Organic Matter in Meteorites and Precambrian Rocks: Clues about the Origin and Development of Living Systems [and Discussion]

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Organic matter in meteorites and Precambrian rocks: clues about the origin and development of living systems

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Discoveries during the last decade in organic geochemistry and palaeochemistry are used to assess concepts and to evaluate current scientific views on the nature and significance of organic matter in meteorites and early Precambrian rocks and its role in the origin and development of living systems. A critical account is given of the various chemical and organic structures contained in various ancient Precambrian rocks and carbonaceous chondrites. Analysis and identification of such organic matter contained in these rocks and meteorites are giving clues about how life originated and also about the nature and evolution of the early atmosphere, hydrosphere and early biological systems.

Introduction

It seems reasonably clear that the surface of planet Earth at one time, some 4.0 Ga ago (1 Ga = 10^9 years), was so hot that no life could exist, nor for that matter could one expect even complex macromolecules such as proteins and nucleic acids to exist in any form remotely resembling that required for life assembly. Consequently at some time there had to be a period when life arose on a sterile planet, and there are several possible ways in which this might have occurred. Modern hypotheses about the origin of life on Earth follow from suggestions made originally by Oparin (1924) and Haldane (1929) about the nature of (*a*) the *de novo* formation of the planet and its atmosphere and environment, and (*b*) chemical synthesis in which building block precursors of biomolecules could be elaborated from a primitive early atmosphere by abiotic chemical reactions.

Our present knowledge of the abiogenesis of organic molecules is derived from (i) identification of organic molecules in astronomical spectra, (ii) the presence of organic compounds in carbonaceous chondrites, (iii) studies of the organic contents in early Precambrian rocks, and (iv) laboratory experiments designed to test abiogenic synthesis theories.

In this paper, I shall examine (ii–iv) and evaluate these results against the Oparin–Haldane hypothesis, using the ancient geological record and information contained in carbonaceous chondrites.

FORMATION OF THE EARTH'S BIOSPHERE, ATMOSPHERE AND HYDROSPHERE

The Earth, like the rest of the Solar System, came into existence 4.5–4.7 Ga ago and is considered to have had no significant atmosphere, but an environment rich in hydrogen may have been present. The Earth's outer crust, the initial atmosphere and hydrosphere were probably formed by the same differentiation and degassing processes of the mantle about 4.0 Ga ago. After quick dispersion of the initial 'primordial' hydrogen environment by diffusion, a secondary atmosphere was introduced by volcanic activity. From occasional outbursts of solid and fluid matter and the release of gases and vapours, an atmosphere formed that had reducing properties and contained no free oxygen. Water vapour (steam) is the most abundant constituent (97 %) of the volcanic gases and it is estimated that the quantity of water and gases released over the last 4.0 Ga more than accounts for the volumes of the oceans and for the nitrogen and other constituents in the present environment. Oxygen originated and increased in the atmosphere by dissociation of water under the action of solar energy. Several mechanisms (see Hesstvedt *et al.* 1974) for the dissociation of water have been proposed and the three most important are photosynthesis, photolysis and oxidation of elements of variable valence. The major process of dissociation is photosynthesis. Like any set of chemical reactions, photosynthesis does not produce a net change in oxidation. Oxygen is produced, except in bacterial photosynthesis, together with a stoichiometric quantity of reduced carbon (photosynthesis $\rightleftharpoons$ respiration/fermentation). Almost all the oxygen is eventually used to oxidize this reduced carbon and the only net gain in oxygen levels equals the amount of reduced carbon material removed from the biogeochemical system and buried as sedimentary organic matter before it can be oxidized. Thus an important mechanism for the fixation of organic carbon in the Earth's crust and the production of free oxygen into the atmosphere was the accumulation of sedimentary organic matter that escaped oxidation by being deposited. These processes have been active since the first presence of photosynthetic organisms in the early Precambrian. The oxygen now in the atmosphere and that combined with a wide range of other elements in the Earth's crust is probably mainly, if not wholly, biological in origin. As the content of free oxygen in the hydrosphere and atmosphere increased, living systems evolved suitable oxygen-mediating enzymes within their cells and developed into more elaborate organisms with more sophisticated metabolic processes. The result of these and other processes is an intimate evolutionary interaction between the biosphere, atmosphere, hydrosphere and lithosphere (Brooks 1978). The hydrosphere, which was probably formed soon after 4.0 Ga ago (Watson 1976), was the main regulator of the cycle of organic matter in the biosphere and sediments. The timing of the build-up of oxygen in the atmosphere and hydrosphere is critical since many weathering and diagenetic processes involve redox reactions. The early presence of living systems on the Earth, which has now been established, implies that geological processes of sedimentation, weathering and diagenesis may have been influenced by organic activity from the earliest times (Watson 1976; Siever 1977).

The origin, composition and evolution of early Precambrian atmospheres have often been discussed (see Oparin 1924; Haldane 1929; Berkner & Marshall 1964; Brooks & Shaw 1973; 1978; Cloud 1976; 1978; Shimizu 1976; Walker 1977; Schidlowksi 1978) and conclusions are normally based on the following indirect evidence:

(i) the primordial or primitive atmosphere was accreted from the hydrogen-dominated solar nebula;

(ii) the secondary atmosphere was produced from volcanic outgassing;

(iii) abiotic synthesis of simple and increasingly complex organic chemicals requires a reducing or at least neutral atmosphere.

Chemical evolution theory (Calvin 1969; Rutten 1971; Brooks & Shaw 1973, 1978; Miller & Orgel 1974; Ponnampuruma 1977; Noda 1978; Day 1979) and the origin of life on Earth is based on the abiotic synthesis of organic molecules and requires that the early Earth's atmosphere was reducing and contained free-hydrogen. So, based upon these theoretical requirements for abiotic synthesis of organic compounds, the idea that a reducing atmosphere existed throughout the early Precambrian has been built up and not until recently questioned or tested by geochemical examination.

PRECAMBRIAN ORGANIC MATTER

Various criteria (Cloud & Licari 1968; Brooks & Shaw 1968) are used to identify the presence of former living systems in the Precambrian, which include the presence of :

(i) organic microstructures and filaments;

(ii) unstructured or partly structured insoluble organic matter (often called kerogen), which can very often be chemically related to materials of known biological origin;

(iii) extractable organic compounds with chemical structures and occurring in ratios characteristic of biologically produced materials.

The relative stability of the insoluble structured and unstructured organic matter (i and ii), together with its abundance and widespread occurrence, makes it an important parameter in studies on the Precambrian. Although most Precambrian sediments have undergone certain amounts of thermal activity, the diagenetic alteration of the contained organic matter is often sufficiently low to allow meaningful palynological and geochemical examination.

Well preserved microstructures, considered to be biogenic remains from bacterial, algae and possibly aquatic fungi, have been described from many areas representing all Precambrian periods (see figure 3). Palynological and geochemical studies in the Archaean (early Precambrian; more than 2.5 Ga old) takes four main forms: the study of stromatolites, Banded Iron Formations, the analysis of rocks for chemical traces of life, and the study of possible micro-fossils.

Archaean stromatolites (*up to* 3.5 Ga *old*)

The word 'stromatolite' should only be applied to organosedimentary structures predominantly accreted by sediment trapping, binding and/or *in situ* precipitation as a result of the growth and metabolic activities of benthic prokaryotic microorganisms (Buick *et al.* 1981). In their critical review of stromatolite recognition in ancient rocks, Buick *et al.* recommend that structures of uncertain origin that resemble stromatolites should be called 'stromatoloids'. Such classification, it is suggested, would prevent the currently common assumption that if structures have mesoscopic morphological similarities with microbially accreted sedimentary structures, then they must be biogenic. Buick *et al.* have proposed a hierarchial series of criteria that assign degrees of confidence of biogenicity to stomatolites.

As early as 1858, W. E. Logan suggested from a study of *Eozoon canadense* that stromatolite structures were evidence for Precambrian life, and since then many studies and correlations have been carried out on these structures (see Walter 1976). Various authors (see Nisbet 1980) consider that stromatolites offer at best 'compelling' evidence for the existence of life, since analogous modern structures are well known and have been studied in detail (e.g. Shark Bay, Western Australia). Stromatolites are found from the Archaean (see figure 3) to present-day deposits. The oldest reported 'compelling' evidence for life on Earth comes from stomatolites about 3.4–3.5 Ga old (Pidgeon 1978; Hamilton 1980) from the Warrawoona Group in the Pilbara Block of Western Australia (Lowe 1980; Walter *et al.* 1980).

Internally laminated conical moulds characterize a regionally extensive chert unit near the top of the 3.4 Ga old Warrawoona Group (Lowe 1980). The chert formed by silicification of a carbonate–evaporite sequence deposited in shallow subtidal to intertidal environments. Lowe's studies show that the morphology and internal organization of the moulds described suggest that they are conical stromatolites similar but not identical to members of the common Proterozoic group *Conophyton* Maslov. Walter *et al.* (1980) reported stromatolites and interpreted them as indicating that a benthic microbiota existed 3.4–3.5 Ga ago, but its biological affinities are unknown. It is often suggested in the literature that the presence of stromatolites establishes the former presence of cyanobacteria, but this may be an unwarranted interpretation, especially for Archaean stromatolites (Walter 1978). There are living examples of bacterial stromatolites built by non-cyanobacteria organisms (e.g. *Chloroflexus*, a green, photosynthetic, filamentous bacterium) in hot springs. This relationship is significant because among bacteria only the cyanobacteria release oxygen during photosynthesis and this makes it possible to equate the presence of stromatolites in Archaean rocks with and without the former presence of oxygen-releasing photosynthesizers (Walter *et al.* 1980).

Banded Iron Formations (*up to* 3.8 Ga *old*)

Siliceous Banded Iron Formations (B.I.Fs.) are widely distributed in Precambrian rocks. B.I.F. includes a variety of rock-types, but all are ferruginous and often cherty (Morris *et al.* 1980). Microorganisms occur in some B.I.Fs (Barghoorn & Tyler 1954; Cloud *et al.* 1965; Auramik 1976), and their presence, coupled with fine regular banding of layered cherts containing many laminae rich in iron oxide gives iron-rich and iron-poor microbands (Trendall 1973). These were caused by seasonal upwelling of nutrients from algal blooms of ferrous iron in solution. Layered B.I.F. cherts occur in some Archaean greenstones, but occur on a much larger scale in slightly younger rocks (Hamerley Group of Western Australia; Krivoi Rog of the Ukraine; Labrador Iron Formations). The oldest reported B.I.F. have been identified in the *ca.* 3.8 Ga old metasediments of west Greenland; these include what is undoubted B.I.F. some hundreds of feet thick and cropping out over tens of miles (Bridgwater *et al.* 1974; Sylvester-Bradley 1975). McGregor (1973) has shown that the Amitsoq gneisses of the Godthaab region and the Isua mantled gneiss dome were derived by deformation of homogeneous porphyritic granites containing inclusions of older rocks. Among these are quartz-magnetic–grunerite rocks that are probably relicts of B.I.F. If so, they are among the oldest sedimentary rocks in the world, and can scarcely be much younger than 4.0 Ga old (Sylvester-Bradley 1975). B.I.F. occur in rocks of all ages until the Carboniferous and then become comparatively rarer in rocks younger than 0.35 Ga old (Grant 1978). Although there have been reports (Cains-Smith 1978; Morris *et al.* 1980) of possible non-biological light-driven mechanisms for the formation of B.I.F., they are generally considered to have a biological or at least biochemical origin. The presence of B.I.F. in Archaean rocks is taken as an indication that microorganisms were active during the early Precambrian. The identification of B.I.F. in early Archaean rocks has interesting implications and confirms early plant evolution (Trendall 1973; Cloud 1976). It suggests that not only life itself, but also a low level of oxygen-producing photosynthesis, was already in existence more than 3.8 Ga ago, when the oldest known B.I.F. were being deposited in south-west Greenland.

Microfossils, filaments and organic chemicals

(i) *Swaziland Supergroup of southern Africa* (3.1–3.4 Ga *old*)

The Swaziland Supergroup, which consists of a complex of folded sediments, can be divided into three major groups: the Moodies Group at the top of the sequence, the Fig-Tree in the middle and the Onverwacht at the base. The Onverwacht Middle Marker Bed, which occurs at the base of the Upper Onverwacht, has been dated at 3.355 Ga old (Hurley *et al.* 1971).

Geochemical analysis have been carried out on the organic chemicals and residue extracted from Onverwacht rocks (Engel *et al.* 1968; Scott *et al.* 1970; Brooks 1970; Brooks & Shaw 1973; Dungworth & Schwartz 1972; Brooks & Muir 1971, 1980; Oehler *et al.* 1972; Brooks *et al.* 1973). Microorganisms with various morphologies and filamentous structures have been identified within the Onverwacht rocks and in extracted samples (Brooks & Muir 1971; Brooks *et al.* 1973; Muir & Hall 1974; Muir *et al.* 1977).

The spheroids in the Onverwacht Formations are brown or black and a variety of morphological types can be distinguished in each formation. Muir & Hall (1974), Muir & Grant (1976) and Muir *et al.* (1977) have described several types of spheroids, filaments, and even colonial structures in the Onverwacht Group. In all their studies (see Muir *et al.* 1977), only spheroids with a repeated and consistent morphology were measured. A number of statistical tests have been applied to the 'simple spheres' of the assemblages in the rocks, including tests for normality of distribution and three tests suggested by Schopf (1975): a size–probability plot; a divisional dispersions index, and a standard deviation (figure 1).

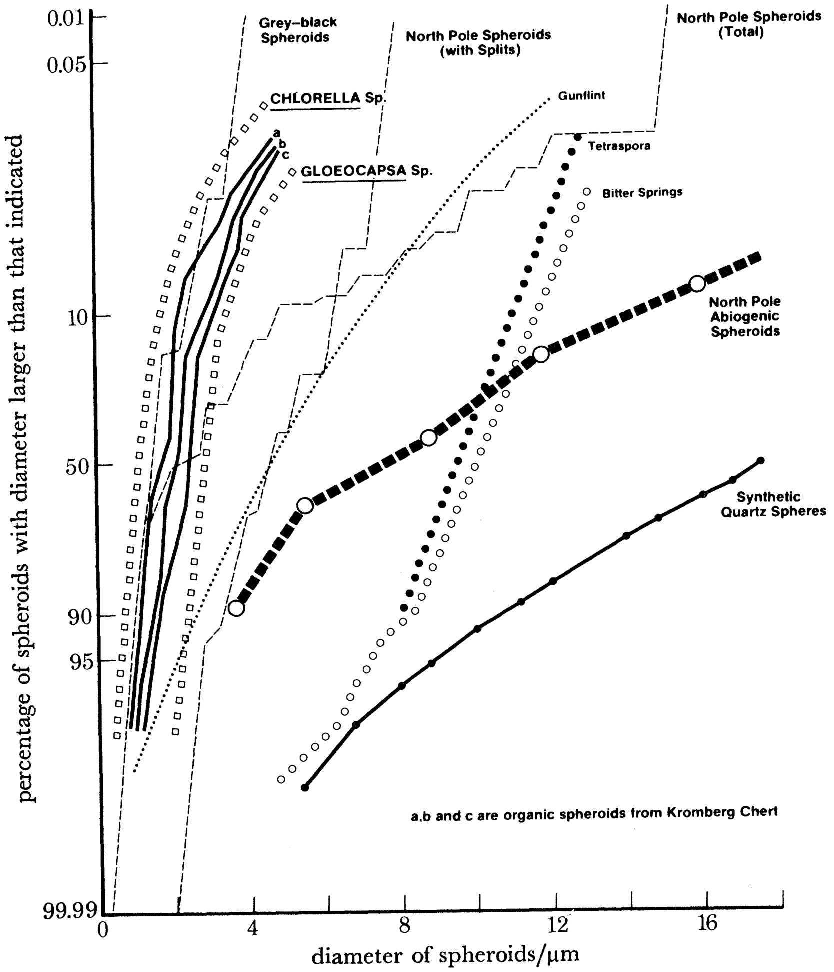

Figure 1. Size-probability plots for several populations of early Precambrian spheroids from North Pole, Australia and Onverwacht samples, Southern Africa (Muir *et al.* 1977; Dunlop *et al.* 1978).

According to Schopf (1975), a monospecific biogenic assemblage will approach a straight-line on the probability plot (figure 1), similar to those of species of the modern algal genera *Chlorella*, *Gloeocapsa* and *Tetraspora*, while more complex heterogenous assemblages should be similar to the plots of the undoubtedly biogenic Gunflint unicells, and the Bitter Spring cells. Muir *et al.* (1977) demonstrated that within the statistical limits imposed by Schopf (1977), these Onverwacht assemblages are all biogenic. In addition to the statistical tests, the biogenicity of the structures also conform to the widely applicable morphological criteria advocated by Cloud & Licari (1968). Statistically, morphologically and chemically, therefore, the spheroids in the Onverwacht sediments appear to be biogenic. The stable carbon isotope ($\delta_{13\mathrm{C}}$) values for sedimentary organic matter of the Lower Fig-Tree Group and Onverwacht Swartkoppie, Kromberg and Komati Formations are similar ($\delta_{13\mathrm{C}} = -25$ to -29‰) and characteristic of Precambrian organic matter produced by biological processes. The $\delta_{13\mathrm{C}}$ values for the Theepruit Formation near the base of the Onverwacht Group are -11.8 to -15.8‰. Assuming that the $\delta_{13\mathrm{C}}$ for the organic matter in the Upper Onverwacht rocks represents 'unaltered or slightly altered' material, then various explanations have been put forward to explain the anomalously high values for the organic matter in the Theepruit Formation. These high $\delta_{13\mathrm{C}}$ are due to geological thermal effects in an environment of mafic volcanic eruptions, while volcanism in the younger Onverwacht Group was more felsic, and thus subject to lower temperature alteration (Brooks 1971; Brooks & Muir 1977). Oehler *et al.* (1972) suggested that the $\delta_{13\mathrm{C}}$ values of the Theepruit organic matter were due to an environment in which the carbon was fixed by pre-photosynthetic mechanisms, and that the values are tending towards those determined for organic matter extracted from carbonaceous chondrites (Smith & Kaplan

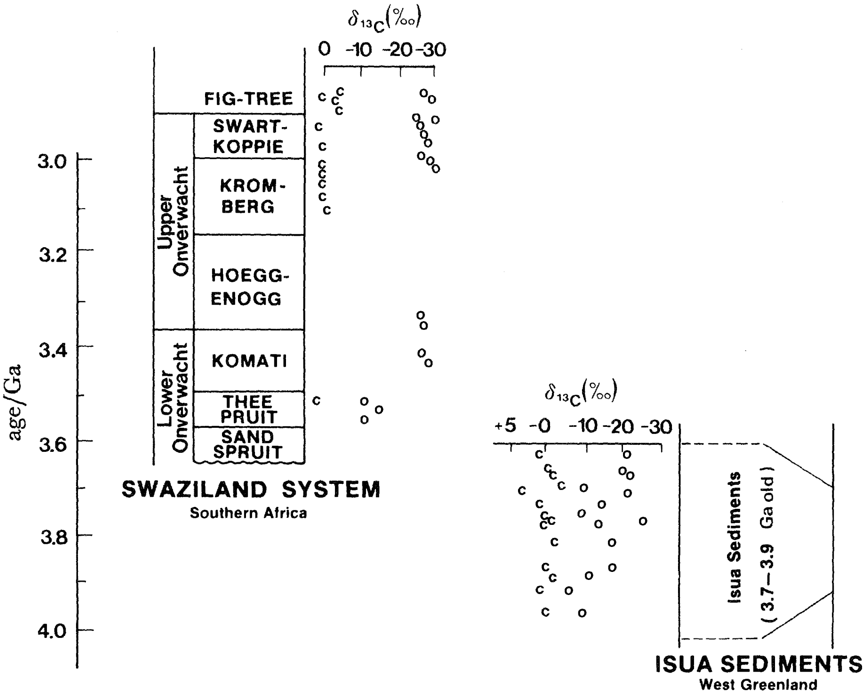

FIGURE 2. Stable carbon isotope data ($\delta_{13\mathrm{C}}$(PDB) of organic matter (O) and Carbonates (C) from the Swaziland System of southern Africa and the Isua Sediments of southwest Greenland (Brooks 1971; Oehler *et al.* 1972; Brooks *et al.* 1973; Schidlowski 1979).

1970). Barghoorn *et al.* (1974) suggested that the variation in $\delta_{^{13}\mathrm{C}}$ in the organic matter of Lower Onverwacht was due to its having been derived from detrital carbon and not from insoluble organic matter. The $\delta_{^{13}\mathrm{C}}$ ratios of the organic matter in the Upper Onverwacht Formations (figure 2) show differences between carbonate and organic carbon of 20–30‰. When such fractionations are compared with those obtained by Fischer–Tropsch syntheses (considered a model for the solar nebula syntheses of organic compounds), these have maximum $\delta_{^{13}\mathrm{C}}$ fractionation of 80‰, showing such comparisons to be invalid. The $\delta_{^{13}\mathrm{C}}$ fractionations of up to 80‰ are found in various types of carbon identified in carbonaceous chondrites, but such fractionations are not known in carbon compounds produced under terrestrial conditions.

Further evidence for the biological origin of the organic matter of the Onverwacht Group can be gained from the depositional environment of the sediments. These were laid down on a surface of pillow lavas and other sub-aqueous volcanics. Although some of the sediments are laterally extensive, most occur in pockets in the surface of the lavas (Viljoen & Viljoen 1969). The juvenile water that accompanies present-day volcanic activity, both at the time of eruption and during the latter fumarole stage, is extremely rich in plant nutrients. The hot springs associated with late Tertiary volcanic activity in the Rocky Mountains (Yellowstone National Park) (Walter *et al.* 1972) contain vast and varied microflora. Bacteria and blue-green algae are particularly common and occur in various microenvironments dependent upon pH, temperature and nutritional factors. Filamentous, rod-like and spheroidal microorganisms occur in water almost at boiling point. Similar conditions may have existed during the formation of the Onverwacht Sediments (Brooks *et al.* 1973), with organisms that could tolerate high temperatures (up to 100 °C) living in shallow depressions on the surface of hot lavas. By analogy with present-day extrusives, the Onverwacht probably maintained high temperatures for considerable periods of time. Such environments would favour production of small, random pockets of microorganisms, whose distribution would be controlled by proximity to the hot spring that produced exceptionally favourable nutritive conditions.

(ii) *Warrawoona Group, Pilbara Block of Western Australia* (*ca.* 3.5 Ga *old*)

The North Pole barite deposits are contained within the lower units of the Warrawoona Group (Hickman & Lipple 1978). Accurate isotopic dating of the barite deposits has not yet been obtained, but their stratigraphic equivalent (the Duffer Formation), has yielded ages between 3.45 and 3.49 Ga. The assemblage of microfossils (Dunlop *et al.* 1978) was present in a *ca.* 3.5 Ga old silicified shallow-water to supratidal carbonate sequence. Five morphologies of carbonaceous spheroids were recognized. Their morphology is very similar to microfossils from the Onverwacht Group, and statistical tests of size distribution (figure 1) support a biogenic origin. A study by Dunlop *et al.* (1978) confirms the presence of the remains of living organisms in ancient rocks of shallow-water origin. The statistical tests, together with the presence of spheroids with slits and rare tetragonal tetrad forms, support the interpretation of the spheroids as biogenic, with sufficient morphological features and range to suggest that Archaean sediments contain a considerable variety in the population of microfossils (Dunlop *et al.* 1978). The North Pole assemblages are similar to those described from rocks of similar age, and supports the view that early Archaean life was much more widespread than was previously considered.

(iii) *Isua and Godthaab Metasediments of southwest Greenland* (*ca.* 3.8 Ga *old*)

The geological history of the Isua supercrustal belt has now been summarized by Bridgewater *et al.* (1981) and radiometrically dated by Appel *et al.* (1978). The Archaean Craton of SW Greenland contains some of the oldest known non-igneous rocks and includes the Amitsoq gneisses of the Godthaab region (McGregor 1973; Bridgewater *et al.* 1974; Windley 1976) and the markedly low-grade Isua belt of metasediments and metavolcanic rocks that appear to have remained at substantially lower temperatures and retain some primary structures (Allaart 1976).

In addition to the B.I.F. in the metasediments, there are also marble (metamorphosed limestones) and graphitic mica schist (metamorphosed organic-rich shale). Cell-like inclusions detected in the cherty layers of a quartzite are interpreted as consisting of biological materials, according to analyses by Raman laser molecular microprobe (Pflug & Jaeschke-Boyer 1979). The fossils occur as individual unicells, filaments or cell colonies. Cells and cell families are usually surrounded by multilaminate sheaths that show a characteristic laminar structure. All species observed apparently belong to the same kind of organism, named *Isuasphaera* (Pflug 1978) and suggested to be related to recent yeast cells (Pflug & Jaeschke-Boyer 1979). Bridgwater *et al.* (1981) critically reviewed these reports on the 'yeast-like microfossils' and conclude that such biogenic interpretation of these structures is inconsistent with the tectonic history of the Isua region, with the petrology of the metaquartzites, and with the morphology of the microstructures themselves. The microstructures present in the Isua samples are considered (Bridgwater *et al.* 1981) to be indistinguishable from limonite-stained fluid inclusions, inorganic and post-depositional in origin, and as such should not be regarded as evidence of early Archaean life forms.

It has been postulated (Walters 1979) that hydrocarbons extracted from Isua rocks are remnants of organisms that existed *ca.* 3.8 Ga ago. Recent work by Nagy *et al.* (1981) shows that such interpretation is inconsistent with the high-temperature history of the rocks. Nagy *et al.* report both hydrocarbons and amino acids in the rock samples, but suggest that the extent of amino acid racemization shows the apparent continuous diffusion of biochemicals into the Isua rocks from encrusting lichens since the end of the last ice-age. Also, the cold-temperature history (which retards racemization) suggests that the amino acids may be modern to about 10000–20000 years old. It has been calculated (Nagy *et al.* 1981) by using kinetic and thermodynamic data from simulated laboratory experiments that amino acids, aromatic and aliphatic hydrocarbons could not have survived the known metamorphic history of the Isua rocks.

CARBONACEOUS CHONDRITES

Much of the solid matter entering the Earth's upper atmosphere is rapidly destroyed by frictional heat and combustion. Such material constitutes meteors. On the other hand, larger particles may survive the heat and combustion and eventually land on Earth. These are the meteorites, and although their outermost parts are often heated to high temperatures during descent, nevertheless the low conductivity of their substance to heat frequently means that, especially in reasonably large specimens, their inner parts have remained unaltered. The stony meteorites that contain organic compounds (up to 4.8 %, with about 20 % water in the Orgueil Meteorite, France) are called carbonaceous chondrites. They are currently the only extraterrestrial material containing organic matter available to us, and they are also the oldest known matter. Radiochemical dating has repeatedly shown meteorites to be 4.5–4.7 Ga old, which makes them at least 0.5 Ga older than the oldest rocks so far found and dated on Earth. About 40 carbonaceous chondrites have been identified since the first known fall at Alais, France, on 15 March 1806. This chondrite was studied by the famous Swedish chemist Berzelius, who later, describing an aqueous extract and pyrolysate of the contained organic material commented 'Does this carbonaceous stone contain humus or other organic substances?' and, 'Does this possibility give a hint concerning the presence of organic structure in other planetary bodies?' Similar questions are still being asked today.

Since this first study, numerous chemical analyses of organic compounds in meteorites have been carried out. A short history of meteorites and studies on their organic compounds has been reviewed by Hayes (1967) and Brooks & Shaw (1973).

In 1961 Claus & Nagy reported the presence of small spherical objects in samples of the Orgueil and Ivuna meteorites and concluded that these organized elements may be microfossils indigenous to the meteorite. These opinions aroused great opposition because the chemical composition of the meteorites did not resemble that of typical microfossil containing terrestrial sediments. During the 1960s, additional claims for finds of structured bodies were made by various groups in studies with crushed fragments, thin sections and acid-resistant extracts of the Orgueil, Murray, Alais, Tonk, Ivuna and Mighei carbonaceous chondrites. The ordinary stony meteorites, Bruderheim and Holbrook, lacked objects. Some of the microfossil objects had simple morphological structures, while others were more complex. Finch & Anders (1963) claimed that some of these objects were recent pollen and spore contamination and also that the structured bodies are most likely to be mineral grains, hydrocarbon droplets as well as contamination.

Brooks & Muir (1971) and Rossignol-Strick & Barghoorn (1971) examined the structured objects in the Orgueil and Murray meteorites by scanning electron microscopy and found that the organic box-like structures have five or six sides. The basic symmetry of all the structures is hexagonal and those structures with a different number of sides, whether it be five or seven, are either imperfect or probably damaged during preparation. The structures are hollow and contain mineral matter, and it is postulated that they were produced by condensation of organic matter round a hexagonal mineral nucleus. Similar structures are present in the Allende meteorite. These structures show no similarities or relationship to any known terrestrial biological organisms.

Extractable organic compounds in carbonaceous chondrites has been studied by Kaplan & Smith (1970) and their stable carbon isotope results indicate a non-random isotope distribution of carbon in the meteorites and show that the insoluble organic matter and perhaps a small portion of the solvent-extractable organic material are indigenous to meteorites. Several reports (see Cronin *et al.* 1980; Harada & Hare 1980) of the occurrence of amino acids in carbonaecous chondrites have appeared in the literature. It is considered very important for concepts of the chemical evolution theory of carbon compounds if amino acids were found to be indigenous to the meteorites. Results (Harada & Hare 1980) indicate that the amino acids from the surface of meteorites are largely terrestrial contamination and that the amino acids from the interior are probably indigenous to the meteorite. Comparison of amino acids in different meteorites and to lunar samples suggest a common mode of origin for these suites of amino acids. These data are readily used to support the view that meteorite organic compounds are the products of an exclusive chemical synthesis from a simple precursors. Although the mechanisms are unknown by which organic compounds of meteorites and postulated primitive Earth were synthesized, the presence of ubiquitous molecules among the meteorite organics suggests at least some analogy between these processes (Cronin *et al.* 1980).

Breger *et al.* (1972) examined the organic matter in the Allende meteorite and reported that the organic material associated with the fusion crusts was probably derived from the formaldehyde which is assumed to occur as paraformaldehyde in the meteorite together with small quantities of hydrocarbons and amino acids. The possible origin of the formaldehyde has been discussed (Breger *et al.* 1972). It could represent part of the initial agglomeration of the meteorite and may be of juvenile character. Alternatively, formaldehyde and formaldehyde polymers are known to exist in interstellar space (Wickramasinghe 1974), and it is possible that it may have been absorbed onto the meteorite surface. Another possibility is that the formaldehyde was abiogenicly synthesized on the surface of the meteorite or could have been absorbed during its fall through the Earth's atmosphere. Breger *et al.* (1972) considered this last source as unlikely.

TABLE 1. ESTIMATED AMOUNTS OF AMINO ACIDS, FORMALDEHYDE AND 'ORGANIC POLYMER' REACHING THE EARTH FROM METEORITES DURING 3.8–4.0 Ga AGO

time between 'cooling of the Earth' and origin of life on Earth	0.2 Ga
daily influx of meteorites on Earth (Kvenvolden *et al.* 1970)	*ca.* 100 t
daily fall of carbonaceous chondrites (50 % of total)	*ca.* 50 t
content of amino-acids in carbonaceous chondrites (Harada & Hare 1980)	*ca.* 5 μg/g
content of formaldehyde in carbonaceous chondrites (Berger *et al.* 1972)	*ca.* 3 μg/g
content of 'high molecular mass organic polymer' in carbonaceous chondrites	*ca.* 1 %
estimated amount of amino acids	0.2×10^{14} g
formaldehyde	10^{13} g
'organic polymer'	10^{18} g

If we accept that carbonaceous chondrites contain some of the important chemical precursors of life (e.g. amino acids, formaldehyde, hydrogen cyanide), then they provide a possible pathway by which the surface of the Earth received significant amounts of these substances. It is estimated that heavy meteorite bombardment onto the early Earth's surface took place 3.8–4.0 Ga ago. Such processes are likely to have contributed large quantities of organic compounds to the Earth's surface before 3.8 Ga ago. Rough estimates can be made of the amounts of amino acids, formaldehyde and organic polymers that might reach the Earth from meteorites. Based on values shown in table 1, it seems that approximately 0.2×10^{14} g of amino acids, 10^{13} g of formaldehyde and 10^{18} g of organic polymers could have reached the Earth's surface between 3.8 and 4.9 Ga ago.

SUMMARY: CLUES ABOUT THE ORIGIN AND DEVELOPMENT OF LIFE

The origin and evolution of life, atmosphere and hydrosphere, as recorded in Precambrian rocks and fossils, is reflected in the composition and biochemical peculiarities of the ancient biosphere. The most favoured hypotheses are based upon a primitive reducing atmosphere leading to a 'primitive soup' in which abiotic chemical reactions produced organic chemicals, which in turn led to the formation of macromolecules required by the living system. Geological evidence from the early Precambrian, however, suggests that such primitive and secondary atmospheres and environments did not exist for any appreciable length of time (Brooks & Shaw 1978). Supporting evidence for the lack of a reducing atmosphere in the early Precambrian is found in the studies on the ultraviolet photolysis of methane to give polymeric materials. Shimizu (1976) suggested that under primitive Earth conditions, the exospheric temperature might have been so high that methane would have disappeared owing to its dissociation into precipitated high molecular mass carbon polymer (deposited on the Earth's surface) and hydrogen (which escaped instantaneously to Space). A reducing atmosphere on primitive Earth, if it existed, would probably have been photodissociated to leave high molecular mass polymeric carbon material behind in too short a time for a living system to have formed in it. The observations led Shimizu (1976) to conclude that the previous optimistic conclusion as to the durability of a reducing atmosphere on the primitive Earth should be cautiously re-evaluated.

If a 'primitive soup' ever existed on Planet Earth for any appreciable time, it would require relatively large quantities of nitrogen-containing organic compounds (amino acids, nucleic acid bases, etc.). It is likely that early Precambrian sediments would undergo normal diagenetic and metamorphic processes, when such nitrogen-rich soups would have been expected to give significant quantities of 'nitrogenous cokes' trapped in various sediments. The formation of such 'cokes' is the normal result obtained by heating organic matter rich in nitrogenous substances (Brooks & Shaw 1978). No such nitrogen-rich materials have yet been found in early Precambrian rocks on this planet. In fact the opposite seems to be true: the nitrogen content of early Precambrian organic matter is relatively low (less than 0.15 %).

There is good evidence in the rocks to indicate that throughout the early Precambrian, living systems were present at the time of their deposition and were photosynthesizing and undergoing biochemical reactions similar to those of current living systems. The oldest preserved sediments probably formed about 4.0 Ga ago, before the major metamorphic events dated at 3.75 Ga ago. The B.I.F. in the Isua and Godthaab metasediments and the stromatolites and microorganisma in the Pilbara Block of Western Australia suggest that living systems were active about 3.8–4.0 Ga ago. Before this time the Earth is considered to have been at too high a temperature (more than 600 °C) to support life, or for that matter to allow the stable existence of complex biomolecules, such as proteins and nucleic acids. This leaves ever-decreasing amounts of time for conventional chemical evolutionary processes to occur. This timescale is very different from that normally suggested for chemical evolution models.

All the chemical evolution hypotheses are speculative and are possibly not applicable to the origin of life on Earth. Life originated on Earth at least 3.8 Ga ago and the evidence for its origin is no longer available (Sylvester-Bradley 1975). The chemical evolution models are not proved and we cannot find Precambrian rocks old enough to test their ideas. None of the vast quantities of early Precambrian rocks contain anything that can be recognized as prebiological organic matter. Since there is no clear evidence on Earth to support current theories of chemical evolution, the organic constituents of carbonaceous chondrities may provide useful clues.

Arrhenius (1903) introduced the 'panspermia' theory, in which he visualized that life could have been transmitted by means of spores carried by meteorites. Evidence shows that spores and remnants of living organisms are *not* constituents of meteorites, but analyses show that the chemical precursors of life can be transported through Space by carbonaceous chondrites. It is interesting to speculate that certain important chemicals (probable precursors of molecules

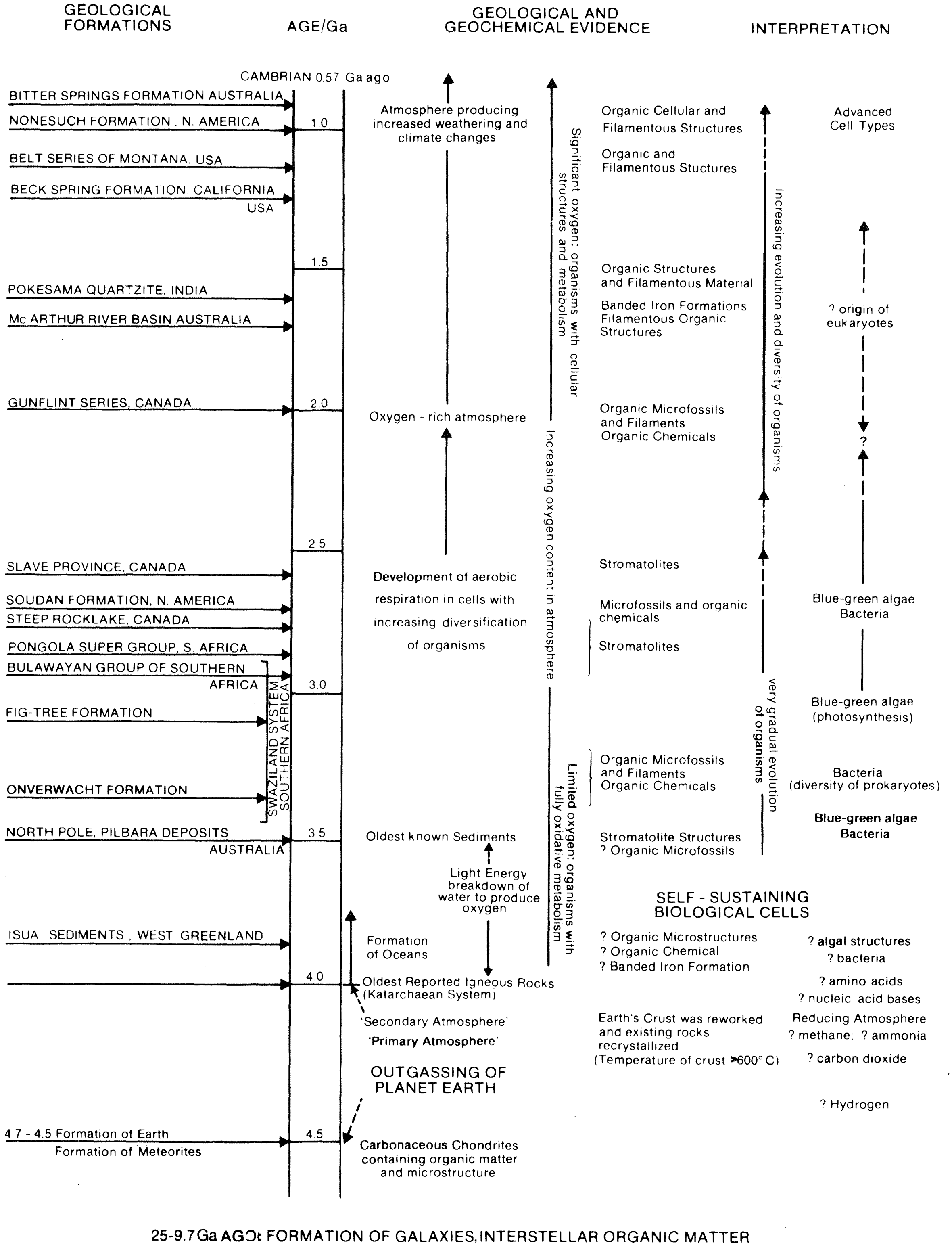

FIGURE 3. Major geological, geochemical and evolutionary events.

required for life) that exist in Space and in carbonaceous chondrites *could* have been distributed by such objects upon landing on Earth some 4.0 Ga ago and *may* have been the precursors of life. Careful studies on interstellar molecules, organic components in carbonaceous chondrites and early Precambrian rocks may yet help us with the mysteries of the origin and development of the living system on Planet Earth. To slightly paraphase the late Sir Robert Robinson, F.R.S. (1968): 'If it can be confirmed that life precursors ('bions') exist in certain meteorites, the further problems that arise are highly intriguing.'

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REFERENCES (Brooks)

Allaart, J. H. 1976 In *The early history of the Earth* (ed. B. F. Windley), pp. 177–190. London: Wiley-Interscience.
Appel, P. W. U., Moorbath, S. & Taylor, P. N. 1978 *Nature, Lond.* **272**, 524–526.
Arrhenius, S. 1903 *Lehrbuch der kosmischem Physik.*
Awramik, S. M. 1976 In *Stromatolites* (ed. M. R. Walter), pp. 311–320. Amsterdam: Elsevier.
Barghoorn, E. S., Troughton, J. H. & Margulis, L. 1974 *Am. Sci.* **62**, 389.
Barghoorn, E. S. & Tyler, S. A. 1954 *Science, N.Y.* **119**, 606–608.
Berkner, L. V. & Marshall, L. C. 1964 *Discuss. Faraday Soc.* **37**, 122–141.
Breger, I. A., Zubovic, P. & Clark, R. J. 1972 *Nature, Lond.* **236**, 155–158.
Bridgwater, D., Keto, L. & McGregor, V. R. 1974 *Gronlands geol. Unders. Rep. Activ.* **65**, 49–54.
Bridgwater, D., Allaart, J. H., Schopf, J. W., Klein, C., Walter, M. R., Barghoorn, E. S., Strother, P., Knoll, A. H. & Gorman, B. E. 1981 *Nature, Lond.* **289**, 51–53.
Brooks, J. 1970 Ph.D. thesis, University of Bradford.
Brooks, J. 1971 In *Sporopollenin* (ed. J. Brooks *et al.*), pp. 351–407. London and New York: Academic Press.
Brooks, J. 1978 In *The geological evidence for the evolution of the atmosphere and hydrosphere* (ed. M. D. Muir & P. R. Grant). London: Imperial College. (In the press.)
Brooks, J. & Muir, M. D. 1971 *Grana* **11**, 9–14.
Brooks, J. & Muir, M. D. 1980 In *Acritarcha: Proc. 4th I.C.P. Congress* 1977, pp. 282–290.
Brooks, J., Muir, M. D. & Shaw, G. 1973 *Nature, Lond.* **244**, 215–217.
Brooks, J. & Shaw, G. 1968 *Nature, Lond.* **220**, 678–680.
Brooks, J. & Shaw, G. 1973 *Origin and development of living systems.* London and New York: Academic Press.
Brooks, J. & Shaw, G. 1978 In *Origin of life* (ed. H. Noda), pp. 597–606. Tokyo: Centre for Academic Publishing.
Buick, R., Dunlop, J. S. R. & Groves, D. I. 1981 *Alchevinga.* (In the press).
Cains-Smith, A. C. 1978 *Nature, Lond.* **276**, 807–808.
Calvin, M. 1969 *Chemical evolution.* Oxford University Press.
Claus, G. & Nagy, B. 1961 *Nature, Lond.* **192**, 594–596.
Cloud, P. 1976 *Paleobiology*, **2**, 351–387.
Cloud, P. 1978 *Cosmos, Earth and Man.* Yale University Press.
Cloud, P., Gruner, J. W. & Hagen, H. 1965 *Science, N.Y.* **148**, 1713–1716.
Cloud, P. & Licari, G. R. 1968 *Proc. natn. Acad. Sci. U.S.A.* **61**, 779–786.
Cloud, P. & Morrison, K. 1979 *Precamb. Res.* **9**, 81–91.
Cronin, J. R., Gandy, W. E. & Pizzarello, S. 1980 In *Biogeochemistry of amino acids* (ed. P. E. Hare, T. C. Hoering & K. King), pp. 153–168. Wiley.
Day, W. 1979 *Genesis on Planet Earth.* Lansing: The House of Talos Publications.
Dungworth, G. & Schwartz, A. 1974 *Chem. Geol.* **14**, 167–171.
Dunlop, J. R. S., Muir, M. D., Milne, V. A. & Groves, D. I. 1978 *Nature, Lond.* **274**, 676–678.
Engel, A. E. J., Nagy, B., Nagy, L. A., Engel, C. G., Kremp, G. O. W. & Drew, C. M. 1968 *Science, N.Y.* **161**, 1005–1008.
Fitch, F. W. & Anders, E. 1963 *Science, N.Y.* **140**, 1097–1100.

Grant, P. R. 1978 In *The Geological evidence for the evolution of the atmosphere and the hydrosphere*. London: Imperial College. (In the press.)
Haldane, J. B. S. 1929 *The origin of life*. Rationalist Annual.
Hamilton, P. J., Eversen, N. M., O'nions, R. K. & Glikson, A. Y. 1980 In *Archaean Symposium*, Perth, Australia (ed. J. E. Glover & D. I. Groves), pp. 11–12. Geol. Soc. Aust. and Int. Geol. Corr. Project.
Harada, K. & Hare, P. E. 1980 In *Biogeochemistry of amino acids* (ed. P. E. Hare, T. C. Hoering & K. King), pp. 169–181. Wiley.
Hayes, J. M. 1967 *Geochim. cosmochim. Acta* **31**, 1395–1440.
Hesstvedt, E., Henriksen, S. E. & Hjartarson, H. 1974 *Geophys. Norv.* **31**, 1–8.
Hurley, P. M., Pinson, W. H., Nagy, B. & Teska, T. M. 1971 *Mass. Inst. Technol. 19th Annual Prog. Rep.*, no. 1381, pp. 1–4.
Kvenvolden, K., Lawless, J., Pering, K., Peterson, E., Flores, J., Ponnamperuma, C., Kaplan, I. R. & Moore, C. 1970 *Nature, Lond.* **228**, 923–926.
Lowe, D. R. 1980 *Nature, Lond.* **284**, 441–443.
McGregor, V. R. 1973 *Phil. Trans. R. Soc. Lond.* A **273**, 343–358.
Miller, S. L. & Orgel, L. E. 1974 *The origin of life on Earth*. Englewood Cliffs: Prentice-Hall.
Morris, R. C., Thornber, M. R. & Ewers, W. E. 1980 *Nature, Lond.* **288**, 250–252.
Muir, M. D. & Hall, D. O. 1974 *Nature, Lond.* **242**, 376–378.
Muir, M. D. & Grant, P. R. 1976 In *Early history of the earth* (ed. B. F. Windley), pp. 595–609. London: Wiley-Interscience.
Muir, M. D., Grant, P. R., Bliss, G. M., Driver, W. L. & Hall, D. O. 1977 In *Chemical evolution of the early Precambrian* (ed. C. Ponnamperuma), pp. 155–170. New York: Academic Press.
Nisbet, E. G. 1980 *Nature, Lond.* **284**, 395–396.
Noda, H. (ed.) 1978 *Origin of life*. Tokyo: Centre for Academic Publishing.
Oehler, D., Schopf, J. W. & Kvenvolden, K. A. 1972 *Science, N.Y.* **175**, 1246–1250.
Oparin, A. I. 1924 *Proiskhozdenic zhizny*. Izd. Moskovski Rabochii.
Pflug, H. D. 1978 *Naturwissenschaften* **65**, 611–615.
Pflug, H. D. & Jaeschke-Boyer, H. 1979 *Nature, Lond.* **280**, 483–486.
Pidgeon, R. T. 1978 *Earth planet Sci. Lett.* **37**, 421–428.
Robinson, R. 1968 *Proc. R. Soc. Lond.* B **171**, 2.
Rossignol-Strick, M. & Barghoorn, E. S. 1971 *Space Life Sci.* **3**, 89–107.
Rutten, M. G. 1971 *The origin of life*. Amsterdam: Elsevier.
Schidlowski, M. 1978 In *Origin of life* (ed. H. Noda), pp. 3–20. Tokyo: Centre for Academic Publishing.
Schopf, J. W. 1975 *Origins of life* **7**, 19–36.
Schopf, J. W., Oehler, D. Z., Horodyski, R. J. & Kvenvolden, K. A. 1971 *J. Paleont.* **45**, 477–485.
Scott, W. M., Nagy, N. & Nagy, L. A. 1970 *Nature, Lond.* **225**, 1129–1130.
Siever, R. 1977 In *Chemical evolution of the early Precambrian* (ed. C. Ponnamperuma), pp. 13–23. New York: Academic Press.
Shimizu, M. 1976 *Precamb. Res.* **3**, 463–470.
Smith, J. W. & Kaplan, I. R. 1970 *Science, N.Y.* **167**, 1367–1370.
Sylvester-Bradley, P. C. 1975 *Proc. R. Soc. Lond.* B **189**, 213–233.
Trendall, A. F. 1973 *Econ. Geol.* **68**, 1080–1097.
Walker, J. C. G. 1977 In *Chemical evolution of the early Precambrian* (ed. C. Ponnamperuma), pp. 1–11. New York: Academic Press.
Walter, M. R. 1972 In *Archaean cherty metasediments: their sedimentology, micropalaeontology, biogeochemistry and Significance to mineralization* (ed. J. E. Glover & D. I. Groves), pp. 1–10. University of Western Australia.
Walter, M. R. (ed.) 1976 *Stromatolites*. Amsterdam: Elsevier.
Walter, M. R., Bauld, R. J. & Block, T. D. 1972 *Science, N.Y.* **178**, 402–405.
Walter, M. R., Buick, R. & Dunlop, J. S. R. 1980 *Nature, Lond.* **284**, 443–445.
Walters, C. 1979 In *Abstr. 178th Am. Chem. Soc., Geoc.* **5**, part 1. Washington, D.C.
Watson, J. 1979 *Yorks. geol. Soc.* **41**, 145–162.
Wickramsinghe, N. C. 1974 *Nature, Lond.* **252**, 462–463.
Viljoen, M. J. & Viljoen, R. P. 1969 *Geol. Soc. S. Africa spec. Pub.* no. 2.

Discussion

L. J. ALLAMANDOLA (*Astrophysics Laboratory, Leiden University, The Netherlands*). Dr Brooks has made the point that, although their origins are not yet known, many complex organic molecules (including ring compounds) have been found in meteorites. While the connection may not be obvious, our experimental results at Leiden on the chemical evolution of grain mantle analogues may provide a clue to the origins of these complex organic molecules.

When a 10 K mixture of $CO:CH_4:NH_3:H_2O$ (mixed in the ratio 10:4:1:2) is irradiated and allowed to warm up to room temperature under vacuum, it is found that 10^{-3} of the original material has been converted into a non-volatile residue that is water and methanol soluble. The infrared spectrum of the residue shows a very broad absorption between 3500 and 2000 cm^{-1}, suggesting the presence of the carboxylic acid functional group while the region between 1200 and 1800 cm^{-1} indicates the presence of amino groups. Professor de Jong, using high resolution mass spectrometric techniques, has found that as the material is put in the direct probe of the mass spectrometer and heated to 400 K, apart from a small amount of urea ($(NH_2)_2CO$), CO_2 is released simultaneously with a material of relative molecular mass 82. This, together with the intensity ratios in the mass spectrum, suggests that amino-pyroline rings make up a substantial part of the residue. Whether they are joined together in a polymeric form with carboxylic acid groups terminating the polymer or in smaller units, cannot be said at this time. The observations that these rings make up only a small part of the material and are not released until a temperature of 350–400 K is reached suggests that, if these or similar ring containing compounds are made in grain mantles, it may be impossible to detect their presence in the interstellar medium with normal submillimetre techniques.