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CHEMICAL EVOLUTION AND ORGANIC GEOCHEMISTRY

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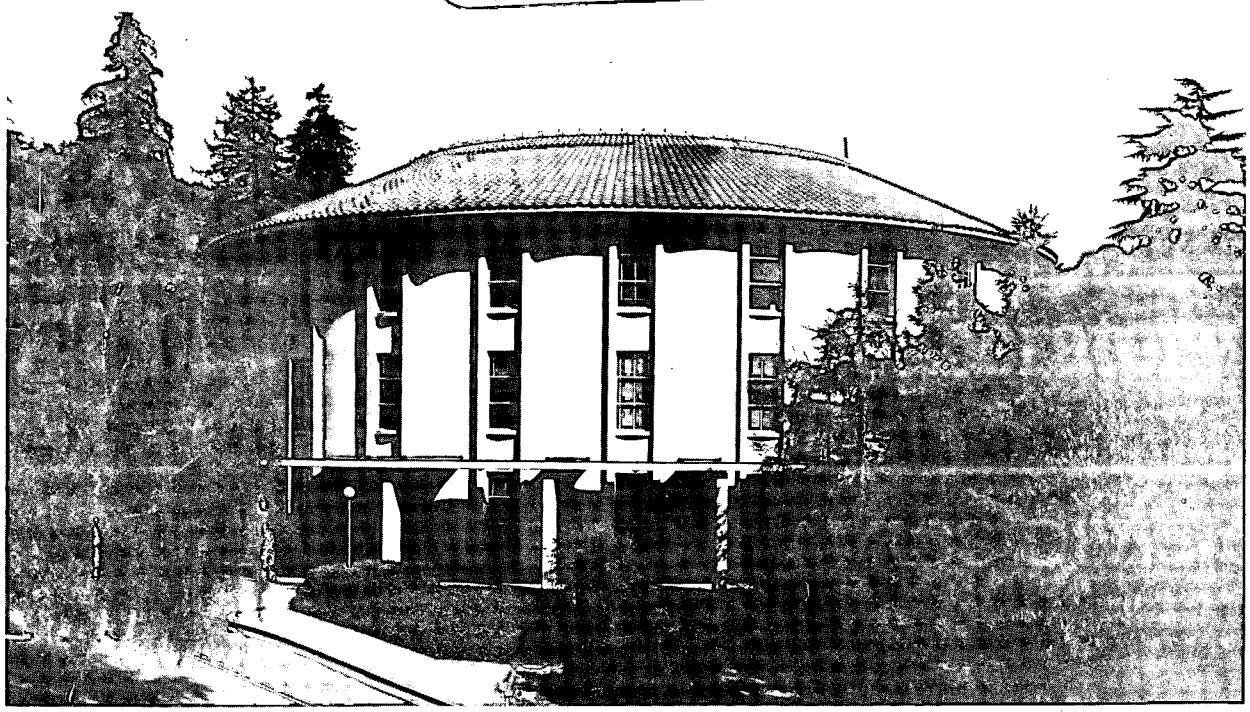
May 1984



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CHEMICAL EVOLUTION AND ORGANIC GEOCHEMISTRY

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Abstract

The relationship is traced between the process of chemical evolution and the evolution of molecular fossils in ancient rocks. The chemical sequences responsible for the construction of the molecular fossils are explained. In addition, the development of biological markers, structures in modern organisms which might be descendants of ancient photosynthetic organisms, are discussed, along with the abiogenic and biogenic origin of modern-day hydrocarbons.

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CHEMICAL EVOLUTION

We had been working on the mechanism of carbon dioxide reduction by green plants, upon which all life on earth today depends.[1] Rather early in that search, back in the late forties, I read a book by George Gaylord Simpson, "The Meaning of Evolution", in which he described the current theories (some of which are still relevant) that life originated on the earth's surface by virtue of the energy inputs from the sun, cosmic rays, lightning and volcanic action.[2] These energy inputs modified the small molecules of the original atmosphere of the earth, randomly creating larger aggregates of atoms, bigger than the original groups which were mostly hydrogen and the simplest of carbon and nitrogen compounds, namely, methane and ammonia. In 1951 we did the first experiments here in Berkeley using the 60-inch cyclotron as the source of a large amount of radiation in a short time. We irradiated not the methane-ammonia-water mixture but carbon dioxide-hydrogen-water; we did not put any nitrogen into this first simulated primitive mixture. We

showed at that time that the input of radiation on a mixture of carbon dioxide-hydrogen-water, with a small bit of iron dissolved in the water, did indeed lead to larger aggregates.[3] Not only did we reduce the CO_2 to carbon monoxide, formic acid and formaldehyde, but the formaldehyde was polymerized to sugar and the formic acid was dimerized to oxalic acid and glyoxylic acid as well as phthalic acid. We thus confirmed the notion that energy inputs on a random collection of primitive molecules which were presumed to have been in the earth's atmosphere would indeed produce reduced molecules of higher molecular weight.

Shortly after those first experiments the physicists came to the conclusion that the primitive atmosphere of the earth was not carbon dioxide and hydrogen, but was mostly methane-ammonia-water. That led to the well known experiment of Stanley Miller and Harold Urey in 1955 in which they performed a similar type of experiment to the one in Berkeley but started with methane and ammonia.[4] Putting nitrogen into the same system which we used originally in 1951 resulted in nitrogen-containing compounds, among them the amino acids. The whole system of primitive energy inputs modifying the initial atmosphere of the earth, whatever it was (carbon dioxide and hydrogen or methane and ammonia) does indeed produce larger aggregations of atoms which could have led to the kinds of molecules which we now find in living organisms.

I felt that we had to perform that initial experiment because of the complications of photosynthesis as we were learning it. I did not feel that photosynthesis could be the first way that life originated on the earth. I intuitively thought that life must have come first by a heterotrophic organism which lived, or was generated, on organic molecules which had been created by this random process. The experiments

which were performed with the 60-inch cyclotron seemed to confirm that notion. As far as I was concerned they were the first actual evidence in that direction. Just to remind you that this is a cycle of thought: I started with carbon dioxide and hydrogen, Urey and Miller came along with ammonia and methane, and that pattern stayed put for many years. Now in the last few years Ponnamperuma has repeated our early experiments. The argument is now going back the other way, that is, the idea that reducing atmosphere escaped very early and the earth's primary atmosphere after it was formed as a solid body for the first billion years was carbon dioxide-water-hydrogen and not methane-ammonia[5,6] Both types of experiments are still valid as far as experiments are concerned. It is, however, now questionable whether the methane-ammonia system is applicable to what is now believed to have been the primitive earth as the initial aggregating materials, particularly molecular hydrogen, were lost to space.

At the national meeting of the American Chemical Society in March 1983 the notion was put forth that the first organisms were indeed photosynthesic, since this random energy input synthetic process does indeed produce porphyrins; that those porphyrins could have been present in the initial environment; and the initial organisms could have been photosynthetic right from the beginning, using porphyrin photosensitizers, particularly if they did not need water as their starting material. These primitive organisms might have used H_2S, for example. The suggestion was made that metal (magnesium) cations, perhaps from sea water, were incorporated into porphyrins. leading to the modern-day chlorophyll molecules that evolve oxygen during photosynthesis.[7]

These are the two introductory streams which led to our concern with chemical evolution and organic geochemistry.[8] I entered this area of research not because I was interested in petroleum, or oil shales, or tar sands. These molecules were residues of ancient times, and we were interested in analyzing really ancient rocks for the possibility of any molecular markers which might have withstood the eons of time.

MOLECULAR FOSSILS

To give you some idea of the time scale when the events we are discussing might have occurred, I would like to point out that it was during the Precambrian period (5 billion years to 500 million years ago) that the initial atmosphere of the earth was presumed to have been lost. The atmosphere in which living organisms were developed during this period was a secondary atmosphere, due to the outgassing of the earth by volcanic action. The secondary atmosphere is now believed to have been more CO_2 than it was ammonia. This argument is ambiguous, but it is the current one.

The time in which the first organisms appeared was in the Cambrian period, evidences for which are available in the rocks themselves. By the time it is possible to find a "form" which can be seen in the rocks, the organisms are pretty well developed. Such organisms appeared in the Bitter Springs Chert in Australia, which is 1.7 billion years old. For about fifteen years it seemed that the Bitter Springs organisms were the oldest microfossil evidence which was available. Recently, however, there appeared evidence for the existence not of individual micro-organisms but what are called stromatolites in geological terms (mats of

blue-green algae, Cyanobacteria) on the surface of a mud in Australia.[9] The mats have a characteristic structure (FIGURE 1) and their age has been found to be 3.4 to 3.5 billion years old. FIGURE 1 shows the stromatolites in the Strelley Pool Chert in Australia, and similar formations have been found in Canada in the older Precambrian rocks. It is easy to see here the surface morphology of the stromatolites, structures formed by the blue-green algae lying one on top of the other. The Strelley Pool stromatolites are similar in morphology and internal structure to younger stromatolites. If the stromatolites do indeed represent at least in part the activities of the blue-green algae, as seems probable based on comparison with modern stromatolites, they would substantiate suggestions that photosynthesis was an effective source of oxygen 3.5 billion years ago. The age of the Strelley Pool stromatolites is 3.5 billion years, which means that living things had evolved before that time and that photosynthetic organisms had evolved as well. Therefore, the whole system of photosynthetic and nonphotosynthetic organisms appeared less than one billion years after the solid earth was formed and had evolved to a fairly substantial level.

To find out which molecular fossils were remnants of these early organisms, we examined the same rocks, or similar ones of the same age, which were rich in organic matter to see if the physical structures of the molecules which the organisms left, subject to some slight ambiguity, would be characteristic. There are a number of arrangements of atoms in a molecule which are clearly not random, not formed by the energy input into single one-carbon-atom molecules which aggregate in a random way, but are very specific structures. We call these "biological

markers" and have been able to find them in very old rocks as well as in petroleum and other high organic residues.

The pathways of construction of molecular fossils are similar to those in modern organisms. Modern organisms make farnesyl pyrophosphate, the C_{15} pyrophosphate, from sugar, and most of the oil-producing plants, such as Euphorbias and Asclepias, put two C_{15} pyrophosphates together as shown in FIGURE 2. The pyrophosphate of one has dropped away and the remaining carbonium is now added on to the double bond, next to the pyrophosphate of the other C_{15} pyrophosphate which is now sticking out of a cyclopropyl ring. The cyclic three-carbon intermediate is the molecule from which a number of different precursors can be formed, following the head-to-head condensation of the two isoprenoid pyrophosphates.

The process involves the removal of one of the pyrophosphates and hooking the remaining farnesyl carbonium ion onto the double bond of another farnesyl pyrophosphate to form the three-membered ring. The second pyrophosphate still remains. This pyrophosphate could drop off and the remaining carbonium ion could migrate in between two carbon atoms of the C_3 ring and then break the ring between C_2 and C_5, in which case there would be four carbon atoms between the two methyl groups marked X. That is, the head-to-head condensation reaction which leads to squalene is the principal way in which the latex-producing plants make the C_{30} hydrocarbon which eventually becomes sterols. Notice the symmetry of the squalene molecule. There are four carbon atoms between the first two branches, which is characteristic of head-to-head condensation reactions. Another way in which this intermediate might open is to break carbon-carbon bond C_2-C_3 without migration, in which case two carbon

atoms would be off to the side and the other two would be connected, leaving a two-carbon-atom branch on the long chain. Between the two bridges there is a quaternary center with a vinyl side chain and two carbon atoms between the two branch points.

If you can visualize the molecule at the bottom of FIGURE 2 without the dotted lines and without the arrows, it forms a structure called Botryococcene which is one of the molecules found in the oil from Botryococcus braunii algae. The oil from that alga was at first thought to be only Botryococcene, a C_{30} compound with six double bonds.[10] However, recently we have found in the oil other compounds ranging from C_{32} to C_{34} and from what we know about the structure we believe that the C_{30} system in this alga can add methyl groups at the double bonds one at a time.

It turns out that one type of structure (squalene) with four single carbon atoms between the two branches, and the other structure with two intervening carbon atoms and the ethyl side chain are found in various natural oils and rocks. We have reason to suppose, therefore, that some of those oils have their origin in microorganisms. There are some even stranger things yet. In FIGURE 2 you can see the head-to-head condensation which can open up in two different ways.[11] You will remember that the farnesyl pyrophosphate itself is formed by head-to-tail condensation and it has only three carbon atoms between the branches, all along the line. It is possible to imagine a head-to-tail condensation of two C_{15} compounds to make a C_{30}, which had only three carbon atoms between the central methyl groups, and it is known. Both of the compounds in FIGURE 2 are the results of head-to-head condensation, but the construction made by head-to-tail condensation is the common prenyl transferase type

of reaction (farnesyl pyrophosphate, C_{15}, geranylgeranylpyrophosphate, C_{30}).

The question is to find out whether there is any evidence for tail-to-tail reactions, and it turns out that they do exist in Archaebacteria and petroleum.[12] If the reaction goes tail-to-tail that would produce two carbon atoms between the branches, creating a compound called biphytenol or biphytane derivative. When the molecule has a C_{30} configuration with two carbon atoms in the middle, we know it is made by the two ends of the molecule way from the phosphates which come together by allylic activation. The oxidase enzyme oxidizes the terminal methyl group, allylic terminal to the double bond, and then those two groups can be hooked together.

These very peculiar molecules are not found as phosphates or acids. In living organisms in a group called Archaebacteria the molecules occur as the diethers of glycerol, very peculiar structures.[13-15] Because glycerol has three hydroxyl groups it is possible to bridge the No. 1 hydroxyl between two glycerines to give a C_{60} compound with two glycerine residues; or it is possible to get a C_{30} which is bridged not between the two glycerines but in a big ring between the No. 1 and No. 2 hydroxyl groups of one glycerine molecule. All of these compounds are known in the Archaebacteria today. By the time petroleum from bacteria of this type appears, the glycerine has long since vanished and the hydrocarbon is all that remains. These particular compounds have been described in the methanogenic Archaebacteria, the oldest kind of living organisms, as well as in various petroleums.[16].

BIOLOGICAL MARKERS

In order to see some relationship between the organic structures that we find in ancient rocks and the organisms which might have created them, we undertook to examine the structures found in modern organisms which might be descendants of ancient photosynthetic organisms.[17] One of these is a green, fresh water alga called Botryococcus braunii which actually forms hydrocarbons (FIGURE 3). This algae is not particularly primitive; it is a nucleated alga so it is quite a long way up the evolutionary scale. The structure of the oil from that alga, called Botryococcene[10,18], has been worked out. We have learned how it is related to some of the other structures in current green plants. There is much interest in this particular alga because of its possible use as a source of hydrocarbons, and experiments have been underway for some time to learn about the structure of the hydrocarbon as well as the methods of its production.[19-24]

Some years ago, even before the advent of the lunar organic material, we began experiments to learn about the hydrocarbon content of various kinds of microorganisms to see whether they could have played a role in the formation of the hydrocarbon markers found in the ancient rocks. Data from some of these experiments is shown in TABLES 1 and 2. The information in TABLE 1 describes the hydrocarbon content of various photosynthetic and nonphotosynthetic bacteria and yeasts. You can see the distribution of hydrocarbons of various kinds, all normalized to 100 for the C_{17} which is the most plentiful. The pristane (C_{19}, an isoprenoid related to phytane (C_{20}) is present in photosynthetic bacteria

Table 1

Hydrocarbons from bacteria and yeast.

Peak heights from mass spectrograms[25]

	Photosynthetic bacteria		Nonphotosynthetic bacteria		Yeast
	Rhodopseudomonas spheroides	*Rhodospirillum rubrum*	*Micrococcus lysodeikticus* (anaerobic)	*E. coli* (anaerobic)	
$n\text{-}C_{15}$	2	0.3	112	10	50
$n\text{-}C_{16}$	7	0.7	95	37	60
Pristane	22	3	55	--	--
ΔC_{17}	--	--	--	--	--
$n\text{-}C_{17}$	100	100	100	100	100
Branched C_{18}	--	--	--	--	--
Phytane	3	--	21	--	--
$n\text{-}C_{18}$	44	10	58	700	500
$n\text{-}C_{19}$	43	13	147	210	450
$n\text{-}C_{20}$	8.8	9	53	200	1000
Alkanes of higher mol. wt. (as fraction of total hydrocarbon)	5%	15%	50%	60%	60% of total hydrocarbons
Major component	$n\text{-}C_{17}$	$n\text{-}C_{17}$	$n\text{-}C_{19}$	$n\text{-}C_{18}$	$n\text{-}C_{20}$

Peak heights are relative to $n\text{-}C_{17}$ peak taken as 100

and Micrococcus while phytane, the hydrocarbon from phytol (the alcohol on chlorophyll, is present in smaller amount. The distribution of these hydrocarbons in bacteria gives a clue as to their various origins and how they might have occurred in petroleum.

The blue-green algae and green algae, both photosynthetic organisms, were also studied (TABLE 2). In the blue-green algae the C_{17} is also the dominant component and also a very peculiar branched C_{18} whose structure we determined along with the normal complement of hydrocarbons in algae.[25,26]

Biological markers are things which are not randomly formed, and if any of the compounds described above are found in an ancient rock or petroleum we can be confident that there was an organism of some type present to produce it.

There are several factors involved in the determination of randomly produced vs. nonrandomly produced structures among the biological markers, both in petroleum and in synthetic systems. A more significant group of biological markers has been defined by my colleague Professor Geoffrey Eglinton.[27] All of these materials have very special structures: cholestane, bis-homohopanoic acid, phytanic acid, etioporphyrin III (from chlorophyll), retene, C_{24} tetracyclic alkane and octamethyldotriacontane, for example. The hydrocarbons are structurally stable enough to be found in ancient rocks and petroleum. More complex structures, such as the vanadium and iron porphyrins, were found many years ago in petroleum by Treibs. One of the major arguments some time ago was that petroleum was biogenic in origin because these particular structures could be formed by biological methods only. We know that the structures are so stable that with random synthesis, in the presence of

Table 2

Hydrocarbons from algae.

Peak heights from mass spectrograms[25]

	Blue-green algae		Green algae	
	Nostoc	Anacystis	Spirogyra	Chlorella
$n\text{-}C_{15}$	0.42	28	--	0.7
$n\text{-}C_{16}$	0.42	3.4	6.7	0.4
Pristane	--	--	22	--
ΔC_{17}	--	--	--	450
$n\text{-}C_{17}$	100	100	100	100
Branched C_{18}	19.4	0.44	--	--
Phytane	--	--	15.5	--
$n\text{-}C_{18}$	0.5	--	58	0.3
$n\text{-}C_{19}$	0.4	--	62	0.1
$n\text{-}C_{20}$	0.4	--	22	--
Alkanes of higher mol.wt.	--	--	Less than 30% of total hydrocarbons	--
Major component	$n\text{-}C_{17}$	$n\text{-}C_{17}$	$n\text{-}C_{17}$	ΔC_{17}

Peak heights are relative to $n\text{-}C_{17}$ peak taken as 100

nitrogen and methane, it is possible to detect the porphyrin structures even if they are present only in trace amounts. The Archaebacteria which produce these compounds today probably existed to produce that same skeleton when the petroleum was laid down or shortly thereafter. That question will come up repeatedly about when the biological markers actually got into the oil.

ABIOGENIC VS. BIOGENIC ORIGIN OF HYDROCARBONS

What would a hydrocarbon collection look like if it were not biological in origin? The lower two curves in FIGURE 4 are hydrocarbon mixtures formed in a nonbiological manner. One of them is formed by a methane discharge, extracting the hexane fraction, and there is an almost continuous distribution of hydrocarbons; no single one dominates. Most of them come out near the C_{17} major peak which is the appearance of the hydrocarbons from an abiogenic synthesis performed on methane. A similar abiogenic synthesis is shown in the Mount Sorrel formation which we believed was a formation partly biogenic and partly abiogenic, but the petroleum formation is mostly abiogenic with random formation, with the dominant peak at the C_{20} position. In a real biogenic rock, however, such as the Posidonian shale (upper curve, FIGURE 4) the hydrocarbons show discrete peaks for each of the molecules; it is not a collection of random structures around some highly favored number, but very discrete peaks. If a sample of hydrocarbon from a rock or oil from a pool contains both biogenic and abiogenic hydrocarbons, the results would have

sharp peaks imposed on top of the continuum (FIGURE 5). This experiment was done on the Onverwacht sedimentary rocks approximately 3.7 billion years old, giving a mixture of both biogenic and abiogenic hydrocarbons as indicated by the continuous background upon which are situated the discrete biogenic molecules, each one characteristically defined.

I feel that the biogenic and biogenic combination represented by the Onverwacht rocks in FIGURE 5 is not characteristic just of ancient rocks. I used to interpret this phenomenon as being the boundary between prebiology and biology, but it may not be. These same processes may be going on today. It is conceivable, and, in fact, there is an argument which I will describe, that the primitive methane which is still oozing out of the center of the deep earth may be the residue of the initial aggregation leading to the formation of the earth. As carbon atoms combine with biological collections which are formed in the last two billion years, they are under pressure and high temperature in contact with the rocks, and they could be integrated into that already-present biogenic material, which could create a modern mixture of abiogenic and biogenic hydrocarbons. The abiogenic hydrocarbons might actually be more recently formed than the biogenic hydrocarbons because of the methane which is known to be oozing out from the deep earth today. The main proponent of the nature of that methane is Professor Thomas Gold, an astrophysicist at Cornell University, and the scientific community is not 100% convinced one way or the other. Gold believes that even today from the deep earth there is a continuous emission of methane which was formed with the primitive earth and which is still escaping from the inside.[28,29]

I thought that question might be answered easily by using the methods of isotopic analysis on the methane which Gold collects from the fissures of the earth. It turns out that there really is not an unambiguous correlation between the ^{13}C defect in the methane from various sources, at least not in my eyes. The primitive methane has several different routes to the atmosphere where it is oxidized, or it can rise through the cracks in the rock, passing through the coal, oil and gas hydrocarbons from the biomass laid down by photosynthesis and be added to the biogenic petroleum and rock formation which we now know to exist.[30]

Professor Geoffrey Eglinton, whose work I described earlier in connection with molecular fossils and biological markers, believes that only about 15% of the known petroleum deposits are unambiguously biogenic. The rest may be biogenic and some of them may actually be abiogenic. He believes this because he finds the oil as being biogenic in terms of the biological markers in the oil, but some of the oils do not have enough biogenic markers to convince him that they are of dominant biogenic origin. This would mean that some of these same processes re underway today. If there are sources of methane that are not biogenic which are contributing to our natural gas supplies and also to the higher hydrocarbons, this would be very significant. We also know that there is carbon dioxide coming out in various ways, going back into the oceans and into the biomass again, affecting long-term evolutionary patterns.

CONCLUSION

The idea of a slow evolutionary process from a nebulous beginning, the concept of aggregation of molecules inside and on the surface of the earth to give rise to all the living things we know today has been expressed. The more recent experiments of chemical evolution and organic geochemistry will indeed bring us closer to an understanding of the evolutionary process.

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FIGURE CAPTIONS

Figure 1 — Surface morphology of conical stromatolites in the Strelley Pool chert, Western Australia (3.5 billion years)[9]

Figure 2 — Structures of terpenoids in plants and algae

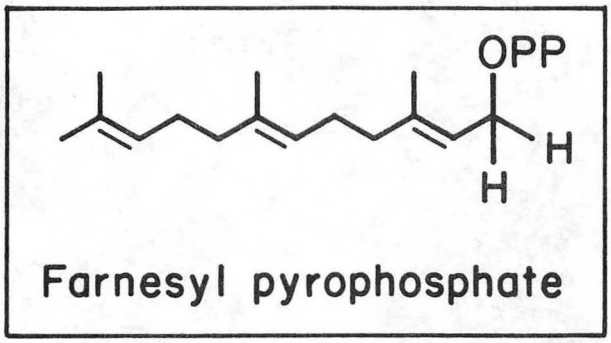
Figure 3 — Botryococcus braunii algae showing formation of hydrocarbons (Wolf[24])

Figure 4 — Gas chromatogram of hydrocarbon fractions from various sources (Ponnamperuma, 1966)

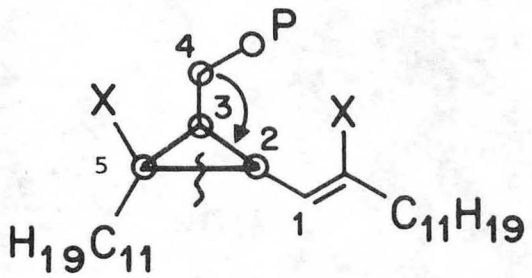
Figure 5 — Gas chromatogram of hydrocarbons from Onverwacht series (3.7 billion years)

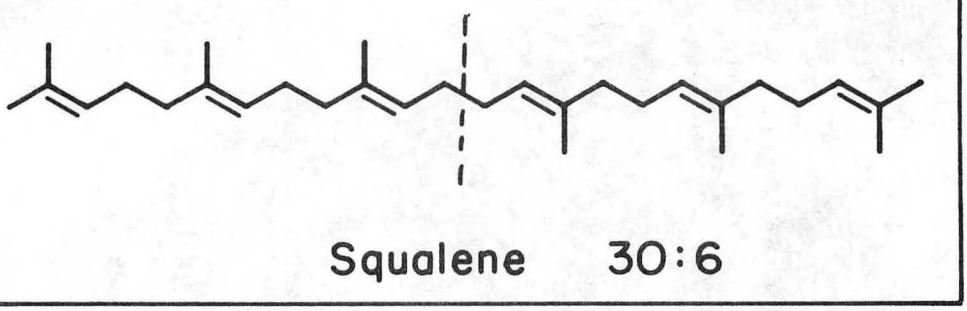
Fig. 1 XBB 834-3549

Surface morphology of conical stromatolites in the Strelley Pool chert. Note elliptical shape of many of the larger cones. This specimen from outcrops west of Strelley Pool at 21°08′ S, 119°00′28″ E. Scale bar, 5 cm.



Farnesyl pyrophosphate





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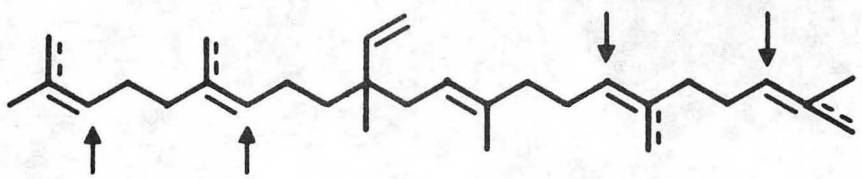

Botrycoccene 30:6

" 34:6

Fig. 2

XBL 834-9444

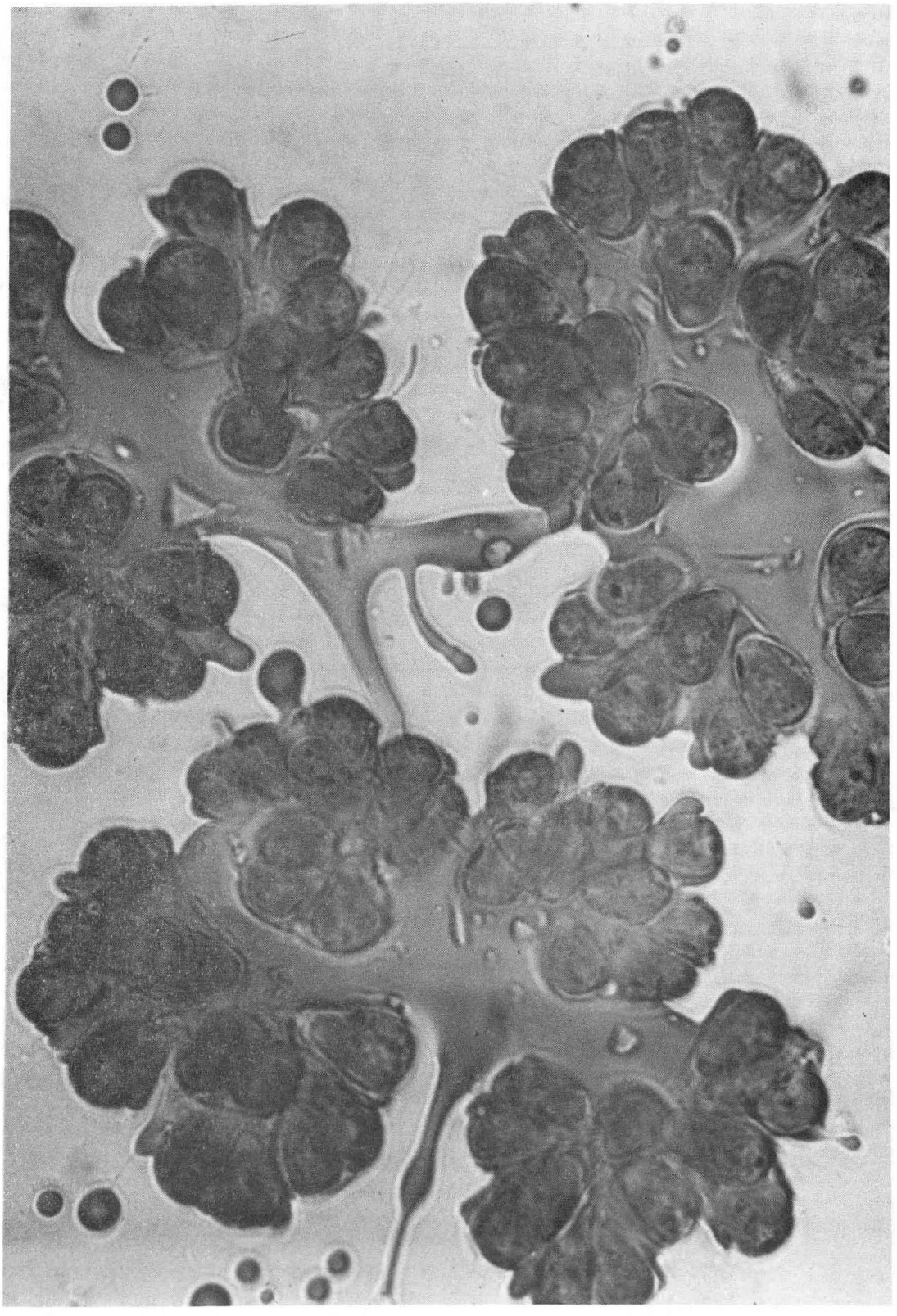

Fig. 3

CBB 835-4582

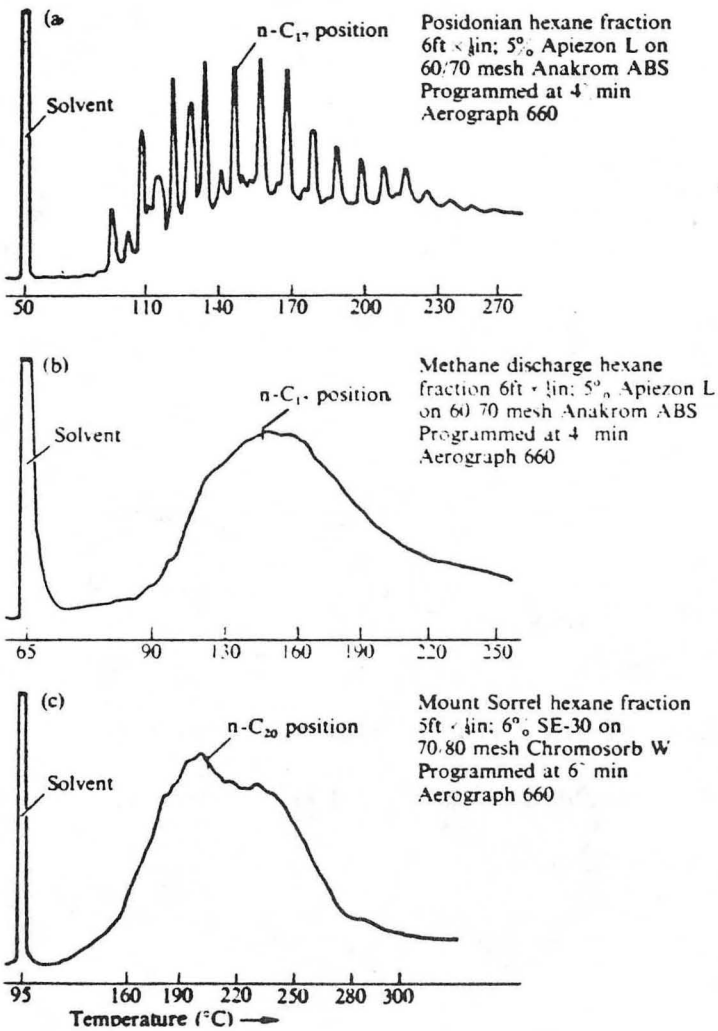

FIGURE 4. Gas chromatogram of hydrocarbon fractions from various sources (Ponnamperuma, 1966).

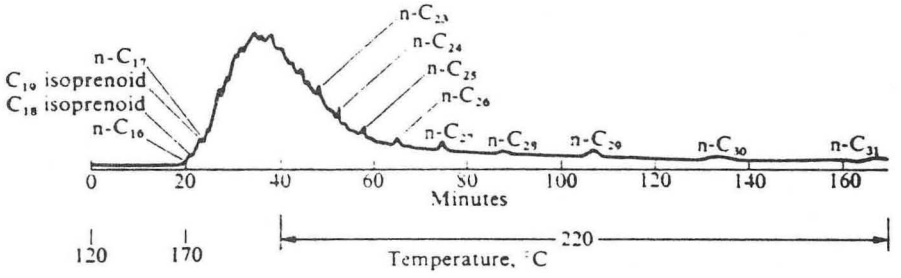

FIGURE 5. Gas chromatogram of hydrocarbons from Onverwacht Series (3.7 billion years)

TECHNICAL INFORMATION DEPARTMENT
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