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4.5 BIOCHEMICAL MARKERS IN STROMATOLITES

by

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INTRODUCTION

Stromatolites still await systematic and detailed organic geochemical study. Apart from the pioneering work of Hoering (1962, 1964, 1967) and a later investigation of the oldest known stromatolites by Schopf et al. (1971), carbonate rocks containing laminated organosedimentary structures built by microscopic algae and bacteria have been largely overlooked by geochemists in their search for chemical and isotopic evidence of the origin and development of biological activity on the Earth's surface (Maxwell et al., 1971; McKirdy, 1974). Analyses of the organic matter in black fossiliferous cherts from several Precambrian stromatolitic beds (Orό et al., 1965; Schopf et al., 1968; Smith et al., 1970) were prompted by the antiquity and remarkable preservation of the fossil assemblages, rather than by their occurrence in stromatolites *per se*. A marked and not altogether explicable sampling bias in favour of argillaceous and siliceous sediments has meant that most of the reported finds of chemical (or molecular) fossils, i.e. hydrocarbons, fatty acids, porphyrins, amino acids, carbohydrates and stable carbon isotopic fractionation of apparent biological origin, have been made in shales and cherts, some older than 3,000 m.y. Consequently, little is yet known about that fossil organic matter which represents the remains of benthonic mat-building communities in ancient carbonate-depositing environments.

Stromatolites are among the most common and long-ranging fossils in the geological record. Their macroscopic size and widespread geographic distribution, their usual occurrence in fine-grained, highly indurated carbonate or chert, and the existence of

"living"analogues in a variety of Recent environments, together make stromatolites extremely attractive materials for organic geochemical investigation. This chapter gathers together biochemical and geochemical data pertinent to our understanding of the composition, derivation and function of the organic content of fossil stromatolites. New analyses of some Australian Palaeozoic and Precambrian stromatolites are reported, and, finally, the potential of organic geochemistry to contribute to future stromatolite research is assessed.

An impressive number and variety of stable organic compounds, interpreted as chemical fossils by virtue of their biologically indicative molecular configuration (Fig. 1) or isotopic composition, have now been extracted from sedimentary rocks of all ages (Maxwell et al., 1971). When found in sufficient concentration in a stromatolite such compounds are likely to have been derived (at least in part) from the organisms that participated in its formation (but see below). Stromatolites are commonly abiophoric (i.e. lacking preserved microfossils: Hofmann, 1973, p.350), in which case indigenous chemical fossils might prove to be the only remaining clues to the identity of the original mat-builders. Of course, a laminated sedimentary structure can be stromatolite-like in appearance and yet abiogenic. Any organic matter it contained would then be allochthonous and largely incidental to its origin.

Despite recent advances in stromatolitology, some fundamental questions remain unresolved or, as is particularly true of abiophoric stromatolite occurrences, can be only tentatively answered (cf. Hofmann, 1973). Are all fossil stromatolites always biogenic? If biogenic, were oxygen-producing cyanophytes mainly responsible? Were the cyanophytes filamentous or coccoid? How can the contribution of eukaryotic algae to a stromatolitic biota be recognized? Did ancient bacteria (and perhaps even fungi) ever build stromatolites? How does one distinguish

such stromatolites from those built by algae? To establish in what way, and to what extent, organic geochemical data may shed light on these problems, we shall consider the various classes of chemical fossil and the potential significance of each for the palaeobiochemistry and palaeoecology of stromatolites.

ORGANIC MATTER IN ALGAL MATS AND STROMATOLITES

The microstructure of most algal laminates and stromatolites, whether Recent or ancient, comprises an alternation of light (sediment-rich) and dark (organic-rich) laminae arising from periodic fluctuation in the relative rates of mat growth and sediment deposition. The sediment-rich layers in Recent stromatolites contain less than 5% organic matter (Gebelein and Hoffman, 1973). The organic matter in the dark laminae is derived mainly from dead blue-green algal cells, filaments and empty gelatinous sheaths, although eukaryotic (green and red) algae and bacteria may also have been present and contributed detritus.

Disseminated organic matter can influence both the grain size and the mineralogy of stromatolitic sediments. Many of the Australian stromatolites described by Walter (1972) "are composed of carbonate with a grain size of less than 30μ, and frequently less than 15μ. Furthermore, the pigmented laminae are nearly always finer grained than contiguous pale laminae" (op. cit., p.97). Similarly Schopf and Blacic (1971, p.929) noted a correlation of finer-grained quartz with regions of relatively high organic content in laminated cherts from the Bitter Springs Formation. In both instances organic matter has presumably inhibited recrystallization. Walter (1972, p.59) also describes a situation in the Bitter Springs Formation at Jay Creek where several stromatolite biostromes contain columns which are black (organic-rich) and consist mainly of calcite, in striking contrast to the pale grey predominantly dolomitic interspaces. In this case, organic matter coating carbonate grains in the stromatolite columns

appears to have helped prevent their post-lithification dolomitization. The completely opposite effect is also possible, in which organic matter acts as a source of Mg for dolomite formation (Gebelein and Hoffman, 1973; Friedman et al., 1973).

The amount of organic matter preserved in a stromatolite upon lithification represents that portion of the primary algal and bacterial production which has survived decomposition by the aerobic and anaerobic bacterial (and sometimes fungal) heterotrophs originally present in the lower zones of the living mat (Golubic, 1974). A measure of this residual organic matter is provided by the total organic carbon (TOC) value of the stromatolitic sediment (Tables 1 and 2).

On the limited data available, Recent laminated algal sediments appear to have TOC values comparable to those for other Recent sediments (Table 1). No organic carbon values have yet been reported for Recent non-stratiform stromatolites such as the club-shaped forms at Shark Bay, Western Australia.

The concentration of organic carbon in fossil stromatolites (Table 2) is generally 1 - 2 orders of magnitude lower than in Recent algal laminates. A Precambrian algal dolomitic limestone containing 1.1% TOC from the Purcell Supergroup, Alberta, (Hodgson et al., 1968) is exceptionally organic-rich. Such high TOC values may reflect a lower energy, less emergent or more poorly drained depositional environment, and hence a more stable anoxic regime below the actively growing mat. TOC values for Precambrian stromatolitic chert, eg. Gunflint Iron Formation, 0.03 - 0.07% (Kvenvolden, 1972); and Skillogalee Dolomite, 0.08 - 0.21% (Table 4 and unpublished results), fall within the same range as those for stromatolitic carbonate. Mean TOC values for carbonates of different ages from the Russian Platform are included in Table 2. By comparison, stromatolitic carbonates are not unusually rich

in organic matter.

The organic content of a sediment may be divided analytically into two major fractions. The material insoluble in organic solvents (kerogen) usually constitutes the bulk of the total organic matter. The solvent-extractable portion (bitumen or geolipids) is an extremely complex mixture of many different compounds. It is in this fraction that chemical fossils have been most commonly sought and found. The chloroform extracts of six fossil (Cambrian to Recent) algae analysed by Das and Smith (1968) amounted to 0.3 - 0.6% of the sample weight. By contrast, exhaustive extraction of the stromatolitic carbonates listed in Table 4 with benzene/methanol gave (with one exception viz. sample 8, 132ppm.) geolipid yields of 2 - 20ppm. These yields vary with the diagenetic grade of the sediments (Fig. 3). A sample of fossiliferous laminated black chert from the stromatolitic Bitter Springs Formation contained 27ppm extractable organic matter (Schopf, 1968) whereas the corresponding yield from the Precambrian stromatolitic cherts analysed by Smith et al. (1970) was less than 0.1ppm.

SYNGENEITY

Most analytical techniques currently employed in organic geochemistry are designed to ensure that the compounds isolated from a rock are indigenous to it and are not field or laboratory artifacts. However, where the chemical fossils are present in very low concentration, as for example in many Precambrian sediments, it is difficult to be certain that they (or their biochemical precursors) were actually deposited with the sediment and did not enter the rock some time after its lithification (Hoering, 1967; Smith et al., 1970; Kvenvolden, 1972; McKirdy, 1974). This uncertainty unfortunately hampers the interpretation of much of the organic geochemical information so far obtained on ancient stromatolitic sediments, especially cherts.

Aliphatic hydrocarbons

The stromatolitic cherts analysed, all Precambrian in age, are from the Gunflint Iron Formation (Oró et al., 1965; Smith, et al., 1970), the Bitter Springs Formation (Smith et al., 1970) and the Paradise Creek Formation (Smith et al., 1970). The concentrations of total alkanes found were variable but generally low (0.005 - 5ppm). Porosity and permeability measurements on ancient cherts (Sanyal et al., 1970; Smith et al., 1970) demonstrate that such sediments are in fact sufficiently porous and permeable to have admitted significant quantities of younger organic compounds from migrating formation fluids under pressure while buried at depth, or later by capillary action when exposed at the surface. Smith et al. (1970) found most of the extractable organic matter to be located along microfractures within the chert matrix and concluded that it was of post-depositional and probably comparatively recent origin. Only trace amounts (several parts per billion) of the alkanes were considered likely to be truly indigenous.

Stromatolitic carbonates (Table 4) yield alkanes in concentrations which are low (1 - 5ppm) but are less variable, and on the average, higher than those for stromatolitic cherts. Moreover, their porosity (0.5 - 4.4%) and nitrogen permeability (3.1×10^{-4} - 1.2×10^{-1} millidarcy) are at least as low (Table 4) as those of the cherts studied by Smith et al. (1970). But are the hydrocarbons isolated from the carbonates any more likely to be syngenetic? An answer to this question can be attempted by turning to the composition of the coexistent insoluble organic matter (kerogen) in the carbonates (Table 4).

The atomic hydrogen to carbon ratio (H/C) of kerogen provides a sensitive measure of its diagenetic (or incipient metamorphic) rank and, by inference, that of the host sediment (Tissot et al., 1974; McKirdy et al., 1975). Kerogen, being insoluble and immobile, is almost certainly syngenetic with the sediment in which it is found. Hence, where

the H/C value of the kerogen is known, the degree of thermal maturation any *syngenetic* hydrocarbons have undergone may be assessed. Both the yield and the distribution pattern of the alkanes in a sedimentary rock change systematically with increasing diagenesis (Brooks and Smith, 1967; Albrecht and Ourisson, 1969) and in a manner dependent on the rock type and the nature of the parent organic material (Powell and McKirdy, 1973a). The degree to which these two parameters (yield and distribution of alkanes) coincide with what might be predicted in view of the rank of the kerogen and the lithofacies of the host sediment may thus in turn indicate whether the alkanes are coeval with the kerogen or have since migrated into the rock (cf. McKirdy, 1974, p.122). Figures 3 and 4, plots of geolipid yield and alkane yield, respectively, against kerogen H/C, show that the stromatolitic carbonates listed in Table 4 conform with the general diagenetic trend for marine carbonates. This is consistent with a syngenetic origin for the stromatolitic alkanes.

Fatty acids

The significance of the fatty acids found by Smith et al. (1970) in stromatolitic cherts of Precambrian age is just as uncertain as that of the alkanes they yielded (see previous section). Both free and bound fatty acids were sought, and again (with the exception of the free fatty acids from the Bitter Springs and Paradise Creek cherts) the highest concentrations were obtained form the surfaces of the chip size fraction. More importantly, however, labile, unsaturated acids were found in unexpectedly high concentration in all extracts, some of which also contained long-chain acids in the range C_{21} - C_{24}. The latter are features more indicative of recent contamination than of a Precambrian microbial source.

Fatty acids interact with carbonate mineral surfaces by way of processes such as chemisorption and form various complexes, including

natural calcium soaps i.e. adipocere (Suess, 1970). Although yet to be specifically investigated in Recent algal mats this fatty acid-carbonate association is probably important in determining the ultimate fate of the fatty acids. Adipocere could be expected to form rapidly following the release of fatty acids from decaying algal cells, and thereafter resist further bacterial decomposition (cf. Berner, 1968). Burlingame and Simoneit (1968) suggest that such mineral-bound fatty acids are more likely to be syngenetic with the sediment in which they are found than are free or interstitially-trapped geolipids.

Amino acids

Amino acids have been recovered by ammonium acetate leach (free acids) and HCl hydrolysis (combined acids) from many ancient sediments, including stromatolitic limestone of the Bulawayan System (Oberlies and Prashnowsky, 1968) and laminated fossiliferous cherts from the Gunflint Iron Formation and Bitter Springs Formation (Schopf et al., 1968). Serine and threonine, both extremely labile amino acids, were found in all three rocks. On stability grounds alone, these two compounds are most unlikely to have survived from the Precambrian. This places in doubt the syngenetic origin of the remaining acids. Stereochemical examination of the amino acids extracted from samples of Gunflint chert (Abelson and Hare, 1969) and Fig Tree chert (Kvenvolden et al., 1969) showed that they comprised only the L-isomers. In the absence of any stabilization by the mineral or kerogen matrix, amino acids in sediments older than about 2 m.y. should be racemic mixtures of the L- and D-isomers. Clay minerals and kerogen may inhibit racemization (Akiyama and Johns, 1972), but the calcareous fraction of Recent marine sediments (Hare, 1972) and the silica of ancient cherts appears to exercise no such stabilizing effect (Abelson and Hare, 1969). A younger biological source for part, if not all, of the extractable amino acids in the above stromatolitic sediments thus appears likely.

ALGAL AND BACTERIAL MARKERS

Aliphatic hydrocarbons

Potential markers

The lipid fraction of algal and bacterial microorganisms includes hydrocarbons, fatty acids (as esters), fatty alcohols (as glycosides), pigments, sterols etc. (Kates, 1964; Nichols, 1973) which together comprise a quantitatively variable (0.3 - 85% of cellular dry weight, mostly < 30%: data from Abelson, 1967), but geochemically highly significant, group of compounds. Of these compounds the hydrocarbons are the least labile and hence the most likely to survive sedimentation and burial with their carbon skeleton more or less intact. Hydrocarbons constitute 0.006 - 0.12% (dry cell weight) of blue-green algae (Oró et al., 1967; Han et al., 1968; Winters et al., 1969). Three algal mats studied by Oró et al. (1967) yielded 2.7 - 5.8% lipid and only 0.001 - 0.01% hydrocarbons. By comparison, the ubiquitous sulphate-reducing bacterium *Desulfovibrio desulfuricans* contains 5 - 9% lipid of which 25% is hydrocarbon (Davis, 1968).

The composition of the aliphatic hydrocarbons present in various extant blue-green (and green) algae and Recent algal mats is summarized in Table 3. The C_{17} n-alkane (and/or alkene) is almost invariably conspicuous and C_{21} to C_{29} n-alkanes are less common than homologues of shorter chain length. Nevertheless, certain algae (blue-green, green and red) (Clark and Blumer, 1967; Gelpi et al., 1970; see also Table 3), bacteria (Albro and Huston, 1964; Davis, 1968; Albro and Dittmer, 1970) and fungi (Weete, 1972) do contain long-chain n-alkanes (or n-alkenes), among which, moreover, the odd-carbon-numbered homologues tend to be dominant. Another possible ultimate source of high molecular weight n-alkanes are the long-chain (C_{26} and C_{28}) polyhydroxy alcohols present as glycosides in the heterocysts of blue-green algae (Nichols, 1973). It is

worth noting here that high molecular weight (>C_{20}) compounds comprise a much greater proportion of the total aliphatic hydrocarbons in non-photosynthetic bacteria (>50%) than in photosynthetic bacteria (<15%) (Han et al., 1968). Non-photosynthetic bacteria are the last viable organisms to populate an algal mat before burial finally removes it from the zone of microbiological activity.

Various aliphatic hydrocarbons appear to be specific to certain taxa of extant microorganisms. These hydrocarbons may well constitute a geochemical basis for recognizing the contribution of a particular biota to stromatolite communities. Examples of such chemotaxonomic markers are 7-methyl and 8-methylheptadecane (Fig. 1) in cyanophytes (Han and Calvin, 1970; Gelpi et al., 1970); and pentacyclic triterpanes of the hopane type (Fig. 1) in prokaryotic algae and bacteria (Kimble et al., 1974). Steroidal alcohols, which readily revert to steranes (Fig. 1) during early diagenesis, are indicative of eukaryotic algae and fungi (although see eg. De Souza and Nes, 1968; Reitz and Hamilton, 1968; Schubert et al., 1968; Gelpi et al., 1970; and Nadal, 1971 for reports of their occurrence in prokaryotes).

The isoprenoid (branched) alkanes pristane (C_{19}) and phytane (C_{20}) (Fig. 1) are two widely occurring biochemical markers usually considered to be products of the diagenesis of the phytyl (C_{20}) side-chain of chlorophyll. Pristane (and rarely phytane) may also occur as discrete hydrocarbons in certain algae (Clark and Blumer, 1967; Oró et al., 1967; Han et al., 1968), bacteria (Oró et al., 1967; Han et al., 1968) and algal mats (Table 3). The precise route to their diagenetic formation in sediments has not yet been fully elucidated, but it appears that their relative concentration depends largely on the degree of oxidation of the parent organic matter during the early stages of chlorophyll decay. In short, the generation of pristane is favoured under oxidizing (aerobic) conditions, whereas a reducing (anaerobic) environment

preferentially gives rise to phytane (Brooks et al., 1968; Powell and McKirdy, 1973b).

Stromatolitic cherts

The normal alkanes isolated from Precambrian stromatolitic cherts by Smith et al. (1970) typically display a smooth unimodal distribution in the range C_{16} to C_{36}, with a maximum concentration at C_{22}. The alkane patterns obtained from the Gunflint chert by Oró et al. (1965), however, tended to be bimodal with maxima at n-C_{18} or $_{19}$ and n-C_{22}. Similar bimodal distributions have been reported from other Precambrian sediments (McKirdy, 1974, p.112).

A slight dominance of odd-over even-carbon-numbered homologues is evident in the n-alkanes larger than C_{26} from the above cherts. A predominance of odd-carbon-numbered n-alkanes is characteristic of many sediments to which higher plants of terrestrial origin have contributed detritus (Powell and McKirdy, 1973a). Its occurrence in the geolipid fraction of Precambrian sediments is unexpected. Even if such an odd-over-even predominance was originally present in the n-alkanes of a precursor Precambrian stromatolitic microbiota (see previous section), it would probably have disappeared during burial diagenesis (Brooks and Smith, 1967).

In view of their doubtful indigeneity, any interpretation of the alkanes isolated from stromatolitic cherts is necessarily equivocal. The alkane distributions (in the absence of data on the diagenetic grade of the cherts) could be equally well explained in terms of either a microbial or a contaminative higher plant source, although the relict odd-over-even predominance strongly favours the latter. Even the low values (<1) for the ratio of the concentrations of the two isoprenoid alkanes, pristane and phytane, are ambiguous. Low pristane to phytane ratios have been found both in marine crude oils derived from aquatic micro-organisms (Powell and McKirdy, 1972b) and in low-rank coals of

non-marine origin (Brooks et al., 1969).

Stromatolitic carbonates

Distributions of n-alkanes obtained from limestones (unlike those from shales) display little variation with advancing diagenesis (Powell and McKirdy, 1973a) and this seems to hold true for stromatolitic carbonates (Table 4). The stromatolitic n-alkanes range from C_{15} to C_{29} with a maximum between C_{18} and C_{25}, and show no noticeable preference for odd- nor even-carbon-numbered molecules. However, certain subtle differences are evident in the total alkane patterns (Fig. 2), and these are largely attributable to diagenetic maturation, as is discussed below.

The least altered stromatolite in Table 4, *Acaciella australica* (sample 8, kerogen H/C = 0.82), gives an alkane pattern (range n-C_{15} to n-C_{23}, maximum, n-C_{18}) considered typical of organic matter derived from blue-green algae (eg. Winters et al., 1969; Gelpi et al., 1970). The straight-chain hydrocarbons (alkanes and alkenes) in modern mat-building cyanophytes, Recent algal mats, and other algae similar to those implicated in certain Precambrian stromatolitic microbiotas (Table 3), generally fall in the same range. In the stromatolites of higher rank (kerogen H/C = 0.7 - 0.2), the n-alkane envelope is somewhat broader (C_{16} to C_{29}) and its maximum is located at a higher carbon mumber (between C_{19} and C_{25}). That is to say, maturation of the organic matter in those stromatolites above a rank equivalent to H/C = 0.8 - 0.7 has resulted in the generation of longer-chain (C_{21} - C_{29}) n-alkanes from the kerogen (cf. Albrecht and Ourisson, 1969; Powell and McKirdy, 1973a). There is a corresponding increase in the proportion of alkanes in the geolipid extract (Fig. 4) but an accompanying diminution of the total geolipid yield (Fig. 3).

The diagenetically more mature stromatolites also differ from *Acaciella australica* in having a much higher proportion of branched and cyclic isomers in their total alkane fraction. (In Fig. 2 the branched/ cyclic alkanes comprise the baseline hump and the peaks between the

n-alkanes). This increase in relative concentration of branched/cyclic alkanes is particularly apparent in *Conophyton f.* (sample 14, kerogen H/C = 0.65) and ?*Baicalia f.* (sample 13, kerogen H/C = 0.23). It may be a result of *catalytic* cracking of hydrocarbons during late diagenesis. Such cracking reactions are facilitated by clay minerals and proceed via carbonium ion intermediates which can undergo alkyl isomerization and β-splitting (Eisma and Jurg, 1969) and lead eventually to the production of branched and cyclic alkanes (McKirdy, 1971). An alternative explanation is that bacteria populating the dark interior of the original mat preferentially metabolized the algal n-alkanes (Bailey et al., 1973).

The stromatolite containing the most highly altered organic matter is *Baicalia burra* (sample 9, kerogen H/C = 0.10). Its alkane distribution (range n-C_{15} to n-C_{24}, maximum n-C_{18}) is similar to that of *Acaciella australica* and presumably reflects the thermal cracking of the longer-chain alkanes generated from the kerogen at an earlier stage of diagenesis into hydrocarbons of lower molecular weight.

Pristane and phytane were identified in the saturated hydrocarbons isolated from many of the stromatolitic carbonates in Table 4. The low pristane to phytane ratios (0.5 - 1.3) reflect the existance of reducing conditions (Powell and McKirdy, 1973b) in the zone of active organic decomposition below the surface of the original algal mat (cf. Sorensen and Conover, 1962; Golubic, 1975).

In such a reducing microenvironment, the unsaturated hydrocarbons (alkenes) which occur in significant concentrations in blue-green algae and Recent algal mats (Table 3) are unlikely to survive for long before undergoing hydrogenation to the corresponding alkanes (Blumer, 1965).

Finally, the remarkable similarity of the alkane patterns of *Tungussia inna* (Wonoka Formation) and *?Tungussia wilkatanna* (Skillogalee Dolomite) (Fig. 2) should be noted. Not only are these hydrocarbon distributions nearly identical, but they are also quite distinct from the patterns obtained from other Precambrian carbonates. The exciting possibility of chemotaxonomic correlation within certain stromatolite form genera is suggested. A lower order of congruence is evident between the alkanes from *Conophyton f.* (Tooganinie Formation) and *?Baicalia f.* (?Skillogalee Dolomite) (Fig. 2). Stratigraphic gradations between these two forms are common (M.R. Walter, pers. comm., 1974).

Fatty acids

Potential markers

Contemporary algae contain fatty acids in appreciably higher concentration than aliphatic hydrocarbons (Schneider et al., 1970). However, algal fatty acids possess shorter chain lengths (C_{10} - C_{22}) than do the hydrocarbons (C_{15} - C_{33}), and exhibit a higher degree of unsaturation. The C_{14}, C_{16} and C_{18} acids occur most frequently, whereas acids with an odd number of carbon atoms in their chain are rare (Table 3). The C_{20} and C_{22} acids found in eukaryotic algae (Ackman et al., 1968) appear to be absent from the blue-green algae (Nichols, 1973).

In contrast to the eukaryotic algae, cyanophytes display a considerable interspecific diversity in fatty acid composition, arising mainly from differences in the relative proportions of the C_{18} (saturated and unsaturated) acids (Nichols, 1973). According to Kenyon and Stanier (1970) many filamentous blue-green algae differ from certain unicellar blue-green algae in containing high concentrations of polyunsaturated fatty acids, particularly the C_{18} series. If it could be shown that the diagenesis of polyunsaturated fatty acids followed a different course (eg. preferential incorporation into an insoluble

kerogen-like polymer) to that of saturated and monounsaturated acids, then the uniformly low concentration (or complete absence) of polyunsaturated acids in unicellular blue-green algae might well provide a geochemical means for identifying stromatolites built by non-filamentous prokaryotic algae. However, the finding of appreciable quantities of the $C_{18:2}$ and $C_{18:3}$ acids in three other unicellular cyanophytes by Schneider et al. (1970) suggests that a chemotaxonomic distinction between coccoid and filamentous blue-green algae, based on fatty acid composition, may not be universally valid.

The chances of recognizing a bacterial contribution to the organic matter in Recent (and possibly ancient) stromatolites are considerably better. Bacteria commonly contain high concentrations of the unusual singly-branched (*iso, anteiso*) fatty acids, in addition to normal (straight-chain) acids (Kates, 1964; Kaneda, 1967; Parker et al., 1967). *Iso* and *anteiso* acids have been identified in Recent marine sediments (Cooper and Blumer, 1968) and algal mats (Table 3). They might be expected to survive for a time in fossil stromatolites, particularly those with a mild thermal history, but will eventually undergo decarboxylation to the corresponding *iso* and *anteiso* alkanes.

The concentration of fatty acids in bethonic algae diminishes rapidly following *post mortem* disintegration of cellular membranes. For example, a living algal mat at Harbor Island (Table 3) contained 0.17% free fatty acids, compared with concentrations of 0.002% and 0.0003%, respectively, in the first two buried mats immediately underneath it (Parker and Leo, 1964). A similarly rapid decrease was also observed in the relative concentration of unsaturated acids, from 39% of the total acids in the living mat to 7% in the second buried mat. The exact fate of the unsaturated fatty acids is unclear. In the anaerobic environment of the mat interior they could be converted to the equivalent saturated acid by hydrogenation of the double bond(s)

(Blumer, 1965; Rhead et al., 1971). Under persistently low Eh and high pH conditions, such as exist in poorly drained algal mats (Golubic, 1973), it is conceivable that the carboxylic acid functional groups of saturated fatty acids might also be reduced, resulting in alkanes with the same number of carbon atoms as the original acids (Blumer, 1965; Welte and Waples, 1973). This latter reaction path would explain the otherwise unexpected presence of small amounts of even carbon-numbered (C_{16}, C_{18}, C_{20}) n-alkanes in Recent algal mats (Table 3). In intermittently aerated mats, unsaturated fatty acids are more likely to disappear into the insoluble kerogen fraction by way of oxidative cross-linking reactions (cf. Abelson, 1967, p.70).

Stromatolites

Fatty acid distributions similar to those in extant microorganisms have been reported from ancient algal sediments. Das and Smith (1968) identified the n-$C_{10:0}$ - n-$C_{20:0}$ acids (n-$C_{16:0}$ being the most prominent) in five fossil algae (presumably preserved in carbonate), ranging in age from Eocene to Cambrian. Included in their suite of samples was the unicellular stromatolite-forming alga *Chlorellopsis coloniata* from the Green River Formation (Bradley, 1929). Predictably, the level of the C_{14}, C_{16} and C_{18} unsaturated acids detected decreased steadily with increasing age so that a trace of the C_{16} unsaturated acid(s) was all that remained in the Cambrian *Girvanella* examined. These data can not yet be interpreted in terms of algal taxonomy.

Recently, organic geochemists have turned their attention to the fatty acids and hydrocarbons which occur in the natural ecosystems and sediments of thermal environments (Jackson and Meinschein, 1973). Both nonbiogenic stromatolite-like structures (geyserite) and biogenic (algal and bacterial) siliceous stromatolites are presently forming around hot springs and geysers in Yellowstone National Park (Walter et al., 1972). This particular hot spring environment was postulated as a Recent analogue for the stromatolitic chert facies of the Gunflint Iron Formation by

Walter (1972). According to Jackson and Meinschein (1973) bacterial-algal mats in streams draining Yellowstone hot springs yield fatty acid distributions similar to those obtained from ancient cherts. However, it is somewhat salutory to note that these workers also report finding syngenetic fatty acids in nonbiogenic geyserite 10^2 - 10^3 years old; the acids have apparently changed little since being trapped in the silica. Nichols (1970, p.114) quotes the fatty acid composition of the important thermophilic blue-green algae *Mastigocladus laminosus;* apart from a minor amount (2.1%) of the $C_{18:2}$ acid, it lacks other polyunsaturated acids. The tendency to synthesize a high proportion of saturated acids is a feature of organisms growing in warm environments (Abelson, 1967).

Pigments

Potential markers

Quantitatively, pigments are the next most important part of the lipid fraction of blue-green algae after the fatty acids and associated acyl lipids (Nichols, 1973). Algal pigments perform such vital functions as mediating photosynthesis, screening out harmful radiation, and preventing photo-oxidation. The major algal photosynthetic pigment is the dihydroporphyrin, chlorophyll *a*. The related bacteriochlorophylls are tetrahydroporphyrins which differ slightly in their peripheral structure. The iron-containing coenzymes (cytochromes, catalase, peroxidase) of microbial photosynthesizers are also porphyrin-based compounds.

Other key chromophores are the phycobilins (eg. phycoerythrin, phycocyanin) present with chlorophyll in the photosynthetic lamellae of blue-green algae (Chapman, 1973) and the chloroplasts of red algae; and various carotenoids, some of which are unique to the Cyanophyta (Nichols, 1973). Carotenoids are cyclic or acyclic isoprenoid compounds, usually containing a series of conjugated double bonds.

The degradation of free, extracellular chlorphyll into porphyrins of the kind found in sedimentary rocks and crude oils has been

documented by Orr et al. (1958). Chlorophylls (and other pigments) that are deposited in intact or partially degraded microbial cells may instead become "grafted" onto a variety of cellular macromolecules (Oehler et al., 1974). With further maturation these "grafted pigment complexes" may fragment into smaller pigment units; or alternatively condense into humic and fulvic acids, or insoluble kerogen. Blumer and Rudrum (1970) predict the presence of polymeric porphyrin structures in kerogen. Early diagenetic oxidation and polymerization of labile carotenoid pigments would likewise tend to result in their incorporation into a kerogen precursor, perhaps resembling sporopollenin (cf. Brooks and Shaw, 1970).

Stromatolites

Reports of fossil pigments in algally-laminated sediments are few. Bacteriochlorophylls *a* and *c* have been identified in organic matter separated from the Yellowstone stromatolites of Recent age (Walter et al., 1972). Whereas trace amounts of presumably indigenous porphyrin-like compounds were found in sediments of the Swaziland Sequence, none could be detected in the stromatolitic Gunflint chert (Kvenvolden and Hodgson, 1969) despite its rich microfossil content. On the other hand, two Precambrian algal limestones examined by Hodgson et al. (1968) yielded chlorins and metal (Ni, V)-chelated porphyrins in small concentration. The presence of chlorins could indicate contamination from modern plants, soils or younger sediments. Chlorin pigments are very abundant in Recent sediments and soils.

Phycobilins are less stable to heat than chlorophyll (Oehler et al., 1974) and so recognition of their geochemical derivatives in ancient stromatolites may be more difficult. Jackson (1973) has nevertheless inferred that original differences in the ratio of phycoerythrin to phycocyanin in fossil algae are still decipherable in geolipid extracts of sediments as old as 3400m.y. He interpreted secular

variations in the spectroscopic (visible and infrared) properties of soluble humic matter in sediments of various ages and depositional environments, in terms of major evolutionary changes in the pigmentation of the algal ecosystems populating those environments. Among the samples studied were cherts from the Gunflint Iron Formation, Paradise Creek Formation and Bitter Springs Formation, and a dolomite from the Beck Spring Dolomite, all stromatolite-bearing units. These four samples help define quite distinct trends in pigment concentration and/or composition over the 1900 - 900 m.y. segment of Precambrian time. Evolutionary developments claimed to be reflected in these changes include: the presence of high concentrations of protective pigments in blue-green algal cells before 2000 m.y., a steady decline in algal production of protective chromophores (or a change in pigment type) between 1900 and 900 m.y., corresponding to the gradual accumulation of atmospheric ozone; and the appearance of eukaryotic algae between 1600 and 1300 m.y. ago.

Amino acids

Carbonate-trapping and precipitating algal mats growing on the shelf of a hypersaline pool adjacent to the Gulf of Aqaba contain organic matter rich in amino acids (Friedman et al., 1973), notably aspartic acid (most abundant), alanine, glutumic acid, glycine, leucine, phenylalanine, serine and valine. These and twelve or so other amino acids are the building blocks of algal and bacterial proteins. Because of their lack of long-term geochemical stability the importance of such peptides and their constituents amino acids lies not so much in their value as biochemical markers *per se* but as in their ability to modify mineralogical equilibria during early diagenesis, particularly in carbonate-depositing environments.

Peptides and free amino acids, like fatty acids, readily form monomolecular layers on the surface of carbonate minerals (Suess, 1970), thereby slowing inorganic carbonate equilibration reactions, eg. the

inversion of aragonite to calcite (Jackson and Bischoff, 1971). Extracellular organic matter produced by blue-green algae is mainly peptide and its ability to chelate metal ions (eg. Ca^{2+}, Mg^{2+}) is well known (Fogg and Westlake, 1955). Acidic amino acids such as aspartic acid and glutamic acid can bind Ca^{2+} ions from solution, and in so doing influence the precipitation of $CaCO_3$ (Mitterer, 1968; Mitterer and Carter, 1973). This may account for the calcitized organic matter in an algal laminate from the Middle Devonian Winnipegosis Formation (Shearman and Fuller, 1969). The high Mg^{2+} concentration in the sheath mucilage (a polysaccharide-peptide complex: Dunn and Wolk, 1970) of stromatolite-building blue-green algae such as *Schizothrix calcicola* has been invoked (Gebelein and Hoffman, 1973) to explain the origin of dolomitic lamination in stromatolitic limestones. Similarly, Friedman et al. (1973) reported algally-precipitated laminae of alternating aragonite and high-Mg calcite, the latter enclosing abundant dispersed organic matter. The organic matter actually contains one third of the total Mg in the laminates and is presumably the source of the Mg in the calcite.

The possibility that amino acids released from the original algal peptides by hydrolysis may still be present, albeit in a less accessible form, cannot be entirely ruled out. Amino acids react with carbohydrates to produce dark, complex polymers [whose] having properties are strikingly similar to natural humic acids (Abelson and Hare, 1971; Hoering, 1973). Humic acids are thought to be intermediates in the generation of kerogen. Once formed both humic acids and kerogen have the capacity to continue taking up free amino acids and peptides by adsorption as well as irreversible reaction (Abelson and Hare, 1970, 1971). Hence it would appear that any truly indigenous algal and bacterial amino acids are likely to be locked away in the kerogen fraction of the sediment.

Thus, although the peptides and amino acids of the precursor algae may not be amenable to preservation as recognizable biochemical

markers, the effects of their original presence are often evident in the mineralogy and texture of the lithified stromatolite.

Kerogen

Potential markers

Kerogen was once aptly and succinctly described by Degens (1967) as a heteropolycondensate. Indeed, all of the biochemical markers so far discussed are capable of incorporation during diagenesis into this amorphous syngenetic substance, making it an important but still largely untapped reservoir of chemical fossils. The mucilaginous secretions of blue-green algae are probably a major progenitor of stromatolite kerogen (Shearman and Shipwith, 1965). Sporopollenin, the resistant and chemically inert carotenoid polymer claimed by Brooks and Shaw (1970, 1972) to be present in "many algal and fungal spore exines", although recently reported in the cell wall of *Chlorella* and other green algae (Atkinson et al., 1972), has not yet been found in blue-green algae. Its contribution to the insoluble organic matter in fossil stromatolites is probably minimal and limited to those in which eukaryotic algae and/or fungi were part of the mat biota.

The main advantage kerogen has over the geolipid extract as a source of palaeobiochemical information, viz. freedom from post-lithification contamination, stems from its particulate, insoluble and relatively unreactive nature. These same attributes, however, make it difficult to analyse except by relatively drastic degradative techniques involving hydrogenation, oxidation, alkali fusion or pyrolysis.

The products of low temperature pyrolysis (Hoering, 1967; Giraud, 1970) or mild oxidation (Burlingame and Simoneit, 1969) provide information about the basic structure of the kerogen, eg. whether it is aliphatic or aromatic. Thermally immature algal kerogens may be expected to yield hydrocarbons (on pyrolysis) and fatty acids (on oxidation) that

are predominantly aliphatic (cf. Brooks and Shaw, 1970). In certain cases it might be possible to recognize more specific clues to the identity of the source material among the degradation products of stromatolitic kerogens. For example, the C_{20} and C_{22} unsaturated fatty acids characteristic of certain eukaryotic algae should give rise to anomalous amounts of C_{19} - C_{21} alkyl residues; high concentrations of dicarboxylic acids following oxidation would be consistent with a sporopollenin-based kerogen (Brooks and Shaw, 1970). Comparison of the hydrocarbons obtained by low-temperature pyrolysis of the kerogen with those in the geolipid extract of the sediment provides a useful check on the syngeneity of the soluble fraction (cf. Hoering, 1967).

The elemental composition of kerogen broadly reflects the nature of its precursor organic matter and the environment of deposition of its host sediment (Tissot et al., 1974). However, the greater the degree of post-depositional thermal alteration the kerogen has undergone, the less diagnostic of both source and environment is its composition.

Stromatolites

Hoering (1964) hydrogenated kerogen from a Precambrian (Bulawayan) stromatolite with phosphorus and anhydrous hydrogen iodide and analysed the resulting low molecular weight ($<C_8$) hydrocarbons. As Hoering (1967, p.103) points out, however, the method "is apparently too destructive to help reveal high molecular-weight compounds, diagnostic of a biological origin".

The elemental compositions of kerogen isolated from some Australian Palaeozoic and Precambrian stromatolites are given in Table 4. Their dry ash-free carbon content varies from 72.7% to 90.9% corresponding to a progressive increase in diagenetic rank (Fig. 5: cf. Tissot et al., 1974, fig. 2). Figure 5 shows that algal kerogens vary widely in composition. Nevertheless, the stromatolitic kerogens are distinctive in that, as a group, they tend to be unusually rich in oxygen. This is

highly indicative of an oxygen-rich precursor, eg. algal mucilage. Three samples (4, 10 and 15, Table 4) actually plot outside the shaded compositional field. These may be derived from algal mats which grew in a more desiccated environment and hence produced greater amounts of mucopolysaccharides (and perhaps other compounds such as unsaturated fatty acids). Mucilaginous secretions help prevent loss of water from algal colonies during desiccation (Fogg et al., 1973, p.320). The envelopes of desiccation-resistant spores from the blue-green alga *Anabaena cylindrica* contain 41% carbohydrate (Dunn and Wolk, 1970).

Stable carbon isotopes

Potential markers

The uptake and fixation of CO_2 by photosynthetic organisms leads to fractionation between ^{12}C and ^{13}C such that the resultant organic matter is richer in the lighter isotope than the inorganic carbon source. For contemporary marine algae that source is dissolved CO_2, and parameters such as CO_2 concentration, pH, water temperature and growth rate have been shown to be major controls of the observed carbon isotopic composition (Degens, 1969). All photoautotrophic organic matter incorporated into sediments is stamped with an isotopic biochemical marker which is largely unaffected by subsequent diagenetic processes. In contrast, marine non-photosynthetic bacterial heterotrophs like *Desulfovibrio desulfuricans* are isotopically only slightly different from their (?algal) carbon source (Kaplan and Rittenberg, 1964). Should the sediment eventually undergo incipient metamorphism the $\delta^{13}C$ value* of its kerogen may become

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

The Chicago PDB carbonate is a commonly used standard.

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appreciably altered as a result of preferential rupture of ^{12}C - ^{12}C bonds and loss of ^{12}C- enriched, low molecular weight hydrocarbons (McKirdy and Powell, 1974; cf. Fig. 6). There is good evidence that the carbon isotopic composition of atmospheric CO_2 has remained relatively constant since the early Precambrian (Weber, 1967; Perry and Tan, 1972). The $\delta^{13}C$ values of most ancient marine carbonates (limestone and dolomite) fall in a narrow (3 per mil) range which overlaps that for the inorganic carbon in present-day seawater (Fig. 6). Hence, the $\delta^{13}C$ values of living and unmetamorphosed fossil organic matter may be directly compared and used for interpreting the origin of the latter.

In laboratory cultures of blue-green algae and other photosynthetic microorganisms, the degree of fractionation between cellular carbon and inorganic substrate, $\Delta\delta^{13}C$, is -24 to -1 per mil (Abelson and Hoering, 1961; Calder and Parker, 1973; Seckbach and Kaplan, 1973; Fig. 6). The maximum fractionation was achieved by the thermophilic mat-forming green alga *Cyanidium caldarium* when growing in pure CO_2 at 45°C. Recent hot spring algal mats tend to be more enriched in ^{12}C ($\delta^{13}C_{PDB}$ = -24 to -11 per mil : Seckbach and Kaplan, 1973) than those inhabiting paralic environments ($\delta^{13}C_{PDB}$ = -17 to -10 per mil: Behrens and Frishman, 1971; Calder and Parker, 1973), although interestingly enough they are no more depleted in ^{13}C than the organic matter (presumably phytoplanktonic detritus) in deep-sea marine sediments ($\delta^{13}C_{PDB}$ = -24 to -16 per mil : Degens, 1969), as shown in Figure 6.

Under conditions of restricted water circulation, direct incorporation of CO_2 derived from the metabolic activity of mat-building algae, or from their decay, into the associated carbonate becomes possible, particularly if the algae involved are carbonate precipitators. Then, both the carbonate matrix of the stromatolite and

its organic matter will be enriched in ^{12}C.

Stromatolites

Hoering (1962, 1967) and Schopf et al. (1971) used carbon isotopic measurements on coexisting carbonate and reduced organic carbon (Table 5) to establish the biogenicity of abiophoric stromatolite-like structures in various Precambrian formations. As Schopf et al. (op.cit., p.483) explain for the oldest known stromatolites: "The large difference in δC^{13} values between coexisting organic and inorganic carbon compounds in the unmetamorphosed Bulawayan sediments is most reasonably interpreted as having resulted from carbon isotopic fractionation during the biological fixation of carbon dioxide by photosynthetic microorganisms". Thus, carbon isotopic data, in conjunction with stromatolite morphology, demonstrates "the existence of photosynthesis and biological activity [early in] the Precambrian era" (Hoering, 1962, p.191).

The carbon isotopic composition of kerogen in Precambrian stromatolites is typical of that found in other unmetamorphosed Precambrian (and most Phanerozoic) sedimentary rocks (Oehler et al., 1972; Fig. 6). On the other hand, it is considerably lighter than algal organic matter in Recent sediments. Various reasons for this have been advanced. Seckbach and Kaplan (1973, p.168) speculated "that low $\delta^{13}C$ values measured in Precambrian kerogen may in part represent organic matter deposited in algal mats growing at elevated temperatures and under atmospheric conditions where P_{CO_2} was substantially greater than at present". Whereas similarities admittedly exist between the Yellowstone hot spring environment, in which algal and bacterial stromatolites composed of silica are presently growing (Walter et al., 1972), and the stromatolitic facies of the Gunflint and Biwabik iron formations (Walter, 1972), thermophilic algae cannot be held responsible for the majority of Precambrian stromatolites which are

preserved in marine carbonates. A possible alternative explanation is that lipids comprised a higher proportion of the Precambrian algal biomass and gave rise to lipid-rich kerogens. The lipids of modern organisms, including blue-green algae, are isotopically very much lighter than the whole organism (Abelson and Hoering, 1961; Degens, 1969; Fig. 6). Nevertheless, Calder and Parker (1973) maintain that incorporation of the lipid of contemporary blue-green algae into kerogen would not, by itself, produce the same low $\delta^{13}C$ values found in Precambrian organic matter. It seems that the correct explanation for the enigmatic isotopic composition of Precambrian kerogens lies in some as yet unknown combination of environmental variables.

The difference in kerogen isotopic composition between unmetamorphosed Precambrian stromatolitic carbonates (10 samples: $\delta^{13}C_{PDB}$ range = -33.5 to -19.9 per mil, mean = -28.4 per mil) and cherts (11 samples: $\delta^{13}C_{PDB}$ range = -37.2 to -24.8 per mil, mean = -29.0 per mil.) illustrated in Figure 6 is probably too small to be of any potential palaeoecological significance, although analyses of more samples are obviously needed to fully explore this possibility. McKirdy and Powell (1974) found the kerogens from two Precambrian evaporitic carbonates, one of which was a stromatolite (sample 9, Table 4), to be some 7-8 per mil heavier than normal marine organic matter of similar diagenetic rank. On the same basis, it may be possible to distinguish peritidal from subtidal fossil stromatolites. The Boetsap River section of the stromatolitic Transvaal Dolomite (Truswell and Erikson, 1973) would seem to be an ideal Precambrian locality in which to test this hypothesis.

Tan and Hudson (1974) report $\delta^{13}C_{PDB}$ values as low as -14.0 per mil for early diagenetic carbonate in algal limestones from the Great Estuarine Series (Jurassic) of Scotland. Restricted water circulation leading to a build-up of organic-derived, ^{12}C-enriched

bicarbonate in their environment of deposition is implied.

ORGANIC GEOCHEMISTRY - A NEW TOOL IN STROMATOLITOLOGY?

Is there such a need? I hope not

If one thing is obvious from this account of the exploratory application of organic geochemical methods to stromatolites, it is perhaps that there have been more failures than successes. The composition of kerogen, the major portion of the organic matter preserved in stromatolites, is as obscure as ever. The syngenetic origin of the extractable geolipids is still equivocal. But most important of all, stromatolites and their associated sediments have yet to be seriously considered as a source of biogeochemical information on the evolution of the mat-building biota and the diagenetic fate of algal and bacterial organic matter in carbonate-depositing environments.

Nonetheless, organic geochemistry has already contributed significantly to our understanding of stromatolites as sediments and the organisms that built them. Carbon isotopic measurements confirm the assignment of a photosynthetic (or chemoautotrophic) physiological mode to ancient stromatolitic biota. Where the geolipid fraction of the total organic matter appears to be largely syngenetic with the host rock, as is apparently more often true of carbonates than cherts, the hydrocarbons and fatty acids are consistent with an algal and/or bacterial derivation. The structure and composition of kerogen (eg. hydrogen to carbon atomic ratio) provides an index of thermal alteration which can be used to monitor other more subtle diagenetic changes in stromatolites, particularly those affecting their microstructure. The interaction of organic matter in the form of fatty acids, amino acids and humic compounds with the surfaces of mineral grains helps explain such important phenomena as lack of recrystallization, preservation of calcite in stromatolite columns, and preferential dolomitization (or calcitization)

of organic-rich laminae.

What then are some of the directions that future organic geochemical research might profitably take in the expanding field of stromatolitology? Continued study of the lipids and other potential chemical fossils present in the organisms of modern algal-mat communities is essential because it is on such biochemical data that interpretation of the molecular fossil record is ultimately based. Particular attention should be paid to compounds that are peculiar to certain classes of microorganisms, viz. coccoid and filamentous blue-green algae, eukaryotic algae, fungi, and photosynthetic and non-photosynthetic bacteria. Non-photosynthetic bacterial decomposers in algal mats are of considerable geochemical importance because they are the last organisms to leave their biochemical imprint (eg. singly-branched fatty acids, high proportion of $>C_{20}$ compounds in their aliphatic hydrocarbons, preferential metabolism of algal straight-chain hydrocarbons) on the residual organic matter. Mats from different environments should be compared to ascertain whether characteristic differences in their "biochemical facies" exist. Several organic geochemical parameters are to a large extent environmentally controlled: pristane to phytane ratio and even-predominance in n-alkanes, by redox potential; and kerogen $\delta^{13}C$, by temperature, pH and CO_2 concentration. In view of the ability of carbonate minerals to form complexes with a wide variety of organic compounds, stromatolitic carbonates appear likely to be more fruitful source of syngenetic chemical fossils than cherts. Finally a concerted attempt, employing a range of analytical techniques (including carbon isotopic analysis), should be made to characterize as many stromatolite kerogens as possible, with the aim of detecting original biochemically-derived (as distinct from geochemically-imposed) differences which may be of evolutionary significance.

Now that biological control of stromatolite microstructure (Gebelein, 1974) and some aspects of gross morphology (Serebryakov and Semikhatov, 1974) has been verified, the potential rewards awaiting further study of stromatolites by organic geochemists would seem to far outweigh the present analytical and interpretational difficulties.

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able 1. Total organic carbon content (TOC) of algal mats and other Recent sediments.

LOCATION	TOC %	REFERENCE
Harbor Island, Texas		Parker and Leo (1965)
living mat	32	
first mud layer	1.1	
second mud layer	0.84	
Kleberg Point Lagoon, Baffin Bay, Texas		Behrens and Frishman (1971)
well developed laminae	2-5	
disrupted, oxidized laminae	1-1.7	
Gulf of Batabano, Cuba		Hunt (1967)
shallow marine carbonate	1.4 (mean)	
Saanich Inlet, British Columbia		Brown et al., (1973)
carbonate-poor, reducing muds	3.4 (mean)	
Choctawhatchee Bay, Florida		Palacas et al., (1972)
estuarine muds	3.6 (mean)	

ble 2. Total organic carbon content (TOC) of stromatolites and other ancient carbonates.

	LOCATION	TOC %	REFERENCE
STROMATOLITES	Cavan Limestone, NSW (Devonian)	0.06 - 0.42	McKirdy (this paper)
	Wilkawillina Limestone, SA (Cambrian)	0.01	McKirdy (this paper)
	Australian stromatolites (Precambrian)	0.01 - 0.05	McKirdy (this paper)
	Purcell Supergroup, Alberta (Precambrian)	1.1	Hodgson et al. (1968)
	Transvaal Dolomite Series, S.Africa (Precambrian)	0.1	Hodgson et al. (1968)
	Bulawayan Group, Rhodesia (Precambrian)	0.5	Hoering (1964)
OTHER CARBONATES	Russian Platform carbonates (mean values)		Ronov and Migdisov (1971)
	Mesozoic and Cainozoic	0.47	
	Palaeozoic	0.26	
	Late Proterozoic	0.06	
	Early and Middle Proterozoic	0.01	

Table 3. Hydrocarbons and fatty acids of geochemical significance in algal mats, mat-building cyanophytes, and extant representatives of algal genera implicated in Precambrian stromatolitic microbiotas.

ALGAE and ALGAL MATS	HYDROCARBONS[1]																						
	15:0	16:0	17:0	17:1	17:2	18:0	ai 18:0	br 18:0	br 18:1	19:0	19:1	pris	20:0	phyt	21:0	21:2	22:0	23:0	23:1	25:1	26:1	27:1	27:2	other
Algal mats, Texas Gulf Coast:-																								
Harbor Island[2]									———		not	determined			———									
Port Aransas	2	2	36	4	32	1		11		1	8													
Oyster Bay[3]	<1	2	12	31		7	10		6**	7		2.5	5	2.5	4		2	2						6
Laguna Atacosa	3		29	43		5				2		3.75	1	1.5	<1		<1							
Padre Island		2	24	22		1	16		21**	1		<1	1		<1		<1	1						9
Mat-building cyanophytes:-																								
Microcoleus chthonoplastes	2	4	92			2																		
Lyngbya aestuarii[4]	2	6	35			1		38*																16
Genera implicated in Precambrian stromatolitic microbiotas:-																								
Chlorella eg. C. pyrenoidosa			19	77																				
Anacystis eg. A. cyanea[5]			87					13*																
A. montana[5]			12													9			8	15	4	35	3	
Spirulina eg. S. platensis	10	20	70	<1																				
yngbya eg. L. lagerhaimii	1	4	86	1				8																
Oscillatoria eg. O. williamsii	9	<1	91	<1		<1																		
Myxosarcina eg. M. chroococcoides									———		not	determined			———									

FATTY ACIDS[1]																			REFERENCES
12:0	i 12:0	i 13:0	14:0	i 14:0	ai 14:0	14:1	15:0	i 15:0	ai 15:0	16:0	i 16:0	16:1	16:2	i 17:0	17:1	18:0	18:1	18:2	18:3	others	
										58		11				2	23	6	<1		Parker and Leo (1965)
								——	not	determined		——									Winters *et al.* (1969)
1		<1		3	4			1	3	24	4	23		4		6	3	4	4	16	Oró *et al.* (1967)
2	<1	4	3	2	4			6	4	17	3	10		1		3	2	3	7	27	Oró *et al.* (1967)
2	2	6	6		7			3	1	22	7	9		3		9		3	2	19	Oró *et al.* (1967)
2			5			<1	3			37		13				4	14	5	18		Parker *et al.* (1967) Winters *et al.* (1969)
										26		15	3				8	17			Gelpi *et al.* (1970) Schneider *et al.* (1970)
			2							21		2	6				17	19	26		Gelpi *et al.* (1970) Schneider *et al.* (1970)
							3			23		20				2	7	10	5		Gelpi *et al.* (1970) Schneider *et al.* (1970)
										21		3					25	18	19		Gelpi *et al.* (1970) Schneider *et al.* (1970)
			2							45		6			2		10	16	13		Gelpi *et al.* (1970) Schneider *et al.* (1970)
<1			2			<1	1			40		15	<1			2	31	7			Parker *et al.* (1967) Winters *et al.* (1969)
<1			2			1	2			36		24	14			2	11	4			Parker *et al.* (1967) Winters *et al.* (1969)
										38		9	1			4	7	9	33		Nichols and Wood (1968)

1. Straight-chain (i.e. normal) isomers except where otherwise indicated viz. i = iso, ai = anteiso, br = branched, pris = pristane, phyt = phytane. Numbers before colon = numbers of carbon atoms in molecule; numbers after colon = number of double bands. Concentrations given as relative percent of total hydrocarbon or fatty acid fraction.

2. Mainly Lyngbya confervoides

3. Mainly Microcoleus chthonoplastes, Lyngbya aestuarii and, in lesser amount, Schizothrix calcicola

4. Morphologically similar to Palaeolyngbya Barghoorniana, Bitter Springs Formation (Schopf, 1968).

5. Morphologically similar to Palaeoanacystis vulgaris, Bitter Springs Formation (Schopf, 1968).

* Mixture of 7-, and 8- methylheptadecane

** Includes some 17:1 hydrocarbon.

Table 4. Preliminary analysis of some Australian Precambrian and Palaeozoic stromatolites (See also Appendix 1)

Sample	TOC %	Geolipid ppm	extract mg/g^C	Alkanes ppm	Alkanes % extract	n-Alkanes range	n-Alkanes max.	Pristane/Phytane	Kerogen C %	Kerogen H ash-free basis	Kerogen N ash-free basis	Kerogen S ash-free basis	Kerogen O* ash-free basis	Ash %	H/C	O/C	Porosity %	Permeability V millidarcy	Permeability H millidarcy
1	0.24	11	4.7	3.3	29.8	C_{19}-C_{29}	C_{25}	-	81.2	3.7	0.9	1.7	12.5	8.4	0.54	0.12	2.3	0.0005	0.12
2	0.42	10	2.7	1.4	13.3	C_{17}-C_{29}	C_{25}	0.5	88.2	1.9	0.3	2.6	7.0	20.2	0.26	0.06	4.4	0.0002	0.00003
3	0.06	8	13.2	1.8	22.2	C_{19}-C_{29}	C_{25}	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.70	n.d.	1.2	0.0002	0.0003
4	0.01	7**	69.3**	3.7**	n.d.	n.d.	n.d.	n.d.	73.0	3.0	2.1	9.0	12.9	6.4	0.49	0.13	1.0	0.005	0.004
5	0.03	5	18.1	1.4	26.1	C_{16}-C_{26}	C_{19}	0.6	77.9	3.1	2.7	6.6	9.7	44.2	0.47	0.09	0.5	0.0004***	
6	0.01	17	173.4	4.7	27.4	C_{18}-C_{28}	C_{21}	-	81.2	3.4	0.9	n.d.	n.d.	15.5	0.49	n.d.	2.2	n.d.	n.d.
7	0.02	10	48.6	2.5	25.9	C_{16}-C_{28}	C_{21}	0.6	84.0	1.7	<0.9	5.7	7.7	44.3	0.24	0.07	2.8	0.006	0.006
8	0.02	132	659.3	1.5	1.2	C_{15}-C_{23}	C_{18}	1.1	72.7	5.0	1.5	7.0	13.8	5.7	0.82	0.14	0.8	0.007	0.006
9	0.02	11	77.2	2.5	10.9	C_{15}-C_{24}	C_{18}	0.8	90.9	0.8	<0.5	3.8	4.0	23.2	0.10	0.03	2.2	0.003***	
10	0.05	6	28.2	3.0	53.8	C_{16}-C_{26}	C_{19}	0.4	75.3	2.1	1.0	1.6	20.0	8.0	0.33	0.20	n.d.	n.d.	n.d.
11	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	85.2	2.2	0.7	2.3	9.6	53.1	0.31	0.08	n.d.	n.d.	n.d.
12	0.08	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	85.2	2.0	0.7	2.0	10.1	54.0	0.27	0.09	n.d.	n.d.	n.d.
13	0.03	8	16.6	1.4	16.7	C_{17}-C_{29}	C_{24}	1.3	88.7	1.7	1.3	1.8	6.5	38.3	0.23	0.06	0.8	0.0008	0.0005
14	0.04	5	12.3	1.9	39.1	C_{17}-C_{29}	C_{24}	1.2	77.2	4.2	1.8	6.2	10.6	16.4	0.65	0.10	1.7	0.0007	0.0006
15	0.01	2	15.0	n.d.	n.d.	n.d.	n.d.	n.d.	73.8	2.7	<0.6	5.8	17.1	20.2	0.43	0.17	2.1	0.005	n.d.

* By difference ** Includes free S *** Orientation unknown n.d. not determined

Table 5. Carbon isotopic composition of some Precambrian stromatolites (after Hoering, 1962, 1967; and Schopf et al., 1971).

LOCATION	$\delta^{13}C_{PDB}$	
	carbonate	TOC
Belt Supergroup, Montana	+0.4	- 24.6
Iron River Formation, Michigan	+ 1.3	- 19.9
Transvaal Dolomite Series, S. Africa	- 0.3	- 31.0
Bulawayan Group, Rhodesia	- 0.1 *	- 32.1 *

* mean values

APPENDIX 1. Australian stromatolites for which new analytical data is presented in text

Sample	Reference No.	Formation	Location	Estimated age (m.y.)	Form	Lithology	Source
1	CMC 80	Flaggy Limestone Mbr, Cavan Limestone, Murrumbidgee Gp.	Taemas, N.S.W.	375 (early Dev.)	crenulate	carbonate	Author
2	CMC 68				linked cumulate	"	"
3	CMC 37				stratiform	"	"
4	S 105	Wilkawillina Limestone Hawker Gp.	Wilkawillina Gorge, S.A.	565 (early €)	cumulate	"	M.R. Walter
5	WP 22	Wonoka Formation Wilpena Gp.	Bunyeroo Gorge, S.A.	600	Tungussia inna	"	W.V. Preiss
6	S 418	"Etina Formation", Umberatana Gp.	Kulpara, S.A.	650	Kulparia kulparensis	"	"
7	S 388	Tapley Hill Formation, Umberatana Gp.	Wilson, S.A.	>700	Gymnosolen ramsayi	"	"
8	S 147	Loves Creek Mbr, Bitter Springs Formation	Williams Bore, N.T.	900	Acaciella australica	"	M.R. Walter
9	S 405		Depot Creek, S.A.		Baicalia burra	"	W.V. Preiss
10	S 172	Skillogalee Dolomite, Burra Gp.	" "	1000	? Tungussia wilkatanna	"	"
11	0 9		" "		cryptalgal laminite	chert	Author
12	0 8		Mundallio Creek, S.A.		" "	"	"
13	WP 64	?Skillogalee Dolomite, Burra Gp.	Unknown	?1000	? Baicalia f.	carbonate	W.V. Preiss
14	MRW 12 (2/9/73)	Tooganinie Formation, McArthur Gp.	Top Crossing, N.T.	1600	Conophyton f.	"	M.R. Walter
15	S 95	Pillingini Tuff, Fortescue Gp.	Mount Herbert, W.A.	2200	Alcheringa narrina	"	"

FIGURE CAPTIONS

1. Carbon skeletons of some potential biochemical markers in stromatolites.

2. Gas chromatograms of saturated hydrocarbons (alkanes) isolated from Australian stromatolites.

3. Influence of diagenesis on geolipid yield from stromatolites and other marine carbonates. Data from Powell and McKirdy (1973a), Powell et al. (1974), McKirdy and Powell (1975), and McKirdy (unpublished results).

4. Influence of diagenesis on alkane yield from stromatolites and other marine carbonates. Data from Powell and McKirdy (1973a), Powell et al. (1974), McKirdy and Powell (1975), and McKirdy (unpublished results).

5. Diagenetic evolution of stromatolitic and other algal kerogens. Data from Powell et al. (1974), McKirdy and Powell (1975), and McKirdy (unpublished results).

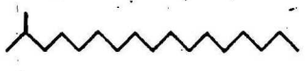
6. Stable carbon isotopic composition of contemporary algae, and algal organic matter in sediments (after Hoering, 1962, 1967; Weber, 1967; Degens, 1969; Behrens and Frishman, 1971, Oehler et al., 1972; Perry and Tan, 1972; Calder and Parker, 1973; Seckbach and Kaplan, 1973; McKirdy and Powell, 1974).

Fig. 1

ALKANES

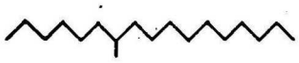
normal

iso

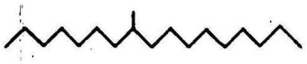


anteiso

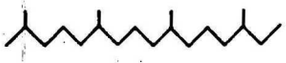
7-methyl



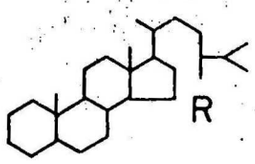
8-methyl



isoprenoid

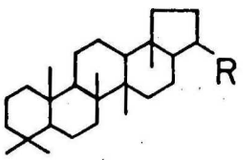


sterane



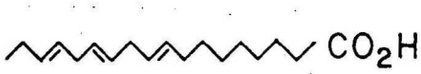
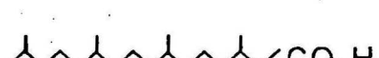
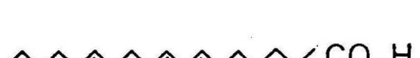
R = H, CH_3, C_2H_5 etc.

hopane



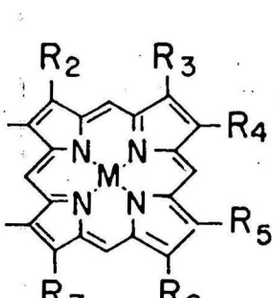
R = H, C_2H_5, iso C_3H_7 etc

FATTY ACIDS

	Saturated		Unsaturated
normal		$C_{18:1}$	
iso		$C_{18:2}$	
anteiso		α-$C_{18:3}$	
isoprenoid		γ-$C_{18:3}$	

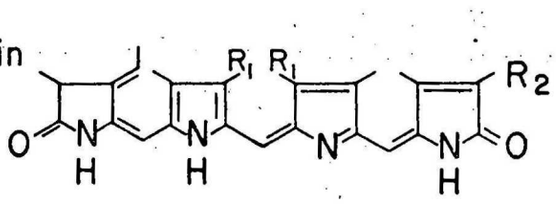
PIGMENTS

porphyrin



R_{2-7} = CH_3, C_2H_5 etc.

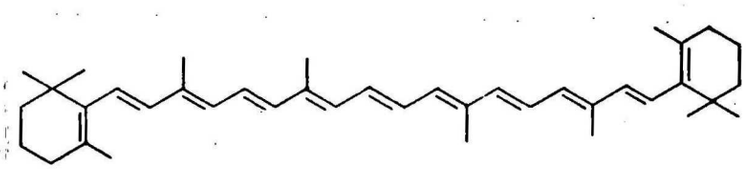
phycobilin



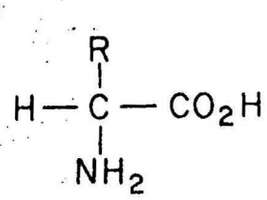
R_1 = $CH_2CH_2CO_2H$

R_2 = $CH:CH_2$ or CH_2CH_3

carotenoid

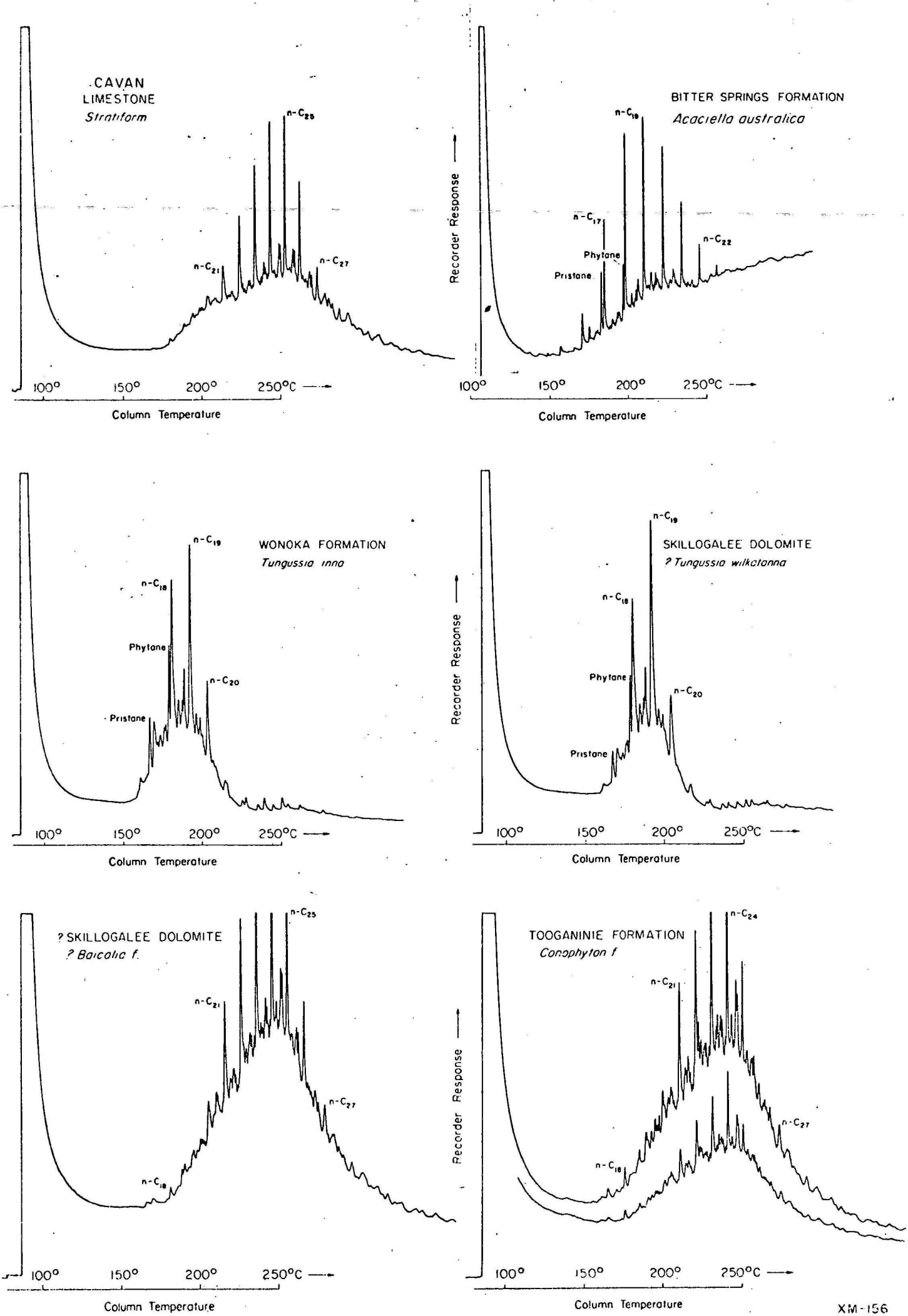


AMINO ACIDS



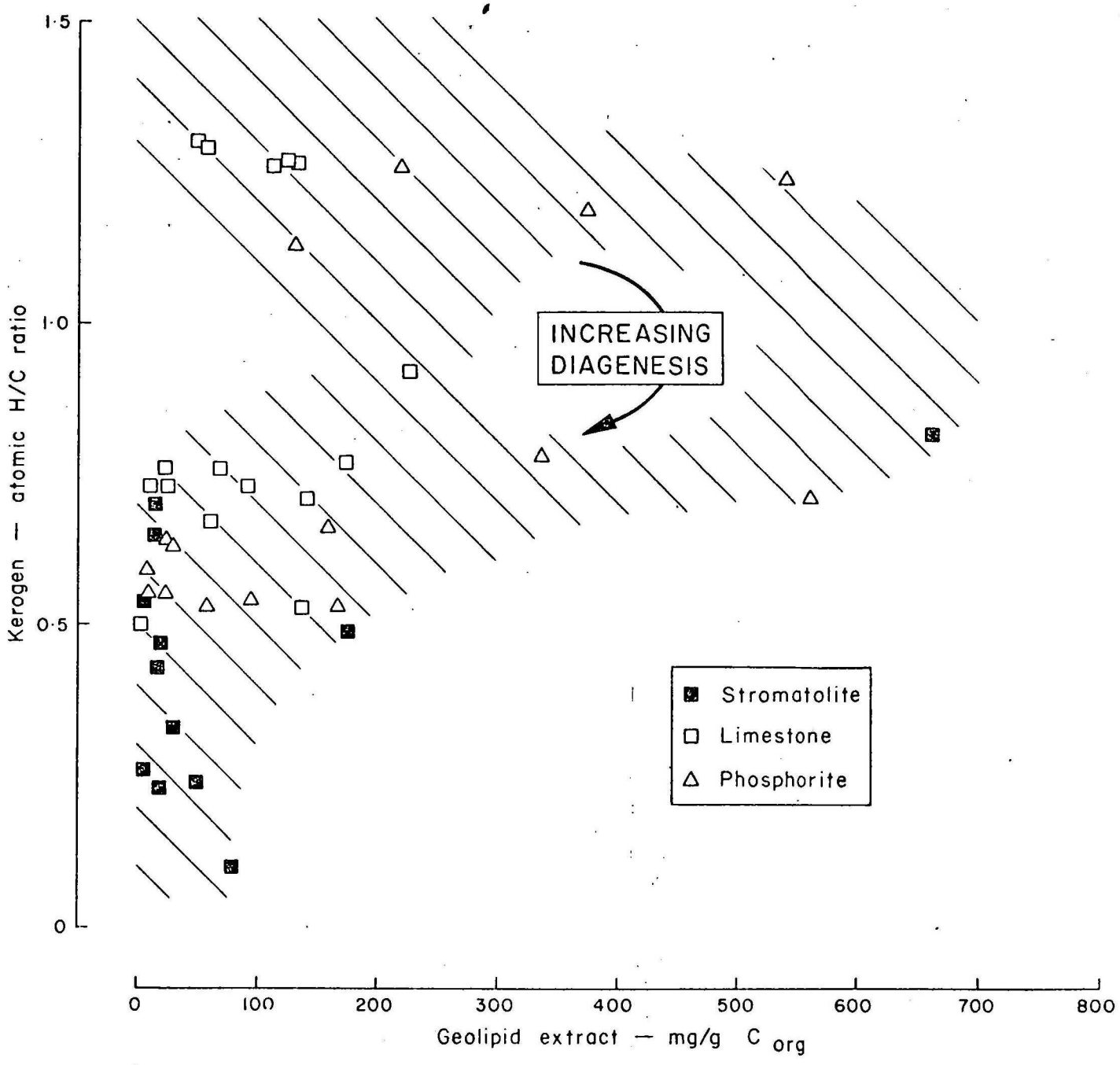
R = H, CH_3, CH_2CO_2H etc.

Fig. 2


CAVAN
LIMESTONE
Stratiform
n-C25
n-C21
n-C27
100°
150°
200°
250°C
Column Temperature
BITTER SPRINGS FORMATION
Acaciella australica
Recorder Response
n-C19
n-C17
Phytane
Pristane
n-C22
100°
150°
200°
250°C
Column Temperature
WONOKA FORMATION
Tungussia inna
n-C19
n-C18
Phytane
n-C20
Pristane
100°
150°
200°
250°C
Column Temperature
SKILLOGALEE DOLOMITE
? Tungussia wilkatonna
Recorder Response
n-C19
n-C18
Phytane
n-C20
Pristane
100°
150°
200°
250°C
Column Temperature
? SKILLOGALEE DOLOMITE
? Baicalia f.
n-C25
n-C21
n-C27
n-C18
100°
150°
200°
250°C
Column Temperature
TOOGANINIE FORMATION
Conophyton f
Recorder Response
n-C24
n-C21
n-C27
n-C18
100°
150°
200°
250°C
Column Temperature
XM-156

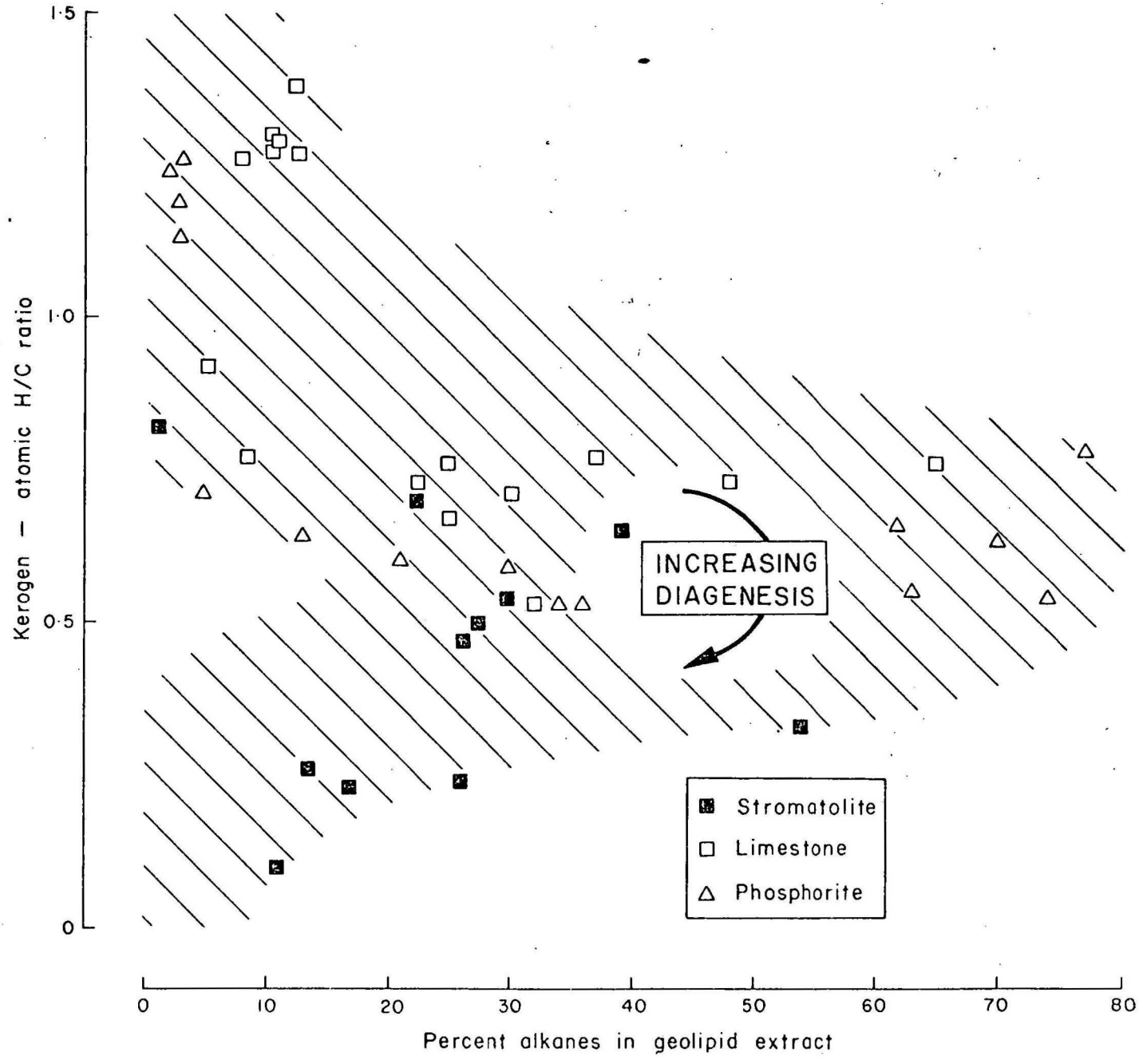
Influence of diagenesis on geolipid content of stromatolites and other marine carbonates

Fig. 3



Influence of diagenesis on alkane content
of stromatolites and other marine carbonates

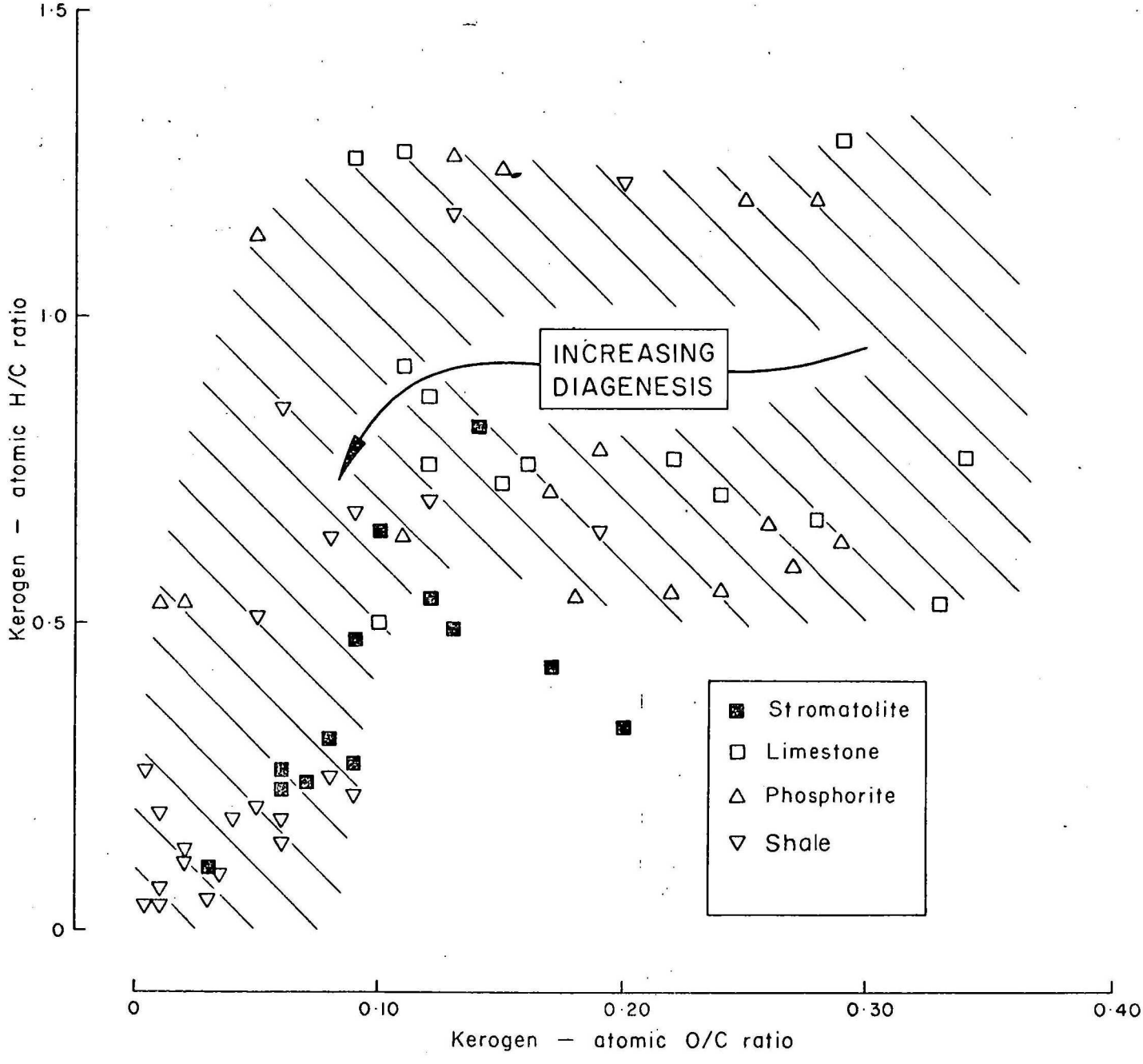
Fig. 4



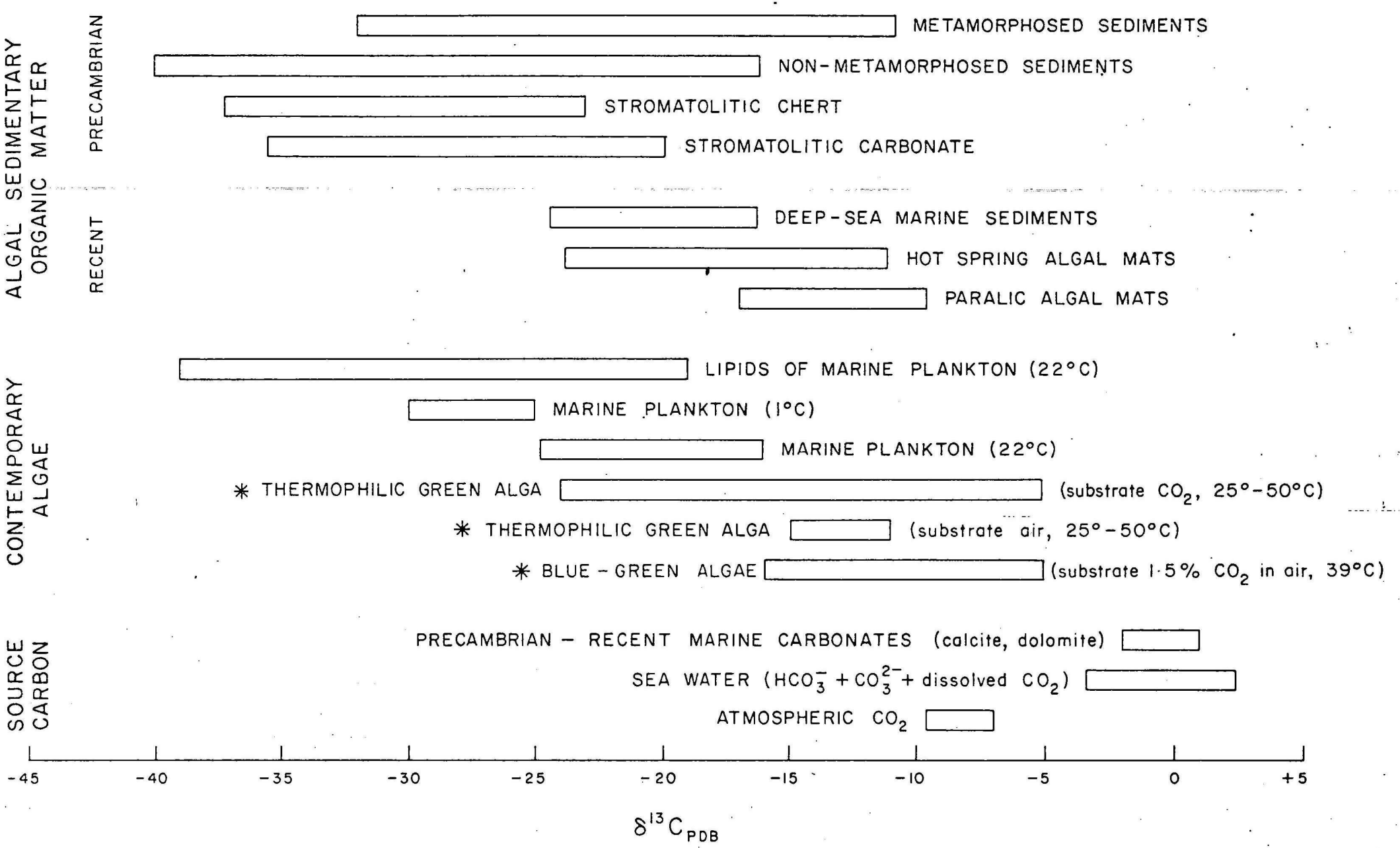
XM-160

Diagenetic evolution of stromatolitic and other kerogens of primarily algal source

Fig. 5



XM-158



* $\Delta\delta^{13}C$ data, where $\Delta\delta^{13}C$ = $\delta^{13}C$ sample – $\delta^{13}C$ substrate

XM-157