentarian)	1.5	Black carbonaceous pyritic shale and silica dolomite	0.97 (Cu ore)	Alkanes (incl. pristane & phytane) Kerogen	Acritarchs	Bennett (1965) Love (1965) Saxby (1970) McKirdy and Powell (in preparation)
McArthur River, N.T. Zn, Pb(Ag)	H.Y.C. Pyritic Shale Member, Barney Creek Formation, McArthur Group (Carpentarian)	1.6	Finely laminated bituminous and tuffaceous pyritic shale, bituminous dolomitic shale	1.0 1.85	Alkanes (incl. pristane & phytane) Kerogen	Stromatolites Acritarchs	Croxford (1968) Saxby (1970) Croxford and Jephcott (1972) Plumb and Brown (1973) Hamilton and Muir (in press) McKirdy and Powell (in preparation)
Broken Hill, N.S.W. Pb, Zn (Ag)	Willyama Complex (Carpentarian)	1.7	Argillaceous metasediments	Up to several % in low-grade equivalents	Methane Graphite $\delta^{13}C$	-	Carruthers (1965) Taylor (1971) Hamilton and Muir (in press)

TABLE IV continued

Alligator River, N.T. U(Au)	Koolpin Formation, South Alligator Group (Nullaginian)	1.8-2.0	Carbonaceous chert and pyritic siltstone	-	$\delta^{13}C$	Stromatolites	Prichard (1965) Dodson (1971) Oehler et al. (1972)
Rum Jungle, N.T. U(Cu)	Golden Dyke Formation, Goodparla Group (Nullaginian)	1.8-2.0	Black pyritic graphitic shale	-	Thucolite	-	Spratt (1965) Dodson (1971)
Woodcutters, N.T. Pb,Zn	Golden Dyke Formation, Goodparla Group (Nullaginian)	1.8-2.0	Carbonaceous dolomitic shale	2.25	Alkanes (incl. pristane & phytane Kerogen	-	Roberts (1973) McKirdy and Powell (in preparation)
Mesabi Range, Minnesota Fe	Biwabik Iron Formation, Animikie Group (Huronian)	1.7-2.2	Carbonaceous (graphitic) slate-like taconite	1-4	Carbohydrates Kerogen	Algae (?)	French (1964, 1968) LaBerge (1967) Cloud and Licari (1968) Swain et al. (1970)
Gunflint Range, Ontario Fe	Gunflint Iron Formation, Animikie Group (Huronian)	1.7-2.2	Black chert and argillite	1 (chert)	Alkanes (incl. pristane & phytane) Fatty acids Amino acids $\delta^{13}C$	Stromatolites Algae Bacteria	Moorhouse and Beales (1962) Barghoorn and Tyler (1965) Cloud (1965) Oró et al. (1965) Schopf et al. (1968) Van Hoeven et al.(1969) Smith et al. (1970)
Hamersley Range, W.A. Fe	Dales Gorge Member, Brockman Iron Formation, Hamersley Group (Nullaginian)	2.0	Carbonaceous chert and d green to black shale	0.15 0.74 1.88 (all shale)	$\delta^{13}C$	Algae (?)	Edgell (196) LaBerge (1967) Trendall and Blockley (1970) Oehler et al. (1972)
Elliot Lake, Ontario U	Various formations, Elliot Lake Group (Huronian)	2.5	Pyritic quartz pebble conglomerate	-	Thucolite	-	Roscoe (1969)

TABLE IV continued.

Kaapvaal Craton, Transvaal & Orange Free State Au,U	Main-Bird Series (Witwatersrand)	2.7	Pyritic quartz pebble conglomerate (often with basal 'carbon' seams of fibrous thucolite)	0.2	Thucolite Alkanes (incl. pristane & phytane) Porphyrins Amino acids Carbohydrates $\delta^{13}C$	Bacteria Algae	Snyman (1965) Hoefs and Schidlowski (1967) Hoering (1967 a,b) Prashnowsky and Schidlowski (1967) Oberlies and Prashnowsky (1968) Hodgson et al. (1968) Schidlowski (1969,1971 Viljoen et al. (1970) J.D. Brooks (1971)
Vermilion Range, Minnesota Fe	Soudan Iron Formation, Keewatin Group (Ontarian)	2.7	Lenticular carbonaceous argillite	0.25-21.8	Alkanes (incl. isoprenoids and steranes) Fatty acids Carbohydrates Kerogen $\delta^{13}C$	Algae (?)	Gruner (1925) Goldich et al. (1961) Cloud et al. (1965) Meinschein (1965) Burlingame et al.(1965 Johns et al. (1966) Hoering (1967 a, b) Cloud and Licari (1968 Van Hoeven et al.(1969 Oró and Nooner (1970) Swain et al. (1970)

Fig. 1. Evolution of Precambrian lithosphere, atmosphere, biota, and organic-rich lithofacies. Lithospheric evolution shown is based on the primitive oceanic crust model of Anhaeusser (1972) and Glikson (1972) for southern Africa.

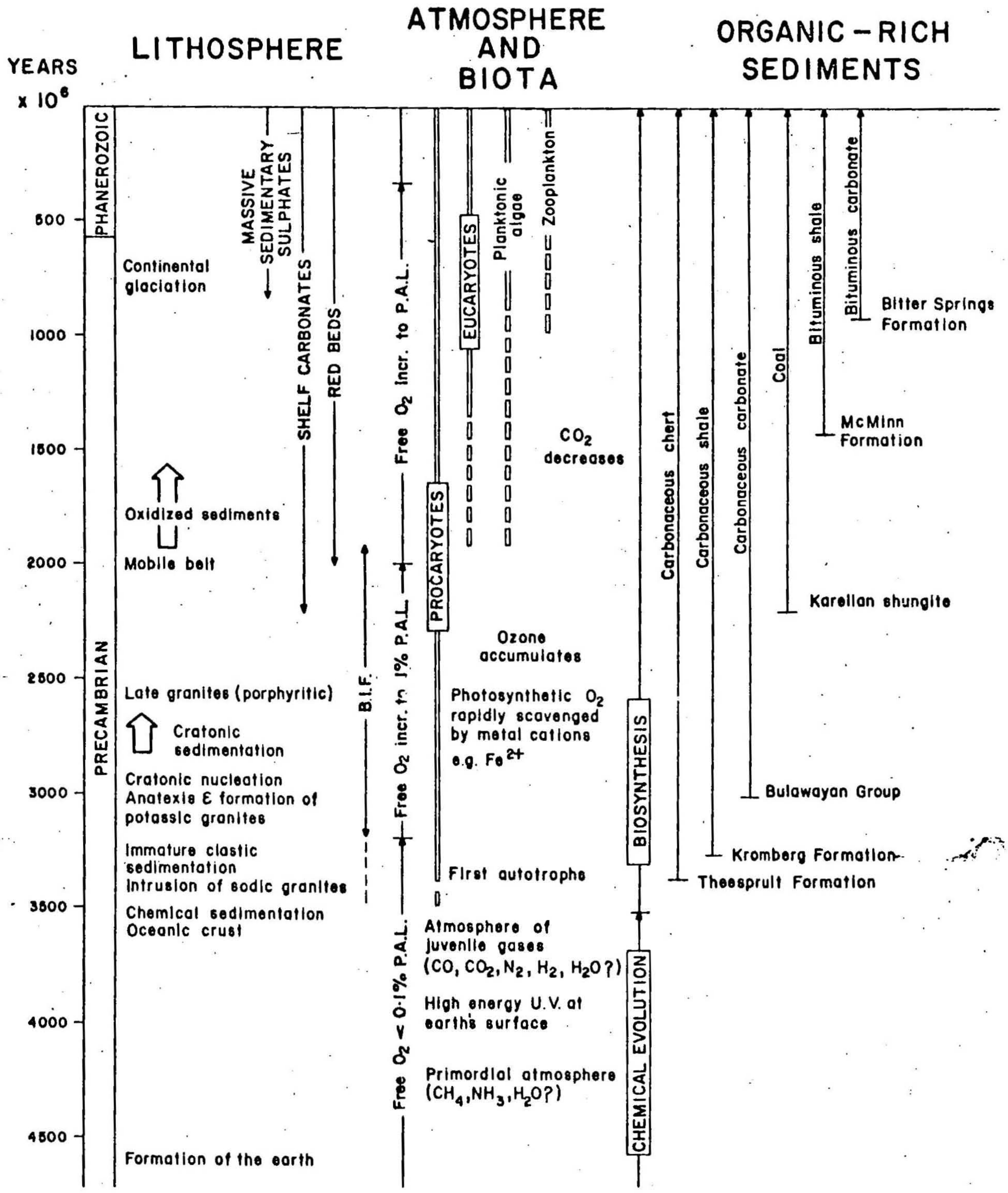

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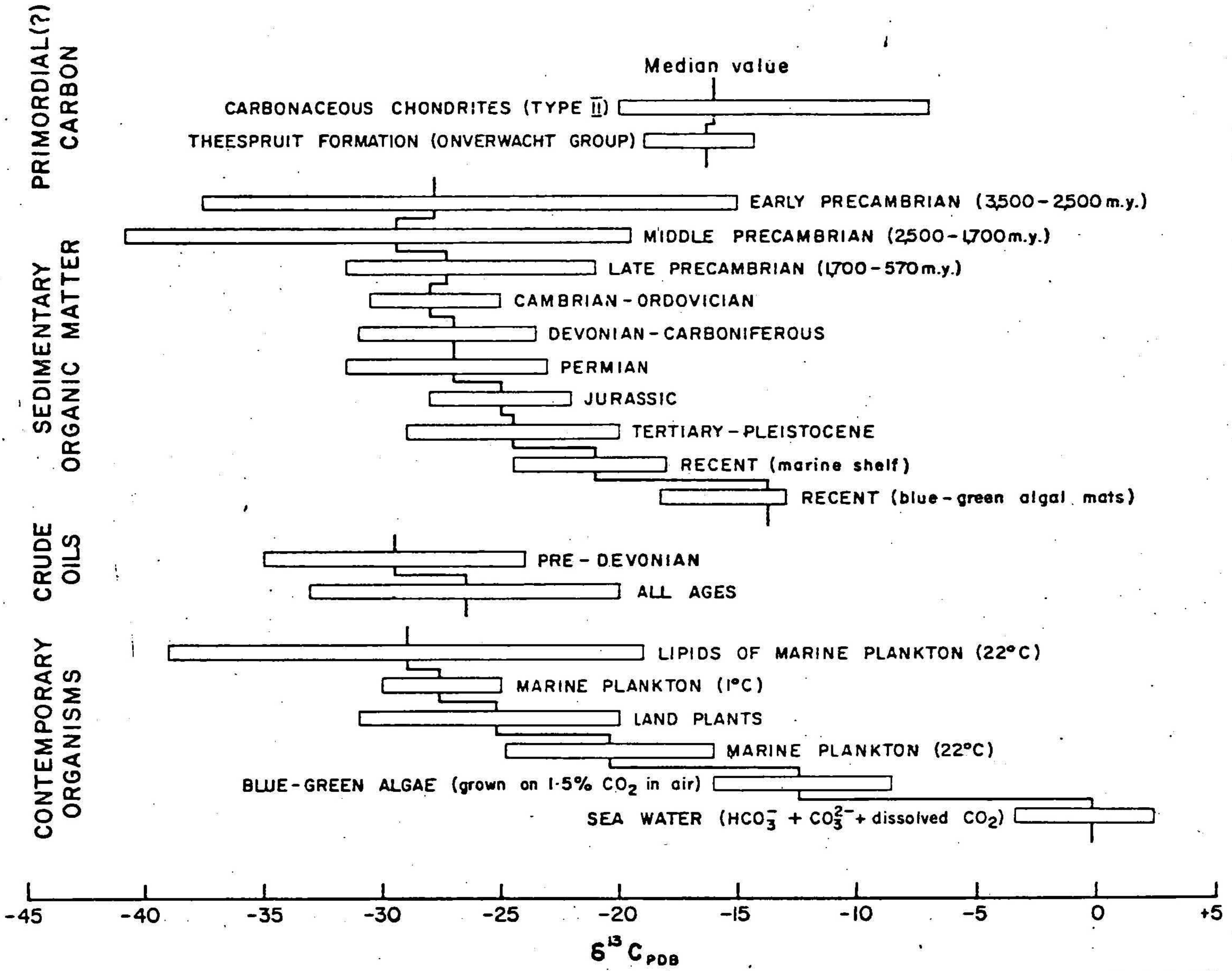
Fig. 2 Carbon isotopic data on various types of organic matter (after Degens, 1969; Behrens and Frishman, 1971; Oehler et al., 1972; and Calder and Parker, 1973). Horizontal bars represent 99% probability ranges.



To accompany Record No 1973/99

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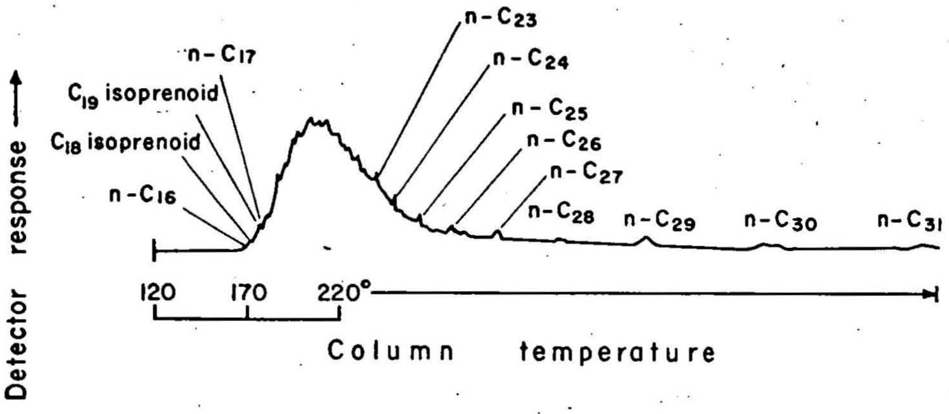
Fig. 3 Gas chromatograms of alkanes from Swaziland System sediments.

A. Onverwacht chert (?). Column conditions: 4.6 m x 0.46 mm i.d. support-coated open-tubular capillary coated with Apiezon L; temperature programmed at 2.5°C/min. over range 120-220°C (after MacLeod, 1968).

B. Fig Tree shale. Column conditions: 70 m x 0.25 mm i.d. capillary coated with Apiezon L ; temperature programmed at 4°C/min. over range 50-350°C (after Hoering, 1967 a, b).

A



B

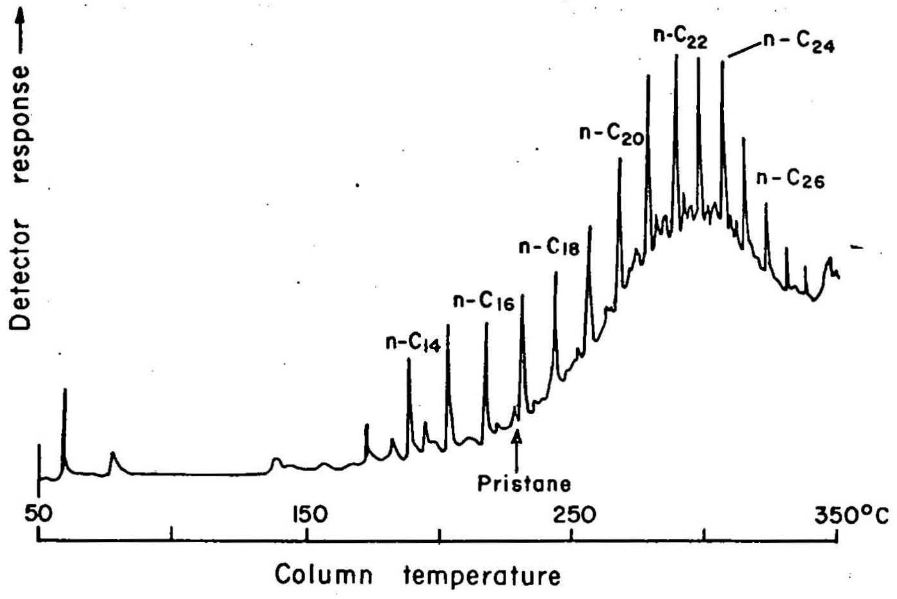


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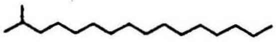
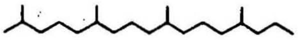
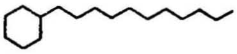
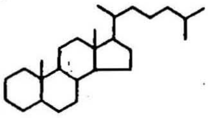
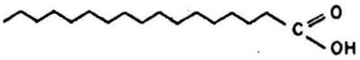
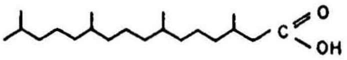
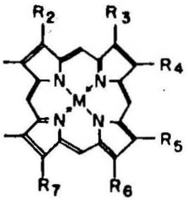
Fig. 4 Some chemical fossils found in Precambrian sediments and their status as biological markers.

COMPOUND TYPE	GENERALIZED CARBON SKELETON	EXAMPLES	SUGGESTED SOURCE(S)	SIGNIFICANCE
ALKANES - normal				
saturated		C_{10} to C_{35}	Algal, bacterial, fungal lipids	Major constituents of geolipid extracts
mono - unsaturated	one double bond in above carbon chain	C_{16}, C_{18}, C_{20}, C_{22}	Biological alcohols Catalytic condensation of ethylene	Probably degraded biolipids but may be partially abiotic in rocks > 3,000 m.y. old
ALKANES - branched				
iso		C_{16}, C_{17}, C_{18}	Bacterial iso & anteiso fatty acids	Evidence of bacterial activity
anteiso		C_{16}, C_{17}, C_{18}		
isoprenoid		C_{14} to C_{16}, C_{18} to C_{21}	Isoprenoid alcohol side-chain of algal and bacterial chlorophylls Phosphatidyl glycerophosphate of halophilic bacteria	Evidence of photosynthesis Origin of C_{21} compound remains obscure
ALKANES - cyclic				
cyclohexyl		C_{16} to C_{19}	Algal unsaturated fatty acids (via diagenetic intramolecular cyclization)	Uncertain
sterane		C_{27}, C_{28}, C_{29}	Algal sterols	Evidence of eucaryotic organisms
FATTY ACIDS - normal				
saturated		C_{11} to C_{24}	Algal bacterial lipids Recent biological origin (if even-carbon-numbered species dominant) ie. contamination	Equivocal biological markers
mono - unsaturated	one double bond in above carbon chain	C_{16}, C_{18}		
FATTY ACIDS - branched				
isoprenoid	 M = metal R_{2-7} = various substituents (e.g. CH_3, C_2H_5)	C_{16}, C_{19}, C_{20}	Isoprenoid alcohol side - chain of algal, bacterial chlorophylls (via diagenetic oxidation) Zooplanktonic lipids (if host rock < 1,000 m.y. old)	Evidence of photosynthesis and possibly zooplankton
PORPHYRINS	 M = metal R_{2-7} = various substituents (e.g. CH_3, C_2H_5)	Vanadyl - chelated porphyrins (detailed peripheral structure unknown)	Algal and bacterial chlorophylls, cytochromes, catalases, and peroxidases Vitamin B_{12}	Evidence of photosynthesis, respiration, protein, and nucleotide synthesis

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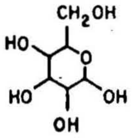
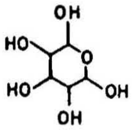
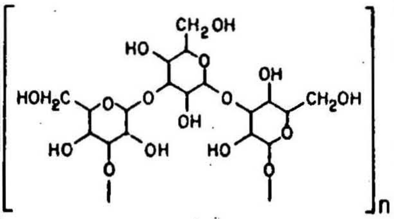
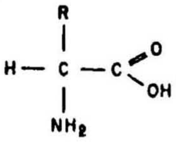
CARBOHYDRATES - monosaccharides hexoses		Galactose Glucose Mannose	Algal, bacterial, fungal carbohydrates Recent biological origin ie. contamination.	Lack geochemical stability Probably not syngenetic
pentoses		Arabinose Xylose Rhamnose Ribose		
CARBOHYDRATES polysaccharides		Starch Cellulose Laminaran		
AMINO ACIDS	 $\mathrm{H{-}\overset{R}{\underset{NH_2}{C}}{-}C\genfrac{}{}{0pt}{}{{=}O}{OH}}$ R = Substituent	Glycine [R = H] Alanine [R = CH_3] Aspartic acid [R = CH_2COOH] Valine [R = $CH(CH_3)_2$] Leucine [R = $CH_2CH(CH_3)_2$] Isoleucine [R=$CH(CH_3)CH_2CH_3$] * Serine [R = CH_2OH] * Threonine [R=$CH(OH)CH_3$] etc. (* thermally labile)	Algal, bacterial protein Recent biological origin (if L - isomers in excess of D - isomers; or serine and threonine present) ie. contamination.	Lack geochemical stability Probably not syngenetic

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Fig. 5 Metamorphic grade of Australian organic-rich Cambrian and Precambrian sediments based on illite crystallinity and chemical composition. Values of Kubler index converted from original Weaver indices using Ferrero's curve (Kubler, 1968, fig. 3).

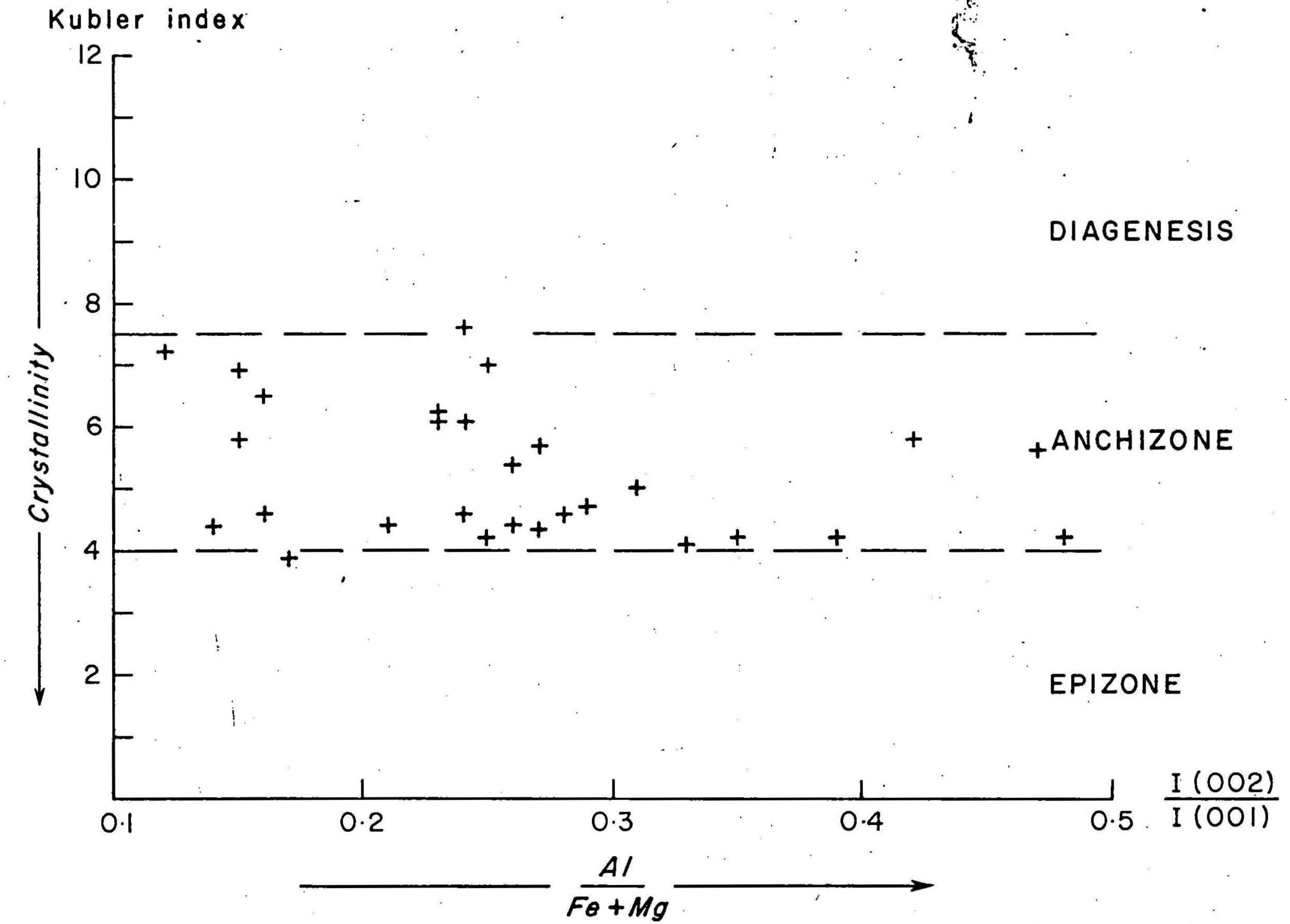

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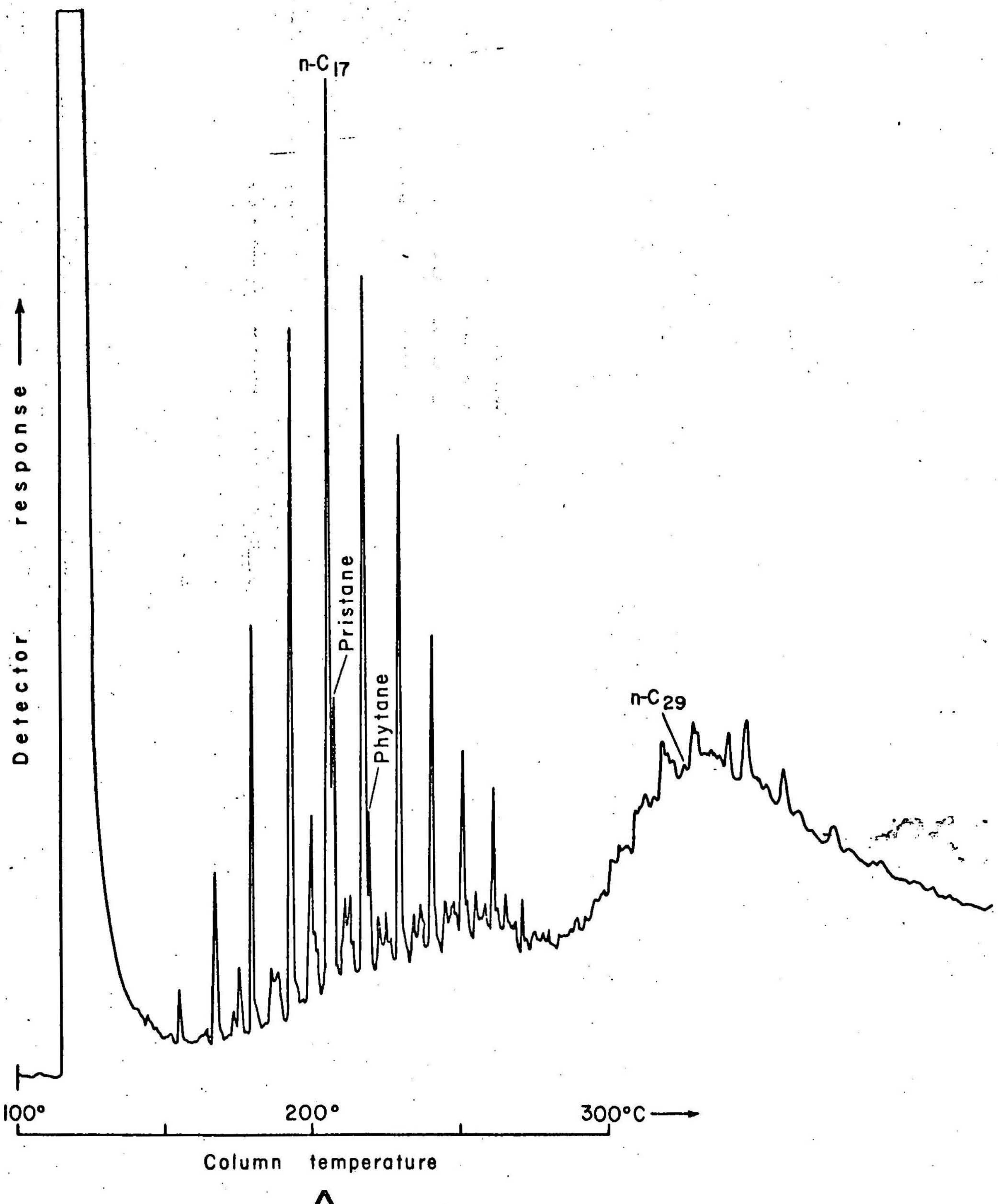
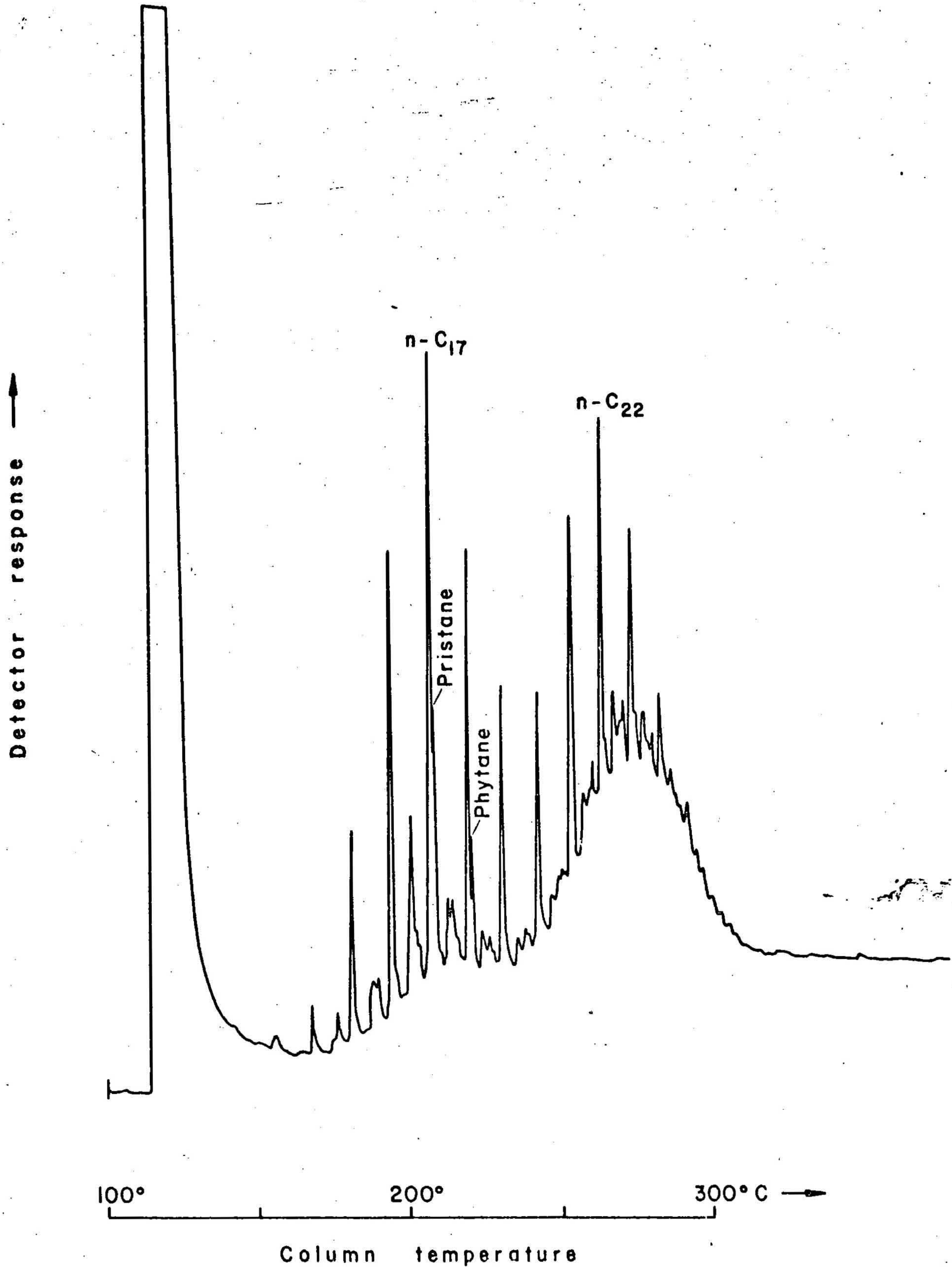
Fig. 6 Examples of bimodal alkane distribution patterns in Precambrian sedimentary rocks. A. Urquhart Shale (ca. 1,500 m.y.), Mount Isa, Queensland. B. Carbonaceous shale (ca. 2,700 m.y.), Eulaminna, Western Australia. Column conditions: 6.1 m x 1.02 mm i.d. stainless steel column packed with 3% OV-1 on 100-120 mesh Gas Chrom Q; temperature programmed at 4° C/min. over range 100-250°C (after McKirdy, 1971).



A

To Accompany Record No 1973/99



B

To accompany Record No 1973/99

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