Organic Geochemistry

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1 Introduction

Organic geochemistry may be broadly defined as the study of the organic matter occurring in geological situations. Organic carbonaceous material is present in sedimentary rocks as old as $3{\cdot}5 \times 10^9$ years. Hence, 'natural product' organic chemistry, through organic geochemistry, is extended in space and time to the whole complex path of carbon in Nature.* The importance of organic geochemistry is self evident from a comparison of the quantities of organic matter existing in contemporary organisms and in the geosphere. Of the estimated total of $6{\cdot}4 \times 10^{15}$ metric tons of organic carbon in or on the Earth's crust, only 3×10^{12} metric tons exist in the biosphere. The organic carbon in the geosphere far outweighs that in the biosphere, even if some allowance is made for the graphitic carbon in the geosphere.[1]

The existence of carbonaceous matter in the geosphere has been recognised for centuries, but it was not until Treibs isolated metalloporphyrin fractions[2,3,4] from a number of crude oils and shales in 1935 that organic chemistry was rigorously applied to the earth sciences. Treibs appreciated that crude oils are mainly biological in origin and his findings precipitated the systematic study of organic compounds in sediments, soils, peats, lignites, coals, crude oils, fossil resins, earth waxes and even in discrete fossils. In sediments most of the organic matter exists as an amorphous polymeric material, kerogen, which is insoluble in organic reagents and solvents. However, a small soluble fraction is invariably associated with the kerogen and many classes of compounds have been recognised in this fraction. The individual classes of compounds in geological samples are frequently very complex,[5] indicating that the reactions forming them must also have been complex. The future of organic geochemistry lies in the study of the complex reaction sequences which determine the geological fate of carbon compounds.

It is impossible in a general review of such a complex topic to enumerate either all of the areas upon which the subject impinges, or all of the known occurrences of particular organic compounds in geological samples. Wherever possible, reference is made only to recent major contributions or to review papers.

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* Nature is defined herein as the whole natural world, including biosphere and geosphere.

[1] D. H. Welte, *Naturwiss.*, 1970, **57**, 17.

[2] A. Treibs, *Annalen*, 1935, **517**, 172.

[3] A. Treibs, *Angew. Chem.*, 1936, **49**, 682.

[4] A. Treibs, *Annalen*, 1945, **510**, 42.

[5] W. K. Seifert and R. M. Teeter, *Analyt. Chem.*, 1970, **42**, 750.

Organic compounds are discussed in terms of their origins and of the chemical reactions which take place over geological time as a result of thermal, catalytic, bacterial and other processes.

The review therefore deals mainly with the lipids found in geological materials, that is geolipids, and discusses the structural and presumed causal relationships between these lipids and the biologically-formed biolipids. Such comparative studies are possible because carbon–carbon covalent bonds often persist through the accumulation, diagenesis,† and maturation of a sediment. Accordingly, all or part of the carbon skeleton of a lipid molecule may be preserved over long periods of geological time although the structure of the molecule may be modified by the complex reactions known to take place during diagenesis and maturation. However, the altered molecule may still be correlated in many cases with that of the original biological precursor by a comparison of their carbon skeletons. Such geological compounds have been termed 'biological markers'. It is only during the last few years that techniques have become available for the isolation, identification and study of the minute quantities of individual organic compounds in geological materials. Organic geochemistry is in its infancy but its *raison d'être* is already evident.

One aspect of the subject concerns comparative biochemistry, studied not only for its relevance to the present day but also to past eras. Paleobiochemistry, the organic geochemist's approach to the biochemistry of organisms in past times, involves the examination of fossil specimens in the hope that some of the information is still present in the form of the structure of the proteins and secondary metabolites. A further approach, evolutionary biochemistry, has had considerable success in comparing the amino-acid sequences of certain key proteins isolated from different living species. Unlike fossil evidence, all of the biochemical information pertains to direct ancestors. For example, it is possible to construct a phylogenetic tree based on the amino-acid sequences of the cytochrome *c* proteins.[6] In this case, changes in sequence (through natural selection) have occurred infrequently. However, less specific polypeptides which have been evolved recently, such as the fibrinopeptides, are changing so rapidly that it is possible that the ancestry of closely related species such as sheep, cattle and several species of deer may be traced.[6,7]

Another facet of organic geochemistry is its role in the understanding of chemical diagenesis and maturation; the problem has been studied in two ways. The indirect method is to compare the structures and distribution of compounds or compound classes in a sediment or fossil with those of biolipids from contemporary organisms. Thus, the alkane fraction (0·01 %) of a fossil *Voltzia* species comprises almost entirely n-octacosane. Although *Voltzia* is now extinct, the major component of the cuticular leaf wax of a related species, *Taxodium*

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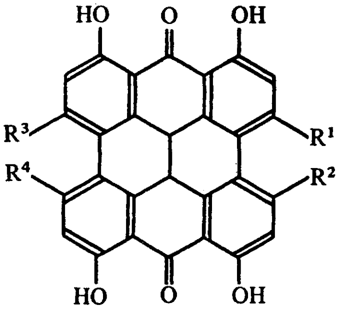
† Diagenesis is the series of chemical and physical changes in a sediment after deposition which converts the sediment to a consolidated rock.

[6] R. V. Eck and M. O. Dayhoff in 'The Atlas of Protein Sequence and Structure', National Biomedical Research Foundation, Silver Spring, Maryland, 1970.

[7] R. F. Doolittle and B. Blomback, *Nature*, 1964, **202**, 147.

distichum is n-octacosanol.[8] Dehydration and reduction appear to be important geochemical reactions.[9] In another example, an animal fossil, a crinoid of Jurassic age, has been shown to contain a number of polyhydroxyquinone pigments, termed fringelites[10,11] (1, R = H or OH). These pigments are somewhat similar in their properties and structure to contemporary pigments, of the aphin[12] (2) and hypericin[13] (3) types. The parent aromatic hydrocarbons were also isolated and identified. Consideration of the structures of the fringelites and the hydrocarbons led to the postulation of a complex geochemical reaction sequence which converted the oxygen-rich pigments to the hydrocarbons.[11,14]



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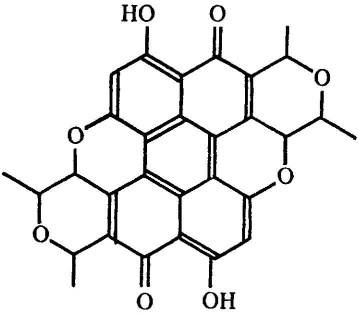

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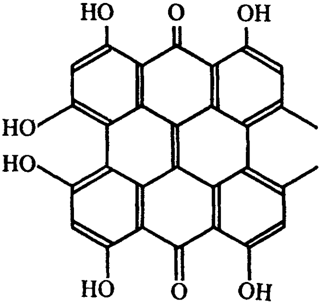

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The direct method of studying geochemical changes is the simulation of diagenesis and maturation under laboratory conditions.

Micro-organisms, and a few multi-cellular organisms, certainly play a major part in the early stages of diagenesis both aerobically and anaerobically. This

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[8] H. Knoche, P. Albrecht, and G. Ourisson, *Angew. Chem. Internat. Edn.*, 1968, **7**, 631.
[9] T. C. Hoering and R. M. M. Mitterer, *Abs. Ann. GSA and Assoc. Soc. Joint Meeting*, New Orleans, 1967, p. 99.
[10] M. Blumer, *Nature*, 1960, **188**, 1100.
[11] M. Blumer, *Geochim. Cosmochim. Acta*, 1962, **26**, 225.
[12] A. R. Todd, *Pure Appl. Chem.*, 1963, **6**, 709.
[13] H. Brockman, *Fortschr. Chem. Org. Naturstoffe*, 1957, **14**, 141.
[14] M. Blumer and D. W. Thomas, *Geochim. Cosmochim. Acta*, 1964, **28**, 1467.

type of activity is amenable to direct experiment using radiolabelled precursors emplaced into Recent sediments *in situ* or in the laboratory. Major developments in this area, including some of importance in relation to pollution control, may be predicted over the next few years.

Thermal alteration (200—300 °C) of docosanoic acid in the presence of bentonite generates a homologous series of n-alkanes and fatty acids with carbon chains both shorter and longer than that of the original acid.[15,16] A similar natural process may in part account for the smooth n-alkane distributions found in most sedimentary rocks and crude oils. Pyrolysis of n-octacosane[17] and certain sediments[18] indicates that thermal and catalytic alteration of the organic material present in sediments in part explains the genesis of petroleum and other hydrocarbon minerals. Thermal treatment of a number of Recent *Mercenaria* shells in the presence of water results in racemisation of the individual amino-acids and alteration of their overall distributions. The resultant distributions parallel those found in older shells of the same species.[19]

Organic geochemistry has potential value in providing palaeochemotaxonomic data on extinct organisms. The n-alkane distribution of an extinct fossil *Equisetum* species almost exactly parallels that of the cuticular wax of a living species.[20] Plant species contributing to a sediment at the time of deposition might be identified, in the future, by comparison of structurally specific geolipids present, such as triterpene hydrocarbons, with the triterpenes abundant in contemporary plant species. The presence of a particular skeleton in the sediment could indicate a contribution from a plant family whose contemporary counterparts contain triterpenes having this skeleton.[21]

Geochemical analysis can also provide other information previously only available from geological techniques. A comparison of the porphyrin–vanadium complexes of the West Venezuelan crude oils and the near-by Cretaceous La Luna formation shows that the latter must have been the source rock.[22] However, it should be emphasised that such chemical studies are in their infancy and have, to date, only been used in a confirmatory fashion.

2 Extraction and Isolation Procedures

A. Extractable Organic Matter (Figure 1).—The extraction and isolation procedures for the study of geolipids are essentially those commonly used in conventional natural product chemistry. Typically, the rock, sediment, or fossil is finely

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[15] J. W. Jurg and E. Eisma, *Science*, 1964, **144**, 1451.

[16] J. W. Jurg and E. Eisma in 'Advances in Organic Geochemistry 1966', ed. G. D. Hobson and G. C. Speers, Pergamon Press, Oxford, 1970, pp. 367, 368.

[17] W. Henderson, G. Eglinton, P. Simmonds, and J. E. Lovelock, *Nature*, 1968, **219**, 1012.

[18] A. G. Douglas, G. Eglinton, and W. Henderson in 'Advances in Organic Geochemistry 1966', ed. G. D. Hobson and G. C. Speers, Pergamon Press, Oxford, 1970, pp. 369–388.

[19] P. E. Hare and R. M. Mitterer, *Carnegie Institution Year Book 1967*, 1968, 205.

[20] H. Knoche and G. Ourisson, *Angew. Chem. Internat. Edn.*, 1967, **6**, 1085.

[21] W. Henderson, V. Wollrab, and G. Eglinton in 'Advances in Organic Geochemistry 1968', ed. P. A. Schenck and I. Havenaar, Pergamon Press, Oxford, 1969, pp. 181–207.

[22] J. A. Gransch and E. Eisma in 'Advances in Organic Geochemistry 1966', ed. G. D. Hobson and G. C. Speers, Pergamon Press, Oxford, 1970, pp. 69–86.

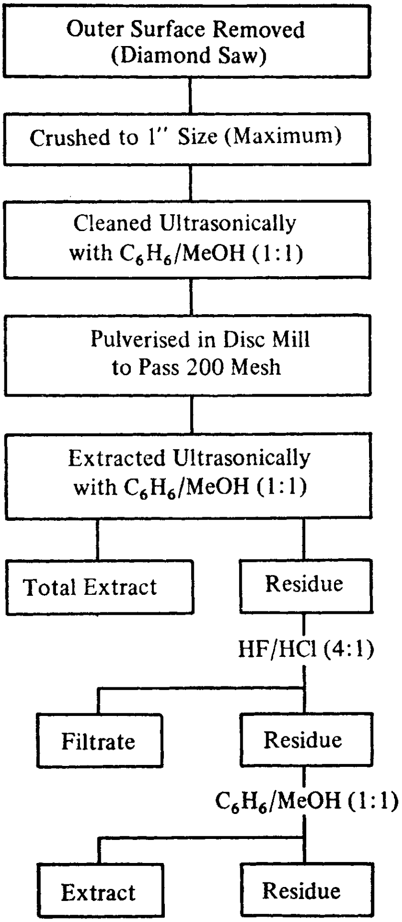

Figure 1 *Procedures typically used to isolate organic matter from sediments*

ground to pass through a 200 mesh sieve and extracted in a soxhlet apparatus with a mixture of benzene and methanol. Alternatively, extraction with solvent agitated by ultrasonic energy is used since it provides a convenient, effective and more rapid method for removing geolipids from sediments.

Soluble organic matter trapped in the mineral matrix may be released by treatment of the residue with a mixture of purified hydrofluoric and hydrochloric acids.[23] Fractionation of the residue from evaporation of the extract is achieved using column or thin-layer chromatography or a combination of both (Figure 2). In particular cases, modified extraction procedures are used;

[23] W. Van Hoeven, J. R. Maxwell, and M. Calvin, *Geochim. Cosmochim. Acta*, 1969, 33, 877.

for example, the free amino-acids present in a number of Precambrian sediments can be leached from the rock with ammonium acetate solution and the bound amino-acids can be isolated from the residue by hydrolysis with hydrochloric acid.[24]

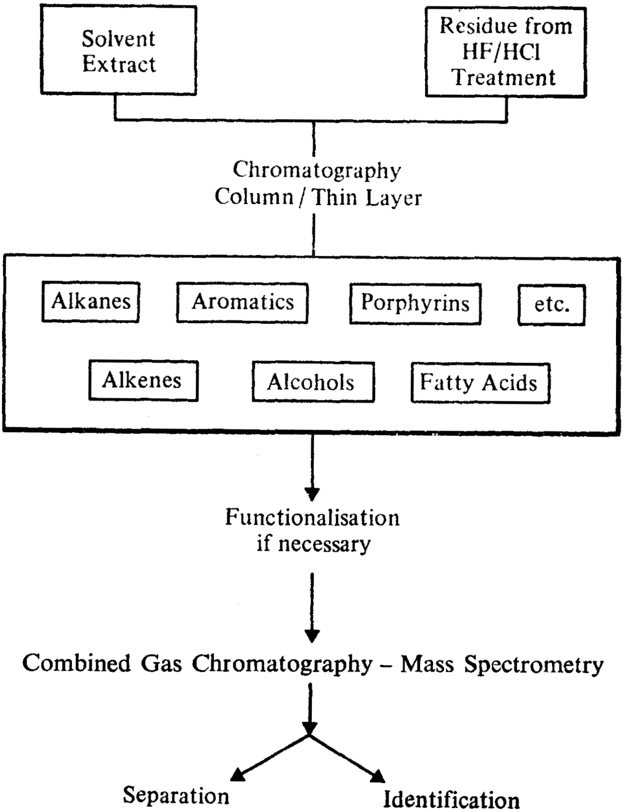

Figure 2 *Procedures typically used to separate and identify organic compounds isolated from sediments*

B. Non-extractable Organic Matter (kerogen).—The residue remaining after removal of the inorganic matrix and subsequent extraction generally contains the bulk of the organic matter as a dark-brown amorphous polymeric material, which can subsequently be degraded by pyrolysis,[25–27] oxidation with chromic

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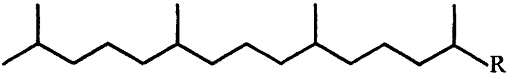
[24] J. W. Schopf, K. A. Kvenvolden, and E. S. Barghoorn, *Proc. Nat. Acad. Sci. U.S.A.*, 1968, **59**, 639.

[25] A. B. Hubbard and W. E. Robinson, *U.S. Bur. of Mines Report of Investigations*, No. 4744, 1950, 24.

[26] D. H. Welte, *Geol. Rundschau*, 1965, **55**, 131.

[27] D. H. Welte, *Bull. Amer. Assoc. Petrol. Geol.*, 1965, **49**, 2246.

acid,[28-32] permanganate[33,34] or ozone,[35,36] or by reduction in an atmosphere of hydrogen in the presence of various catalysts.[37,38] Treatment of the kerogen of the Green River Shale (Eocene) with tetralin in an atmosphere of hydrogen at elevated temperature and pressure affords substantial quantities of alkanes (6% by weight), including 2,6,10,14-tetramethylpentadecane (4, R = CH_3) and 2,6,10,14-tetramethylhexadecane (5, R = CH_3) with carbon skeletons representative of the presumed original biological precursors.[39] The study of kerogens, particularly in rocks of a low carbon content, is important since kerogen is likely to represent indigenous organic matter and not contamination. Kerogen degradation studies may also be of some commercial interest. The Green River Shale of Wyoming and Colorado represents one of the largest known hydrocarbon reserves and could be used to provide shale oil on a commercial scale. However, at present it is cheaper to use crude oil, although this situation could change in the future.



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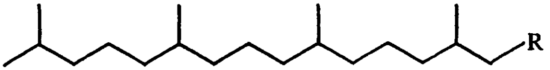

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The methods employed in the isolation and study of humic acids, the polyfunctional aromatic materials in soils, are similar to those used in kerogen analysis and will not be discussed here.

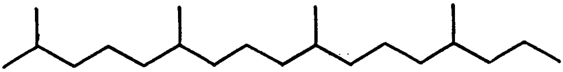
3 Analytical Methods

The application of methods available to the natural product chemist is often restricted in organic geochemistry, where geolipid characterisation is frequently required at the microgram level.

[28] T. C. Hoering and P. H. Abelson, *Carnegie Institution Year Book 1965*, 1966, 218.
[29] A. L. Burlingame and B. R. Simoneit, *Nature*, 1968, **218**, 252.
[30] A. L. Burlingame and B. R. Simoneit, *Nature*, 1969, **222**, 741.
[31] A. L. Burlingame, P. A. Haug, H. K. Schnoes, and B. R. Simoneit in 'Advances in Organic Geochemistry 1968', ed. P. A. Schenck and I. Havenaar, Pergamon Press, Oxford, 1969, pp. 85–129.
[32] A. L. Burlingame, P. C. Wszolek, and B. R. Simoneit in 'Advances in Organic Geochemistry 1968', ed. P. A. Schenck and I. Havenaar, Pergamon Press, Oxford, 1969, pp. 131–155.
[33] W. E. Robinson, H. H. Heady, and A. B. Hubbard, *Ind. and Eng. Chem.*, 1953, **45**, 788.
[34] C. R. Kenney and J. T. Leonard, *J. Chem. Eng. Data*, 1961, **6**, 474.
[35] B. Nagy and M. C. Bitz, *Proc. Nat. Acad. Sci. U.S.A.*, 1966, **56**, 1383.
[36] M. C. Bitz and B. Nagy, *Analyt. Chem.*, 1967, **39**, 1310.
[37] A. B. Hubbard and J. I. Fester, *Chem. Eng. Data Series*, 1958, **3**, 147.
[38] J. E. Flinn and G. F. Sachsel, *Ind. and Eng. Chem.* (*Process Design*), 1968, **7**, 143.
[39] G. S. Bayliss, private communication.

Of the available spectral methods, mass spectrometry is the most useful since it can provide structural information on submicrogram quantities of individual geolipids. Low resolution mass spectrometry has been used to identify numerous geolipids trapped from preparative gas chromatographs.[40-42] High-resolution mass spectrometry with computer-controlled data acquisition can provide structural information on components of different fractions isolated from various sediments.[43,44]

Mass spectrometry alone is often not sufficient to identify isomeric structures. The geological acyclic isoprenoid alkane, 2,6,10,14-tetramethylheptadecane (6)[45-47] has a mass spectrum almost identical to that of one of its structural isomers, 2,6,10,15-tetramethylheptadecane (7). However, the two isomers are easily separable by high-resolution gas chromatography.[48] The most efficient method for the characterisation of microquantities of geolipids has proved to be combined gas chromatography–mass spectrometry (Figure 2). High-efficiency capillary columns effect good separation of compounds, and low-resolution mass spectra, when recorded on small segments of the gas chromatographic peaks, provide detailed information on molecular structure.[21,49,50] A high-resolution mass spectrometer interfaced with a gas chromatograph equipped with packed columns has been used to study the nitrogen-containing compounds in the Green River Shale.[51] Obviously the most powerful analytical method for



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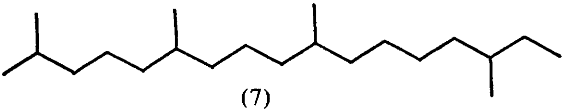

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[40] G. Eglinton, P. M. Scott, T. Belsky, A. L. Burlingame, W. Richter, and M. Calvin, *Science*, 1964, **145**, 263.

[41] G. Eglinton, P. M. Scott, T. Belsky, A. L. Burlingame, W. Richter, and M. Calvin in 'Advances in Organic Geochemistry 1964', ed. G. D. Hobson and M. C. Louis, Pergamon Press, Oxford, 1966, p. 41–74.

[42] P. Haug, H. K. Schnoes, and A. L. Burlingame, *Science*, 1967, **158**, 772.

[43] B. R. Simoneit, H. K. Schnoes, P. Haug, and A. L. Burlingame, *Chem. Geol.*, 1971, **7**, 123.

[44] A. L. Burlingame and H. K. Schnoes in 'Organic Geochemistry Methods and Results', ed. G. Eglinton and Sister M. T. J. Murphy, Springer-Verlag, Heidelberg, 1969, pp. 89–160.

[45] J. G. Bendoraitis, B. L. Brown, and L. S. Hepner, *Analyt. Chem.*, 1962, **34**, 49.

[46] R. B. Johns, T. Belsky, E. D. McCarthy, A. L. Burlingame, P. Haug, H. K. Schnoes, W. Richter, and M. Calvin, *Geochim. Cosmochim. Acta*, 1966, **30**, 1191.

[47] W. Van Hoeven, P. Haug, A. L. Burlingame, and M. Calvin, *Nature*, 1966, **211**, 1361.

[48] E. D. McCarthy, W. Van Hoeven, and M. Calvin, *Tetrahedron Letters*, 1967, 4437.

[49] J. Oró, D. W. Nooner, A. Zlatkis, S. A. Wikstrom, and E. S. Barghoorn, *Science*, 1965, **148**, 77.

[50] J. Oró and D. W. Nooner, *Nature*, 1967, **213**, 1082.

[51] S. P. Markey, Ph.D. Thesis, 1968, Massachusetts Institute of Technology.

the separation and identification of geolipids is combined capillary gas chromatography–high-resolution mass spectrometry but this has as yet been little used in organic geochemistry because of difficulties in obtaining capillary columns with a high enough loading to provide enough sample for high-resolution mass spectrometry.

When a few micrograms of a compound are available, infrared spectroscopy provides useful information about functional groups. The methyl bending region near 1380 cm^{-1} has been used to differentiate a geological triterpene hydrocarbon and lupane although their mass spectra are very similar.[52] Ultraviolet and visible spectroscopy are of particular value in dealing with porphyrins and aromatic compounds[10,11,14,53–55] which are ubiquitous geological compounds. Seifert and Teeter[5] have recently used a combination of spectroscopic methods to study the carboxylic acids of a Californian petroleum. A combination of computer-averaged nuclear magnetic resonance spectroscopy, high-resolution mass spectrometry, ultraviolet, fluorescence, and infrared spectroscopy, and gas chromatography–mass spectrometry was used to show that the carboxylic acid fraction of this crude oil contains over forty compound types, each type comprising a complex mixture of components.

Urea and thiourea adduction are useful techniques for handling geolipids. Urea adducts straight-chain compounds but not branched or cyclic compounds and provides a separation of the two classes. Thiourea adducts acyclic branched compounds, but not straight-chain or cyclic compounds, although there are some exceptions.[56] Molecular sieves offer more effective separations although their applicability to a wide range of compound classes appears to be limited. However, 5 Å molecular sieve is commonly used for occluding n-alkanes to the exclusion of branched and cyclic alkanes.[57] Branched alkanes may be in turn separated from cyclic alkanes by treatment of a mixture of both in tri-isopropylbenzene with 7 Å molecular sieve.[58] Fractionation of geological alkane mixtures can also be carried out on Sephadex; branched alkanes and steranes have been separated from triterpanes in this way.[59]

X-Ray crystallography has been used to elucidate the structures and absolute stereochemistries of a number of geological triterpene hydrocarbons. This has been done without the use of heavy-atom derivatives.[60,61] Structurally-preserved

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[52] A. G. Douglas, G. Eglinton, and J. R. Maxwell, *Geochim. Cosmochim. Acta*, 1969, **33**, 579.

[53] M. Blumer and G. S. Omenn, *Nature*, 1961, **191**, 161.

[54] D. W. Thomas and M. Blumer, *Geochim. Cosmochim. Acta*, 1964, **28**, 1147.

[55] G. W. Hodgson, B. Hitchon, K. Taguchi, B. L. Baker, and E. Peake, *Geochim. Cosmochim. Acta*, 1968, **32**, 757.

[56] Sister M. T. J. Murphy, A. McCormick, and G. Eglinton, *Science*, 1967, **157**, 1040.

[57] J. G. O'Connor, F. H. Burrow, and M. S. Norris, *Analyt. Chem.*, 1962, **34**, 82.

[58] R. Curran, G. Eglinton, I. McLean, A. G. Douglas, and G. Dungworth, *Tetrahedron Letters*, 1968, 1669.

[59] B. S. Cooper, *J. Chromatog.*, 1970, **46**, 112.

[60] I. R. Hills, E. V. Whitehead, D. E. Anders, J. J. Cummins, and W. E. Robinson, *Chem. Comm.*, 1966, **20**, 752.

[61] I. R. Hills, G. W. Smith, and E. V. Whitehead, *Nature*, 1968, **219**, 243.

fossil biopolymers have been recognised by electron microscopy and their organic nature confirmed by analysis of their amino-acid contents.[62–68]

4 Types of Geolipids

The geological time scale is outlined in Figure 3.

	Approximate oldest age in millions of years before present
	Cenozoic[a]
Quaternary	
Pleistocene	2
Tertiary	
Pliocene	7
Miocene	26
Oligocene	38
Eocene	54
Palaeocene	65
	Mesozoic[a]
Cretaceous	
Upper	100
Lower	162
Jurassic	
Upper	162
Middle	172
Lower	195
Triassic	
Upper	205
Middle	215
Lower	225

[a] 'Era' the sub-headings, *e.g.* Quaternary, correspond to 'Periods' and the remainder to 'Epochs'. The table is based on English usage and is drawn from the Geological Society literature.

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[62] M. Florkin, C. Grégoire, S. Bricteux-Grégoire, and E. Schoffeniels, *Compt. rend.*, 1961, **252**, 440.

[63] R. W. G. Wyckoff, E. Wagner, P. Matter, and A. R. Doberenz, *Proc. Nat. Acad. Sci. U.S.A.*, 1963, **50**, 215.

[64] J. M. Shackleford and R. W. G. Wyckoff, *J. Ultrastruct. Res.*, 1964, **11**, 173.

[65] R. W. G. Wyckoff and A. R. Doberenz, *Proc. Nat. Acad. Sci. U.S.A.*, 1965, **53**, 230.

[66] R. W. G. Wyckoff and A. R. Doberenz, *J. Microscop.*, 1965, **4**, 271.

[67] T. Y. Ho, *Comp. Biochem. Physiol.*, 1966, **18**, 353.

[68] M. F. Voss-Foucart, *Comp. Biochem. Physiol.*, 1968, **26**, 877.

	Palaeozoic[a]
Permian	
Upper	240
Lower	280
Carboniferous	
Upper (Silesian)	325
Lower (Dinantian)	345
Devonian	
Upper	359
Middle	370
Lower	395
Silurian	440
Ordovician	
Upper	445
Lower	500
Cambrian	
Upper	515
Middle	540
Lower	570

Figure 3 *Geological society Phanerozoic time scale, 1964*

A. Acyclic type—Polyacetate.—n-Alkanes are ubiquitous components of geological materials and are probably present in most samples containing organic matter. When the isolation procedure outlined above is used, the distributions observed are generally within the range C_{10} to C_{36}; higher members of the homologous series are often present, but their relative abundance is low.

Surface waxes of contemporary higher plants show a very marked odd/even predominance of n-alkanes and a bias towards the higher molecular weight components (n-C_{27}, n-C_{29}, n-C_{31}, n-C_{33}).[69-71] The n-alkane fractions of young sediments,[72-75] and a fossil *Equisetum* species[20] show these characteristics, although they are often less pronounced. Crude oils and Ancient sediments generally have a much smoother distribution with a maximum at lower molecular

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[69] G. Eglinton and R. J. Hamilton in 'Chemical Plant Taxonomy', ed. T. Swain, Academic Press, London, 1963, pp. 187–217.

[70] A. G. Douglas and G. Eglinton in 'Comparative Phytochemistry', ed. T. Swain, Academic Press, London, 1966, pp. 57–77.

[71] K. Stransky, M. Streibl, and V. Herout, *Coll. Czech. Chem. Comm.*, 1967, **32**, 3213.

[72] J. J. Cummins and W. E. Robinson, *J. Chem. Eng. Data*, 1964, **9**, 304.

[73] E. E. Bray and E. D. Evans, *Bull. Amer. Assoc. Petrol. Geol.*, 1965, **49**, 248.

[74] K. A. Kvenvolden, *Nature*, 1966, **209**, 573.

[73] V. Wollrab, M. Streibl, and F. Šorm, *Coll. Czech. Chem. Comm.*, 1963, **28**, 1904.

weight, and in many cases there is no observed predominance of odd carbon numbers.[40,41,46,49,50,73] Evidently, diagenesis and maturation of the original straight-chain alcohols, fatty acids, and alkanes, probably by thermal and catalytic alteration, leads to a decrease in the carbon preference index*.[15-17] The differences observed for the distributions of n-alkanes in similar sediments at increasing depths in single formations are explicable in terms of this hypothesis.[26,27,76-79] The studies of Albrecht and Ourisson[78] are of particular significance since the long core of sediment from Douala, Cameroun (Cretaceous)

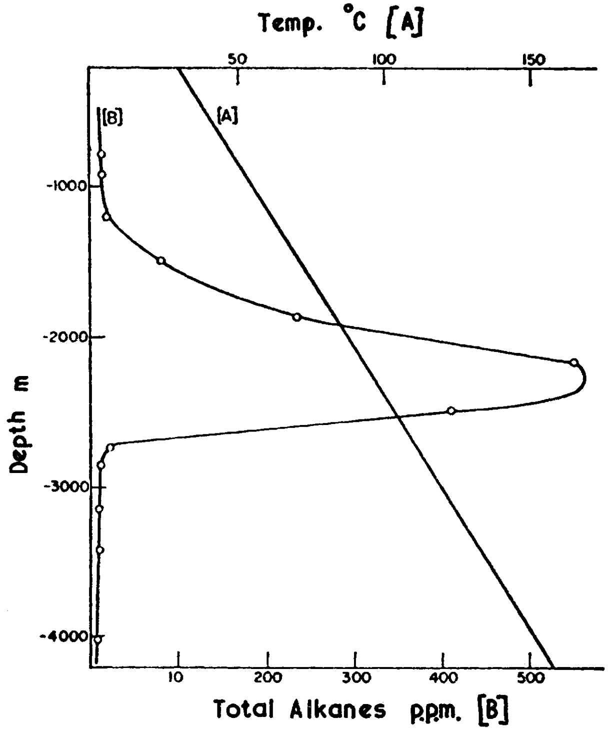

Figure 4 *Variations in temperature and concentration of total alkanes with depth in a Cretaceous sedimentary formation from Douala, Cameroun.* (Reproduced by permission from *Geochim. Cosmochim. Acta*, 1969, **33**, 138.)

$$\text{* Carbon preference index, CPI} = \tfrac{1}{2}\left(\frac{\Sigma \text{ concentrations of odd n-alkanes } C_{17} \text{ to } C_{31}}{\Sigma \text{ concentrations of even n-alkanes } C_{16} \text{ to } C_{30}} + \frac{\Sigma \text{ concentrations of odd n-alkanes } C_{17} \text{ to } C_{31}}{\Sigma \text{ concentrations of even n-alkanes } C_{18} \text{ to } C_{32}}\right)$$

[76] J. D. Brooks and J. W. Smith, *Geochim. Cosmochim. Acta*, 1967, **31**, 2389.

[77] W. E. Robinson, J. J. Cummins, and G. V. Dineen, *Geochim. Cosmochim. Acta*, 1965, **29**, 249.

[78] P. Albrecht and G. Ourisson, *Geochim. Cosmochim. Acta*, 1969, **33**, 138.

[79] G. T. Philippi, *Geochim. Cosmochim. Acta*, 1965, **29**, 1021.

which they examined had been deposited in a relatively short time. The lithology is such that any observed variations in the organic matter are unlikely to arise from variations in the deposition conditions. It was found that the concentration of alkanes was constant to 1200 m depth. Below 1200 m the concentration increased sharply (Figure 4) and reached a maximum at 2200 m, after which depth the concentration suddenly decreased and reached a constant level about 3000 m down. This indicated that alkanes were being generated between 1200 m and 2200 m from the degradation of oxygenated compounds and/or straight-chain material in the kerogen. At the higher temperatures existing below 2200 m the decrease in alkane concentration was interpreted as being the result of thermal catalytic cracking of the higher molecular weight components. These conclusions were also reflected in the n-alkane distributions observed at the various depths. The generation of alkanes was paralleled by an increase in the high molecular weight n-alkanes. The decrease in the alkane concentration was paralleled by an increase in the low molecular weight n-alkanes at the expense of the higher members, consistent with the increase in temperature with depth.

The n-alkane fractions of very old sediments, especially Precambrian, may never have had any marked odd/even predominance; the n-alkanes of very primitive plants do not often show this characteristic[71,80-82] and such organisms are most likely representative of those present in Precambrian times. The n-alkane fraction of the Green River Shale (Eocene) is particularly interesting because an examination of the distribution provides a useful indication of the plant types which contributed to this sediment at the time of deposition. There is a marked dominance of the odd carbon numbers in the C_{30} region of the distribution, corresponding to a contribution from higher plants. Also, the n-C_{17} alkane is a very prominent component, indicating an extensive algal contribution[40,41,72] since this hydrocarbon is a prominent constituent of contemporary algal lipids.[71,80-82]

There are few reports of the isolation of iso-(2-methyl)- and anteiso-(3-methyl)-alkanes.[46,47] Their presence in geological samples may be explained in part by their occurrence in plant waxes.[69,70] The iso and anteiso branched acids in bacteria and marine lipids are also possible precursors.[83-85] n-Alkyl cyclohexanes are present in a number of sediments and crude oils.[46,86,87] Such structures are not common in the biosphere and it is difficult to postulate biological precursors for these compounds, although intramolecular cyclisation of unsaturated fatty acids could account for their presence in geological situations.[46]

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[80] J. Han, E. D. McCarthy, W. Van Hoeven, M. Calvin, and W. H. Bradley, *Proc. Nat. Acad. Sci. U.S.A.*, 1968, **59**, 29.

[81] R. C. Clark and M. Blumer, *Limnol. Oceanog.*, 1967, **12**, 79.

[82] J. Oró, T. G. Tornabene, D. W. Nooner, and E. Gelpi, *J. Bacteriol.*, 1967, **93**, 1811.

[83] R. G. Ackman and J. C. Sipos, *Comp. Biochem. Physiol.*, 1965, **15**, 445.

[84] F. B. Shorland in 'Comparative Biochemistry', ed. M. Florkin and H. S. Mason, Academic Press, London, 1962, Vol. 3, p. 1–102.

[85] T. Kaneda, *J. Biol. Chem.*, 1963, **238**, 1222.

[86] B. Nagy and G. C. Gagnon, *Geochim. Cosmochim. Acta*, 1961, **23**, 155.

[87] G. J. Levy, R. R. Doyle, R. R. Brown, and F. W. Molpolder, *Analyt. Chem.*, 1961, **33**, 698.

There are few reports of the occurrence of n-alkenes in sediments.[88-90] These components could represent products of thermal and catalytic alteration of alkanes,[18] and/or intermediates in the diagenetic dehydration of n-alcohols, and/or unaltered biolipids.

Geological n-fatty-acids have been extensively studied and a wide variety of distributions observed. In crude oils the CPI* is generally about 1 (no even/odd predominance). In modern sediments the CPI is generally high (in the region of 2—5), reflecting the contribution from the fatty acids of plant lipids.[91-93] In Ancient sediments high CPI values are sometimes observed but, in general, they are much less (around 1) than those of modern sediments.[91-93] Thus, the chemical transformations taking place in sediments tend to increase the relative abundances of odd-numbered n-fatty-acids compared to even-numbered fatty acids. Likewise, the relative abundances of odd-numbered n-alkanes tend to increase relative to even-numbered n-alkanes. It has been suggested that the n-fatty-acids have a genetic relationship with the n-alkanes in sediments.[92,93] Thus, comparison of the n-fatty-acid and n-alkane distributions for certain sediments indicates that decarboxylation of an acid, during diagenesis and maturation, provides the corresponding alkane.[93-95] This relationship may be applicable to some sediments but in other cases comparison of the respective distributions indicates that decarboxylation cannot be the only mechanism operating.[93] Kvenvolden and Weiser[96] have developed a mathematical model which describes a possible role of n-fatty-acids in the formation of n-alkanes in sediments. The model assumes that n-fatty-acids are the only source of geochemically generated n-alkanes and that n-fatty-acids may react in one of three ways: (*i*) they may reduce directly to n-alkanes with the same number of carbon atoms, (*ii*) they may lose CO_2 and oxidise to a lower-carbon-numbered fatty acid, (*iii*) they may lose CO_2 and reduce to a lower carbon-numbered n-alkane. Many of the n-alkane and n-fatty acid distributions observed in sediments can be explained by the model but it is probably an oversimplification of the true situation; no account is taken of the possible formation of alkanes from alcohols or of lower molecular weight alkanes arising

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$$\text{* CPI (fatty acids)} = \tfrac{1}{2}\left(\frac{\Sigma \text{ concentrations of even n-fatty-acids } C_{16} \text{ to } C_{30}}{\Sigma \text{ concentrations of odd n-fatty-acids } C_{15} \text{ to } C_{29}} + \frac{\Sigma \text{ concentrations of even n-fatty-acids } C_{16} \text{ to } C_{30}}{\Sigma \text{ concentrations of odd n-fatty-acids } C_{17} \text{ to } C_{31}}\right)$$

[88] M. Streibl and F. Sŏrm. *Coll. Czech. Chem. Comm.*, 1966, **31**, 1585.

[89] W. Henderson, Ph.D. Thesis, University of Glasgow, 1968.

[90] A. G. Douglas and T. G. Powell, personal communication.

[91] A. G. Douglas, K. Douraghi-Zadeh, G. Eglinton, J. R. Maxwell, and J. N. Ramsay in 'Advances in Organic Geochemistry 1966', ed. G. D. Hobson and G. C. Speers, Pergamon Press, Oxford, 1970, p. 315-334.

[92] J. E. Cooper and E. E. Bray, *Geochim. Cosmochim. Acta*, 1963, **27**, 1113.

[93] K. A. Kvenvolden in 'Advances in Organic Geochemistry 1966', ed. G. D. Hobson and G. C. Speers, Pergamon Press, Oxford, 1970, p. 335-366.

[94] D. L. Lawlor and W. E. Robinson, Division Pet. Chem. Amer. Chem. Soc. (Detroit Meeting), 1965, 5.

[95] K. A. Kvenvolden, *Nature*, 1966, **208**, 573.

[96] K. A. Kvenvolden and D. Weiser, *Geochim. Cosmochim. Acta*, 1967, **31**, 1281.

from higher molecular weight alkanes by thermal alteration. However, consideration of the relative amounts and distributions of n-alkanes and n-fatty-acids in sediments and crude oils indicates that it is likely that n-fatty-acids are at least in part the precursors of geochemically formed n-alkanes. Apart from the evidence above, absolute concentrations of n-alkanes increase in geological samples in parallel with a decrease in the concentrations of n-fatty-acids.

The presence of iso and anteiso branched-chain fatty acids has been reported in a number of Recent marine sediments[97,98] and one freshwater sediment of Eocene Age (the Green River Shale).[97] The occurrence of these compounds in the former is hardly surprising since they are common constituents of the lipids of higher marine organisms and bacteria.[83-85] Bacterial lipids are rich in branched-chain acids and are thought to give rise to the branched acids in the freshwater sediment.[97]

αω-Dicarboxylic acids within the range C_9 to C_{21} have been isolated from Scottish Torbanite (Carboniferous),[91] Alaskan Tasmanite (Late Jurassic–Early Cretaceous)[32] and Green River Shale.[43,99] Such acids are found in Nature, either as the free acids or as glycerides, although they are rather rare. Since microbial oxidation of hydrocarbons or monocarboxylic acids can lead to dicarboxylic acids it has been suggested that the occurrence of these acids might arise from such transformations.[43,99]

Hydroxy-acids occur widely as constituents of plant cutins[100] and have been isolated from young sediments. The ω-hydroxy-acids in the hydroxy-acid fraction of a 5000-year-old lacustrine sediment parallel those of contemporary cutin and suberin. The presence of 10,16-dihydroxyhexadecanoic acid as a major component tended to confirm this origin. Unexpectedly, α- and β-hydroxy-acids were also identified. It is thought that these components derive from n-fatty-acids by α- and β-oxidation. In this particular sediment, the αω-dicarboxylic acids are thought to arise from the oxidation of the ω-hydroxy-acids and not from oxidation of alkanes or mono-carboxylic acids.[101] Haug *et al.*[43] have identified a number of (ω − 1)-keto acids (C_{11}—C_{14}) in the extractable acids of the Green River Shale. The compounds are uncommon natural products and may represent the products of microbial hydroxylation of alkanes, alkenes, or carboxylic acids followed by oxidation (enzymatic or chemical) of the hydroxy-function.

Unsaturated fatty acids have rarely been isolated from a geological sample. Parker and Leo[102] have examined the fatty acid content of an algal mat community. The living mat was found to contain substantial proportions of unsaturated acids but the underlying layers were progressively depleted in these components. It appears that unsaturated acids are amongst the first biolipids to

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[97] R. F. Leo and P. L. Parker, *Science*, 1966, **152**, 649.

[98] T. C. Hoering, *Carnegie Institution Year Book 1967*, 1968, 201.

[99] A. G. Douglas, M. Blumer, G. Eglinton, and K. Douraghi-Zadeh, *Tetrahedron*, 1971, **27**, 1071.

[100] J. T. Martin and B. E. Juniper in 'The Cuticles of Plants', Arnold, London, 1970.

[101] G. Eglinton, D. H. Hunneman, and K. Douraghi-Zadeh, *Tetrahedron*, 1968, **24**, 5929.

[102] P. L. Parker and R. F. Leo, *Science*, 1965, **148**, 3668.

be modified by diagenesis. Preliminary results obtained recently by Draffan *et al.*[103] suggest that microbial transformation plays a major role in the disappearance of unsaturated fatty acids in the earliest stages of diagenesis. Addition of ^{14}C-labelled oleic acid to a core of a modern estuarine sediment resulted in a small conversion to saturated fatty acids in seven days. Addition of [$^{14}C,^{3}H$]-labelled oleic acid showed that the radiolabelled saturated acids arose both through chain degradation and *de novo* synthesis, presumably by the anaerobes present. Extension of these studies to a variety of radiolabelled biolipids should provide valuable information about the early fate of biolipids in the geosphere.

n-Alcohols have not been studied as extensively as n-alkanes or n-fatty-acids, but it is known that Recent marine sediments contain saturated and unsaturated n-alcohols with a strong even/odd predominance, reflecting a plant origin. However, their source is uncertain. They could arise either from bacteria or other marine organisms, or from land plants *via* freshwater run-off, or from both.[98,104] Amongst freshwater sediments, Czechoslovakian lignite (Miocene)[105] and the Green River Shale[98,104] contain n-alcohols which probably derive from plant waxes. The distribution in the relatively unaltered lignite deposit parallels the distributions of the n-alcohols found in higher plant waxes, with a strong even/odd predominance and abundance of higher molecular weight components.

B. Acyclic Type—Isoprenoids*.—Geolipids having an isoprenoid-type skeleton are of great geochemical interest because they are almost certainly related to the abundant and varied isoprenoid compounds present in contemporary organisms. This interest centres around the diagenetic and maturation reaction sequences giving rise to such geolipids and their extensive use as 'biological markers'.

The alkanes, 2,6,10,14-tetramethylpentadecane (4, R = CH_3, pristane) and 2,6,10,14-tetramethylhexadecane (5, R = CH_3, phytane), are the most widely distributed acyclic isoprenoid geolipids and have been identified in crude oils and sediments of all ages, including the Precambrian.[40,41,45-47,49,50,52] Often they are by far the most abundant components of the branched/cyclic alkane fractions. The co-occurrence of these compounds with other isoprenoids in sediments is frequently taken as chemical evidence for the existence of living organisms at the time of deposition of the sediments.

Pristane has been isolated from the lipids of plants[106] and marine organisms[107,108] and from Bute Inlet Wax, an unusual jelly-like material found floating in the Gulf of Georgia;[109] these and other occurrences could account in part for

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* The term isoprenoid, strictly speaking, describes only those compounds based on isoprenoid C_5 units. However, it is convenient to use the same term to describe those compounds which have major portions of their skeletons showing the isoprenoid pattern.

[103] M. M. Rhead, G. Eglinton, G. H. Draffan, and P. J. England, *Nature*, 1971, **231**, 327.

[104] J. Sever and P. L. Parker, *Science*, 1969,**164**,, 1052,

[105] V. Wollrab, M. Streibl, and F. Sŏrm, *Chem. Ind.*, 1962. **81**, 1762.

[106] C. H. Brieskorn and K. Zimmerman, *Phytochem*, 1965, **7**, 385.

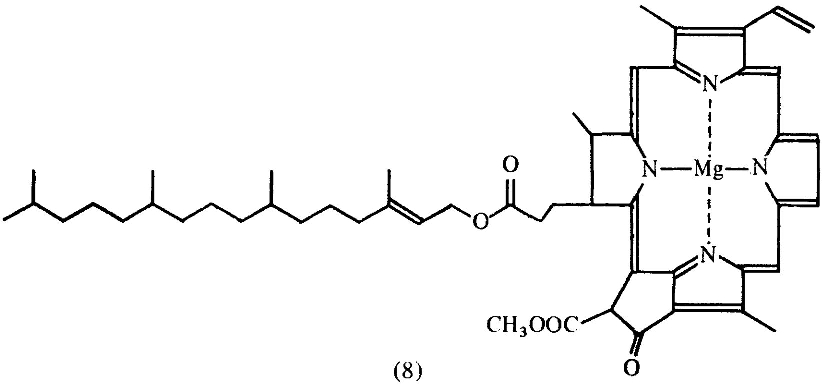
[107] M. Blumer, M. M. Mullin, and D. W. Thomas, *Helgolaender Wiss. Meeresuntersuch.*, 1964, **10**, 187.

[108] M. Blumer and D. W. Thomas, *Science*, 1965, **148**, 370.

[109] T. C. Jain, G. L. Owen, and R. J. Striha, *Phytochem.*, 1969, **8**, 785.

its occurrence in the geosphere. Phytane, unlike pristane, has not been found in Recent marine sediments[110] and appears to be very rare in contemporary organisms[111] so it is likely that this ubiquitous geolipid is formed during diagenesis.

There is strong presumptive evidence that pristane and phytane derive in part from the phytyl side-chain of chlorophyll (8).[45] The first step in the diagenetic reaction sequence would probably be the hydrolysis of chlorophyll to give phytol (9). Subsequent oxidation, decarboxylation, and reduction in the sediment could give rise to pristane. Phytane could be formed from phytol by dehydration and reduction. A somewhat distant laboratory analogy is provided by the perhydrogenation of chlorophyll in the presence of tetralin and hydrogen at elevated temperature and pressure which affords an alkane fraction containing substantial quantities of pristane and phytane.[39]



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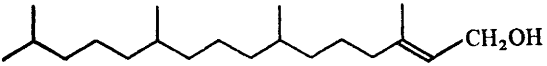

(9)

Zooplankton contain a number of C_{19} mono-olefins having the pristane skeleton. Reduction of these hydrocarbons under geological conditions would give rise to stereoisomers of pristane.[107,112] Likewise the isomeric dienes (10,11,12) apparently derived from phytol in the diet of zooplankton, could give rise to phytane.[113] Phytane could also be formed from the glycerol derivative, 2,3-di-*O*-[3′,7′,11′,15′ - tetramethylhexadecyl] glyceryl - 1 - phosphoryl - [1″(3″) - glyceryl-3″(1″)-phosphate] (13), found in the lipids of halophilic bacteria.[114] The C_{15}

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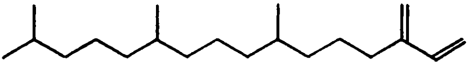
[110] M. Blumer and W. D. Snyder, *Science*, 1965, **150**, 1588.

[111] G. W. Hodgson, B. L. Baker, and E. Peake, Proc. Seventh World Petroleum Congress, 1967, 116.

[112] M. Blumer, J. C. Robertson, J. E. Gordon, and J. Sass, *Biochemistry*, 1969, **8**, 4067.

[113] M. Blumer and D. W. Thomas, *Science*, 1965, **147**, 1148.

[114] M. Kates, L. S. Yengoyan, and P. S. Sastry, *Biochim. Biophys. Acta*, 1965, **98**, 252.



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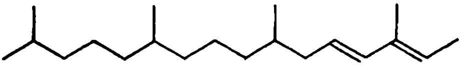

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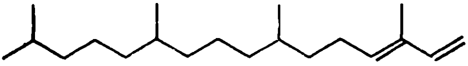

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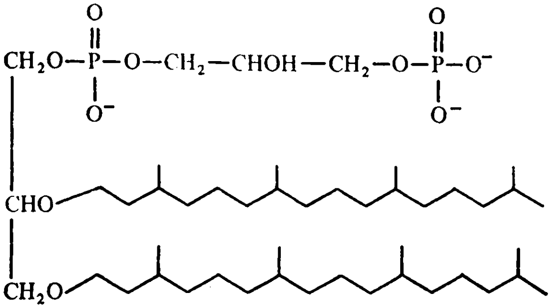

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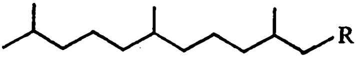
(farnesane), C_{16} and C_{18} regular isoprenoids (14, R = CH_3; 15, R = CH_3; 16, R = CH_3) have also been found in sediments and crude oils.[46] Farnesane could



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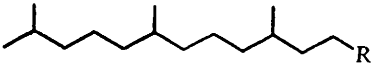

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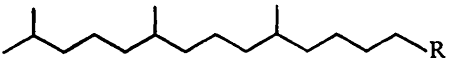
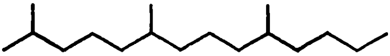


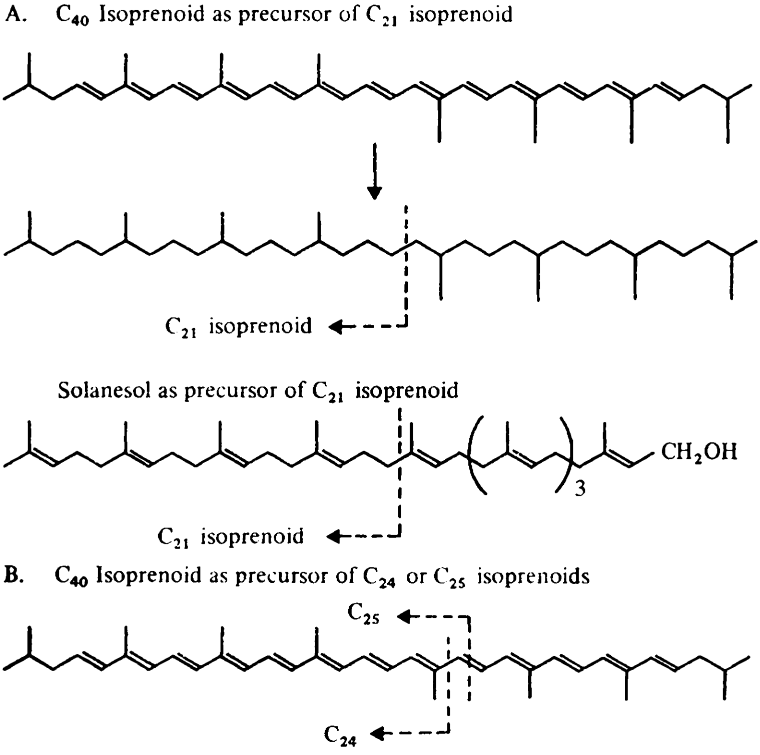
(16)

arise from the farnesane or the C_{15} isoprenoid olefin in plants,[70] or from farnesol (15, R = OH) which is abundantly distributed in the biosphere. A reaction scheme leading from phytol to the C_{16} and C_{18} isoprenoids has been proposed by Johns *et al.*[46] This scheme also takes into account the low abundance of the C_{17} isoprenoid alkane (17) in the geosphere.[115]



(17)

Regular head-to-tail isoprenoid alkanes of higher molecular weight than phytane have been found in the geosphere. The regular C_{21} isoprenoid alkane, 2,6,10,14-tetramethylheptadecane (6), has been found in crude oils and sediments as old as the Precambrian.[46,48] Diagenetic reaction schemes involving reduction and subsequent thermal cracking of high molecular weight terpenes such as lycopene and solanesol have been proposed[48] (Figure 5A) to account for the presence of this alkane. The occurrence of C_{21} to C_{25} regular isoprenoids has been reported in a Lower Cretaceous crude oil.[116] Reaction schemes involv-



A. C_{40} Isoprenoid as precursor of C_{21} isoprenoid

Solanesol as precursor of C_{21} isoprenoid

B. C_{40} Isoprenoid as precursor of C_{24} or C_{25} isoprenoids

Figure 5 *Postulated relationships* (via *reduction and thermal cracking*) *between geological isoprenoid alkanes and some isoprenoid compounds in the biosphere.*

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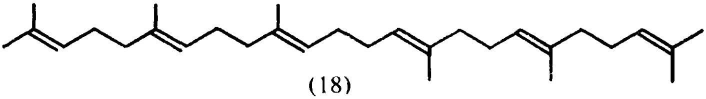
[115] E. D. McCarthy and M. Calvin, *Tetrahedron*, 1967, **23**, 2609.

[116] J. Han and M. Calvin, *Geochim. Cosmochim. Acta*, 1969, **33**, 733.

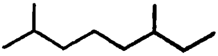
ing lycopene as a precursor can be postulated for the lower molecular weight isoprenoids of this series but these would necessarily lead to the formation of the irregular C_{24} and C_{25} isoprenoids (2,6,10,14,19-pentamethylnonadecane and 2,6,10,14,19-pentamethyleicosane) (Figure 5B). The latter were not detected in the alkane fraction of the crude oil; therefore, it seems unlikely that lycopene [and squalene (18)] played an important role in the geochemical pathway to the


(18)

isoprenoid alkanes in this crude oil. Isoprenoid alcohols such as solanesol, abundant in the biosphere, have been suggested as more plausible precursors.

A series of 2,6-dimethylalkanes (19—24) has been isolated from a Cretaceous


(19)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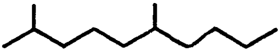
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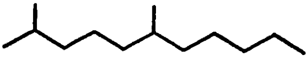
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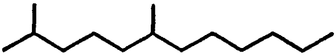
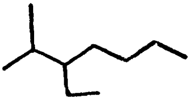

(24)

sediment and a Nigerian crude oil. Squalene and/or the carotenoids have been suggested as the precursors of these skeletons.[117] Mair *et al.*[118] have identified relatively large quantities of 2,6-dimethyloctane (20) and 2-methyl-3-ethylheptane (25) in petroleum and consider that monoterpenes are the precursors (*e.g.* rupture of the ring double-bond of limonene (26) could lead to the 2-methyl-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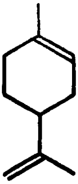
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[117] K. E. H. Gohring, P. A. Schenck, and E. D. Engelhardt, *Nature*, 1967, **215**, 503.

[118] B. J. Mair, Z. Ronen, E. J. Eisenbraun, and A. G. Horodysky, *Science*, 1966, **154**, 1339.

3-ethylheptane skeleton). As yet, there have been few attempts to correlate the geologically abundant acyclic isoprenoid alkanes with the abundant terpenes of the biosphere by laboratory simulation of the various postulated geochemical pathways. Detailed studies of the stereochemistries of these isoprenoid geolipids are also necessary to allow an appraisal of these pathways. For example, phytane derived from natural phytol (9) [3,7(*R*),11(*R*),15-tetramethylhexadec-*trans*-2-en-1-ol][119-121] *via* a series of chemical (non-biological) reactions would comprise a mixture of the 6(*R*),10(*S*),14(*R*)- and 6(*R*),10(*S*),14(*S*)-isomers in equal proportions, assuming no epimerisation of the 6- and 10-positions over geological time. Phytane derived from lycopene or solanesol *via* non-biological reduction and thermal cracking would contain all eight possible isomers. Until recently there was no method for separating stereoisomers of acyclic isoprenoid alkanes. However, direct gas chromatographic analysis of pristane (4, R = CH_3) from the Green River Shale has now shown that it comprises almost entirely the 6(*R*),10(*S*) configuration,[122] compatible with a chlorophyll origin. In addition, Cox *et al.*[122] have recently determined the absolute configuration of pristane isolated from the liver of the basking shark, by oxidation to isoprenoid acids whose stereochemistry could be determined, but the method awaits application to geological isoprenoid alkanes.

In the geosphere the isoprenoid acids are not as widely distributed as the corresponding alkanes and have not been detected in some sediments in which the alkanes are abundant.[91] Various isoprenoid acids have been isolated from Recent marine sediments,[123] the Green River Shale,[43,91,124,125] the Triassic Serpiano Shale[99] (*ca.* 210 × 10^6 years), and crude petroleum.[126] These acids are geochemically interesting because they possibly represent diagenetic intermediates in the formation of alkanes.

The occurrence in Recent marine sediments of 4,8,12-trimethyltridecanoic acid (15, R = CO_2H), 2,6,10,14-tetramethylpentadecanoic acid (4, R = CO_2H) and 3,7,11,15-tetramethylhexadecanoic acid (5, R = CO_2H) is not surprising, since these acids are present in the lipids of higher marine organisms.[127,128] In Ancient sedimentary rocks the complete series of isoprenoid acids from C_{11} to C_{22} has been identified. The relative and absolute configurations of the C_{14} (27), C_{15} (3,7,11-trimethyltridecanoic acid; 14, R = CO_2H), C_{16} (15, R = CO_2H), C_{19} (4, R = CO_2H), and C_{20} (5, R = CO_2H) acids from the Green River Shale have been examined by capillary gas chromatography of their methyl and

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[119] J. W. K. Burrell, L. M. Jackman, and B. C. L. Weedon, *Proc. Chem. Soc.*, 1959, 263.

[120] P. Crabbé, C. Djerassi, E. J. Eisenbraun, and S. Liv, *Proc. Chem. Soc.*, 1959, 264.

[121] J. W. K. Burrell, R. F. Garwood, L. M. Jackman, E. Oskay, and B. C. L. Weedon, *J. Chem. Soc. (C)*, 1966, 2144.

[122] R. E. Cox, J. R. Maxwell, R. G. Ackman, and S. N. Hooper, in preparation.

[123] M. Blumer and W. J. Cooper, *Science*, 1967, **158**, 1463.

[124] G. Eglinton, A. G. Douglas, J. R. Maxwell, J. N. Ramsay, and S. Ställberg-Stenhagen, *Science*, 1966, **153**, 1133.

[125] R. C. Murphy, M. V. Djuricic, S. P. Markey, and K. Biemann, *Science*, 1969, **165**, 695.

[126] J. Cason, and A. I. A. Khodair, *J. Org. Chem.*, 1967, **32**, 3430.

[127] A. K. Sen Gupta and H. Peters, *Fette, Seifen, Anstrichmittel*, 1966, **68**, 349.

[128] R. G. Ackman and R. P. Hansen, *Lipids*, 1967, **2**, 357.

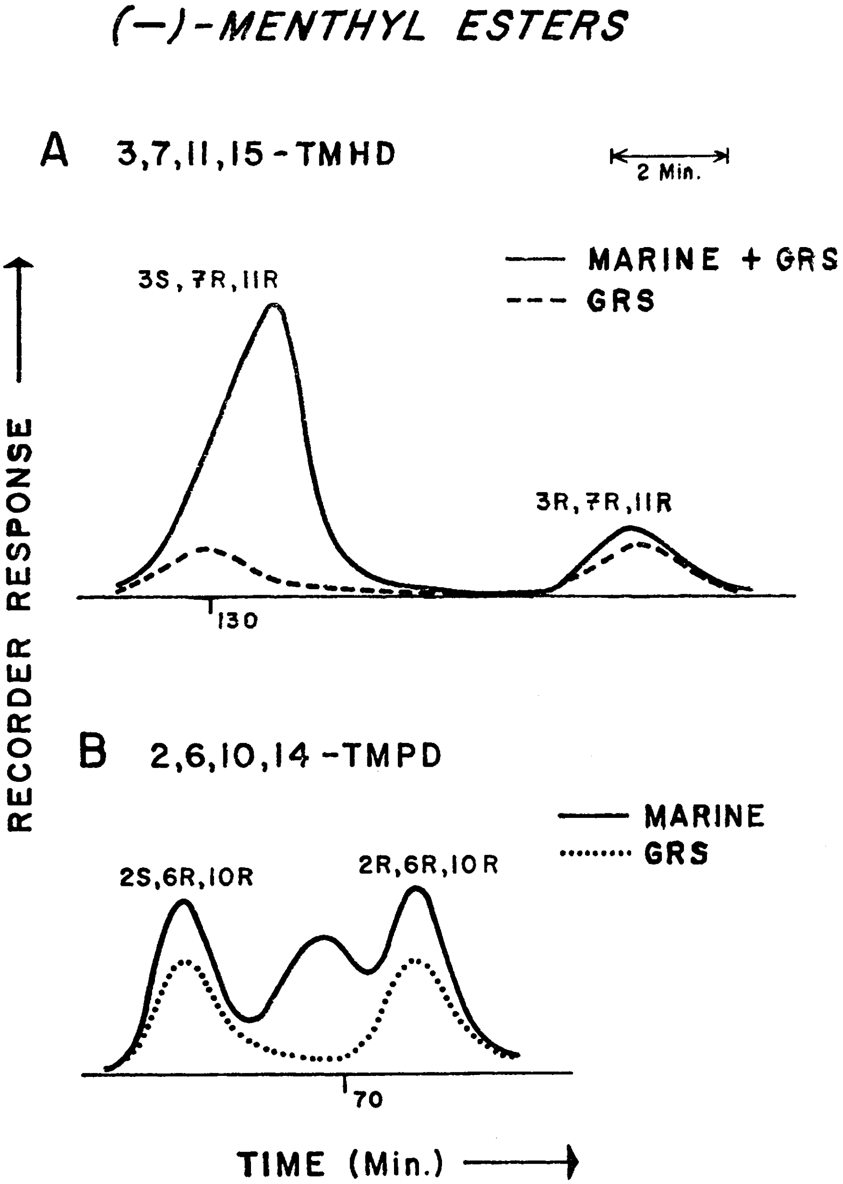
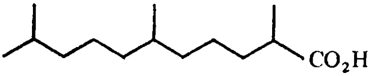


Figure 6 *Gas chromatographic separations of diastereoisomeric* (—)*-menthyl esters of isoprenoid acids.* (A) *menthyl ester of* 3,7,11,15*-tetramethylhexadecanoic acid from the Green River Shale* (*GRS*) *before and after coinjection with the ester of the same acid of contemporary marine origin.* (B) *comparison between the* (—)*-menthyl ester of* 2,6,10,14*-tetramethylpentadecanoic acid of contemporary marine origin and that isolated from the Green River Shale. Separations achieved on a* 150 *ft* × 0·01 *inch stainless steel capillary coated with butanediol succinate.*



(27)

(−)-menthyl esters and are compatible with a phytol origin.[129,130] Figure 6 shows gas chromatograms of the (−)-menthyl esters of the C_{19} and C_{20} acids. The C_{20} acid has a ratio of the 3(*S*),7(*R*),11(*R*)- and 3(*R*),7(*R*),11(*R*)-isomers of approximately 0·8:1; the C_{19} acid comprises the 2(*S*),6(*R*),10(*R*)- and 2(*R*),6(*R*),10(*R*)-isomers in a ratio of approximately 1:1. The C_{19} and C_{20} acids arising from natural phytol as a result of non-stereospecific reactions during diagenesis and maturation would comprise 1:1 mixtures of these stereoisomers. Other natural products based on the isoprenoid skeleton could conceivably have given rise to the Green River Shale isoprenoid acids. The dihydrophytyl glyceryl ether in some bacterial lipids would give only the *RRR*-isomers of the C_{19} and C_{20} acids.[114] Poly-unsaturated compounds such as the carotenoids, undergoing reduction and subsequent oxidation, would require stereospecific reduction to give the *RRR* and *SSS* isomers only and non-stereospecific reduction to give all the possible isomers. Therefore, chlorophyll is the most likely precursor of these acids. Stereochemical considerations indicate that the C_{15} and C_{16} acids in the Green River Shale also derive in the main from chlorophyll.[129,130]

The C_{20} alcohol, dihydrophytol, is the only isoprenoid alcohol which has been identified in sediments.[104] It is unknown in the biosphere and probably represents an early intermediate in the diagenesis of phytol. The observed geological occurrences of acyclic isoprenoid compounds and studies of the stereochemistry of these compounds are slowly providing information about the exceedingly complex reaction sequences involved in the geological alteration of chlorophyll (8) (see later section). Dilcher *et al.*[131] have recently identified methylphaeophorbide *a* in an Eocene lignite (Geisel, Germany) which has had a particularly mild thermal history. Thus, loss of phytol (9) probably occurs at an early stage in the breakdown of chlorophyll. The next step in the degradation of the phytol side-chain may be reduction to dihydrophytol, which can undergo oxidative cleavage to isoprenoid acids. The stereochemistry[130] of the pristanic acid (4, R = CO_2H) in the Green River Shale indicates that pristane (4, R = CH_3) is unlikely to be an intermediate in the pathway leading to the acid, if only non-biological transformations are involved. More detailed information about the geological fate of chlorophyll could be obtained by a comprehensive study of the acyclic isoprenoid compounds which probably co-occur with the phorbins in Geisel lignite.

C. Cyclic Type.—Although cyclic terpenoids are generally less abundant in

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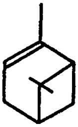
[129] I. McLean, G. Eglinton, K. Douraghi-Zadeh, R. G. Ackman, and S. N. Hooper, *Nature*, 1968, **218**, 1019.

[130] J. R. Maxwell, R. E. Cox, G. Eglinton, C. T. Pillinger, R. G. Ackman, and S. N. Hooper, *Chem. Comm.*, 1970, 1639.

[131] D. L. Dilcher, R. J. Pavlick, and J. Mitchell, *Science*, 1970, **168**, 1447.

the geosphere than are acyclic terpenoids, they have been extensively studied because they are widely distributed in the plant kingdom and they offer the opportunity for detailed skeletal comparisons. The carbon skeleton approach to organic geochemistry outlined in the Introduction is well illustrated by studies of the structurally complex cyclic terpenoids. For example, the diagenesis of α-pinene (28) in peat-covered pine stumps has been followed by analysis of the monoterpene content. With increasing depth of burial the content of *p*-cymene (29) and *p*-menthane (30) increases at the expense of the α-pinene, a major component of the turpentine of pine trees.[132] Similarly, the abietic acid (31) in buried pine trees is apparently converted to the geolipids fichtelite (32) and retene (33), which are unknown as plant products.[133] In this context, it is interesting



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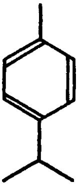

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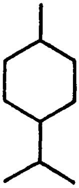

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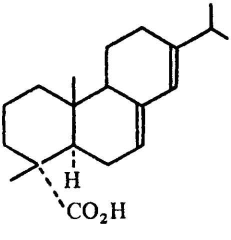

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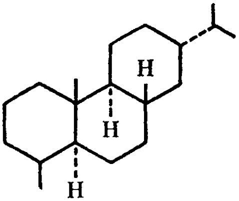

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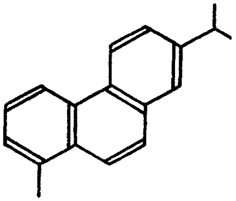

(33)

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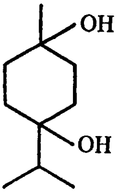
[132] A. I. Skrigan, *Doklady Akad. Nauk S.S.S.R.*, 1951, **80**, 607.
[133] A. I. Skrigan, *Chem. Abs.*, 1965, **62**, 10664.

that *Flavobacterium resinovarum* isolated from pine forest soil can, under aerobic conditions, utilise the diterpene fraction of pine trees as the sole source of carbon.[134] Micro-organisms, operating under both aerobic and anaerobic conditions, may play an important role in the early stages of diagenesis of cyclic terpenes.

Diagenesis and maturation of terpenoid biolipids leads to geolipids with skeletons which are stable over long periods of geological time. The most widely distributed cyclic terpenoids in the geosphere are alkanes; the occurrence of a number of aromatic compounds in crude oils and sediments is also explicable in terms of cyclic terpene precursors (see below).

Monoterpenes are abundant in the biosphere but, surprisingly, have not been encountered frequently in the geosphere, possibly as a result of their volatility.[132] *p*-Cymene, *p*-menthane, and terpin hydrate (34) have been isolated from decaying pine stumps preserved in peat.[135] Shale from the Precambrian Ketilidian fold belt of South West Greenland contains camphor (35), borneol (36) and a number of unidentified monoterpenoids.[136] The presence of these functionalised monoterpene skeletons may indicate that this sediment has had a mild metamorphic and diagenetic history, although infiltration in geologically recent times is another possibility.



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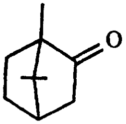

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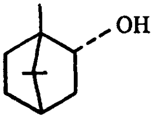

(36)

Sesquiterpenes are rarely found in geological samples; however, a number of unidentified sesquiterpenoid hydrocarbons have been isolated from lignite deposits.[137,138]

Diterpenes are widely distributed in the plant kingdom and are particularly abundant in conifer resins. Consequently, fossil conifer resins (earth resins) and associated lignite deposits often contain a wide variety of diterpenoids. Fichtelite (32) and iosene (37) have been frequently identified in lignite.[139–141] A number

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[134] J. F. Bullmann, R. Wennig, P. Daste, and M. Raynaud, *Chem. Comm.*, 1968, 168.

[135] F. N. Guild, *J. Amer. Chem. Soc.*, 1922, **44**, 216.

[136] K. R. Pedersen and J. Lam, *Med. Grønland*, 1968, **185**, No. 5, 1.

[137] R. Ciusa and A. Gallizi, *Gazzetta*, 1921, **51**, 55.

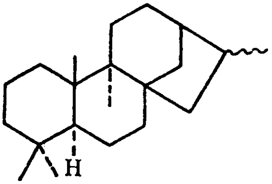
[138] A. Soltys, *Monatsh.*, 1929, **53–54**, 175.

[139] J. L. Simonsen and D. H. R. Barton in 'The Terpenes', Cambridge University Press, 1952, Vol. 3, p. 337.

[140] L. H. Briggs, *J. Chem. Soc.*, 1937, 1035.

[141] J. R. Maxwell, Ph.D. Thesis, University of Glasgow, 1967.

of contemporary resins from various conifer species (*Agathis*) have been examined.[142,143] Fossilisation of the resins is accompanied by a decrease in the solvent-soluble proportion as a result of polymerisation and other reactions undergone by the less stable components.[142] The soluble diterpene fractions of a few of the fossil resins (kauri resins) have been analysed and contain a number of components including agathic acid (38), sandaracopimaric acid (39, R = CO_2H) and sandaracopimarinol (39, R = CH_2OH).[144,145] These compounds are also present in the fresh resin of *Agathis Australis*,[142] the probable source of the kauri resins in question. These preliminary results indicate that it may be possible to relate fossil resins to the resins of contemporary species through comparison of their respective diterpene skeletons.



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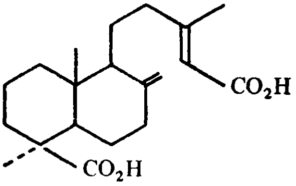

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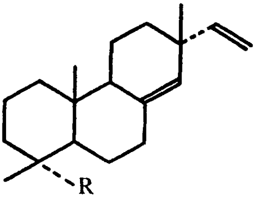

(39)

The abundance of triterpenes in the plant kingdom is well known, and geolipids which appear to have been derived from them occur widely in sediments and crude oils of all ages. The triterpenoids are frequently invoked as biological markers because of the high structural specificity of the stable polycyclic skeleton. Accordingly, their occurrence in older geological samples provides cogent evidence of a plant derivation for at least part of the organic matter present. They have not yet been recognised in the products of simple abiogenic synthesis and their chief limitation as geochemical markers is that they are not as widely distributed as some of the other geolipid classes. The carbon skeletons persist

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[142] B. R. Thomas, *Acta Chem. Scand.*, 1966, **20**, 1074.

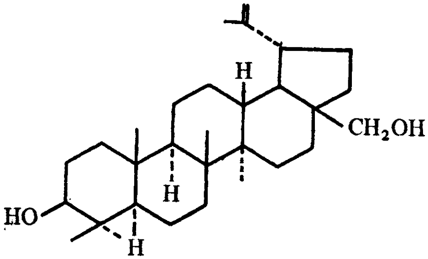
[143] R. M. Carman and D. E. Cowley, *Austral. J. Chem.*, 1967, **20**, 193.

[144] L. J. Gough, *Chem. and Ind.*, 1964, 2059.

[145] B. R. Thomas in 'Phytochemical Phylogeny', ed. J. B. Harbourne, Academic Press, London, 1970, pp. 59–79.

over geological time and the optical rotations observed for crude oils principally derive from the presence of triterpenoid and steroid hydrocarbons.[146–150]

A number of oxygenated triterpenes, including betulin (40), friedelin (41), and ursolic acid (42) have been isolated from Central European lignite.[151–155] A few



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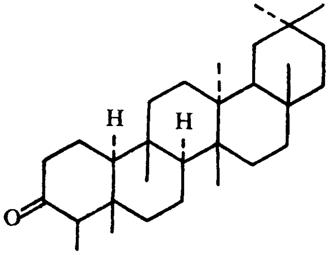

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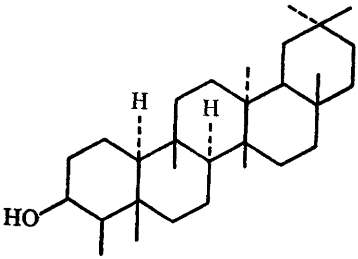

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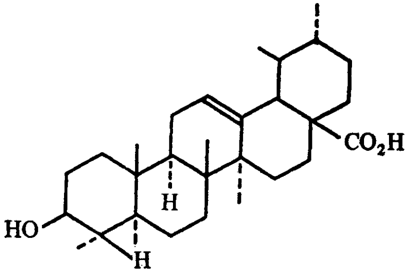

(42)

unidentified triterpanes have also been found in Czechoslovakian lignite of Miocene age,[141,156] but the predominance of the oxygenated species provides chemical evidence that the lignite deposit has suffered only mild alteration, in agreement with its waxy appearance and the great variety and quantity of plant debris present.[157] Friedelin (41) and friedelan-3β-ol (41a) have been

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[146] W. G. Meinschein, *Bull. Amer. Assoc. Petrol. Geol.*, 1955, **43**, 925.

[147] M. Louis, *Rev. Inst. Franç. Petrole*, 1964, **19**, 277.

[148] W. G. Meinschein, *Geochim. Cosmochim. Acta*, 1961, **22**, 58.

[149] N. Danieli, E. Gil-Av, and M. Louis, *Nature*, 1968, **217**, 731.

[150] I. R. Hills and E. V. Whitehead, in 'Advances in Organic Geochemistry 1966', ed. G. D. Hobson and G. C. Speers, Pergamon Press, Oxford, 1970, pp. 89–110.

[151] S. Ruhemann and H. Raud, *Brenstoff-Chem.*, 1932, **13**, 341.

[152] V. Jarolim, M. Streibl, K. Hejno, and F. Sŏrm, *Coll. Czech. Chem. Comm.*, 1961, **26**, 451.

[153] V. Jarolim, K. Hejno, M. Streibl, M. Horak, and F. Sŏrm, *Coll. Czech. Chem. Comm.*, 1961, **26**, 459.

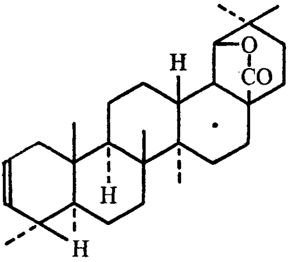
[154] V. Jarolim, K. Hejno, and F. Sŏrm, *Coll. Czech. Chem. Comm.*, 1963, **28**, 2318.

[155] V. Jarolim, K. Hejno, and F. Sŏrm, *Coll. Czech. Chem. Comm.*, 1963, **28**, 2443.

[156] V. Jarolim, K. Hejno, F. Hemmert, and F. Sŏrm, *Coll. Czech. Chem. Comm.*, 1965, **30**, 873.

[157] W. Francis, 'Coal', Arnold, London, 1961.

identified in Scottish lignite[158] and in Israeli peat.[159] Friedelan-3β-ol has also been found in Scottish peat.[160] Oxyallobetul-2-ene (43) has been isolated from an American crude oil.[161]



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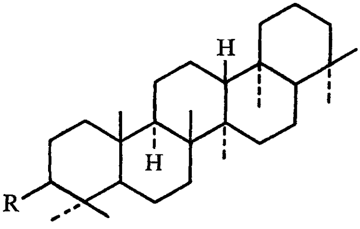

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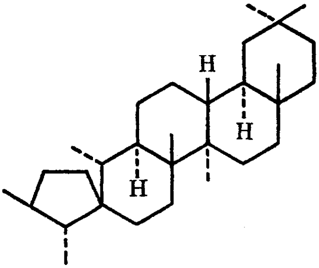

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The Green River Shale has proved to be a fruitful source of triterpane hydrocarbons. Two different approaches to the analysis of these alkanes have been employed. The first is to isolate and purify individual components and obtain rigorous structural identification using many of the physical analytical techniques available, notably high-resolution gas chromatography, mass spectrometry, X-ray crystallography, and optical rotation measurements. The structure and absolute stereochemistry of the triterpane, gammacerane (44, R = H), isolated from the Green River Shale[60] has been elucidated in this way. Although gammacerane has not been identified in living organisms, it is noteworthy that the corresponding 3β-alcohol, tetrahymanol (44, R = OH), has been isolated from a primitive protozoan, *Tetrahymena pyriformis*,[162] and the fern, *Oleandra Wallichi*.[163] Another example of the use of this approach is the structural deter-

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[158] R. Ikan and J. McLean, *J. Chem. Soc.*, 1960, 893.

[159] R. Ikan and J. Kashman, *Israel J. Chem.*, 1963, **1**, 502.

[160] J. McLean, G. H. Rettii, and F. S. Spring, *Chem. and Ind.*, 1958, 1515.

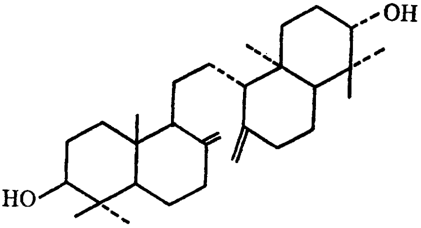
[161] D. H. R. Barton, W. Carruthers, and K. H. Overton, *J. Chem. Soc.*, 1956, 788.

[162] Y. Tsuda, A. Morimoto, T. Sano, Y. Inubushi, F. B. Mallory, and J. T. Gordon, *Tetrahedron Letters*, 1965, 1427.

[163] J. M. Zander, E. Caspi, G. N. Pandey, and C. R. Mitra, *Phytochem.*, 1969, **8**, 2265.

mination of an optically active spirotriterpane (45) isolated from a Nigerian crude oil.[61] No triterpene containing a spiro A:B ring junction has been found in contemporary organisms; such a structure may await recognition in the biosphere, may have existed in the plants of Eocene times, or may have been formed from a common triterpenoid by a geochemical rearrangement. The second approach to the analysis of geological triterpanes is the identification of individual components in a mixture by high-resolution gas chromatography–mass spectrometry.[21,164,165] This procedure relies on the availability of a substantial number of pure compounds for use as reference standards in the identification of components by comparison of gas chromatographic and mass spectrometric data. Although it does not always provide an absolute structural identification, this approach avoids a tedious isolation scheme and can be directly applied to samples of mixtures containing only submicrogram quantities of individual compounds. A study of the mass spectral fragmentation patterns of the standards can identify the skeletal type of an unknown triterpane even when the necessary standard for complete identification is not available.

Gammacerane, onocerane II*, and onocerane III* (48) have been identified in the alkane fraction of the Green River Shale by coinjection of standards and by g.c.–m.s. Lupane (49, R = Me, R^1 = H, R^2 = i-Pr, R^3 = H), onocerane I*, moretane† (49, R = H, R^1 = β-i-Pr, R^2 = H, R^3 = Me), adiantane† (30-norhopane, 49, R = H, R^1 = α-Et, R^2 = H, R^3 = Me) and friedelane (50) were shown to be absent, or present in very low concentrations relative to the other triterpanes present.[21,164] It should be pointed out that the absence of a particular triterpane should be just as significant in a palaeochemotaxonomic sense as its presence (see below).



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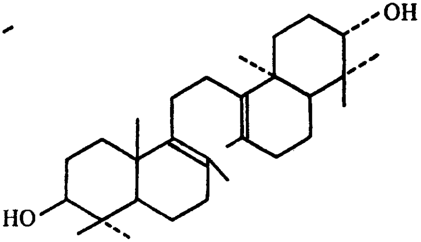

(47)

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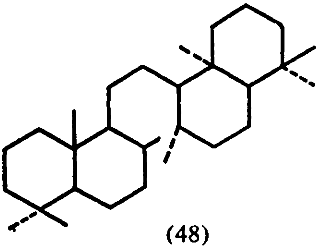
* Reduction of the unsaturated α- and β-onocerins (46) and (47) to alkanes gives a mixture of isomers, *e.g.* onoceranes I, II, and III from α-onocerin. The orientation of the methyl groups at positions 8 and 14 in onocerane I and onocerane II has not been defined.

† The absolute configuration of C-21 in moretane and adiantane is in dispute. The original names are used here; *X*-ray crystallography is required to determine the relative stereochemistry of the C-21 isopropyl group.

[164] W. Henderson, V. Wollrab, and G. Eglinton, *Chem. Comm.*, 1968, 10.

[165] S. C. Pakrashi, S. K. Roi, and J. Bhattacharya, *J. Indian Chem. Soc.*, 1964, **41**, 651.



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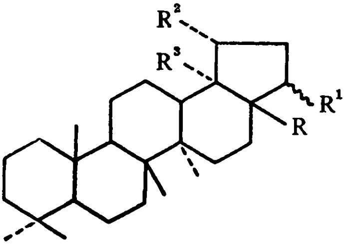

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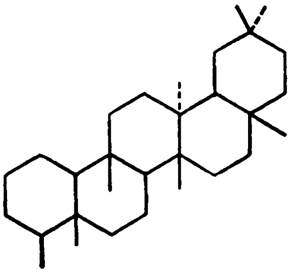
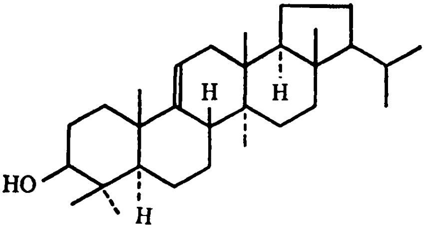


(50)

Oxygenated triterpenoids, the presumed precursors of the triterpanes, may still be encountered in Ancient sediments which have had a mild history. The triterpene alcohol, isoarborinol (51), which occurs in tropical plants,[165-168] has been found in the Messel Oil Shale of Germany.[169] There is a close correlation here between the paleontological and geochemical studies because the fossil flora of this Eocene sediment closely resemble contemporary tropical flora found in South East Asia.



(51)

The distribution of triterpene skeletons in contemporary organisms has been

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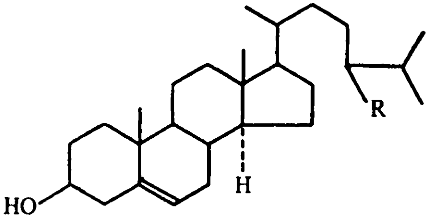
[166] H. Vorbruggen, S. C. Pakrashi, and C. Djerassi, *Annalen*, 1963, **688**, 57.
[167] W. H. Hui and C. N. Lamb, *Phytochem.*, 1965, **4**, 333.
[168] K. Nishimoto, M. Ho, S. Natori, and T. Ohmoto, *Tetrahedron*, 1968, **24**, 735.
[169] P. Albrecht and G. Ourisson, *Science*, 1969, **163**, 1192.

reviewed by several authors.[89,150,170] A comparison of the carbon skeletons of fossil triterpenoids and those of living organisms could provide valuable palaeochemotaxonomic data, bearing in mind the particular geological situations. Such data could provide (*a*) information on the types of plants contributing to a sediment for which there is no adequate fossil record, and (*b*) correlations between extinct plants and their modern counterparts.

Triterpanes are less volatile and less susceptible to microbial attack than the branched- and straight-chain components of crude oil. Thus the triterpane 'fingerprint' of a particular oil should remain relatively unchanged after spillage at sea in comparison with the branched/straight chain alkane 'fingerprint' which may be altered as a result of evaporation losses and microbial attack. This could make possible the identification of pollution sources.

Steroids occur in the plant and animal kingdom as free sterols or as sterol esters. Free sterols, notably β-sitosterol (52, $R = C_2H_5$) and its saturated analogue, β-sitostanol, have been isolated from young geological samples, including Recent sediments,[171] peat,[169,172] and lignite.[168] Attaway and Parker[173] have tentatively identified β-sitosterol, cholesterol (52, R = H), stigmasterol (Δ^{22}-sitosterol), and campesterol (52, $R = CH_3$) in two Recent marine sediments. More detailed studies should allow assessment of the relative contributions to such sediments of phytogenic and zoogenous organisms, and perhaps the individual species themselves.



(52)

Steranes appear to be reasonably abundant as a class of geolipids and mass spectrometric evidence indicates that they occur in crude petroleum and sediments as old as the Precambrian.[146,148,174] However, there are few reports of the firm identification of individual steranes in geological samples. High-resolution gas chromatography and g.c.–m.s. have shown that 5α- and 5β-cholestane, stig-

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[170] T. G. Halsall and R. T. Aplin in 'Progress in the Chemistry of Organic Natural Products', ed. L. Zechmeister, Springer-Verlag, Heidelberg, 1964, Vol. 22, pp. 153–202.

[171] R. B. Schwendinger and J. G. Erdman, *Science*, 1964, **144**, 1575.

[172] P. I. Be'kevich, G. P. Verkholetova, F. L. Kaganovich, and I. V. Torgov, *Chem. Abs.*, 1963, **58**, 10011.

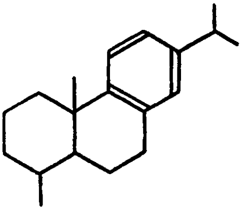
[173] D. Attaway and P. L. Parker, *Science*, 1970, **169**, 674.

[174] A. L. Burlingame, P. Haug, T. Belsky, and M. Calvin, *Proc. Nat. Acad. Sci. U.S.A.*, 1965, **54**, 1406.

mastane, and a $C_{28}H_{50}$ sterane are present in the Green River Shale.[21,164] Individual steranes have also been isolated from this sediment by distillation and preparative gas chromatography; cholestane, stigmastane, and ergostane (campesterol skeleton) were identified.[175]

D. Aromatic Compounds.—The concentrations of aromatic compounds in organisms are low; however, these compounds, especially the hydrocarbons, are among the most abundant in the geosphere. In this section emphasis will be placed on those compounds whose occurrence is at present readily explicable in terms of derivations from biolipids.

The apparent transformations of α-pinene (28) to *p*-cymene (29) and of abietic acid (31) to retene (33) in fossil pine stumps suggest that dehydrogenation of aliphatic compounds to aromatic compounds is an important geochemical reaction. With respect to the abietic acid (31) → fichtelite (32) → retene (33) transformation sequence, it is noteworthy that the aromatic hydrocarbon dehydroabietin (53) has been isolated from pine forest soil.[176] The structural similarity existing between dehydroabietin, fichtelite, and retene indicates that dehydroabietin may be an intermediate in the diagenesis of abietic acid. Hence, this hydrocarbon should be sought whenever fichtelite and retene are encountered in the geosphere. Other aromatic compounds whose structures indicate that they probably derive from cyclic terpenes and steroids are found in geological samples. Examples include certain alkylbenzenes[177,178] and methyl-substituted naphthalenes.[179]



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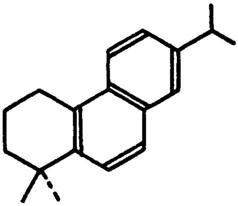

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A fossil conifer lignite (1 × 10^5 years) has been shown to contain the tricyclic aromatic hydrocarbon simonellite (54) whose skeleton is closely related to that of a number of naturally occurring diterpenes.[180,181] Other tricyclic aromatic

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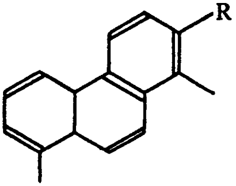
[175] P. C. Anderson, P. M. Gardner, E. V. Whitehead, D. E. Anders, and W. E. Robinson, *Geochim. Cosmochim. Acta*, 1969, **33**, 1304.
[176] E. P. Swan, *Forest Prod. J.*, 1965, **15**, 272.
[177] B. J. Mair and J. M. Barnewall, *J. Chem. Eng. Data*, 1964, **9**, 282.
[178] B. J. Mair and J. M. Barnewall, *J. Chem. Eng. Data*, 1967, **12**, 126.
[179] B. J. Mair and T. J. Mayer, *Analyt. Chem.*, 1964, **36**, 351.
[180] E. Ghighi and G. Fabbri, *Atti Accad. Sci. Inst. Bologna*, 1965, **12**, 1.
[181] E. Ghighi, L. Plessi, A. Drusiani, and G. Giovanninetti, *Analyt. Chim. Rome*, 1969, **59**, 510.

hydrocarbons which may be related to steroid or terpenoid precursors have been found in crude oil, notably 1,8-dimethylphenanthrene (55, R = H), 1,2,8-trimethylphenanthrene (55, R = CH_3), 1,2-cyclopentenophenanthrene (56, R = H),[182] and 3′-methyl-1,2-cyclopentenophenanthrene (56, R = CH_3).[182,183]



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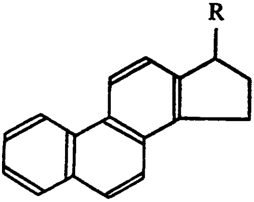
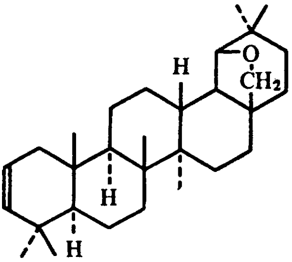


(56)

Laboratory dehydrogenation of lanosterol with selenium yields 1,2,8-trimethylphenanthrene (55, R = CH_3), indicating that diagenesis of plant sterols could have given rise to this hydrocarbon.[183] The occurrence of the cyclopentenophenanthrenes in petroleum is particularly noteworthy since they have a cyclic skeleton similar to those of steroids and some tetracyclic triterpenes. In fact, dehydrogenation of cholesterol with selenium affords 3′-methyl-1,2-cyclopentenophenanthrene.[183] Further indirect evidence for steroids and other polycyclic terpenoids as progenitors of alkyl phenanthrenes is provided by the high ratios of phenanthrenes to anthracenes in many petroleums.[184] Mair and Martinez-Pico have pointed out that geochemical alteration of alkaloids related to morphine could also give rise to phenanthrene derivatives.[183] More compelling evidence for the triterpene/aromatic hydrocarbon relationship has been obtained from a study of Czechoslovakian lignite of Miocene age. A number of biologically-occurring triterpenes (see above) are accompanied by a range of pentacyclic compounds (57—60) of varying degrees of aromaticity,



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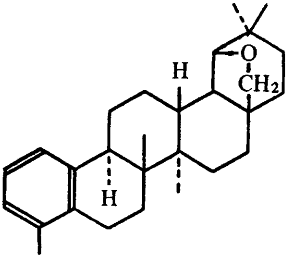

(58)

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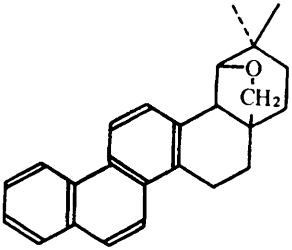
[182] W. Carruthers and A. G. Douglas, *J. Chem. Soc.*, 1957, 278.

[183] B. J. Mair and J. L. Martinez-Pico, *Proc. Amer. Petrol. Inst.*, 1962, **42**, 173.

[184] B. J. Mair, *Geochim. Cosmochim. Acta*, 1964, **28**, 1303.

indicating that stepwise aromatisation of the originally deposited triterpenes may be occurring in the sediment.[185]



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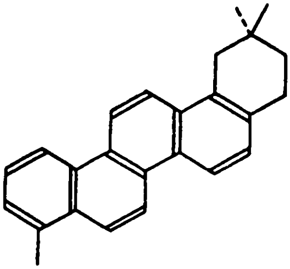

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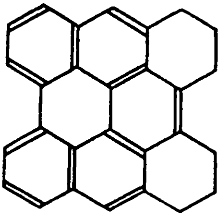
The aromatic hydrocarbons mentioned above are thought to result from dehydrogenation processes. It appears that polycyclic aromatic hydrocarbons can also be formed from quinones under reducing conditions. Pink-coloured specimens of a fossil sea lily (*Apocrinus* sp)—actually an animal crinoid—contain a number of polycyclic aromatic hydrocarbons and quinone pigments (1, R = H or OH).[10,11,14] The fringelites D, E, F, and H (1, R^1,R^2,R^3,R^4 = OH; R^1,R^2,R^3 = OH, R^4 = H; R^1,R^2 = OH, R^3,R^4 = H; R^1,R^2,R^3,R^4 = H respectively) are present, increasing in abundance in that order, suggesting that, under the reducing conditions prevailing during diagenesis and maturation, stabilisation has occurred by elimination of sterically congested hydroxy-groups. Fringelite H is thought to be stable but further reduction is indicated by the presence of the aromatic hydrocarbon (61), which may arise *via* (62). A wide range of other aromatic hydrocarbons is also present and the occurrence of two of these (63 and 64) can be explained by the presence in the fossil of other as yet undetected pigments.[11,14,186]



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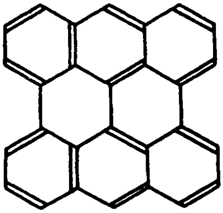

(62)

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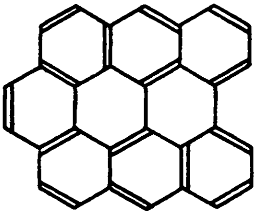
[185] M. Streibl and V. Herout in 'Organic Geochemistry: Methods and Results', ed. G. Eglinton and M. T. J. Murphy, Springer-Verlag, Heidelberg, 1969, pp. 401–424.
[186] M. Blumer, *Science*, 1965, **149**, 722.



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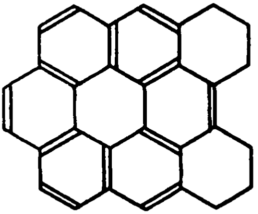
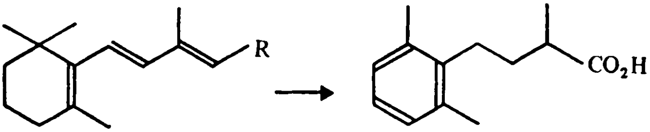


(64)

Alkylbenzenes occur in crude oils[177,178,184] (and probably in sediments); the structures of some of these compounds suggest terpenoid precursors. However, the origin of other alkylbenzenes having long n-alkyl substituents is uncertain. Haug *et al.*[43] have tentatively identified, by high-resolution mass spectrometry, a number of aromatic carboxylic acids in the extractable acids of the Green River Shale. Again, the proposed structures suggest an origin from terpenoid precursors. The suggested structure for one of these acids indicates that it might be the end product of the degradation of carotenoids:



Little is known about the aromatic structures which constitute a major part of petroleum asphaltenes (fractions of petroleum insoluble in n-pentane). Infrared, nuclear magnetic resonance, electron spin resonance, and *X*-ray diffraction analysis indicate the presence of high molecular weight systems containing flat sheets of condensed aromatic rings.[187]

E. Pigments.—Pigments isolated from geological sources include porphyrins, chlorins, carotenoids and, to a lesser extent, quinones. Naturally occurring plant pigments, such as flavones and anthocyanins, are not normally sought presumably because of their water solubility or tendency towards rapid alteration in the geological environment. Open-chain tetrapyrrole pigments which occur in species of algae, bacteria, flagellates, annelids, crustaceans, and molluscs, and in bile and animal faeces, have not been detected in sediments or fossils.[188] However, the paucity of reports of the geological occurrence of pigments other than

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[187] G. C. Speers and E. V. Whitehead in 'Organic Geochemistry: Methods and Results', ed. G. Eglinton and M. T. J. Murphy, Springer-Verlag, Heidelberg, 1969, pp. 638–675.

[188] H. N. Dunning in 'Organic Geochemistry', ed. I. Breger, Pergamon Press, Oxford, 1963, pp. 367–430.

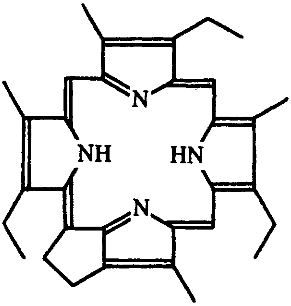
porphyrins and carotenoids is no indication of their absence. Colourations in sedimentary rocks, usually due to the presence of inorganic minerals, may also arise from the presence of organic pigments. The intense pink colouration in quincite, a limestone from Quincy, France, is not due to the presence of rhodochrosite ($MnCO_3$) but arises from a mixture of uncharacterised organic pigments which are not porphyrins or carotenoids.[189]

Quinones

Quinones have been rarely encountered in the geological environment. Polycyclic quinones have been found in a fossil crinoid (see above). A mixture of anthraquinone pigments has been isolated from a Permian–Carboniferous shale.[190] The individual compounds present were not identified, so the geochemical significance of their occurrence is not certain.

Porphyrins and chlorins (dihydroporphyrins)

The macrocyclic moiety of porphyrins and chlorins confers great stability on these molecules; consequently they are found in sediments and crude oils of all ages[111] and can occur either as the free bases or as metal (notably vanadyl and nickel complexes. The most common biological compound of this type is chlorophyll and as such it may be a major precursor of a number of porphyrins and chlorins in sediments. Chlorophyll (8) itself is unstable and there is no authenticated report of its occurrence in geological samples. However, the presence of methylphaeophorbide *a* and other green pigments in an Eocene lignite (Geisel, Germany) indicates that, under mild geological conditions, the chlorophyll nucleus can survive relatively unchanged for long periods of geological time.[131,191] These findings also indicate that hydrolysis and demetallation are probably two of the earliest diagenetic reactions to take place.



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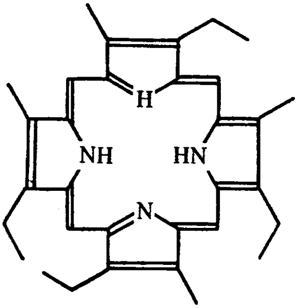
[189] M. Louis, C. J. Guillemin, J. C. Goni, and J. P. Ragot in 'Advances in Organic Geochemistry 1968', ed. P. A. Schenck and I. Havenaar, Pergamon Press, Oxford, 1969, pp. 553–566.
[190] A. Treibs and E. Steinmetz, *Annalen*, 1933, **506**, 171.
[191] D. Dilcher, *Natur. Mus.*, 1967, **97**, 124.

Treibs[2-4] interpreted the occurrence of geological porphyrins (petroporphyrins in terms of a diagenetic pathway from chlorophyll or haemin *via* demetallation, ester hydrolysis, reduction, aromatisation, decarboxylation, and chelation. Thus, chlorophyll *a* (8) would give rise to a metal complex of deoxophylloerythroetioporphyrin (DPEP) (65).

Treibs' scheme appears to be an over-simplification of the true situation. It is thought that the chelation step occurs at an earlier stage than that proposed by Treibs since metal chlorins have been isolated from lake sediments.[192] Thomas and Blumer[54] isolated a series (C_{29}—C_{34}) of porphyrins related to DPEP from a Triassic sediment (Serpiano, Switzerland); the highest molecular weight member contained two carbon atoms more than DPEP and the lowest three carbon atoms fewer than DPEP. Dean and Whitehead[193] have also observed a similar distribution (C_{28}—C_{32}) for the vanadyl complexes of the DPEP pigments in a crude petroleum. Such a series could conceivably arise from a range of pigments not known to occur in the biosphere today, but Thomas and Blumer have stated that an extension of Treibs' scheme to include reduction of carboxy-groups, loss of vinyl groups, and decarboxylation with radical intermediates would provide a more satisfactory explanation of the occurrence of a series of DPEP-type pigments. However, the asphaltene fraction of the Boscan crude oil (Cretaceous) shows a range (C_{27}—C_{38}) of DPEP pigments having a Gaussian distribution.[194] This molecular weight range cannot be accounted for by the scheme outlined by Thomas and Blumer. Further reactions, possibly free-radical alkylation and dealkylation may take place in the process leading from chlorophyll to geological DPEP pigments.[194] Alternatively, the petroporphyrins with carbon numbers greater than 34 could arise, *via* the schemes proposed by Treibs[2-4] and Thomas and Blumer,[54] from aberrant chlorophylls such as those found in some photosynthetic bacteria.[189] Similar observations have been made for petroporphyrins of the etioporphyrin (66) type, which



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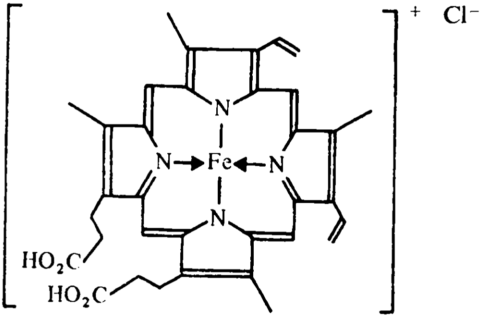
[192] G. W. Hodgson and E. Peake, *Nature*, 1961, **191**, 766.

[193] R. A. Dean and E. V. Whitehead, Paper V-9, 6th World Petroleum Congress, Frankfurt, Germany, 1963.

[194] E. W. Baker, *J. Amer. Chem. Soc.*, 1966, **88**, 2311.

presumably arise from the diagenesis of haemin (67).[2-4,64,194,195] Other geochemical reactions leading to petroporphyrins undoubtedly take place. Blumer and Snyder,[197] and Blumer and Rudrum[198] have recently used gel permeation chromatography to examine the porphyrin fractions in the asphaltenes of a Triassic sediment (Serpiano, Switzerland) and a sediment of Pennsylvanian age. The chromatographic behaviour of these fractions, taken in conjunction with visible and mass spectrometric evidence, indicates that the porphyrins can extend as continuous homologous series with molecular weights up to 20 000 and perhaps beyond this in the kerogen. It was estimated that a typical oil shale may contain at least 10^5 different individual porphyrins. Mass spectrometric analysis of the lower molecular weight components indicated the presence of homologous porphyrins with side-chains carrying up to 44 carbon atoms more than the basic porphin nucleus. These findings suggest that the reactions leading to geological porphyrins are more complex than the relatively minor stepwise alterations (outlined above) from chlorophyll and haemin. Blumer and Rudrum[198] suggest that more complex reactions may take place which convert chlorophyll and haemin to polymeric moieties which are subsequently thermally depolymerised to give complex mixtures of porphyrins. It was also suggested that similar polymerisation–depolymerisation reactions could in part explain the occurrences and distributions of other geolipids such as the alkanes.



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A number of amino-acids have been isolated from hydrolysates of the porphyrin fractions of several geological samples. Hodgson *et al.*[199] believe that these amino-acids represent the residues derived from protein entities originally

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[195] R. Morandi and H. B. Jensen, *J. Chem. Eng. Data*, 1966, **11**, 81.

[196] E. W. Baker, T. F. Yen, J. P. Dickie, R. E. Rhodes, and L. F. Clark, *J. Amer. Chem. Soc.*, 1967, **89**, 3631.

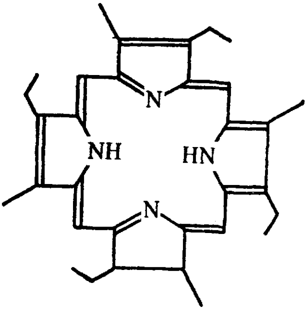
[197] M. Blumer and W. D. Snyder, *Chem. Geol.*, 1967, **2**, 35.

[198] M. Blumer and M. Rudrum, *J. Inst. Petrol.*, 1970, **56**, 99.

[199] G. W. Hodgson, J. Flores, and B. L. Baker, *Geochim. Cosmochim. Acta*, 1969, **33**, 532.

associated with plant chlorins and that the porphyrins arise from biological chlorins rather than the commonly-occurring chlorophylls.

Chlorins are also widely distributed in the geosphere. The etiochlorin (68) isolated from Serpiano shale is a derivative of haemin (67) and as such is thought to have a secondary origin, *via* geochemical reduction of the corresponding porphyrin (66). The origin of the corresponding dihydro-DPEP found in the sediment is less clear since it could derive either directly from a chlorophyll (8) precursor or from chlorophyll *via* DPEP (65).[200] However, chlorins have not been studied as extensively as porphyrins and they undoubtedly also comprise complex mixtures; it appears likely that fossil chlorins may also extend up to the molecular weight ranges reported for the porphyrins.



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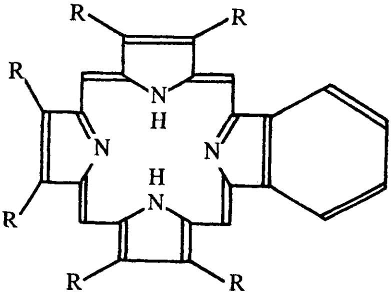
Although DPEP porphyrins and etioporphyrins form the major porphyrin series found in the geosphere, a third porphyrin series, the rhodo-type series, is present in some samples. The rhodoporphyrins are thought to be alkylbenzoporphyrins (69, R = Alkyl) and may arise from a geochemical ring closure and aromatisation step.[196]



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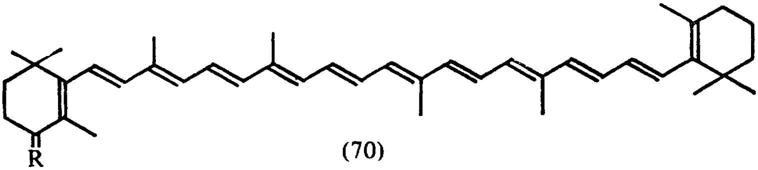
[200] M. Blumer and G. S. Omenn, *Geochim. Cosmochim. Acta*, 1961, **25**, 81.

Studies of petroporphyrin distributions may provide a chemical method for differentiating between marine and non-marine origins for petroleums and sediments. Marine geological samples appear to contain porphyrins having a wide range of molecular weights and a low DPEP/etioporphyrin ratio, whereas a narrow molecular weight range and a high DPEP/etioporphyrin ratio appears to be indicative of a lacustrine origin.[196] Geochemical studies of porphyrins exemplify the difficulties encountered in the analysis of geological organic compounds. At present it is not possible to separate individual porphyrins from complex geological mixtures to allow more detailed studies, although gas chromatographic analysis of the porphyrins themselves[201] or of volatile derivatives[202] may eventually allow proper analysis of the lower molecular weight homologues.

Carotenoids and related compounds

Carotenoids occur widely in nature but their relative instability is possibly reflected in the lack of reports of their occurrence in sediments older than 20 000 years. Carotenes [*e.g.* β-carotene (70, R = H_2)] and xanthophylls [*e.g.* echinenone (70, R = O)] have been characterised in a number of very Recent marine and nonmarine sediments.[188,203,204] At present, the oldest sediment reported to contain carotenoids is an interglacial gyttja estimated to be 100 000 years old.[205] However, the fully reduced analogue of α- or β-carotene, carotane, has been isolated from Green River Shale.[56] The fully saturated analogue of lycopene, lycopane (71), has also been isolated from another Eocene sediment (Messel Shale, Darmstadt, Germany).[206] Carotane and lycopane are unknown as constituents of contemporary organisms and their occurrence in the geosphere represents further evidence that the reduction of carbon–carbon double bonds is a likely and widespread geochemical reaction. Carotenoids may play



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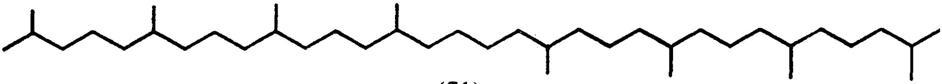

(71)

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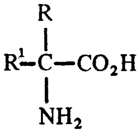
[201] A. H. Corwin and N. M. Karayannis, *Analyt. Biochem.*, 1968, **26**, 34.
[202] D. B. Boylan and M. Calvin, *J. Amer. Chem. Soc.*, 1967, **89**, 5472.
[203] J. R. Vallentyne in 'Symposia on Comparative Biology', Vol. 1. 'Comparative Biochemistry of Photoreactive Systems', ed. M. B. Allen, Academic Press, New York, 1960.
[204] E. D. McCarthy, Ph.D. Thesis, University of California, Berkeley, 1967.
[205] S. T. Anderson and G. K. Gundersen, *Experientia*, 1955, **11**, 345.
[206] P. Albrecht and G. Ourisson, personal communication.

an important role as the precursors of lower molecular weight isoprenoid compounds [48,115,184] (see above).

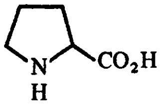
Among the more resistant organic materials of direct biological origin found in the geosphere are the walls of pollen grains and of spores. This resistance to degradation permits study of the morphology and microstructure of the pollen grains and spores (the field of palynology). The chemical constitution of the wall materials, collectively termed sporopollenins, has received surprisingly little attention. However, it has recently been suggested that sporopollenins are formed by polymerisation of carotenoids and carotenoid esters and that these polymeric carotenoids may represent a significant fraction of the high molecular weight polymeric material found in sedimentary rocks.[207–209] The comparison has been made on the basis of similarities between the elemental compositions and some of the oxidative degradation products of contemporary sporopollenin and kerogen. However, Cooper and Murchison[210] are of the opinion that sporopollenin would be altered over geological time and that comparison cannot be made between the degradation products of the contemporary polymeric material and the (presumably) thermally altered geological material.

F. Amino-acids.—Amino-acids in both free and polymeric forms are present in all living cells and consequently are potentially valuable for geochemical study. Abelson surveyed the thermal stability of amino-acids at various temperatures; in particular, kinetic studies of the thermal degradation of dilute aqueous solutions of alanine (72, $R = CH_3$, $R^1 = H$) showed that the degradation followed first-order kinetics and that this amino-acid could possibly survive in geological samples older than 3×10^9 years providing it was not exposed to temperatures $>40\,°C$.[211] Glutamic acid (72, $R = CH_2CH_2CO_2H$, $R^1 = H$), glycine (72, $R = R^1 = H$), isoleucine [72, $R = CH(CH_3)CH_2CH_3$, $R^1 = H$], leucine [72, $R = CH_2CH(CH_3)_2$, $R^1 = H$], proline (73), valine [72, $R = CH(CH_3)_2$, $R^1 = H$], and α-aminobutyric acid (72, $R = CH_2CH_3$, $R^1 = H$) were shown to possess comparable stability. Threonine [72, $R = CH(OH)CH_3$, $R^1 = H$], lysine [72, $R = (CH_2)_4NH_2$, $R^1 = H$], tyrosine (72, $R = CH_2C_6H_4OH$, $R^1 = H$), and phenylalanine (72, $R = CH_2C_6H_5$, $R^1 = H$)



$$R^1-\overset{\displaystyle R}{\underset{\displaystyle NH_2}{C}}-CO_2H$$

(72)



(73)

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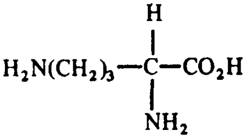
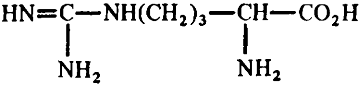
[207] J. Brooks and G. Shaw, *Nature*, 1968, **219**, 352.
[208] J. Brooks and G. Shaw, *Nature*, 1968, **220**, 678.
[209] J. Brooks, Ph.D. Thesis, University of Bradford, 1970.
[210] B. S. Cooper and D. G. Murchison, *Nature*, 1970, **227**, 194.
[211] P. H. Abelson in 'Organic Geochemistry', ed. I. A. Breger, Pergamon Press, Oxford, 1963, pp. 431–455.

were moderately stable under the same conditions. However, serine (72, R = CH_2OH, R^1 = H) underwent facile degradation. Although these simulation studies cannot duplicate the complex situations occurring in the geosphere, the results paralleled the gradual disappearance of serine and threonine observed in *Mercenaria mercenaria* shells ranging in age from Recent to Miocene.[212] The non-protein amino-acid ornithine (74) appeared in the fossil shells at the expense of arginine (75) such that the ornithine/arginine ratio was essentially infinity in the shells of Miocene age.[212]



$H_2N(CH_2)_3-\overset{H}{\underset{NH_2}{C}}-CO_2H$

(74)



$HN{=}\underset{NH_2}{C}-NH(CH_2)_3-\underset{NH_2}{CH}-CO_2H$

(75)

The distribution observed in the *Mercenaria* shells were also closely paralleled by the results of a series of thermal alteration experiments. For example, the distributions of amino-acids observed in the fossil shells of Miocene age were virtually duplicated when the Recent shells were heated to 160 °C for 10 h in the presence of water.

Changes in stereochemistry were also observed in both studies. The amino-acids in the untreated shells indicated gradual racemisation and those in the shells of Miocene age were found to be fully racemised. Also the non-protein amino-acid *allo*-isoleucine [72, R = $CH(CH_3)CH_2CH_3$, R^1 = H] which was absent in the contemporary shells appeared at the expense of its diastereoisomer, isoleucine, in the older shells. In a 1000-year-old shell the *allo*-isoleucine/isoleucine ratio was found to be 0·1. Once again, the observed situation could be duplicated by thermal alteration of the Recent shells.[212] Further evidence that amino-acids racemise over relatively short periods of geological time is indicated by studies of the Eocene Green River Shale.[213] All of the ten identified chiral amino-acids had measurable concentrations of both (*R*)- and (*S*)-enantiomers, the (*R*)-enantiomer representing 10—35% of individual amino-acids. Since the Green River Shale appears to have had a particularly mild geological history, it seems most likely that this represents partial racemisation, but there remains the possibility that the amino-acids represent a mixture of totally racemised amino-acids and (*S*)-amino-acids arising from Recent biological contamination. Contamination may not represent an appreciable contribution to the organic-rich Green River Shale but it is a serious problem in studies of Precambrian sedimentary rocks (see below). Kvenvolden and Peterson[214] have recently examined the bound amino-acids in samples of Recent marine sedi-

[212] P. E. Hare and R. M. Mitterer, *Carnegie Institution Year Book 1967-68*, 1969, 205.
[213] K. A. Kvenvolden and E. Peterson, *Geol. Soc. Amer. Abs.*, part 7, 132, 1969.
[214] K. A. Kvenvolden and E. Peterson, *Science*, 1970, **169**, 1079.

ments (Saanich Inlet, British Columbia) spanning the last 9000 years. Gas chromatographic analysis indicated that the proportions of (*R*)-enantiomers increase with the age of the sediment. This study also indicates that all α-amino-acids indigenous to sediments older than 2 × 10^6 years should be racemic, although this will depend on the history of a particular sediment.

The organic matrix of tooth dentine and bone is largely made up of the protein collagen. Electron microscope studies of a number of mammalian bones and teeth as old as the Jurassic have shown that the morphology of the proteinaceous matrix can be preserved over millions of years.[63–66,215] Amino-acid analyses of fossil collagen concentrates[67,216] have been carried out in an attempt to provide palaeochemotaxonomic data by interrelating the amino-acid compositions and correlating these with those of present-day collagens. In a number of cases the relative abundances of individual amino-acids in collagen isolated from fossils are similar to those observed in the collagen of contemporary counterparts. For example, the amino-acid composition of a collagen sample from *Equus occidentalis* (Pleistocene) is markedly similar to that of collagen from the Recent horse, *Equus caballus*, except that it shows a much lower histidine content.[67]

Electron microscope studies of fossil molluscan shells[217,218] have shown the presence of lace-like structures similar to those observed in the nacreous conchiolin of modern shells. Analyses of these fossil structures show amino-acid distributions similar to that of a modern conchiolin.[219] The distribution typical of conchiolin has also been observed in a mother-of-pearl sample of Eocene age.[219] A number of fossil graptolites of Silurian and Ordovician age afforded amino-acids on hydrolysis, indicating a possible proteinoid nature for the material of the fossil.[220]

Similar comparative studies have been carried out with fossil brachiopod shells and their nearest Recent contemporary relatives,[221–224] and with mastodon tooth enamel protein and fresh mammalian tooth enamel protein.[225] Also, the amino-acid composition of proteinaceous material isolated from slices of Dinosaur eggs shows similarities to that of the shell matrix of hens' eggs.[226] The major problem in such studies is that it is not certain if subtle differences observed between the amino-acid compositions of the fossil and modern proteins are significant in a chemotaxonomic sense or are indicative of contamination or of alterations brought about during fossilisation. What is clear, however, is

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[215] A. R. Doberenz and R. Lund, *Nature*, 1966, **212**, 1502.

[216] T. Y. Ho, *Biochim. Biophys. Acta*, 1967, **133**, 568.

[217] C. Grégoire, *Arch. Internat. Physiol. Biochim.*, 1958, **66**, 674.

[218] C. Grégoire, *Inst. Roy. Sci. Natl. Belg. Bull.*, 1959, **35**, 1.

[219] M. Florkin, C. Grégoire, S. Bricteux-Grégoire, and E. Schoffeniels, *Compt. rend.*, 1961, **252**, 440.

[220] M. F. Foucart, S. Bricteux-Grégoire, J. Jeuniaux, and M. Florkin, *Life Sci.*, 1965, **4**, 467.

[221] M. Jope, *Comp. Biochem. Physiol.*, 1967, **20**, 593.

[222] M. Jope, *Comp. Biochem. Physiol.*, 1967, **20**, 601.

[223] M. Jope, *Comp. Biochem. Physiol.*, 1969, **30**, 209.

[224] M. Jope, *Comp. Biochem. Physiol.*, 1969, **30**, 225.

[225] A. R. Doberenz, M. F. Miller, and R. W. G. Wyckoff, *Calc. Tiss. Res.*, 1969, **3**, 93.

[226] M. F. Voss-Foucart, *Comp. Biochem. Physiol.*, 1968, **24**, 31.

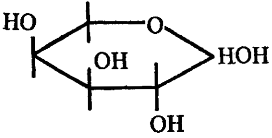
that well-preserved morphology in a fossil is not paralleled by preservation of protein structure, much of the amino-acid content being lost and/or modified.

G. Carbohydrates.—The carbohydrate residues of a number of fossils, Recent sediments, and sedimentary rocks have been examined in order to evaluate their potential as stratigraphic, palaeoenvironmental, and palaeotaxonomic marker compounds.

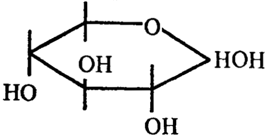
Comparative studies of the monosaccharides in various types of modern non-marine sediments and in the associated living plants show that the individual monosaccharides in the sediments can be partly related to those in the contributing plant species. The stratigraphic distributions also show relationships to the sedimentary and palaeoenvironmental history of the sediments but these relationships have not yet been rationalised.[227-229] The distribution of monosaccharides from hydrolysis of the oligosaccharides and polysaccharides in a Recent sediment from the Pacific Ocean near Santa Barbara, California, suggests that the carbohydrates arose from marine sources, probably algae and other micro-organisms, rather than terrestrial sources.[230]

The total carbohydrate content (determined by the phenol–sulphuric acid test) of limestones, shales, and cherts of the Devonian Onondaga Beds (Pennsylvania and New York) has been examined. The observed distribution of carbohydrates provides a correlation with the known stratigraphy, and indicates that these compounds may be used to provide information about palaeoenvironments. For example, one area of the Onondaga has particularly high carbohydrate concentrations, possibly arising from the accumulation of marine vegetation, and the low carbohydrate content of the mudbank face in the Beds may be due to early diagenetic activity of scavengers during deposition.[231]

The types and ratios of monosaccharides in fossil Psilophytales and Lycopodiales (Devonian to Pennsylvanian) are similar to those of modern ferns.



(76)



(77)

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[227] M. A. Rogers, *Geochim. Cosmochim. Acta*, 1965, **29**, 183.

[228] F. M. Swain, in 'Essays in Palaeontology and Stratigraphy', ed. C. Teichert and E. Yochelson, University of Kansas Press, 1967, pp. 445–475.

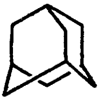
[229] F. M. Swain, *Bull. Minn. Geol. Surv.*, in press.

[230] A. Prashnowsky, E. T. Degens, K. O. Emery, and J. Pimenta, *Neues. Jahrb. Geol. Palaeontol. Min.*, 1961, **8**, 400.

[231] F. M. Swain and M. A. Rogers, *Geochim. Cosmochim. Acta*, 1966, **30**, 497.

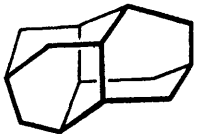
However, fossil *Calamites* appears to contain more galactose (76) than glucose (77); this suggests that galactan may have been the main structural polysaccharide rather than cellulose, the predominant polysaccharide in the modern counterpart, *Equisetum*.[232]

H. Miscellaneous.—The tricyclic alkane adamantane (78) has not been described in any of the sections dealing with geolipid types, but deserves special mention for two reasons: first, it is widely distributed in crude oils[233–235] in concentrations of up to 0·03%[236,237] although there is, as yet, no report of its occurrence in sediments; and secondly, it has not been found in contemporary organisms. It has been suggested that adamantane arises in petroleum from geochemical rearrangement of biologically-derived compounds such as terpenoids.[238] Several observations support this hypothesis: thermal alteration of crude oils increases the concentration of adamantane present;[237,238] and thermal alteration of a number of isoprenoid compounds in the presence of Lewis acids consistently affords alkyladamantane mixtures.[239] Thia-adamantane (79)[240] and diamantane (80),[241] which have been isolated pure from crude oil, may also represent rearrangement products.



(78)

(79)



(80)

Fossil plant cutins, in many cases with the gross morphology preserved, are widespread in sediments.[242–247] However, there are significant differences in the chemical reactions of fossil cutins and contemporary plant cutins. The latter

[232] F. M. Swain in 'Advances in Organic Geochemistry 1968', ed. P. A. Schenck and I. Havenaar, Pergamon Press, Oxford. 1969, pp. 167–180.

[233] S. Landa and V. Machacek, *Coll. Czech. Chem. Comm.*, 1935, **5**, 1.

[234] B. J. Mair, M. Shamaiengar, N. C. Krouskop, and F. D. Rossini, *Analyt. Chem.*, 1959, **31**, 2082.

[235] E. I. Bagrii, E. I. Amosova, and P. I. Sanin, *Neftekhimiya*, 1966, **6**, 665.

[236] S. Landa and S. Hala, *Erdöl u Kohle*, 1958, **11**, 693.

[237] S. Landa, *Ropa Uhlie*, 1959, **1**, 5.

[238] A. I. Bogomolov, *Trudy Vses. Neft. Nauchn.-Issled. Geologorazvěd, Inst.*, 1964, 10; (*Chem. Abs.*, 1965, **62**, 7549).

[239] M. Nomura, P. von R. Schleyer, and A. A. Arz, *J. Amer. Chem. Soc.*, 1967, **89**, 3657.

[240] S. F. Birch, T. V. Cullum, R. A. Dean, and R. L. Denyer, *Nature*, 1952, **170**, 629.

[241] S. Hala and S. Landa, *Angew. Chem. Internat. Edn.*, 1966, **5**, 1045.

[242] T. M. Harris, *Endeavour*, 1956, **15**, 59.

[243] H. H. Thomas and N. Bancroft, *Trans. Linn. Soc. Lond.*, 1913, **8**, 155.

[244] D. Edwards, *Phil. Trans.*, 1970, **258**, 225.

[245] G. Roselt and W. Schneider, *Paläont. Abh. B.*, 1969, **3** **(1)**, 1.

[246] D. L. Dilcher and G. E. Dolph, *Amer. J. Bot.*, 1970, **57**, 153.

[247] M. C. Boulter, *Biol. J. Linn. Soc.*, 1970, **2**, 41.

are readily hydrolysed to hydroxy-acids[248,249] under alkaline conditions. Preliminary examination of some fossil cutins indicates that they are resistant to alkaline hydrolysis, even when drastic conditions are used.[249,250] The i.r. spectra of modern cutins show an ester carbonyl absorption which is absent in the spectra of the fossil cutins.[249,251] Nitric acid oxidation of modern cutins[249,252] affords mixtures of dicarboxylic acids with distributions different from those obtained by oxidation of fossil cutins.[249] At present there is no detailed information available on the chemical constitution of the insoluble matrix of plant fossils because the methods of analysis of these polymeric materials have not reached a sufficient degree of refinement.

5 Stable Carbon Isotope Measurements

Carbon-14 measurements, although invaluable for dating purposes in archaeology, are of little value in geochemical studies; the half-life ($t_{\frac{1}{2}} = 9000$ yr) is short in comparison to the ages of geological samples other than the youngest Recent sediments. However, measurement of stable carbon isotopes (^{12}C, ^{13}C) can provide information about the cycle of carbon in Nature and complements the carbon skeleton approach to organic geochemistry. Absolute amounts of these isotopes are not measured since ^{13}C has a low natural abundance. Conversion of total sample to carbon dioxide allows mass spectrometric measurement of a $^{13}C/^{12}C$ ratio. Comparison of this ratio to that of carbon dioxide from a standard carbonate sample (PDB, Belemnite from the Peedee Formation, S. Carolina) indicates whether the material is enriched or depleted in ^{13}C.†

The biosynthetic pathways in living organisms tend to discriminate against ^{13}C; thus negative $\delta^{13}C$ values are generally observed for the organic compounds in living organisms, although the numerical values may vary considerably. The $\delta^{13}C$ values for Recent sediments reflect the values observed in associated organisms. The mean $\delta^{13}C$ of freshwater sediments is -25 per mil whereas the values for the organic matter in marine muds are around -20 per mil, the differences being compatible with those observed in terrestrial and marine plants.[253] More detailed correlations have also been observed with Recent sediments. Sackett and Thompson[254] examined the $\delta^{13}C$ values of the organic matter in sediment samples taken at increasing distances from the coastline in the Gulf of Mexico. It was found that the ^{13}C content increased with increasing distance from the shore; the most probable explanation of this gradation is that the $\delta^{13}C$ values reflect the relative contributions of terrestrial and marine organic matter to the sediments.[254] Temperature effects also appear to be significant in

† Data are reported as δ-values.
i.e. $\delta^{13}C$ ‰ (per mil) $= \{1000 \times [^{13}C/^{12}C\ (\text{sample}) - {}^{13}C/^{12}C\ (\text{PDB})]\}/[^{13}C/^{12}C\ (\text{PDB})]$

[248] G. Eglinton and D. H. Hunneman, *Phytochem.*, 1968, **7**, 313.

[249] D. H. Hunneman, Ph.D. Thesis, University of Bristol, 1970.

[250] G. Eglinton and T. A. Maclachlan, unpublished results.

[251] G. Eglinton and A. Caldicott, unpublished results.

[252] V. H. Legg and R. V. Wheeler, *J. Chem. Soc.*, 1929, 2449.

[253] E. T. Degens, in 'Organic Geochemistry: Methods and Results', ed. G. Eglinton and M. T. J. Murphy, Springer-Verlag, Heidelberg, 1970, pp. 304–329.

[254] W. M. Sackett and R. R. Thompson, *Bull. Amer. Assoc. Petrol. Geologists*, 1963, **47**, 525.

affecting the $\delta^{13}C$ values of Recent sediments. Samples of marine plankton from high latitudes of the South Atlantic (surface temperatures about 0 °C) show a ^{12}C enrichment relative to those collected where the temperatures are higher (*ca.* 25 °C). This enrichment is reflected in the $\delta^{13}C$ values of sediments from Drake Passage (South Atlantic) and the Argentine Basin respectively, which also show ^{12}C enrichment relative to the values observed in sediments from warmer areas.[255]

Many $\delta^{13}C$ values have been recorded for the organic matter in ancient sediments. It appears that diagenesis and maturation concentrate ^{12}C since the $\delta^{13}C$ values of Ancient marine sediments are generally lower than those observed for Recent marine sediments.[253] However, the organic matter in Precambrian sediments has even lower $\delta^{13}C$ values than that in other sedimentary rocks. It has been suggested[253] that this discrepancy reflects either a higher abundance of molecular carbon dioxide in the Precambrian sea (lower pH) or colder temperatures relative to present-day conditions. A lowering of pH or a change in temperature would affect the solubility characteristics of calcium carbonate, so the appearance of shell-forming organisms at the Cambrian–Precambrian boundary may be linked with the low $\delta^{13}C$ values of Precambrian sediments.[253]

6 Precambrian Sedimentary Rocks

Organic geochemists have been particularly active in recent years in isolating and identifying 'biological marker compounds' from Precambrian sedimentary rocks, the prime incentive being the search for the earliest signs of life. Geochemically stable compounds with structurally specific carbon skeletons (*e.g.* acyclic isoprenoid alkanes) have been extensively used as 'biological marker compounds', that is, compounds which were originally synthesised by living organisms, or whose precursors were synthesised by living organisms.

The co-occurrence of these carbon compounds and of discrete micro-objects, interpreted as fossil algae and bacteria, has been taken as evidence that living organisms flourished on the Earth's surface as early as 3×10^9 years ago. However, both the chemical evidence and the micropalaeontological evidence are somewhat controversial, especially for the oldest rocks. One problem is that organic matter extractable with solvents may not be truly syngenetic (the organic compounds themselves or their precursors were present at the time of deposition). Thus α-amino-acids, including the unstable serine, are present in a number of Precambrian rocks,[256,257] and stereochemical examination of fractions from samples of two of these rocks has shown that the amino-acids are almost entirely the (*S*)-enantiomers.[257,258] However, there is evidence[212,214] (see above) that over the periods of geological time in question the amino-acids ought to have been racemised, and that unstable amino-acids such as serine should have long since

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[255] W. M. Sackett, W. R. Eckelmann, M. L. Bender, and A. W. H. Bé, *Science*, 1965, **148**, 235.

[256] J. W. Schopf, K. A. Kvenvolden, and E. S. Barghoorn, *Proc. Nat. Acad. Sci. U.S.A.*, 1968, **59**, 639.

[257] K. A. Kvenvolden, E. Peterson, and G. E. Pollock, *Nature*, 1969, **221**, 141.

[258] P. H. Abelson and P. E. Hare, *Carnegie Institute Year Book 1967-68*, 1969, **67**, 208.

disappeared. It therefore appears that the amino-acids in these samples are *not* syngenetic, and must have entered the sediments relatively recently, either through geological processes, sample collection methods, or bacterial contamination. Smith *et al.*[259] have recently studied the alkanes and fatty acids in three Precambrian chert samples. Freshly broken chips were extracted with solvent, crushed, and further extracted. It was found that the yield of alkanes was significantly higher for the chips (with external surfaces) than from the powdered residue, indicating that by far the major proportion of the alkanes was associated with exterior surfaces. Also, the alkane fractions exhibited a marked odd-number predominance for n-alkanes above n-heptacosane. These results indicate that the alkanes and their precursors, like the amino-acids, may not be syngenetic. A similar situation might exist for the fatty acid distributions observed in extracts of Precambrian samples. Van Hoeven *et al.*[23] examined the free and bound saturated fatty acids in the Gunflint Chert, Ontario (*ca.* $1{\cdot}9 \times 10^9$ years old) and the Soudan Shale of Minnesota (*ca.* $2{\cdot}5 \times 10^9$ years old) and concluded that these fatty acids were possibly syngenetic, although the possibility could not be excluded that they represented younger contamination. Smith *et al.*[259] examined the free and bound fatty acid fractions of the Gunflint Chert and two other Precambrian samples and concluded that the presence of small quantities of unsaturated fatty acids argued against a syngenetic origin for the acids. Furthermore, the yields of the Gunflint saturated acids were highest for the rock chips before crushing.

The supposition that apparently impermeable rocks, such as cherts, are traversed by micropores and cracks has been confirmed by autoradiography with radioactive solutions.[260] Porosity and permeability studies with the Early Precambrian Onverwacht chert (*ca.* $3{\cdot}2 \times 10^9$ years old) show a porosity of $0{\cdot}5\%$ and permeability of $5{\cdot}7 \times 10^{-7}$ millidarcy.[261] These results indicate that, over a period of 3×10^9 years, at least 0·35 g of C_9—C_{30} n-alkanes could have been in solution in the water which might have flowed through 1 m^3 of this rock. The few milligrams of isoprenoid alkanes which can be detected in 1 m^3 of the chert might therefore not be syngenetic. Permeability and porosity measurements of the three Precambrian cherts mentioned above were also made by Smith *et al.*,[259] and these measurements show that the cherts in question are not impermeable, as had been thought previously.

Apart from the contamination problems, abiological synthesis of biological markers has to be considered; some amino-acids can be synthesised from mixtures of methane, ammonia, and water vapour under the action of various forms of energy.[262] Porphyrins—or at least fractions exhibiting the appropriate light absorption—have been synthesised in a similar manner.[263] Studier *et al.*[264] have claimed that the low molecular weight (C_9—C_{14}) perdeuterio counterparts

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[259] J. W. Smith, J. W. Schopf, and I. R. Kaplan, *Geochim. Cosmochim. Acta*, 1970, **34**, 659.
[260] G. Eglinton and M. M. Rhead, unpublished results.
[261] B. Nagy, *Geochim. Cosmochim. Acta*, 1970, **34**, 525.
[262] C. Ponnamperuma and N. W. Gabel, *Space Life Sci.*, 1968, **1**, 64.
[263] G. W. Hodgson and C. Ponnamperuma, *Proc. Nat. Acad. Sci. U.S.A.*, 1968, **59**, 22.
[264] M. H. Studier, R. Hayatsu, and E. Anders, *Geochim. Cosmochim. Acta*, 1968, **32**, 151.

of the regular acyclic isoprenoid alkanes can be synthesised in trace amounts from carbon monoxide and deuterium by a modified Fischer–Tropsch process, although Oró *et al.*[265] have been unable to confirm these findings. Irradiation of isoprene adsorbed on vermiculite with ^{60}Co γ-rays produces hydrocarbon mixtures with a high predominance of regular isoprenoid structures.[266] Although these and similar syntheses which have been carried out may not be truly representative of natural syntheses which might possibly have occurred in the primitive Earth environment, they indicate—as might be expected—that some of the structures used as 'biological markers' are not uniquely biological. More rigorous criteria are necessary for defining the origin of 'biological markers' in Precambrian samples. Since the biosynthetic pathways in living organisms discriminate against ^{13}C, it has been suggested[267] that measurements of δ^{13}C values of individual compounds in Precambrian sediments could be used to indicate whether the compounds had a biological or non-biological origin. Thus the δ^{13}C values of geochemically-stable molecules (*e.g.* alkanes), which preserved their original carbon skeletons (*i.e.* minimal isotopic fractionation over geological time) would reflect their original values. As yet this method has not been applied to Precambrian sediments, presumably because of the technical difficulties involved. Extension of the gas chromatographic method for the stereochemical determination of isoprenoid acids (see above) to the isoprenoid alkanes found in Precambrian samples could also provide another criterion for distinguishing a biological origin from an abiological origin. A product of biological synthesis—presumably a non-random mixture of stereoisomers—would thus be easily distinguished from an abiological product—presumably a random mixture of stereoisomers. Again, only technical difficulties in such an analysis remain. The major problem to be overcome still appears to be that of contamination of the extractable organic matter. One possible method of obtaining indigenous extractable organic matter for analysis would be to isolate a microfossil concentrate. Methods for obtaining such a concentrate from a sediment would certainly be tedious. However, the effort ought to be justifiable since a number of Precambrian microfossils retain their morphology after dissolution of the matrix with hydrofluoric acid.[268] Immunity to the hydrofluoric acid treatment suggests that some organic matter is still present, though carbonisation must surely be very extensive.

An alternative approach would be the analysis of the organic matter in kerogens, which are more likely to be indigenous to the sediment than the solvent-extractable fraction (although this is by no means certain). However, this requires a refinement of the methods presently available for the degradation of these polymeric materials. It is difficult to propose a procedure which would (*a*) provide rigorous criteria for the origin of organic compounds in Precambrian samples, and (*b*) overcome the contamination problems. One procedure might

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[265] E. Gelpi, J. Han, D. W. Nooner, and J. Oró, *Geochim. Cosmochim. Acta*, 1970, **34,** 965.
[266] C. Munday, K. Pering, and C. Ponnamperuma, *Nature*, 1969, **223,** 867.
[267] D. H. Welte, *Naturwiss*, 1969, **56,** 133.
[268] J. W. Schopf, *J. Palaeont.*, 1968, **42,** 651.

be to isolate compounds with isoprenoid skeletons (assuming such skeletons are present) by oxidation or thermal alteration of kerogen and then determine the stereochemistries of the isoprenoids by gas chromatographic analysis.

7 Extraterrestrial Samples

A. Meteorites.—The organic matter in carbonaceous chondrites will not be discussed in detail here because the subject has been recently reviewed.[269] Carbonaceous chondrites contain up to 30 mg g^{-1} of solvent-extractable material but the greater proportion of the organic matter appears to be polymeric. Many of the contamination problems encountered in the analysis of terrestrial Precambrian sediments also appear to apply to meteorites. Most of the carbonaceous chondrites which have been examined were exposed to terrestrial contamination through storage in museums for many years. Only one carbonaceous chondrite, that falling at Pueblito de Allende, has been collected immediately after arrival on Earth. Han *et al.*[270] analysed the organic extract of this type III carbonaceous chondrite only a few days after it fell and found, by means of gas chromatography and combined gas chromatography–mass spectrometry, alkanes (*ca.* 0·5 p.p.m.), fatty acids (0·1 p.p.m.), and a number of unidentified compounds in a benzene–methanol extract of the exterior surface. Acyclic isoprenoid alkanes, including pristane (4, R = CH_3) and phytane (5, R = CH_3) were present in the alkane fraction, and saturated and unsaturated normal fatty acids were found in the fatty acid fraction. The extract of an interior sample of the meteorite showed the concentrations of these compounds to be barely above the detection limits of the gas chromatograph. This indicated that the organic matter on the surface sample represented contamination and that contamination of meteorites could occur rapidly. However, Levy *et al.*[271] have recently studied the organic matter in the Pueblito de Allende carbonaceous chondrite, using pyrolysis gas chromatography and pyrolysis gas chromatography–mass spectrometry. A range of low molecular weight alkanes (up to C_{11}) and low molecular weight aromatic hydrocarbons (toluene, xylene, C_3 alkylbenzenes, styrenes, *etc.*) were identified in pyrograms (up to 460 °C) of exterior and interior samples of the meteorite. The concentrations of organic matter released by pyrolysis were as high as 70 p.p.m. and were greater for the interior samples. Two explanations are possible for the apparent contradiction in the results of Han *et al.* and those of Levy *et al.*:

(i) Evaporation of the solvent extract resulted in the loss of the low molecular weight compounds observed in the pyrolysis experiments.

(ii) The low molecular weight compounds observed in the pyrograms represent breakdown products of polymeric material.

It appears that the interior of the meteorite does contain indigenous organic matter comprising low molecular weight hydrocarbons or polymeric material,

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[269] J. M. Hayes, *Geochim. Cosmochim. Acta*, 1967, **31**, 1395.

[270] J. Han, B. R. Simoneit, A. L. Burlingame, and M. Calvin, *Nature*, 1969, **222**, 364.

[271] R. J. Levy, C. J. Wolf, M. A. Grayson, J. Gibert, E. Gelpi, W. S. Updegrove, W. Zlatkis, and J. Oró, *Nature*, 1970, **224**, 148.

but that the exterior surface is severely contaminated with biologically-derived terrestrial contaminants. Stable carbon isotope measurements have also been recently used to study the contamination problem in carbonaceous chondrites. A recent study[272] of the carbonate, soluble organic, and insoluble organic fractions of seven carbonaceous chondrites indicates that the extractable components from three of them are highly contaminated with terrestrial organic matter. Carbon isotope measurements of these fractions in three of the other meteorites suggest that there may be a generic relationship between the extractable and non-extractable components; therefore the extractable components may, in some cases, be indigenous. It is thought that the non-extractable components ($\delta^{13}C$ $-14{\cdot}8$ to $-17{\cdot}1$) may have formed rapidly, under highly energetic conditions (high temperature or plasma irradiation), from reduced carbon (such as methane).

One other carbonaceous chondrite, the Murchison meteorite (Murchison, Victoria, Australia, 1969), appears to contain indigenous organic matter extractable with organic solvents.[273] The acid hydrolysate of the extract was found to contain amino-acids with almost equal proportions of the (*R*)- and (*S*)-enantiomers. Other amino-acids, including sarcosine (81) and 2-methylalanine

$$CH_3NHCH_2CO_2H$$

(81)

(72, $R = R^1 = CH_3$), which are rare in biological systems, were also isolated. A gas chromatogram of the alkane fraction of the extract showed an extremely complex mixture which was not resolved by the chromatograph. The distribution was similar to that obtained in the laboratory by the action of electrical discharges in methane. The $\delta^{13}C$ values ($+4{\cdot}43$ to $+5{\cdot}93$) of the extractable organic matter were outside those observed for terrestrial organic matter. This evidence indicates that the amino-acids and alkanes may be truly extraterrestrial in origin and not terrestrial contaminants. The findings thus appear to substantiate the Oparin–Haldane hypothesis of chemical evolution that organic compounds were formed before the appearance of life on Earth.

B. The Moon.—Closely related to terrestrial organic geochemical studies is the study of the carbon compounds in returned extraterrestrial samples. The close parallelism exists in the microanalytical methods used for characterisation of the carbon compounds and in elucidating their origins.

Measurement of the total carbon content of the Apollo 11 fines afforded values of the order of 150—200 p.p.m. Values were measured by analysis of the carbon dioxide produced after combustion of samples at 1800 °C in an atmosphere of

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[272] J. W. Smith and I. R. Kaplan, *Science*, 1970, **167**, 1367.

[273] K. Kvenvolden, J. Lawless, K. Pering, E. Peterson, J. Flores, C. Ponnamperuma, I. R. Kaplan, and C. B. Moore, *Nature*, 1970, **228**, 923.

oxygen.[274] Measurement of the organic carbon content gave values much lower than the total carbon values. Mass spectrometric analysis of the products evolved by heating samples to 500 °C indicated that the concentrations of organic matter in the Apollo 11 samples were less than 1 p.p.m.[274] In another series of experiments, pyrolysis of various samples, followed by detection of the volatile products with a hydrogen flame ionisation detector, placed an upper limit of 10 p.p.m. upon possible indigenous organic matter.[275]

Analysis of the fines for the presence of a number of the individual compound classes mentioned above was carried out using various extraction and pyrolysis techniques, followed by gas chromatography, mass spectrometry, or combined gas chromatography–mass spectrometry. No alkanes in the volatility range corresponding to approximately n-C_{12} to n-C_{32} were observed at concentrations corresponding to the detection limits of the methods used; that is, no individual alkane was observed at concentrations corresponding to *ca.* 1—5 parts in 10^9.[276–281] One report[282] of the occurrence of n-alkanes gave a level of *ca.* 1 p.p.m. total, but the sample had probably been contaminated. No alcohols,[279] fatty acids,[279,280] sugars,[280] or nucleic acid bases[280] were found. No indigenous aromatic hydrocarbons were found in solvent extracts of untreated fines[276,278–282] or of the residues remaining after hydrofluoric acid treatment.[276,278] However, benzene, toluene and other alkylbenzenes, thiophen and alkylthiophens, indene, naphthalene and methylnaphthalenes, styrene, and biphenyl were observed when the fines were heated to temperatures up to 700 °C.[282] The origin(s) of these compounds is not yet certain. They could be degradation products of polymeric material, contaminants, or synthetic products derived from low molecular weight compounds such as methane.

Examination of a benzene–methanol extract of Apollo 11 fines by Hodgson *et al.*[283] indicated the presence of porphyrin-like material (at a concentration of *ca.* 0·1 ng g^{-1}) which showed fluorescence excitation at 390 nm. However, similar material was found in the mineral dunnite exposed to the Lunar Module (LM) descent engine in terrestrial trials. Rho *et al.*[284] also used spectrofluorimetric techniques on extracts of Apollo 11 fines but found no porphyrin-like material at a limit of 0·1 ng g^{-1}. However, material with absorption maxima at

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[274] Lunar Sample Preliminary Examination Team, *Science*, 1969, **165**, 1211.

[275] R. D. Johnson and C. C. Davis in 'Proceedings of the Apollo 11 Lunar Science Conference', ed. A. A. Levinson, Pergamon Press, New York, 1970, Vol. 2, pp. 1805–1812.

[276] A. L. Burlingame, M. Calvin, J. Han, W. Henderson, W. Reed, and B. R. Simoneit, ref. 275, pp. 1779–1791.

[277] W. G. Meinschein, E. Cordes, and V. J. Shiner, ref. 275, pp. 1875–1877.

[278] R. C. Murphy, G. Preti, M. M. Nafissi-V, and K. Biemann, ref. 275, pp. 1891-1900.

[279] P. I. Abell, G. H. Draffan, G. Eglinton, J. M. Hayes, J. R. Maxwell, and C. T. Pillinger, ref. 275, pp. 1757–1773.

[280] K. A. Kvenvolden, S. Chang, J. W. Smith, J. Flores, K. Pering, C. Savinger, F. Woeller, K. Keil, I. Breger, and C. Ponnamperuma, ref. 275, pp. 1813–1828.

[281] J. Oró, W. S. Updegrove, J. Gibert, J. McReynolds, E. Gil-Av, J. Ibanez, A. Zlatkis, D. A. Florey, R. L. Levy, and C. Wolf, ref. 275, pp. 1901–1920.

[282] M. E. Murphy, V. E. Modzeleski, B. Nagy, W. M. Scott, M. Young, C. M. Drew, P. B. Hamilton, and H. C. Urey, ref. 275, pp. 1879–1890.

[283] G. W. Hodgson, E. Bunnenberg, and B. Halpern, ref. 275, pp. 1829–1844.

[284] J. H. Rho, A. J. Bauman, T. F. Yen, and J. Bonner, ref. 275, pp. 1929–1932.

310 and 350 nm and fluorescence excitation at 410 nm was found[284] at a level of about 10 ng g^{-1}. The origin of this material is not yet certain.

Amino-acid analyses were carried out by a number of investigators.[280–282,285] Aqueous extraction of a lunar fines sample, followed by ion-exchange chromatography and treatment with n-butanol and trifluoroacetic anhydride, followed by gas chromatography of the product, showed that the fines contained no free amino-acids.[280] Individual *N*-trifluoracetyl derivatives at a concentration corresponding to 1 ng g^{-1} would have been detected by this method. Hydrolysis of the sample with hydrochloric acid and similar workup revealed no bound amino-acids at concentrations of 100 ng g^{-1} of individual components.[280,281] Hare *et al.*[285] found, using an amino-acid analyser instead of a gas chromatograph, glycine (72, $R = R^1 = H$), alanine (72, $R = CH_3$, $R^1 = H$), glutamic acid (72, $R = CH_2CH_2CO_2H$, $R^1 = H$), serine (72, $R = CH_2OH$, $R^1 = H$), aspartic acid (72, $R = CH_2CO_2H$, $R^1 = H$), threonine [72, $R = CH(OH)CH_3$, $R^1 = H$), and *β*-diaminopropionic acid (72, $R = CH_2NH_2$, $R^1 = H$) in acid hydrolysates of aqueous extracts of lunar fines. Murphy *et al.*[282] detected urea, glycine (72, $R = R^1 = H$), alanine (72, $R = CH_3$, $R^1 = H$), and ethanolamine (82) at concentrations of *ca.* 30 ng g^{-1} in a water extract of the lunar fines. However, identifications were based only on retention times in the amino-acid analyser, and further investigation by g.c.–m.s. is clearly necessary. Hare *et al.*[285] and Murphy *et al.*[282] believe that the amino-acids may be the result of abiotic synthesis brought about on the lunar surface by the rocket exhaust or by irradiation of indigenous carbon matter. Analysis of Apollo 12 and 14 samples collected at a considerable distance from the LM should help to eliminate the possibility of rocket exhaust synthesis. Also, terrestrial contamination appears to be present in Apollo 12 samples at lower concentrations than in Apollo 11 samples. Much of the interest of organic chemists in lunar samples is now centred on the analysis and origin of the gaseous organic compounds which can be released from the samples. A number of gaseous rocket exhaust contaminants[286] have been identified in Apollo 11 lunar fines[276,278] but these can be removed by degassing the samples at 150 °C *in vacuo*. Carbon monoxide is rapidly evolved when the fines[276,279,281,287,288] are heated above 400 °C and nearly all the carbon is driven off as carbon monoxide (and carbon dioxide to some extent) by heating Apollo 11 fines to the melting point (*ca.* 1100 °C).[276] Some of this carbon monoxide possibly arises from reduction of silicates or metal oxides by elemental carbon in the samples.[287]

$$HOCH_2CH_2NH_2$$

(82)

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[285] P. E. Hare, K. Harada, and S. W. Fox, ref. 275, pp. 1799-1803.

[286] B. R. Simoneit, A. L. Burlingame, D. A. Flory, and I. D. Smith, *Science*, 1969, **166**, 733.

[287] S. Chang, J. W. Smith, I. Kaplan, J. Lawless, K. A. Kvenvolden, and C. Ponnamperuma, ref. 275, pp. 1857–1869.

[288] S. R. Linsky, R. J. Cushley, C. G. Horvath, and W. J. McMurray, ref. 275, pp. 1871–1873.

Approximately 66 p.p.m. of carbon monoxide, accounting for about one third of the total carbon, has been liberated by hydrofluoric acid dissolution of one sample of the fines.[276] However, this CO was later reported to be an artifact.[289] Pyrolysis of the Apollo 11 fines also releases small amounts of low molecular weight alkanes, including methane[276,279,282] and ethane.[282] Acid treatment of the fines followed by mass spectrometry, gas chromatography, or combined gas chromatography–mass spectrometry produces these alkanes in addition to ethylene, acetylene, propene, and propane.[280,290] Small quantities of allene, methylacetylene, and isobutane have been tentatively identified on hydrofluoric acid treatment.[290] The products arise from two sources: treatment of the fines with deuteriated hydrochloric acid showed that *ca.* 15% of the methane and ethane released was released as CH_4 and C_2H_6, indicating that this fraction was indigenous to the sample;[291] the remainder of the methane and ethane was released as fully deuteriated or almost fully deuteriated (CD_3H and C_2D_5H) species, indicating that these were products of the acid reaction. It is likely that these compounds and the other hydrocarbon gases released are the products of acid hydrolysis of carbides. Further studies of the indigenous hydrocarbon gases and lunar carbides are in progress. The origin of the carbides and trapped gaseous hydrocarbons is of paramount interest. They could have a lunar origin, an extralunar origin, or both. Thus the indigenous hydrocarbons could represent (*a*) primordial gases, (*b*) products of hydrolysis of carbides *in situ* on the Moon, (*c*) products of thermal or radiation-induced alteration of indigenous organic matter, or (*d*) solar wind products; for example, they could arise from hydrogenation of indigenous or solar wind carbon by hydrogen implanted by the solar wind.[291] Preliminary examination of a number of Apollo 12 lunar samples having different lunar surface exposure histories indicates[290,292] that the major fraction of the indigenous methane has an extralunar origin, possibly from the solar wind. The investigation of one lunar igneous rock suggests[290,292] that the CH_4 may have a small primordial contribution. The carbide may arise by contributions from meteorite impact and from 'carbide-like' materials generated by solar wind implantation.[290,292] It is likely, therefore, that a more detailed study will provide information about the history and radiation environment of the Moon.

Mars

The automated, miniature laboratory to be landed on the surface of Mars by the 1975 Viking Mission will be equipped with a pyrolyser–gas chromatograph–mass spectrometer–computer combination instrument. This tiny but powerful instrument will be used in an attempt to recognise any biological order in the

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[289] W. Henderson, W. C. Kray, W. A. Newman, W. E. Reed, A. L. Burlingame, B. R. Simoneit, and M. Calvin, unpublished results.

[290] P. I. Abell, P. Cadogan, G. Eglinton, J. R. Maxwell, and C. T. Pillinger, unpublished results.

[291] P. I. Abell, G. Eglinton, J. R. Maxwell, C. T. Pillinger, and J. M. Hayes, *Nature*, 1970, **226**, 251.

[292] P. Cadogan, G. Eglinton, J. R. Maxwell, and C. T. Pillinger, *Nature*, 1971, **231**, 28.

structures of the compounds identified or non-random distribution of compound classes.

8 Silicate Mineral Determination by Gas Chromatography

Treatment of silicates with concentrated hydrochloric acid, isopropanol, and hexamethyldisiloxane results in the formation of volatile trimethylsilyl derivatives of silicate anions. The derivatives may be characterised by gas chromatography[293] and combined gas chromatography–mass spectrometry.[294,295] However, the mineral olivine $(Mg,Fe)_2SiO_4$, containing $SiO_4{}^{4-}$ as the only anion, does not yield $Si[OSi(CH_3)_3]_4$ as sole product. This is the major product of the reaction, but linear and cyclic polymeric products, characterised by combined gas chromatography–mass spectrometry, are also formed.[295] Natrolite, $Na_2(Al_2Si_3O_{10})$,-$2H_2O$, which might be expected to yield only the trimethylsilyl derivative of the linear $Si_3O_{10}{}^{8-}$ anion, also affords a mixture of derivatives.[294,295] At present, the method is only useful for determination of large structural differences in silicates (*e.g.* between olivine and serpentine), of large-scale variations in the amount of one silicate mineral in another silicate mineral, and for the examination of geological glasses. However, the method is potentially important for silicate analysis if the polymerisation reactions occurring can be minimised; for example, the routine determination of the metamorphism in a sequence of metamorphic rocks.

This borderline area, wherein the methods of organic chemistry are applied to the problems of inorganic geochemistry, merits increased attention and may be expected to yield major scientific returns.

One further example may be quoted: the highest sensitivity yet recorded for the determination of metal cations is obtained by chelation followed by gas chromatography of the volatile metal chelates. Thus, the lower limit for electron capture detection of the beryllium chelate, $Be(CF_3COCHCOCH_3)_2$, is 4×10^{-13} g.[296]

9 The Future

The past 10 years have seen major developments in our knowledge of the precise chemical structures of the organic compounds present in geological and environmental materials. The rapid pace of development owes much to the impact of modern instrumentation and to the methods of natural product organic chemistry Just as in the latter field, a variety of approaches can be used:

(i) The improvement of existing analytical methods and the development of new techniques specifically designed for the problem area.
(ii) The search for compounds not previously recognised in geological samples.
(iii) The comparative or taxonomic study whereby the components from one

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[293] C. W. Lentz, *Inorg. Chem.*, 1964, **3**, 574.

[294] F. F. H. Wu, J. Götz, W. D. Jamieson, and C. R. Masson, *J. Chromatog.*, 1970, **48**, 515.

[295] G. Eglinton, J. N. M. Firth, and B. L. Welters, unpublished results; B. L. Welters, B.Sc. thesis, University of Bristol, 1970.

[296] W. D. Ross and R. E. Sievers, *Talanta*, 1968, **15**, 87.

source are compared qualitatively and quantitatively with those from others.

(iv) The study of the actual site wherein compounds are retained in the matrix and how this may relate to the history of the material.

(v) The inductive and experimental study of the mechanisms whereby compounds are interconverted.

It is becoming increasingly apparent that most carbon compounds encountered in the geosphere are indirectly or directly derived from biological materials. These materials were originally incorporated into the material at the time of formation of the sediment or entered subsequently as a result of geological contamination. As in classical natural product chemistry, emphasis is shifting from mere trophy-hunting, in the form of the characterisation of individual organic compounds or compound-types present, to an understanding of the origin and mode of formation of such compounds.

The short-term fate of organic material in sediments is of interest to the organic geochemist but it is of vital concern to the environmental scientist investigating pollution problems. The materials may be naturally derived or may be man-made, but the same methods of study may be used, together with a knowledge of the chemical and bacteriological factors involved. Particular micro-organisms, so far little studied, may prove to be of great significance geochemically and in their effect on the degradation of organic pollutants.

All of these fields of study (natural product chemistry, organic geochemistry, and environmental chemistry) are part of a wider study—that of the planetary-wide cycles of such elements as carbon, hydrogen, oxygen, nitrogen, sulphur, and phosphorus. Dynamic equilibria involve the input of solar energy, the loss of energy by radiation, and the interaction of many compounds in the atmosphere, hydrosphere, geosphere, and biosphere.

The lunar sample analysis programme has also involved a considerable effort by organic geochemists, who have had to modify their techniques to allow analyses at the parts per billion (10^9) level. The 'inorganic' type of organic geochemistry which has emerged from these lunar studies is now leading to renewed interest in terrestrial igneous rocks. This work should further increase our knowledge of the cycle of carbon in Nature.

Finally, in planetary exploration, the vast expenditure of some 800 million dollars on the Viking mission for the remote analysis of the surface of Mars in 1975 is one indication of the need for increased laboratory studies related to planetary surfaces. Organic geochemical techniques are being used in the Viking mission in an attempt to detect the past or present existence of 'life'. Improved information on the meaning of such organic geochemical experiments will be of crucial importance in interpreting the data eventually telemetered back from this mission.

A. Isolation Techniques and Analysis.—Improved methods for the isolation and identification of individual compounds are required. Any increase in sensitivity and precision of identification would be valuable, for the quantities of individual components which can be isolated are often very small. At present, most emphasis lies in the application of chromatographic and spectrometric techniques, and there seems every indication this will continue.

The organic compounds found in the geosphere generally occur as complex mixtures. The problem is to recognise known compounds and to characterise new ones present in these complex mixtures. Currently, the only suitable method is that of combined gas chromatography–mass spectrometry and coupled computer handling of the data. Work is in progress at the University of Bristol and elsewhere on computer sorting techniques which will classify the components of the mixture by on-line computer treatment of the mass spectra. This approach should be invaluable in the analysis of complex mixtures derived from any source, including bio-medical samples and industrial products. Another of the most desirable developments would be to utilise the full potential of high-resolution mass spectrometry, which is also dependent on extensive computer treatment.

X-Ray crystallography is a powerful method when crystals are available, and ^{13}C n.m.r. spectroscopy promises well. There is also scope for improvement in chemical procedures for derivatisation, which will assist in chromatography and in structural elucidation by spectrometric methods. Isotopic labelling techniques should be most informative, especially when used to follow the pathway of individual compounds through geological processes. However, much more information from biological materials is necessary before this kind of data can be interpreted unambiguously.

The problem of dealing with the ubiquitous insoluble organic debris present in sediments is one which will require considerable chemical effort, for the contemporary techniques for degradation of polymeric materials result in extensive loss of information. A somewhat similar problem is involved in the removal of the mineral matrix. An especially interesting question is whether or not the organic content can be correlated specifically with the morphology of fossils.

B. Nature and Distribution of Carbon Compounds in the Geosphere.—One major problem is that of contamination of rocks by the slow diffusion of organic materials into them. This is one aspect of the redistribution process which complicates the correlation of presumed source rocks with petroleum deposits. Contamination can be geological (involving slow permeation of the rock) or accidental (as a result of sampling in the field or handling in the laboratory). Progress has been made in recognising Recent contamination by amino-acids but any definitive work with materials containing only traces of organic compounds will be difficult for some time to come—this is so with Precambrian materials and meteorites.

It is now clear that there are several classes of compounds which are widespread in the geosphere. These include straight-chain compounds such as hydrocarbons and fatty acids, branched-chain compounds such as the isoprenoids and porphyrins, aromatic hydrocarbons, and cyclic isoprenoids, particularly steranes and triterpanes. However, some compound classes have not yet been studied in any detail; these include organometallic compounds other than the metallo-porphyrins, alkaloids, and many of the more complex bio-organic compounds. It is possible that the existence of 'new' biological compounds will be inferred from the presence of geological counterparts. This suggestion has already been made in relation to certain triterpanes found in the geosphere.

We can also expect progress in the recognition of individual compounds, or groups of compounds, as being characteristic of different environments, palaeoenvironments, and of the different conditions to which a rock has been subjected since the time of deposition. Organic geochemical data should then prove to be of value to geologists. At present the geological information is of more value to geochemists in that it allows interpretation of the emerging mass of organic geochemical data.

C. Reactions Occurring in the Geosphere.—It is probable that reactions occur in the short-term (a few days or weeks), medium-term (months to many years), and the long-term (millions of years). In short-term changes taking place during diagenesis it is likely that microbial action, involving catabolism of deposited materials, plays an important part. Other environmental factors, such as acidity, the presence of clay minerals, *etc.*, may induce quite rapid changes. Thus Recent sediments show an increase in saturated fatty acids relative to unsaturated fatty acids with increasing depth. In medium- and long-term maturation processes, the presence of aromatic systems, particularly those related to steroids, triterpenoids, and carotenoids provides some evidence. It is clear from the presence of perhydro-derivatives of unstable biolipids such as carotenoids that hydrogenation reactions occur and that there is a progressive loss of oxygen and nitrogen from the compounds in the maturing rock. Carbon atoms appear to be both added to and removed from the carbon chains of hydrocarbons, fatty acids, and possibly porphyrins in sediments. It is necessary to study these processes in detail since the reactions involved lead to the formation of oil, gas, and coal. One method is to examine the cores taken from rock formations and search for systematic changes in the organic material with depth, age, temperature, *etc.* Studies of this type should allow some distinction between biological, altered biological, and abiological material. Stereochemical investigations will be particularly important in this respect.

D. Industrial and Economic Importance.—As indicated, the study of organic geochemistry should provide information on the origin of minerals, such as ores, oil, gas, and coal. Already correlations between source rocks and crude petroleum are used by petroleum exploration groups. The ocean floor exploration, involving deep-drilling of the ocean bed, also requires organic geochemical study. Cores from the JOIDES programme (Joint Oceanographic Institutes for Deep Earth Sampling) taken from the Black Sea, Texas Gulf, Pacific Ocean, and Red Sea are currently under analysis using high-resolution mass spectrometry and other techniques. These studies should provide some understanding of the history of the sediments and of the adjoining continents.