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Search for Biochemical Fossils on Earth and Non-Biological Organic Molecules on Jupiter, Saturn and Titan

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Recognizable remnants of ancient biochemicals may survive under mild/moderate geological environments. Acyclic isoprenoid hydrocarbons, cyclic hydrocarbons with terpenoid carbon skeletons (e.g. hopanes) and vanadyl and nickel porphyrins have been isolated from organic matter, including petroleum, in Phanerozoic sedimentary rocks. Remnants of lignin have also been found. Usually, carbohydrates do not survive long; they degrade and/or react with other organic substances to form macromolecular matter. Proteins, e.g. apparently those in dinosaur bone collagen, break down relatively rapidly. Life arose during the Precambrian and potential biochemical fossils, e.g. n-alkanes, 2,5-dimethylfuran have been isolated from Precambrian kerogens. Traces of hydrocarbons, NH_3, PH_3 occur on Jupiter and Saturn. Hydrocarbons, N_2 and HCN, the latter a key intermediary in the laboratory abiological syntheses of amino acids and nucleic acid bases, are present on Titan where life could not have evolved. Precursor abiological organic molecules of some complexity may have been synthesized on Titan and the Jovian planets.

Definitive remnants of syngenetic biochemicals are of increasing interest to earth scientists. The reason for this is that biochemical fossils can elucidate paleobiological environments which existed during parts of the Earth's history. Furthermore, if well preserved, these chemical substances may indicate the types of organisms that lived in the past and they may also help to explain constraints of the diagenesis, catagenesis and metagenesis of organic matter. Biochemical fossils are defined as organic molecules which preserved the basic structural entities or the carbon skeletons of their parent biochemicals, or which are known degradation products of such biochemicals. Pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane) are probably the best known and most thoroughly studied biochemical fossils in sedimentary rocks and petroleum [1, 2]. These acyclic saturated isoprenoid hydrocarbons are generally considered to be derived mainly from the phytyl chain of chlorophyll [3–6]. These isoprenoid structures occur in nature as minor or trace components of a number of organisms. For example, pristane had been detected in marine benthonic and planktonic algae [7] and pristane and phytane in zooplankton [8, 9]. Furthermore, squalene, an unsaturated acyclic isoprenoid hydrocarbon ($C_{30}H_{50}$), occurs in relatively large quantities in shark liver oil [10], and in numerous plant and animal tissues; a number of prominent pentacyclic terpenoid molecules (oleanane-, lupane-, ursane-types) may be derived from squalene. Some fossil pentacyclic terpenoid hydrocarbons in sediments may have been ultimately derived from squalene. Pristane and phytane and the pentacyclic hydrocarbons serve as illustrations of the generic, structural relationships between precursor biochemicals and biochemical fossils.

Because hydrocarbon and heteroatomic biochemical fossils may enhance the understanding and evaluation of paleontological and micropaleontological findings, they need to be analyzed and treated with appropriate constraints.

(a) Identifications, of course, need to be unambiguous, e.g. gas chromatographic characterization without mass spectrometric confirmation no longer suffices.

(b) Rock samples should be collected after the regional stratigraphy, sedimentary petrology and structural geology have been determined in detail; the assistance of local field geologists familiar with the area is usually of considerable benefit in selecting proper samples [11].

(c) The ages of rocks need to be known from isotopic age determinations [12]. If this is not possible, stratigraphic correlations between rocks to be sampled and isotope-dated rocks need to be unambiguous; this, of course, involves considerations of small-scaled details of regional structural geology.
(d) Prolonged heating and pressure after deposition will not only affect the mineral composition and texture of sediments, but organic substances are progressively and severely altered as they approach the graphitic stage [13, 14]. Biochemical fossils are destroyed by severe metamorphism.
(e) Weathered and contaminated rocks will, of course, yield biochemical fossils of undeterminable ages, with the possible presence of modern biochemicals.
(f) There is yet another problem to be considered. Most sedimentary rocks are porous and permeable and they can serve as conduits of fluids through geological time [15–18]. Therefore, soluble organic substances which can be readily extracted with solvents could have been introduced into sedimentary rocks any time after deposition, thus their syngenetic nature is of serious concern.
The latter problem implies that the identification of biochemical fossils in solvent-soluble substances, with the exception of those in petroleum which provide limited alternatives for determination, is not the optimum approach [12]. Even though analysis of solvent-soluble organic matter, usually performed by solvent extraction, other chemical steps, elution chromatography and followed by combined gas chromatography-mass spectrometry, is a relatively straightforward process, the more time-consuming analysis of the immobile kerogen is preferable.

Kerogens: Prime Candidates for the Search of Biochemical Fossils

Biochemical fossils are often sought in kerogens because these solid organic substances virtually do not migrate at all. Kerogens are insoluble in common organic or aqueous alkaline solvents and are formed from biochemicals released by decayed organisms. It seems preferable to refer to kerogens in the plural form because the nature of these polymer-like substances varies, often within the same unit of rock. Kerogens usually occur finely disseminated in sedimentary rocks, and constitute the most abundant organic substance on Earth, $\approx 10^{21}$ g in sedimentary rocks [19–21] vs. $\approx 10^{18}$ g of coal on Earth plus the estimated petroleum in reservoir rocks [22].
The analysis of the immobile kerogens is a rather complex and time-consuming procedure. Bulk properties of kerogens can be established from H/C, O/C atomic ratios [23–25] (where the former may be plotted against the latter to give "van Krevelen diagrams" [26]), transmitted light, reflectance and fluorescence microscopy [27–29], ^{13}C-NMR cross polarization with magic angle spinning [30], electron and x-ray diffraction studies [13, 31], differential thermal analysis [32], infrared spectroscopy [33], etc. The results of a number of these analytical procedures indicate that kerogens, at least those which do not have minimal H/C, O/C ratios, bear some resemblance to proposed structural models of asphaltenes [34], the suspended colloidal solids in petroleum. In many kerogens, stacks of a few aromatic sheets with cycloalkane, heterocyclic and acyclic components seem to appear either randomly oriented or in clusters [35]. The stacks may be connected by aliphatic hydrocarbon, ether, ester, ketone or sulfide, etc. bridges. Increasing temperatures and pressures promote an increasingly parallel orientation of the aromatic sheets, loss of heteroatomic components [35] and the rearrangement of the randomly oriented stacks into aggregates or clusters [31]. Even kerogens containing very low H/C, O/C ratios may accomodate some aliphatic and heteroatomic moieties, depending on the sizes and relative spatial configurations of the atomic sheets. The origin and evolution of kerogens, together with their demonstrated hydrocarbon and heteroatomic constituents, suggests that these polymer-like substances may act as protective enclaves for syngenetic biochemical fossils. To identify such structures, it is necessary to differentiate those moieties which are integral parts of the macromolecules from the components that are bound to kerogen surfaces or are entrapped in the kerogen matrix (in the latter case as in a molecular sieve).
The identification of specific organic moieties, which may be candidates for biochemical fossils, needs other analytical approaches than those noted above. Such organic compounds are generally determined by standard techniques used in polymer chemistry for the degradation of macromolecules. Oxidative degradations with e.g. H_2CrO_4, O_3, $KMnO_4$, have been used as well as hydrogenation [36–40]. The problem with these procedures is that they introduce or subtract heteroatoms from the kerogenous polymer-like matter. Pyrolytic degradation has been widely used [12, 41, 42] and, on a number of occasions, with considerable success. Vacuum pyrolysis of kerogens looks promising [43–45] and has yielded potential biochemical fossils even from Precambrian rocks. Pyrolytic degradation does produce, however, inter- and intramolecular rearrangements. Primary moieties, which were originally present in kerogens, can be liberated only if the experimental conditions are optimized to ensure the evolution of minimal abundances of secondary products. This often involves vacuum pyroly-

sis at sequentially increasing temperatures [45] and the selection of the most favorable temperatures, pressures, pyrolysis time, sample mass and thickness [46].

Phanerozoic Biochemical Fossils

The Phanerozoic eon spans the last ≈13% of the Earth's history and it contains numerous well-characterized sedimentary rocks. Generally, these sediments and their organic constituents begin to become increasingly abundant and well-defined, respectively, during the Paleozoic and proceeding through the Mesozoic and Cenozoic eras to the very present. The types of organisms which evolved or became extinct during the various periods of the Phanerozoic and parts of the Precambrian, are either known or can be estimated with reasonable assurance. Therefore, one has a concept of permissible biochemical precursors within a framework of given time intervals. This is based, of course, on the biochemistry of extant species, with assistance of "evolutionary trees". These are constructed by the comparison of similar sequences of the molecular constituent units of the protein and nucleic acid biopolymers from different organisms, by using mathematical methods of numerical taxonomy [47, 48]. Effectively, a dual approach has evolved in the quest of identifying biochemical fossils. One involves studies of modern biochemicals, and then proceeds to the characterization of the older biochemical fossils. The other approach starts from the examination of the most ancient carbonaceous matter on Earth and then proceeds to studies of progressively younger organic substances. After a sufficient body of data has been secured from both of these experimental processes and the results reconciled within a framework of continuum, the search for paleobiochemicals and the understanding of evolutionary trends will be enhanced; it is expected that the diagenesis, catagenesis and metagenesis of organic substances will also be elucidated.

It is well known that the major organic components of extant organisms are proteins, lipids and carbohydrates, with lesser amounts of DNA, RNA and other biochemicals, such as the various porphyrin moieties. However, it is no longer sufficient to refer to proteins per se. Different amino acids assembled in different sequences in the biopolymers determine the physiological functions of peptides and proteins, however, complete sequencing data is not yet available for many proteins and peptides. The available nucleic acid sequencing information is also far from sufficient. A number of macromolecules containing/consisting of carbohydrates and lipids are somewhat better understood.

After the death of organisms, degradation of biochemicals proceeds relatively rapidly. First, tissues disintegrate and then the organic constituents are depolymerized. Bacteria and other microorganisms exert a major role in these processes [49]. Next, a random repolymerization and polycondensation of molecular moieties occur leading to humic substances [50] and protokerogens. It is not known for certain but macromolecular substances/protokerogens may be formed in a few decades or even more rapidly [51]. The changes which occur during this stage are complex; they involve the modification of the carbon skeletons of many molecules and often alterations of the compositions of heteroatomic groups. Bacteria again play an important role during this diagenetic stage. If the environment is aerobic for a reasonable length of time the organic matter is, of course, fully oxidized and lost from the system; CO_2, H_2O are the major oxidation products.

Carbohydrate molecules may not survive very long as syngenetic biochemical fossils in the ordinary geological milieu, even when the environments are anaerobic. For example, the quantity of carbohydrate hydrolyzates was depleted by 50% between ≈ 50 years and ≈ 750 years in two marine sediments from the Santa Barbara Basin. The total organic content of the two sediments remained approximately the same [52]. Glucose, galactose, mannose, ribose, xylose, arabinose, fucose and rhamnose were liberated from both samples by hydrolysis at 100 °C for 90 min with $2N$ H_2SO_4 after free sugars and water-soluble polysaccharides had been removed by repeated water extraction. Carbohydrates readily react with other substances, such as amino acids, to form humic acids [53, 54], and then probably protokerogens. However, virtually all known biological hexoses and pentoses can be degraded to only two specific substances: 2,5-dimethylfuran and 2-methylfuran, respectively. Hexoses and pentoses are first degraded to 5-hydroxymethylfurfural (and then to 5-methylfurfural) or furfural, respectively [55], which then yield 2,5-dimethylfuran or 2-methylfuran by the reduction of alcohol and aldehyde groups (Fig. 1). Furans are stable com-

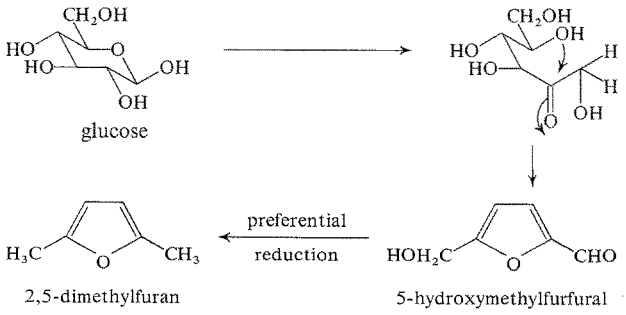

Fig. 1. Reactions yielding 2,5-dimethylfuran from glucose; some of the intermediate compounds and steps are illustrated

pounds; they are known to survive for reasonable lengths of time up to 700 °C in the laboratory [56]. 2,5-Dimethylfuran has been considered to be a biochemical fossil of carbohydrate precursors in sediments [57].

Proteins and peptides are easily hydrolyzed in unprotected, open, geological systems. Probably the most meaningful fossil biochemicals would be proteins and peptides preserved intact in sealed systems. Such environments will largely ensure the syngenetic origin of the components of these biopolymers and thus offer hope for indicating biological species specificity through sequencing of the amino acid constituents. The proteins (collagens) in well-preserved fossil bones are likely candidates for such fossil biochemicals. Modern collagens are organized at four molecular and supramolecular levels. First, the monomer α-chain, which consists of some 1055 amino acids; second, the trimer, a coiled assemblage of three parallel α-chains; third, the microfibril consisting of staggered repeating units of five trimer coils; fourth, the fibril, which is a bundle of aligned microfibrils. Attempts have been made to establish taxonomic differences between species of animals based on modern collagens [58]. Since some proteins seemed to have been preserved in Cretaceous and Jurassic dinosaur bones, collagen analysis appeared promising, even though peptides of uniform lengths could not be extracted from fossil collagens (this may hamper the sequencing of the amino acids [59]). Then the results of a number of analytical techniques have shown that extensive peptide cleavages occurred in the collagen molecules in fossil bones; however, the fragments remained in situ in the fibrils. Perhaps lysyl- and hydroxylysyl-derived cross-links stabilized the structure of the breakdown products in the fibrils [60]. Another aspect of protein/amino acid paleobiochemistry is the racemization of old or ancient amino acids, used for dating fossil materials. Aspartic acid obeyed reversible first-order kinetics in bones of known ages collected from localities which had similar to present temperatures but whose other environmental conditions showed considerable differences. Racemization rates of these samples were consistent with the expected rates, based on the temperature of the localities [61]. Amino acid racemization in various fossils has been widely studied and described in the literature [62–66].

Lignin in woody tissues is attacked almost exclusively by some of the fungi [67]. Apparently lignin degradation occurs in aerobic environments, or at least under conditions where oxygen can be transferred or dehydrogenation can take place [50]. However, lignin may survive reasonably intact if it is enclosed in protective environments before fungal degradation commences or becomes effective. The silicified conifer, *Araucarioxylon arizonicum,* from the Triassic Chinle formation ($\approx$ 200 million years old) in the Petrified Forest in Arizona, provides one example [44]. Vacuum pyrolysis of the organic matter liberated from interior sections of black silicified wood yielded a number of characteristic moieties. The pyrolyzates obtained at 600 °C included alkylbenzenes, phenol, cresols, xylenols, indenes, benzofurans and naphthalenes. Traces of one of the key lignin indicator compounds in geological environments, syringaldehyde (3,5-dimethoxy-4-hydroxybenzaldehyde) [68], were obtained by vacuum pyrolysis at 450 °C. A modern spruce lignin standard, prepared and pyrolyzed identically, yielded the same products. Thus, characteristic lignin degradation products may have long lifetimes under suitable environments in the geological record.

Although there are many possible structures for porphyrins, only a limited number occur in sediments and petroleum; their concentration varies from less than 1 ppm to $\approx$0.4% [69]. Porphyrin paleobiochemistry has a historical significance. Treibs in 1934 identified some of these specific pigments in a Triassic shale of $\approx$ 200 million years old [70]. This finding, followed up by further definition of these compounds by Treibs in 1935 and 1936 [71, 72] provided the necessary impetus for modern studies on biochemical fossils. Probably the most common porphyrins in sedimentary rocks consist of tetrapyrrole nuclei, where the four pyrrole molecules are joined by methine bridges and where methyl, ethyl substitutions, and one isocyclic ring are attached to respective pyrrole units. Nickel or vanadyl (VO^{2+}) ions are held in the center of the tetrapyrrole nuclei. The chlorophylls [69, 70, 73], hemin, bacteriochlorophylls and porphyrin enzyme systems [69] are the probable precursors of the porphyrin biochemical fossils. The evolution of the vanadyl and nickel complexes is not yet sufficiently understood and it appears to be a complex process. It has been proposed [69] that chlorophyll *a* is converted to pheophytin *a* by the loss of Mg^{2+}; next the removal of the phytyl ester chain yields pheophorbide *a*, which through a number of steps, mainly involving loss of CH_3OH, CO_2 and O, finally yields deoxophylloerythroetioporphyrin. The nickel or vanadyl complexes of the latter, and their various alkyl-substituted homologs [74], are the common porphyrin biochemical fossils. This degradation pathway is based on diverse laboratory studies [75–77] which did not closely simulate geological environments. Still, the basic structure of porphyrins in rocks resembles the molecular configurations of their modern analogs; also, they are stable structures which are expected to survive for reasonable lengths of time in sediments.

The most extensively studied compounds of paleobiological significance are the hydrocarbons, particularly the alkanes and some of the lipids. Part of the reason for this is that hydrocarbons virtually always constitute the major components of petroleum. Also, recent emphasis on petroleum source substances, such as the hydrocarbon products of wet-pyrolysis of kerogens, is because of their industrial significance. The relatively new exploration methods consisting of comparative source rock-crude oil and crude oil-crude oil correlations based on hydrocarbons, further enhance the importance of these compounds. Among the lipids, decarboxylation of fatty acids to n- and branched alkanes has been studied by numerous investigators in the laboratory [78–80]. As a result of these and other experiments, most acyclic alkanes are usually considered to be decarboxylated fatty acids. They may also be derived from alcohols and esters. Traces of acyclic alkanes also occur in a great variety of extant organisms, including microorganisms, e.g. bacteria [81]. One example for higher plants is the isolation of the n-alkanes and some alkyl-substituted aromatic hydrocarbons from the leaves of the banana plant, *Musa sapientum* [82]. Series of n-alkanes with odd carbon number preference have been commonly observed in living organisms and Recent sediments [82–86]. The odd carbon number preference usually decreases/disappears with progressive catagenesis and age, and is usually absent or diminished in petroleum [85, 87]. With improved instrumentation, mainly mass spectrometry, increasing attention has been focused on another class of hydrocarbons, the various terpenes; these molecules contain two or more isoprene units. Two of the isoprenoid hydrocarbons, pristane and phytane, have been noted before. Cyclic terpenes, both the hydrocarbons and particularly those with oxygen-bearing functional groups, are widely recognized constituents of plants and many animal tissues. Steroids are tetracyclic triterpenoids; the corresponding hydrocarbons are the steranes, found in sediments and petroleum. Relatively large abundances of the pentacyclic hopane series have been found in cyanobacteria [88]; they also occur in ferns [89]. The C_{28}-pentacyclic triterpane hydrocarbon, 17α(H),18α(H),21β(H),28,30-bisnorhopane has been isolated from the Montery shale, offshore in the vicinity of Santa Barbara, California, as well as in many California crude oils [90]. Certain projections have been made about the chemical pathways leading to this biochemical fossil during diagenesis. It is possible that this compound was derived from adipedatol, a fern triterpenoid of the 30-norhopane type which possessed a hemiacetal linkage between C-22 and C-28. Hydrolysis would result in a CH_2OH group at C-18, which after oxidation to the corresponding carboxylic acid and subsequent decarboxylation would produce the C_{28}-pentacyclic hydrocarbon. This can be accomplished by accepted geochemical processes, but other feasible diagenetic pathways have also been considered [90]. This may serve as yet another illustration that the diagenesis of organic matter and the evolution of biochemical fossils involve complex processes. Other examples of this are the chemical pathways leading to the aromatic hydrocarbons, hydrochrysenes and hydropicenes, probably from the pentacyclic triterpenoids, amyrins [91], and the thermal isomerization and variations in the abundances of steranes [92]. Reactions implicated in the evolution of the isomers of methyl- and dimethylphenanthrenes and methyldibenzothiophenes in sedimentary rocks in Western Canada also attest the complexity of the maturation of biological precursors [93].

Finally, one virtually unexplored aspect of Phanerozoic and Precambrian paleobiochemistry needs to be briefly considered. This is the effect of microorganisms and biochemicals on the evolution of certain ore deposits [94–96]. It is known that some of the uranium minerals and part of the gold is chemically related to kerogens in the Precambrian Witwatersrand carbon seams [97]. Also, certain species of cyanobacteria can accumulate a significant amount of copper from aqueous solutions [98] and *Pedomicrobium*-like budding bacteria may affect manganese and iron deposition [99]. Searching for pertinent biochemical fossils and associated biological/organic chemical processes relevant to the concentration of metals into ore deposits could be beneficial.

Search for Precambrian Biochemical Fossils

It is more difficult to find biochemical fossils in the Precambrian than in the Phanerozoic because outcrops of rocks which remained substantially unaltered by heat and pressure are far less abundant in the Precambrian record than in younger geological eras. Also, it appears that syngenetic organic matter is less well preserved in Precambrian than in Phanerozoic rocks; this is particularly noticeable in the Archean ($> 2.5 \times 10^9$ years ago). Still, biochemical fossils and potential biochemical fossils have been described from the Precambrian [36, 37, 39, 40, 42, 45, 100, 101]. According to several investigators, paleobiochemical information from this period of time is of considerable significance because life on Earth must have arisen during the Precambrian. This is one of the reasons why the identification of Precambrian biochemical fossils must be supported by strict and compelling evidence. There are a number of problems which make the search and identification of Precambrian biochemical fossils difficult under such strict

Fig. 2. A photograph of one of the Belingwe stromatolites in Zimbabwe. These sedimentary rock structures were built with the aid of cyanobacteria $\approx 2.7 \times 10^9$ years ago. The structure shown in this photograph is often considered to be the oldest best preserved stromatolite. Scale bar shows 20 cm (photographed by and reproduced with the permission of A. Martin)

constraints. First, several of the biochemical fossils reported in the literature are solvent-soluble substances which may have entered the rocks any time after deposition. This is particularly true for early analytical studies. Second, most Precambrian kerogens, particularly those in the oldest Archean rocks, have very low H/C, O/C atomic ratios attesting to considerable aromatization and loss of heteroatoms during this long period of geological time. Third, the diagenesis and catagenesis of organic matter is not yet sufficiently understood; the proper understanding of these processes would greatly aid the critical evaluation of the analytical results and identifications. Finally, many Precambrian rock samples analyzed in the laboratory have not been collected with appropriate stratigraphic and structural controls and, on occasions, even the accuracy of their ages are open to question.

Precambrian kerogens consist basically of aromatic moieties [102]. However, the isolation of series of acyclic hydrocarbons and heteroatomic molecules has been reported by various investigators [100–103]. The latter consist of thiophenes, furans, tetrahydrofuran and tetrahydropyran, all occurring as minor constituents. 2,5-Dimethylfuran isolated by vacuum pyrolysis from the kerogen in a 2.7×10^9 years old Belingwe stromatolite in Zimbabwe, and analyzed by gas chromatography-mass spectrometry, constitutes an interesting challenge [45]. A series of control experiments points to the possibility that this moiety is not a contamination and the lack of all other dimethylfuran isomers suggests biological origin. Also, the abundance of 2,5-dimethylfuran in the Belingwe stromatolite kerogen is considerably higher than the maximum experimentally determined uptake of the likely precursor sugars by kerogens [104]. Still, without proper knowledge of kerogen diagenesis/catagenesis and because of the great antiquity of this rock (Fig. 2), one may only refer to this organic moiety as a potential biochemical fossil.

The oldest generally accepted microfossils occur in the $\approx 2.0 \times 10^9$ years old Gunflint iron formation in Ontario, Canada [105, 106]. There are reports that morphologically much simpler microfossils are present in various older rocks, some approaching 3.5×10^9 years in age. Thus, it would be beneficial to gain paleobiochemical data, established by compelling evidence and supportive of these very old and simple microstructures/microfossils. A conservative approach to the identity of the early remnants of life appears to be appropriate.

There is another aspect which is of increasing interest. The Moon was subjected to heavy bombardment by relatively large objects until $3.9–4.0 \times 10^9$ years ago [107, 108]. The surfaces of Mercury, Mars and apparently Venus are also covered by an abundance of impact craters. Is it likely that the Earth was unique and avoided these catastrophic events? The oldest known rocks on Earth are found in the Isua area in Southwestern Greenland and they are $\approx 3.8 \times 10^9$ years old [109, 110]. These rocks consist of gneisses and metamorphosed sediments. The latter attest the existence of a hydrosphere and atmosphere at the time of deposition. It seems that prior heavy bombardment of the Earth with probably its considerable effects on the atmosphere, hydrosphere and lithosphere should have also affected prebiological organic syntheses. Such syntheses are necessary precursors to life and so is the assemblage of abiological monomers into functional biopolymers in primordial soups. These catastrophic conditions would not have boded well to the survival of the first fragile protocells or living cells. But then life may have evolved rapidly on Earth.

Search for Non-Biological Organic Molecules on Jupiter, Saturn and Titan

Laboratory simulation experiments conducted under various environments resulted in the non-biological syntheses of various organic compounds, including biochemicals. This leads to the question of whether it is worthwhile to examine the essence of the accumulated body of simulation data in view of information obtained by space probes to other members of the solar system. This may widen the scope of insight into chemical evolution. Mars appeared at first as

the prime candidate for the search for organic compounds on a relatively large body in the solar system. The two Viking landers on Mars returned a wealth of data, but found no carbon compounds [111] and any experimental implications for life are extremely weak and, in fact, can be explained by plausible inorganic processes [112, 113]. Unfortunately, the data returned by the landers were unable to answer the questions whether life or suitable conditions for prebiological syntheses ever existed on Mars, perhaps during a period of time which would have corresponded to the Precambrian eon on Earth. The Viking landers found that Mars is a bleak, arid land. The temperature at the Viking 2 landing site dropped to about -130 °C during the winter. However, temperatures as high as $+17$ °C have been noted at times at the Solis Planum plain [114], a point closest to the Sun when Mars is at the most sunward point of its orbit. Temperatures as warm as $+25$ °C have been detected in nearby equatorial regions during summer at noon. The atmosphere of Mars is thin; the surface pressure is 6–8 mb [115]. It consists of some 95% CO_2, 3% N_2, 1.5% Ar, 0.1% each of O_2 and CO, with traces of Kr, Ne and Xe. Very little H_2O is present in the Martian atmosphere, yet the polar caps contain both H_2O and CO_2 ices. Most of the water on Mars may lie frozen beneath the surface as permafrost near the polar regions and at greater depths at lower latitudes, and possibly as seasonably varying permafrost ("tempofrost") in widespread regions extending much closer to the equator. Still, there are unmistakable flow structures on the surface, such as scoured channels, river beds and flood plains [115]. Most investigators consider that these structures are the results of flowing water. Perhaps meteorite impacts or subsurface magma intrusions and other surface pressure episodes disrupted the permafrost layer and the overlying rocks, resulting in the release of large quantities of water, causing rather extensive flooding [116]; this may have lasted for only a few days. The surface of Mars is strongly oxidizing; photolysis of H_2O in the atmosphere near the surface produces OH, HO_2 and probably superoxides [117]. The absence of carbon compounds (e.g. from carbonaceous meteorite infall) points to the oxidative destruction of organic substances.

The atmosphere of Jupiter contains small amounts of CH_4, CH_3D, NH_3, PH_3, GeH_4, H_2O, C_2H_6 and C_2H_2 [118, 119]. The main component of Jupiter's atmosphere is hydrogen. Helium is an abundant component; its concentration above the clouds is $\approx 19\%$ [120]. Some of the swirling clouds on Jupiter show a belt-like pattern, and indicate winds blowing from both east and west. The clouds have orange, brown and grey colors. Lightning bolts on Jovian cloud tops have been detected [121]. There is also the Great Red Spot and its associated structures rotating in a counterclockwise motion in the atmosphere. Many of the colors are similar to the colors of the composite organic substance formed by electrical discharges from CH_4, NH_3, H_2O (and on occasion H_2), at much lower hydrogen dilution, in simulated laboratory chemical evolution experiments [122, 123]. Perhaps the highly reducing Jovian clouds contain complex organic substances formed by solar ultraviolet irradiation [124, 125] and possibly lightning.

The bulk of Saturn's atmosphere is hydrogen; He is depleted relative to Jupiter to $\approx 11\%$ above the clouds. Traces of CH_4, C_2H_6, C_2H_2, NH_3 and PH_3 have been positively identified and methylacetylene (C_3H_4) and propane (C_3H_8) have been tentatively identified. NH_3 is strongly depleted in the upper troposphere in comparison with its abundance on Jupiter; this appears to be the results of the condensation of NH_3 as a consequence of low temperatures. The concentrations of CH_4, C_2H_6 and C_2H_2 are approximately the same in both Saturn's and Jupiter's atmospheres [126]. The wind profile of Saturn shows eastward and westward jets; a broad equatorial jet has a maximum eastward velocity of $\approx$ two-thirds of the speed of sound at ≈ -173 °C [127]. Voyagers 1 and 2 also showed huge irregular storm systems. Storms on Saturn and Jupiter last much longer than on Earth. The colors of the cloudtop levels are reminiscent of those of Jupiter, but their generally muted tones may be due to the better mixing of atmospheric chromophores on Saturn [128]. A red oval-shaped spot and other similar features on Saturn, the largest $\approx$ one-tenth the size of Jupiter's Great Red Spot, have been detected [127]. The most remarkable feature of Saturn is its very complex ring system; apparently, water ice is present in the ring material [120].

Titan, one of Saturn's moons, is the only satellite in the solar system which has a substantial atmosphere above its solid surface. The density of Titan is $\approx$ twice the density of water, indicating an $\approx 50:50$ mixture of water ice and rocks. The atmospheric pressure at Titan's surface is 60% higher than at the Earth's surface; it is 1.6 bars. The temperature at the surface of Titan is close to the triple point of CH_4. The temperature decreases to ≈ -200 °C at ≈ 50 km above the surface; at higher altitudes it increases to ≈ -100 °C (Fig. 3). The bulk of the atmosphere is nitrogen, with $\approx 10\%$ methane at the surface and $\approx 1\%$ in the upper atmosphere [120]. Also, lesser amounts of C_2H_6, C_2H_2, C_2H_4 and HCN have been positively identified in the atmosphere of Titan and C_3H_4 and C_3H_8 have been tentatively identified. The hydrocarbon abundances on Titan are substantially higher than on Saturn and Jupiter [126]. Titan has

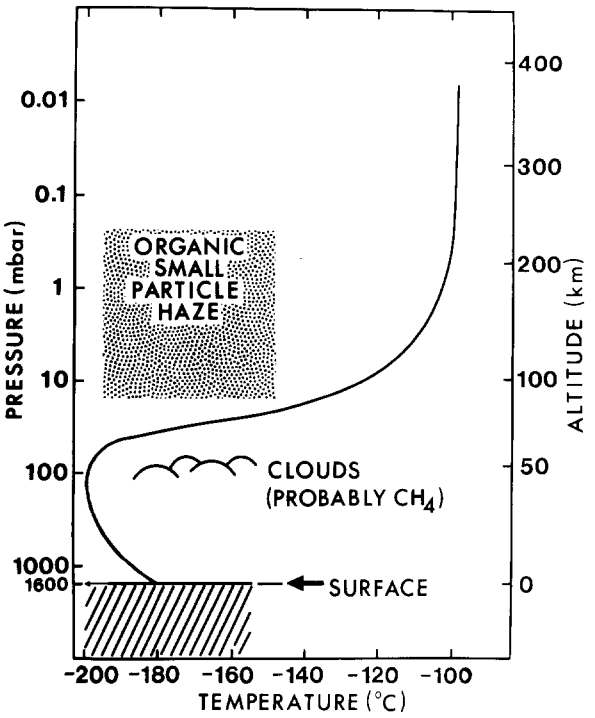

Fig. 3. Temperature profile of Titan. The atmosphere consists mainly of nitrogen. The lowest altitudes of the clouds and the organic haze is not sufficiently known (modified after [126, 127])

an orangish atmosphere which seems to be composed, at least in part, of complex organic molecules. At an altitude of $\approx$ 80–230 km there is a haze layer consisting of very small-sized particulate matter and at $\approx$ 10–$\approx$ 50 km there appear to be clouds of methane [126, 127]. HCN can be produced from N_2 and CH_4 by energetic electron chemistry. This is shown by Titan's ultraviolet dayglow of N_2, N^+ and N [120]. It is interesting in this context that HCN is a key intermediary product of the abiological syntheses of amino acids and nucleic acid bases in the laboratory [126]. Titan and the Jovian planets may be ongoing natural "laboratories" for such abiological synthesis reactions [129–132].

It is generally believed, of course, that organic matter in carbonaceous meteorites has also been produced by abiological syntheses on the meteorite parent body(ies) and/or during the condensation of the solar nebula. It has been recently reported that the $\delta^{15}N$, $\delta^{13}C$ and δD values are different in the acid-insoluble residues from those in the solvent-soluble organic matter (e.g. amino acids, other nitrogenous compounds) of these objects. Both of these fractions were indicative of extraterrestrial origin but it was considered unlikely that these two types of substances were produced from the same reservoirs of C, H and N [133, 134]. This may be significant regarding the complexity of extraterrestrial syntheses. Still, abiological chemical syntheses can persist under harsh conditions in the solar system. This could be significant to considerations of prebiological syntheses on the Early Earth.

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