

# The origin of life

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## Abstract

Microfossil finds have been firmly established at about 3.5 Ga (giga annee =  $10^9$  years), but no rocks older than about 4.0 Ga have been demonstrated, leaving the history of the first 0.6 Ga missing. This gap has been filled by models of the solar system. The origin of the ocean, atmosphere, and much crustal material apparently lies in a heavy rain of comets, subsequent to the catastrophic Moon-forming event. The earliest microfossils are those of the Apex chert in Australia, about 3.5 Ga old. 'Prebiotic' simulations of possible biochemistry have made some progress in recent years, but many obstacles remain, and there is no agreement as to the course of development. The 'ribose nucleic acid (RNA) World', aboriginal 'clay genes', and catalysis on iron-sulfide precipitates are not ruled out. The search for the 'last common ancestor' has reached a point between the Bacteria and the Archaea. It is possible that this organism may have been a thermophile, similar to many modern hot spring organisms. But it is likely to have been an autotroph, and a late development after the true origin of life. Even more speculative are suggestions about the origins of metabolic sequences, in particular the origin of the genetic code. Since all modern organisms share this code (and many other things), there had to be a long history of development during the blank period of Earth history. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The volume edited by Schopf (1983), is still a major source of information on the origin of life, and the text by Miller and Orgel (1974) is still useful, but in the meantime a number of volumes have appeared on this subject, in addition to the periodical litera-

ture. Some are single-author summaries, according to the particular author's interests (Holland, 1984; Shapiro, 1986; Cloud, 1988; Fox, 1988; de Duve, 1991, 1995; Morowitz, 1992; Zubay, 1996; McSween, 1997; Delsemme, 1998). Others are compendia or reports of symposia (Hartman et al., 1985; Schopf, 1992a; Greenberg et al., 1993, 1995; Bengtson, 1994; Deamer and Fleischaker, 1994; Chela-Flores et al., 1995; Bock and Goode, 1996; Chela-Flores and Raulin, 1996; Thomas et al., 1996; Cosmovici et al., 1997). In this review, I will attempt to make sense of these developments, in a few areas in

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particular. There have been two general reviews of this subject in the last decade (Oró et al., 1990; Chyba and McDonald, 1995). Oró (1994), Lazcano (1997), and Lifson (1997) have considered the probable order of the steps leading to life. Deamer (1997) and Russell and Hall (1997) have reviewed many data regarding the possible first cell.

The most impressive thing about the topic of the origin of life is that it is the most interdisciplinary of any science. The subject matter ranges from cosmology and astrophysics to organic chemistry, molecular biology and mathematical theory. Some topics, such as the origin of the elements, are adequately covered elsewhere (McClendon, 1980; Oró, 1994; Zubay, 1996; Delsemme, 1998), but from the beginning of the solar nebula, to the diversification of the last common ancestor, all comes in our purview. And each of the above-mentioned volumes is different in scope and in detail. I will organize this discussion around several, more or less independent, topics, emphasizing recent reviews and other recent developments. However, since the original literature is so voluminous, I have been selective.

## 2. Fossils, chemical and morphological

There are two aspects of the fossil evidence, namely, when did life arise, and what was its nature?

The existence of Archean fossils, both microfossils and stromatolites, is well established by now. This subject has been thoroughly reviewed by Walter (1983), Schopf and Walter (1983), and more recently by Schopf (1992b, 1994).

The oldest well established microfossils seem to be those of the Apex chert of Western Australia (Schopf, 1993; see Figs. 1 and 2. These are cellular, filamentous structures dated at about 3.465 Ga. Many of these resemble modern Cyanobacteria in size and shape (but see below). The fossils are demonstrably indigenous to the chert, shown in petrographic thin sections. Some 11 different taxa were described, but some of these could be developmental variants. Spherical microfossils are also present but are not distinctive and so are only possibly biogenic. Certainly, unicellular organisms preceded filamentous

ones, but no reports of fossils older than those of the Apex chert appear to exist. Other fossils previously described from Warrawoona in Australia are discounted because the collection site could not be relocated. Early stromatolites are found in similar formations and are about as old as the cellular microfossils, but the stromatolites themselves do not contain recognizable fossils.

The usual implication of this and other descriptions of early Archean, allegedly cyanobacterial, fossils is that oxygenic photosynthesis was already extant at that time.

An alternative view is that these fossils may in fact not be of Cyanobacteria but perhaps of anoxygenic (but photosynthetic), filamentous bacteria (Pierson, 1994; Blankenship et al., 1995) or of something entirely different. Pierson (1994) has outlined the diversity of anoxygenic photosynthetic bacteria and their possible involvement in stromatolites. The cells of other bacteria are usually (but not always) narrower than Cyanobacteria; the former may possibly be illustrated in Fig. 1D,E.

Other evidence cited for the early existence of oxygenic photosynthesis is the  $\delta^{13}\text{C}$  of ancient kerogens (Schidlowski et al., 1983; Schopf, 1992b, 1994), so this is useful even in the absence of microfossils. The primary carbon dioxide fixing enzyme of green plants (including Cyanobacteria and many other bacteria) is called, for short, 'Rubisco' (see a modern plant biochemistry text such as in Dey and Harborne, 1997). This enzyme necessarily generates a discrimination against  $^{13}\text{CO}_2$ . The kerogens in the Apex formation and that immediately earlier (Towers) have a  $\delta^{13}\text{C}$  value at least  $-20\%$ , and mostly  $-25$  to  $-35\%$  (Schopf, 1993), in agreement with modern plants. It is worth noting that the presumed high  $\text{CO}_2$  content of the early atmosphere would not relieve, but rather increase, the discrimination against  $^{13}\text{C}$  by Rubisco (Smith and Boutton, 1981).

Other recent reports concern the oldest known sedimentary deposit, the Isua formation in western Greenland. A recent reinvestigation (Moorbath and Whitehouse, 1996) of the age of the Isua supracrustal sequence gave an age of  $3772 \pm 33$  Ma. This is metamorphic and so not fossiliferous, but contains carbon. Mojzsis et al. (1996) and Eiler et al. (1997) have analyzed graphite inclusions in apatite, from these rocks, under the electron microscope and found

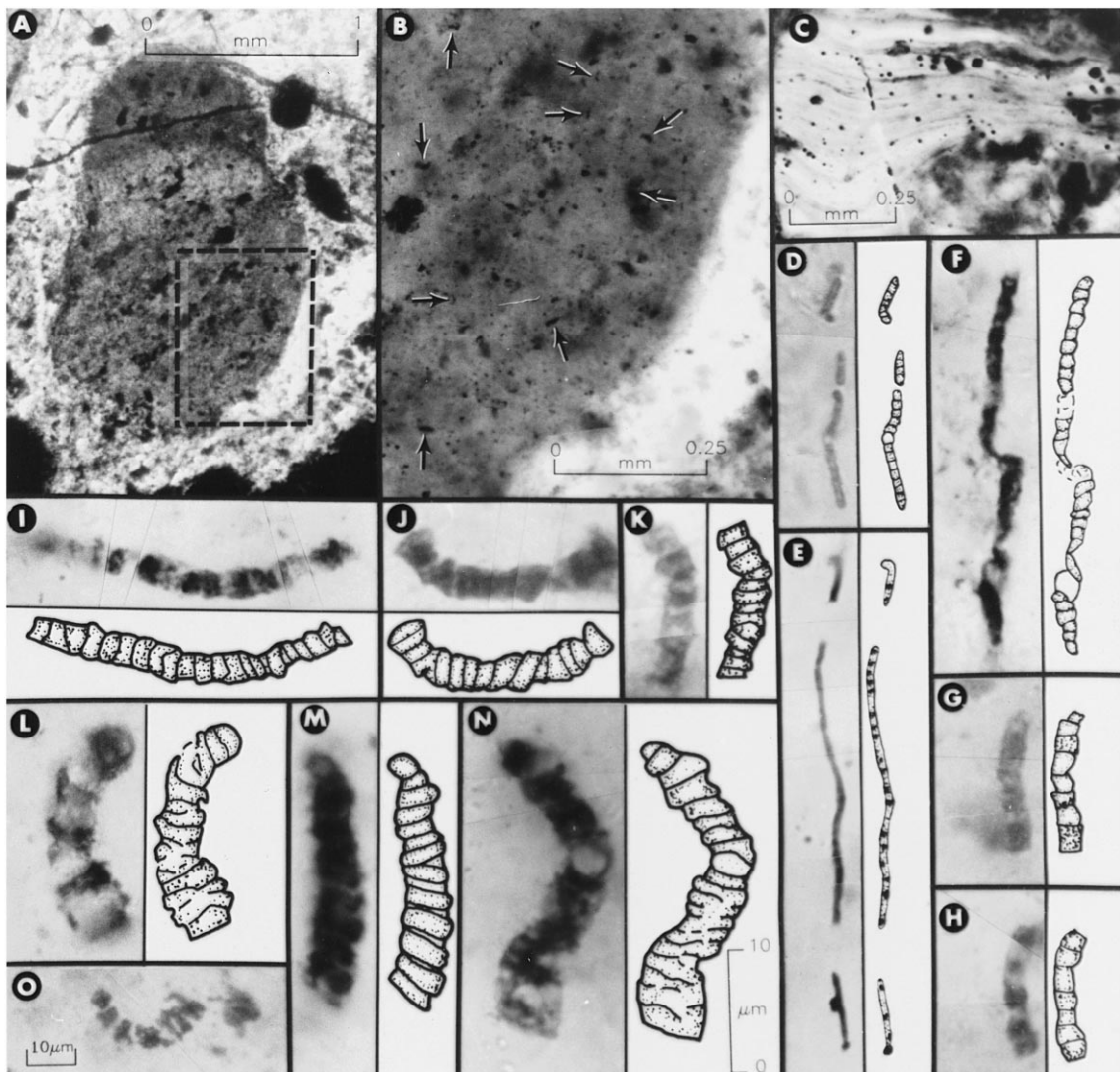


Fig. 1. Microfossils from the early Archean Apex Chert of Australia (from Schopf, 1993, by permission). Stromatolite-like clasts (A,B,C) and micro fossils (D–O, holotypes) with interpretative drawings. Except as indicated, magnification is as shown in (N). (A) shows clast, with boxed area enlarged in (B); arrows point to minute filamentous microfossils. (C) is another clast showing stromatolite-like laminae. (D,E) *Archaeotrichion septatum*; (F) *Eoleptonema apex*; (G,H) *Primaevifilum minutum*; (I,J,K) *Primaevifilum delicatum*; (L,M,N,O) *Archaeosclatorioropsis disciformis*.

discrimination against  $^{13}\text{C}$ , similar to that above. This sample is claimed to be more reliably biogenic than the whole rocks analyzed previously.

Caution is advised, however, because meteoritic carbon can have isotope ratios in the same range as biogenic organic matter.

So, very likely after 1.0 Ga after accretion of the Earth (fossils exist), and possibly after 0.7 Ga (iso-

tope discrimination exists), fully competent life existed on Earth. It was probably photosynthetic, but this cannot be considered the first organism, nor even the last common ancestor (Section 9).

It seems unlikely that significantly older sedimentary deposits will ever be found, since the oldest known igneous rocks are only 4.0 Ga (see table 1 in Nutman et al., 1996).

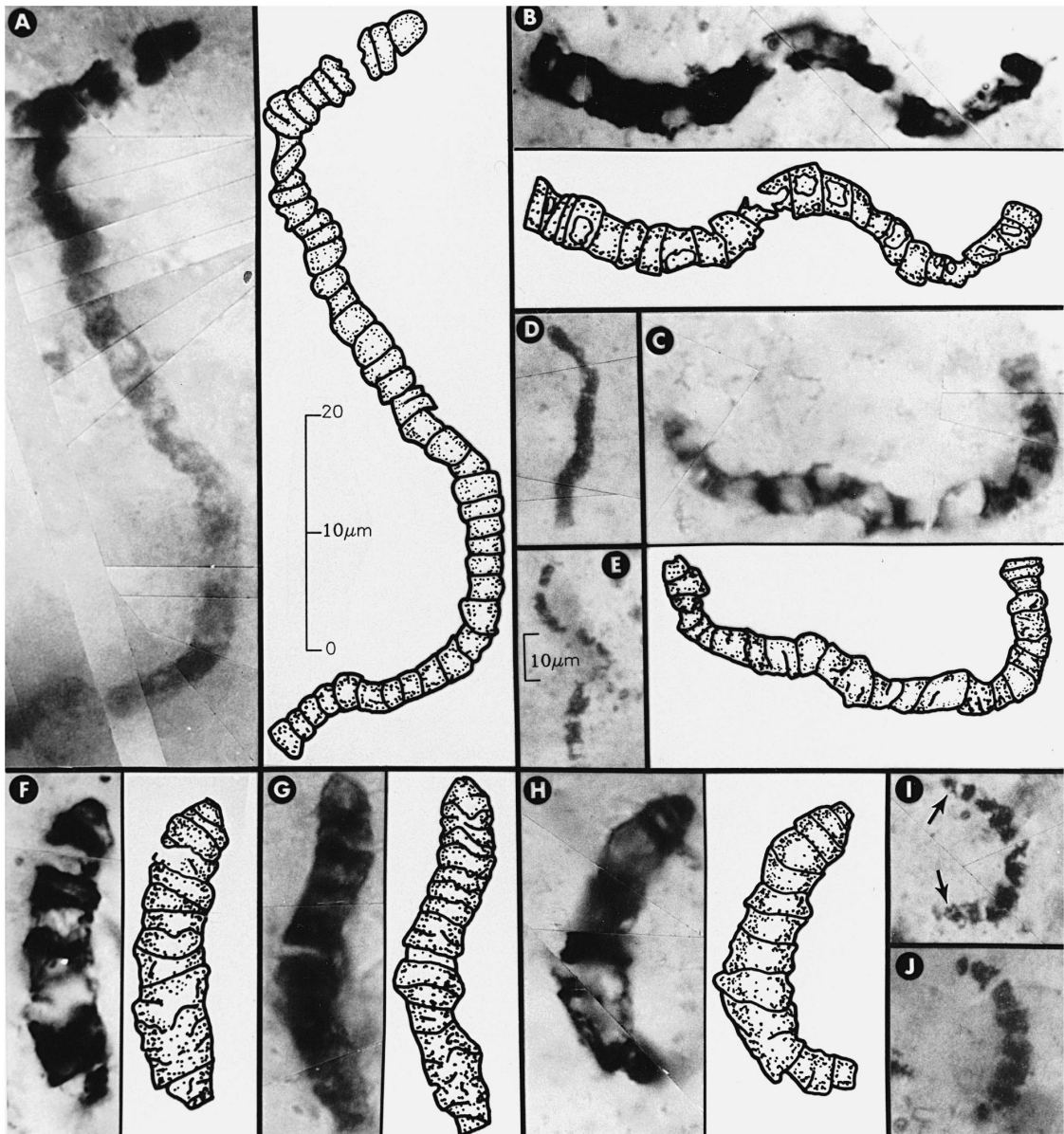


Fig. 2. More microfossils from the Apex Chert (from Schopf, 1993, by permission). Magnification of (D,E,I,J) as in (E); others as in (A). (A–E) *Primaevifilum amoenum*; (F–J) *Primaevifilum conicoterminatum*.

The other major item of contention in the early Archean is the evidence for lack of oxygen in the atmosphere. This evidence, sedimentary pyrite and uraninite (Walker et al., 1983; Schopf, 1992b; Lowe, 1994), is strongly indicative of very low oxygen

concentrations in the atmosphere before the early Proterozoic. The problem is, this does not tell us the local concentration of oxygen in the ocean, nor the possible presence of  $H_2$  or  $CH_4$ . Iron was being dissolved in one location (presumably as ferrous

carbonate or sulfate, or as acidic ferric compounds, in submarine hot springs), and the uraninite and pyrite were being abraded in streams in another location, while iron was being precipitated by oxidation in a third location as banded iron formations (BIF). Thus, the latest occurrence of pyrite conglomerate is much later (ca. 2.0 Ga) than the earliest BIF (ca. 3.8 Ga). It is not unreasonable to suppose that the cyanobacterial oxygen did not diffuse rapidly into the atmosphere, but was more rapidly consumed by iron oxidation. If we can assume that the only source of oxygen in these waters was photosynthesis, the early date for BIF may support the early date for cyanobacterial fossils. Not until the abundant crustal reduced iron was used up would we expect much oxygen to accumulate in the air, eliminating sedimentary pyrite and producing fully oxidized red beds.

Lowe (1994) and Towe (1994) suggest that the deep layers of the stratified ocean were filled with ferrous iron newly dissolved from hydrothermal systems. At the same time, the upper layers could have been more oxygenated, producing BIF, but leaving the atmosphere unknown.

One aspect that receives little attention is the oxidation of sulfur. If some of the primordial iron was troilite or pyrite, to dissolve this iron it would probably first be necessary to oxidize the sulfide to sulfate. Free  $H_2S$  in the ocean, while attractive from an early metabolism point of view, would not survive in the presence of any dissolved iron. Some of the sulfur could also be emitted by volcanoes, and perhaps oxidized in the atmosphere. Massive amounts of sulfate minerals were deposited in the Archean (Lowe, 1994). On this basis, Towe (1994) maintains that the amount of oxygen in the Archean atmosphere was not zero.

Walker (1990) gives a recent estimate of the amounts of reduced and oxidized components of the Earth's surface. Sulfate (sedimentary and oceanic) is about double the amount of ferric iron, with elemental oxygen many times less. Organic carbon is about double the sum of the oxidized components, leaving us somewhat in doubt.

The time of origin of eukaryotes is sometimes equated with the accumulation of oxygen in the air. But atmospheric oxygen was not actually necessary for respiratory organisms. With Cyanobacteria pro-

ducing locally oxygenated water, a variety of respiratory organisms, both prokaryotes and eukaryotes, could have coexisted with the Cyanobacteria, before significant accumulation in the atmosphere.

### 3. The origin of the ocean

It has been thought that the ocean arose by degassing from incoming planetesimals, either on impact or later from the interior. However, the recognition of the origin of the Moon by the glancing impact of a perhaps Mars-size body (Newsom and Jones, 1990; Kasting, 1993a; Taylor, 1994) has changed this view. This extreme impact, shortly after the accretion of the Earth, would have dissipated all of any ocean and atmosphere that were present, either actually or potentially, because of the extreme heat produced. The iron core of the smaller body would have joined that of the Earth, and the surface layers of the Earth and of the Moon would have been molten.

Whether or not you accept that scenario, there is another reason why the water of the ocean did not arrive at the beginning. The thermal history of the solar nebula (Delsemme, 1996) is such that the planetesimals near 1 A.U. were at over 1000 K, eliminating any water other than vapor. The nebular temperature gradient was calibrated by an estimate of the temperatures of formation of the minerals in meteorites. The relatively dry ordinary chondrites, assumed to correspond to the lighter colored asteroids at about 2 A.U. have formation temperatures around 510 K, while the carbonaceous chondrites, corresponding to the darker asteroids above 2.6 A.U., have formation temperatures of around 450 K. The large planets and comets, in which water is ice, are beyond 5 A.U. Thus, since the Earth accumulated primarily from dust and planetesimals at about 1 A.U., the initial accretion of the planet Earth would have been largely from dry materials.

So where did all the water come from? Comets (see Thomas et al., 1996). After the formation of the Moon, a rain of impacts fell on the Moon, as we can observe, and therefore also on Earth. Oró and Lazcano (1996) have reviewed the disparate estimates of

how many comet impacts there were and conclude that if only 10% of the probable impacts were comets, enough water would have been delivered for the present oceans. Delsemme (1996) agrees and details a mathematical model of how the large planets (Jupiter and Saturn) were formed mainly out of comets and subsequently threw the remaining comets out of nearby orbits, crossing those of the terrestrial planets and (if they did not strike the sun or one of the planets), either ejecting them from the solar system or adding them to the Oort cloud. The amount of terrestrial water from that rain of comets was estimated at an order of magnitude greater than that of the present ocean (thus agreeing with Oró and Lazcano). Some 85% of that would have come from the vicinity of Jupiter, the rest from further out. The present deficiency of oceanic volume is attributed to loss from massive impacts which ejected water out of the Earth's gravity.

An interesting consequence of these calculations is that essentially all of the old craters on the moon were from comet impacts.

Owen (1997) also discusses the arrival of water from comets, but emphasizes the isotope ratio evidence ( $^{36}\text{Ar}/^{132}\text{Xe}$  vs.  $^{84}\text{Kr}/^{132}\text{Xe}$ ). These are such that chondrites could not have been the exclusive source of these noble gasses to our atmosphere. These ratios on Earth and Mars indicate that they arrived from two different sources ('external' and 'internal'), in different amounts in each planet. Venus may have gotten its in part from a third source. Owen notes that ice condensed at different temperatures (30–54 K) traps noble gasses in different ratios. He identifies the external source with ice condensed at 50 K in the region of formation of Uranus and Neptune (the internal source being gasses trapped in the minerals accreting). If we extrapolate the diagram of Delsemme (1996) to this temperature, we get a heliocentric distance of 25 to 30 A.U. for the condensation of the comets, in the region of Uranus and Neptune. I note that the 'internal source' refers only to the noble gasses, and not necessarily to water.

The timing of these events is important for consideration of a habitat for the origin of life. Delsemme (1996) gives details from his model, including the following times after the sedimentation of solids into the mid-plane of the solar nebula: (1) until 99% of

Earth accumulation, 40 million years; and (2) for the orbital diffusion of the comets from the zone of Jupiter, 70 million years. In other words, the ocean would have accumulated for the most part before 4.45 Ga. The impact that formed the Moon could have been during this time, dissipating much of the early ocean. The continued, slower, rain of impacts would have been comets from the zones of Uranus and Neptune or from the Oort cloud.

The general picture, then, is this. Earth, Mars, Venus and Mercury all accumulated from dry planetesimals. They then acquired a thin veneer, both of solids (iron, silicates, etc.) and of liquid water, plus an atmosphere. According to Delsemme (1996), this explains both the excess of volatiles pointed out by Rubey, and the excess of siderophiles in the crust and mantle. An analysis of comets in general has yet to be accomplished, but comet Halley (from the Oort cloud) was found to be 23% rocks, 41% water, and 36% 'CHON'.

The Moon would also have been pelted by comets, but the water dissipated in the low gravity (unless some is present as buried ice). Venus, and to a lesser extent Mars, however, would have retained the water. Venus presumably lost its water by dissociation (UV light) during a runaway greenhouse effect. Mars, on the other hand, has water, with evidence of enormous floods, and small channels. Carr (1996) reviewed the situation on Mars and concluded that the massive floods came from sudden outbreaks of liquid water from below the permafrost. The small channels seem to him to be the result, not of rainfall, but of springs moving earthy matter downslope, 'mass wasting'. He believes that most of the water is still there, frozen more thoroughly due to cooling of the planet and a decline in volcanism.

The depth of the early ocean is important in considering the origin of life. If Delsemme (1996) is correct, most of the ocean accumulated before about 4.4 Ga. This is a worry, because it would have diluted any organic matter that was there, making further synthetic reactions less probable (see Deamer, 1997). Some authors (notably Darwin himself, in a letter, quoted by Calvin, 1969) have postulated 'a warm little pond' in which to start life. However, it is clear that no extensive continents (with ponds) existed very early (Allegre and Schneider, 1994; Lowe, 1994). The oldest datable rocks [the Acasta

Gneiss in Canada, the Itsaq Gneiss in Greenland, etc., (Nutman et al., 1996)] are only 3.8–4.0 Ga, 500 or 700 million years after the beginnings. This makes the prior surface conditions speculative.

Presumably, as soon as the Earth cooled a bit, a crust formed on the surface rock, and it rained. Immediately, plate tectonics began, to accommodate the convective cooling of the interior. Fig. 3 illustrates what the crust might have looked like then. The biggest pieces of dry land would have been tiny accumulations at subduction zones, and volcanic islands of unknown size. At the submarine spreading centers, hot springs would develop, which might have been important in the origin of life (Bock and Goode, 1996). Lowe (1994) reviewed the geology of the Archean.

A view supplementary to the above is that of Meier et al. (1998); they conclude from spectroscopic analyses of deuterated water in comets Hale–Bopp, Hyakutake, and Halley, that long-period comets such as these cannot be the only source of water in terrestrial oceans. They suggest that the solar nebula was not homogeneous and that much of the ocean arose from water adsorbed on the rocky matter that originally accreted. However, short-period comets, which would be more representative of the Jupiter zone, and which are more likely to have contributed to the ocean (Delsemme, 1996), have not been analyzed. Also, Mumma (1997) cautions that only about half of the D + H in comets is in the water; the rest is in organics.

One aspect of the early ocean which gets little or no attention is the suspended mineral content. The

oldest surface of the moon is ‘gardened’ by impacts, leaving a thick layer of breccia. At least some of the terrestrial impacts, contemporary with that age of the moon, would have had the same effect on the oceanic crust. Those impacts too small to penetrate the ocean would also add to the fines suspended in the ocean. The result of this would be the alteration of the crustal, cometic and meteoritic matter by water, and much clay would be formed, in part kept in suspension by wind. This is my interpretation of a reference to the ‘clay soup’ instead of the more common ‘primordial soup’ (Schmitt, 1998). This is important with respect to the suggestions that clay surfaces were essential catalysts in the origin of life (Section 8).

The stratification of the ocean has been emphasized by both Lowe (1994) and Towe (1994). This has to do with oxygen, and was taken up in Section 2.

Some authors warn (Maher and Stevenson, 1988; Sleep et al., 1989; Zahnle and Sleep, 1996) about impacts massive enough to vaporize the whole ocean, and postulate a need for multiple origins of life, or at least the survival of only thermophilic organisms (Sections 6 and 9). However, many impacts that we would now consider massive did not have that effect, as shown by the Chicxulub impact, which must have had severe environmental effects, but did not boil the entire ocean. In contrast, Bada et al. (1995) suggest that the heating by the early impacts only served to melt a frozen ocean. Even so, to accommodate the data on comet input, much of the ocean has to have been lost to space.

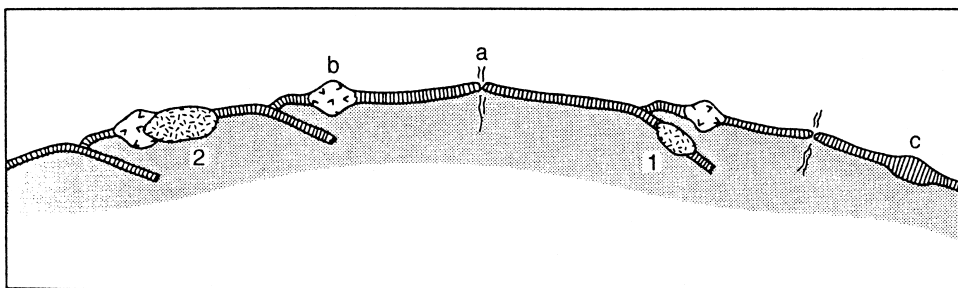


Fig. 3. Schematic diagram of the probable nature of the Hadean and early Archean lithospheric crust. ‘a’ Indicates a spreading center with hot springs; ‘b’ indicates a subduction zone with microcontinent; ‘c’ indicates a hot spot volcano. ‘1’ Is a bit of crust being subducted, as was all the Hadean crust. After about 3.8 Ga, the continents began to grow (‘2’). From Lowe (1994), with permission. Except for small areas, the whole world would be overlaid with ocean.

#### 4. The origin of the atmosphere

At present, most of the carbon in the surface of Earth is locked up as carbonate rocks, but those rocks are the result of weathering of silicates. The earliest sedimentary rocks (Isua) include some carbonates, presumably from submarine weathering of the oceanic crust. If all the CO<sub>2</sub> in carbonates were in the gas state, there would be an atmosphere of 60–80 bars, comparable to that on Venus. Likewise, if the ocean boiled, there would be a steam atmosphere of some 270 bars. Kasting (1993a,b), Kasting et al. (1993), Lowe (1994), and Towe (1994) have recently reviewed the early atmosphere.

There is still uncertainty as to the original composition of the atmosphere. Most of those attempting 'prebiotic chemistry' used atmospheres strongly reducing, with methane and ammonia, rather than carbon dioxide and nitrogen. Chyba and Sagan (1996), in their discussion of the sources of early organics, make their calculation both on the basis of a strongly reducing atmosphere and on the basis of an intermediate atmosphere (carbon as CO<sub>2</sub>, nitrogen as N<sub>2</sub>). Furthermore, I have found no recent authors who support the strongly reducing atmosphere model, attractive as it is from a chemical synthesis point of view. Kasting (1993a) and Kasting et al. (1993) debate the question in some detail, and supports a composition in which H<sub>2</sub> was present, but at very low concentrations. The key factors in determining the atmospheric composition were photochemical processes and outgassing from the interior via volcanoes. Kasting considers that the volatiles generated on impact were soon 'in-gassed' by reaction with the subducting surface rock. Eventually, the ocean and atmosphere came to a steady state between in- and out-gassing. Kasting uses modern values for volcanic emission, the redox state of which is apparently set by equilibration with rather oxidized iron-containing minerals (FeO + Fe<sub>2</sub>O<sub>3</sub>; the quartz–fayalite–magnetite buffer). However, a more reducing atmosphere would have been produced if the volatiles had equilibrated with a metallic iron–FeO (iron-wustite) buffer. The evidence from BIF (above), is that much reduced iron existed until well after the origin of life.

An important feature of the review of Kasting (1993a,b) is the effect of the atmospheric composition on the surface temperature. If the early sun was

only 70% as strong as at present (as derived from cosmology), a greenhouse effect would be necessary to warm the Earth above the freezing point of water, at the same time avoiding boiling the ocean. If CO<sub>2</sub> produced this effect, it would have had to be between about 1 and 20 bars pressure. Chyba and Sagan (1997) suggest that ammonia could also have been an early greenhouse gas, if shielded from solar UV by organic solids produced from methane photolysis. Alternatively, Bada et al. (1995) have suggested that the influx of comets, etc., would have melted a frozen ocean sufficiently to compensate for the low solar input.

Although much evidence has been presented (Section 5) for the deposition of organic matter from interplanetary dust or comets, presumably the early atmosphere was formed by the destructive impact of comets and carbonaceous asteroids on the surface. The very earliest atmosphere would have disappeared with the impact that formed the moon. Aside from such massive impacts, only half of comet collisions occur with sufficient velocity to cause erosion of the atmosphere (Chyba and Sagan, 1996). However, Steel (1997) seems to get a much higher speed of impact by some comets.

#### 5. Organic input to the Earth

The volume of the bodies of water in which the early organics accumulated, is very important (Deamer, 1997). Ponds might have existed on the sides of the early volcanoes, but continents did not exist, and the ocean was apparently massive very early. Miller's experiments (Miller and Orgel, 1974; Miller, 1992) assumed, following Oparin et al., that the atmosphere was full of methane and ammonia, but the discussion above again puts this in grave doubt. Since we know that life did arise, we are obligated to find mechanisms to accumulate enough organic matter to start life.

There are three places to look for the origin of organics: extraterrestrial sources such as comets; the atmosphere of the Earth; and the ocean itself.

There has been much discussion about comets or meteorites being a source of organic compounds on the early Earth (Anders, 1989; Chyba and Sagan, 1996; Thomas et al., 1996; Mumma, 1997; Oró and



Cosmovici, 1997). The proportion of survival of this material upon impact is an unknown factor, but analysis of meteorites, especially the Murchison, shows that some fraction of impacts would have delivered amino acids at least. In addition, and apparently much more important quantitatively, is the rain of interplanetary dust (Chyba and Sagan, 1996), which I presume has a current origin in comets, ablated from them during their travel near the sun.

Steel (1997) makes the point that the speed of impact of comets from the Oort cloud is generally too high for any organics to have survived. These calculations, however, would not apply to the comets in the neighborhood of Saturn, etc., providing the early ocean.

Another possible source is catastrophic airbursts. The Tunguska event in 1908 has variously been attributed to a comet or asteroid, but no samples were recovered. Chyba et al. (1993) give a careful numerical analysis of what happens to an incoming bolide, and conclude that the Tunguska one was probably a stony asteroid, exploding at about 8.5 km. Contrary to what one might expect, apparently a bolide does not explode by sudden boiling, but by catastrophic failure due to the pressure on the front surface. Comets and carbonaceous chondrites of comparable size explode at higher elevations, due to their lower strength; strong iron meteorites do not explode before they strike the ground. The height of explosion depends on the inclination and speed of attack as well. Objects much bigger than 1 km in diameter do not explode because they do not react quickly enough. Small objects and interplanetary dust decelerate and/or ablate and fall more gently.

Chyba et al. (1993) also discuss the few other observed airbursts. In 1965 (Follinsbee et al., 1967) a bolide exploded (at about 30 km) over Revelstoke, B.C., Canada (just west of Glacier National Park), depositing millimeter sized fragments of a type I carbonaceous chondrite on the snow. These have been found to have unheated interiors, permitting organics to have survived. Less well known are the Kinkardine and College objects, exploding over Ontario in 1966 and Alaska in 1969. These airbursts were so high (just over 60 km) that they could have been comets.

Other evidence from Phanerozoic impacts indicates the possible survivability or synthesis of or-

ganic compounds from major impacts. The Cretaceous/Tertiary boundary sediments in Denmark (associated with the impact crater at Chicxulub, Mexico) have been reported to contain non-biological amino acids (Zhao and Bada, 1989). Chyba and Sagan (1996) question, however, that these came in with the bolide, instead suggesting atmospheric synthesis in the shock of impact. Sudbury, Ont., in Canada is the site of another of the most massive impacts known. This impact structure has been found to contain carbon in the form of fullerenes, ball-shaped carbon compounds with a central hole trapping helium. When a sample of the Sudbury fullerenes was analyzed, it was found that the ratio of helium-3 to helium-4 was 20 times greater than any other terrestrial sample (Becker et al., 1996). Two conclusions may be drawn from this: first, the fullerenes themselves and the helium in the fullerenes (trapped when the balls were formed) came from somewhere in the solar nebula or interstellar space; and second, the heat of the impact of the meteorite did not break up all the fullerenes. But fullerenes are more resistant than amino acids.

The origins of the primordial matter that formed the solar nebula and its products has been studied by spectroscopy. This is too far afield for this review, so I shall only mention that interstellar carbon compounds have been found and evidence for their incorporation into comets has been cited. Kissel et al. (1996) and Mumma (1997) have reviewed many of these data (see also Thomas et al., 1996).

Chang (1993) has reviewed the possible sources of atmospheric synthesis, including not only electric effects (lightning and corona discharges) but impact shocks and solar UV. All of these appear capable of adding to the oceanic stock, even with a less reduced atmospheric composition. The susceptibility of the carbon compounds to solar UV means that if they were to survive, they would have to be quickly deposited in the ocean. However, unless impact synthesis was in a reducing atmosphere, interplanetary dust would provide a much greater source. Navarro-González et al. (1996) have added to the possible environments for synthesis by pointing out the probable presence of lightning in volcanic gas/ash-clouds.

Chyba and Sagan (1996) have also reviewed shock synthesis in the atmosphere. In their inventory of

major sources of prebiotic organic inputs they find a total almost a thousand times more with a reducing atmosphere than with an intermediate atmosphere ( $[H_2]/[CO_2] = 0.1$ ). The three most important sources under the latter conditions are: UV photolysis, interplanetary dust particles, and an extrapolation from the K/T deposits (major impact shocks). Each of these come to 2 to  $3 \times 10^8$  kg/yr. Electric discharge is 10-fold less, while other shocks are 6 orders of magnitude less.

Compounds formed in the atmosphere or found in comets would undergo further reactions on deposition in the ocean. The best known of these reactions is the Strecker synthesis, forming amino acids from HCN and aldehydes. Chang (1993) discusses such reactions.

The uncertainties involved with the rates of input (orders of magnitude) are exacerbated by the uncertainties involved with impact erosion of atmosphere and ocean. The latter is caused by an unknown number of impacts of sufficient size, during the first half billion years of the existence of the Earth. The only means of estimating such impacts is from the record of impacts on the moon, but the only sure radiometric date on the moon is near the end of the Hadean, when life had already begun.

Gold (1997) continues his contrary view of the origin of petroleum, extending it to the origin of life in the depths of a crust (Earth or Mars). His view of the abiotic origin of liquid hydrocarbons at a depth of 150 km does not seem to be conformable with the above scenario of the origin of the ocean. The 1000 K temperature of the solar nebula would presumably eliminate many carbon compounds as well as water, while the moon-forming impact would likewise destroy any primordial hydrocarbons.

## 6. Submarine hot springs–hydrothermal systems

With the discovery of large ecosystems surrounding deep-sea hot springs, the immediate interpretation was that here we have life going on without photosynthesis and perhaps giving a site for the origin of life. A word of caution is necessary. Most of the chemosynthetic energy in the modern sites is derived from the oxidation of sulfur compounds,

upon mixing with sea water. The oxygen for that process is made by photosynthesis. Nevertheless, anaerobes also exist in these hot springs, and what we are interested in is the possibility of hot springs being important in the origin of life.

The entire volume edited by Bock and Goode (1996) is devoted to hydrothermal systems. The early history of the crust and ocean (above) indicates that they were present in abundance.

An early suggestion that life may have actually arisen in hot springs is due to Woese (Woese, 1981, Woese et al., 1990) because some of the most primitive organisms, defined as being close to the base of the phylogenetic tree, are now thermophilic bacteria of the domain Archaea (Archaeobacteria). This tree will be discussed in Section 9.

Shock (1996) has reviewed the thermodynamics of hydrothermal vent fluid components, showing that energy could certainly be gained by organisms, for instance by reacting  $H_2$  with  $CO_2$ . The fluid from a vent on the East Pacific Rise was at  $350^\circ C$ , with  $H_2$  at 1.2 millimolal, and  $CO_2$  at 5.72 mM.

Shock (see also Chang, 1993, 1994; Russell and Hall, 1997) has also described the course of reactions occurring in the flow of water through the rocks near a spreading center. Walter (1996) described fossil thermal spring deposits.

Nisbet and Fowler (1996) propose that modern organisms retain the imprint of their hydrothermal origins in the existence of 'heat-shock proteins'. These are proteins that are formed in response to sudden heating (not growth at high temperatures), an early requirement being due to the very variable environments. They also suggest that the metals (Mg, Fe, Mn, Mo, etc.) now required for metabolism, would most easily be obtained in the primordial period from the hot vents. However, clays and other debris, suspended in the ocean (Section 3) would also have been a good source of many metals. Furthermore, abundance alone cannot account for the modern mineral requirements (McClendon, 1976).

A cautionary view is that of Pace (1991) and Levy and Miller (1998) who question the stability of ribose nucleic acid (RNA) and its monomers under hyperthermal conditions. The half-lives of the bases at  $100^\circ C$  ranged from 19 days to 12 years (Levy and Miller, 1998). Also, Lazcano (1997) points out that if the origin of life were delayed long enough, all the

complex organic compounds in the ocean would be destroyed by passage through the hot spring channels. These reports emphasize the possible importance of smaller bodies of water as loci for the origin of life, or else the very early encapsulation of metabolism (Deamer, 1997; Russell and Hall, 1997).

## 7. Chemical simulations

Chemical syntheses occurring in interstellar space, the solar nebula or the interior of comets or asteroids, were important but perhaps limited in scope. The delivery to the surface of Earth was discussed above. Here, we must consider the model experiments aimed at elucidating steps in the origin of life. The *sine qua non* of chemistry pertinent to the origin of life is that the reaction conditions must be plausibly present around the time of Earth's origin.

A major obstacle to knowledge about synthesis on the early Earth is uncertainty about the composition of the atmosphere. Most of the experimental work has been done in a reducing atmosphere, including methane, or if not, including H<sub>2</sub> with CO<sub>2</sub>. This may or may not be realistic, as outlined above.

This topic has been reviewed in general by Miller and Orgel (1974), Chang et al. (1983), Miller (1992), Deamer and Fleischaker (1994), Oró (1994), Chyba and McDonald (1995) and Zubay (1996).

The defining feature of cells is the cell membrane, a bilayer lipid. The prebiotic synthesis of lipid materials has been demonstrated, and Deamer and Fleischaker (1994), Deamer et al. (1994), and Deamer (1997) have discussed the formation of primitive lipid membrane structures. The necessary chemical nature of the constituents is limited to having a lipophilic tail and a hydrophilic head (polar lipids). A great variety of these is present among extant organisms, and various prebiotic analogs are possible. Two patterns of the non-polar parts of membrane lipids are now present, straight-chain fatty acids, and branched-chain isoprenoids. The latter are typical of membranes of the Archaea, the former of all other membranes, including those of the Eukaryotes, probable sisters to the Archaea (Section 9). However, the ability to biosynthesize fatty acids and isoprenoids is found in both groups, for instance

carotenoids and sterols in eukaryotes. This emphasizes the uncertainty about the original membranes. The iron-sulfide membranes postulated by Russell and Hall (1997) would have to have been superseded by organic ones.

Since the physicochemical properties of the membrane are the most important, it may not be crucial to have had a particular chemical structure. But since all organisms make part of their ATP by a mechanism utilizing the proton gradient across a membrane, membranes are especially important. If this was an early discovery, it would provide energy for many processes (Koch and Schmidt, 1991). This use of the proton gradient for ATP synthesis is found in all major groups, showing it was present in the last common ancestor. Deamer (1997) reviews many experiments dealing with the formation of lipid vesicles and their possible functions as energy storing mechanisms. Primitive pigments may also have been important in photochemical reactions.

For prebiotic amino acids, the situation is this: these are easy to make if you do not worry about chirality (D vs. L). Since the original report by Miller and Urey, who used a spark synthesis, many repetitions have been performed. In addition, it has been proposed that the interstellar synthesis occurred via a Fischer–Tropsch type synthesis, similar to that producing synthetic gasoline from hydrogen and carbon monoxide (Anders et al., 1973; see Table 1—a blank does not necessarily mean absence of the compound, it may not have been sought). Chang and Bunch (1986) point out that isotope ratios show that the meteoritic carbon compounds had diverse origins.

Meteorites, in particular the Murchison, contain much the same amino acids as Miller obtained in his spark synthesis in an atmosphere of methane, ammonia and water (Table 1). However, these are all close to racemic, while proteins are only made from L-amino acids. In addition, some of the protein amino acids, such as lysine, histidine and arginine, are not found in detectable amounts (Weber and Miller, 1981; Miller, 1992). On the other hand, many amino acids are found which have no role in modern proteins, such as norvaline and norleucine (straight chain analogs of their namesakes) (Table 1).

Many authors have worried about getting chiral amino acids (etc.) from the racemic mixtures found in abiotic syntheses, and have looked for cosmic

Table 1  
Occurrence of amino acids in various syntheses

	PRO	SPK <sup>a</sup>	FTT	MET <sup>a</sup>
Alanine	x	++++	x	+++
Arginine	x		x	
Aspartic acid	x	++	x	+++
Cysteine	x			
Glutamic acid	x	++	x	+++
Glycine	x	++++	x	++++
Histidine	x		x	
Isoleucine	x	++	?	
Leucine	x	++		
Lysine	x	?	x	
Methionine	x	+		
Phenylalanine	x			
Proline	x	+	?	+++
Serine	x	++		
Threonine	x	+		
Tryptophan	x			
Tyrosine	x		x	
Valine	x	++	?	+++
α-Amino isobutyric acid		++	?	+++
α-Amino <i>n</i> -butyric acid		++	?	+++
β-Alanine		++	x	+++
β-Amino isobutyric acid		+	?	++
γ-Amino <i>n</i> -butyric acid		+	?	++
Norvaline		+++	x	+++
Ornithine		?	x	
β-Amino <i>n</i> -butyric acid		+		++
Pipecolic acid		+	?	+++
α,β-Diaminopropionic acid		++		
α,γ-Diaminobutyric acid		++		
α-Amino <i>n</i> -heptanoic acid		+		
Alloisoleucine		++		
Allothreonine		+		
Homocysteine		+		
Homoserine		+		
Isoleucine		++		
Norleucine		++		
Tertiary leucine		?		

<sup>a</sup>Relative yield is: 100 = + + + +, 10 = + + +, 1 = + +, 0.1 = +, < 0.01 = ?.

PRO = found in proteins; SPK = found in spark syntheses; FTT = found in Fischer–Tropsch type syntheses; MET = found in the Murchison meteorite; ? = tentative identification.

Data from Weber and Miller, 1981, and from Anders et al., 1973.

sources. In a recent reexamination of the amino acids of the Murchison meteorite, Cronin and Pizzarello (1997) studied several amino acids not known to occur on Earth, so as to avoid any chance of terrestrial contamination. Their chief subject was 2-amino-2,3-dimethyl pentanoic acid, which has four

stereoisomers. Their careful quantitative work showed that the two L-isomers from the meteorite represented 52 to 54% of the total, while their synthetic control sample showed no significant difference. Isovaline and α-methylnorvaline gave similar results. All these have a methyl group on the same carbon as the amino group. But, two amino acids that have an H instead of a methyl (α-amino-*n*-butyric acid and norvaline), showed no excess of the L-isomer. However these results may be interpreted, with respect to the origin of the discrimination, they do not give much basis for an extraterrestrial origin of the biological use of exclusive L-isomers. Furthermore, choosing, say, L-alanine vs. D-alanine is no harder nor easier than choosing L-alanine vs. L-norvaline.

As for the amino acid polymers, i.e., proteins, Sidney Fox (Fox and Dose, 1977) has demonstrated the ease of polymerization into ‘proteinoids’ by hot dehydration, but although some catalytic activity was expressed, no regular structure was present. Chyba and McDonald (1995) were particularly critical of the need for dehydrating conditions for this and other syntheses, as unlikely on the Hadean Earth. The only likely location would be on the sides of volcanoes emergent from the ocean, but maybe this would be important.

In modern proteins, the order of the monomers in the protein determines its function. In the above proteinoids, more or less random order is obtained, which is further degraded by the occurrence of racemic monomers (giving an irregular chain) and the possibility of cross-links between the double function amino acids: aspartic and glutamic acids and lysine. The only way out of this dilemma is the use of surface catalysts to determine the structure of the polymer (see Section 8).

For nucleic acids, adenine is easy to make from HCN (on paper, it is a simple polymer of HCN), but pyrimidines are not so easy (Miller, 1992). HCN is an essential precursor of both purines and amino acids, and is found in spark syntheses and outer space. The purines adenine, guanine, hypoxanthine and xanthine, have been found in carbonaceous meteorites. Of the pyrimidines, only uracil has been found.

For the polymerization into nucleic acids, many difficulties exist. The nucleic acid polymer consists

of an alternating chain of pentose sugar and phosphate, to which are attached the purines and pyrimidines. Although many ingenious experiments have been performed, it is not yet clear how this polymerization might have occurred under plausible conditions.

The main difficulty with nucleic acids is with the sugars, ribose and deoxyribose (Miller, 1992; Chyba and McDonald, 1995; Rizzotti, 1997). (In addition, phosphate is in short supply in modern waters and soils.) Sugars form spontaneously from formaldehyde in alkaline solution over calcium carbonate, but we have an embarrassment of riches. One author found more than 40 different sugars present in his reaction mixture (Miller, 1992). This makes the choice of ribose problematic; the modern constituents are only D-ribose and D-deoxyribose. Since the three-dimensional structure of the DNA and RNA, upon which the hereditary system depends, is in turn dependent on the chirality of the ribose, to which the phosphate and base are attached, some deterministic choice seems to be required. Non-sugar substitutes (such as glycerol) seem likely but their plausibility has not been shown. One interesting suggestion is for a peptide chain, instead of a sugar–phosphate chain (peptide nucleic acids, or PNA; Lazcano, 1997). Although DNA is the current hereditary material, it is more than likely that RNA preceded it historically (below).

The relative importance of various energy inputs is also uncertain. Miller used a spark discharge, simulating lightning. Lightning may be relatively rare, but Navarro-González et al. (1996) point out the abundance of lightning in volcanic gas/ash-clouds, which may have compositions different from the general atmosphere. Chang (1993) compared a variety of energy inputs, including impacts, and find that for HCN and formaldehyde rain-out, the most important source was solar UV.

## 8. Hypothetical schemes

Eigen et al. (Eigen and Schuster, 1979; Eigen and Winkler-Oswatitsch, 1992) have constructed mathematical models of positive feed-back mechanisms (hypercycles) which may have some relevance to the origin of life.

Many authors have taken the primordial soup for granted and have considered the next step. Deamer et al. (1994), Deamer (1997) consider the origin of cells as a primary step. Chang (1993) proposes bubble formation and breaking in the ocean–atmosphere interface as a likely mechanism for closing vesicles. The spontaneous formation of vesicles is a characteristic of phospholipids and similar materials and alternate drying and wetting serve to encapsulate interesting polymers. Deamer (1997) reviews this idea and the associated problems of permeability of the membrane, needed to permit small organic molecules to penetrate and be acted upon.

Russell, Hall, et al. (Russell and Hall, 1997), have proposed iron sulfide membranes, precipitated as bubbles at submarine hydrothermal vents, as the primordial cell membranes in a step leading to life. Russell and Hall (1997) reviewed a great deal of metabolism required in modern and presumed primordial cells.

Others center on the genetic/protein-synthesis mechanism, which could be encapsulated by the primordial cells. In recent years it has become popular to consider the RNAs as the first genetic system, the ‘RNA World’ (Lazcano, 1994b; Zubay, 1996). Ever since the first reports of RNA being able to *do* something, rather than merely being acted upon (Cech, 1987), it has increasingly become popular to consider that RNAs were not only the early genetic material, but also the early enzymes (‘ribozymes’). What was initially observed was the self cleavage and self splicing of certain naturally occurring RNAs. Ferris (1993), Schwartz (1993) and Lazcano (1994b) review this topic. Rizzotti (1997) outlines reasons why the RNA world could not be very early. Pace (1991), accepting the hyperthermic origin, postulates that the early RNAs had to be protected somehow from hydrolysis.

The RNA world requires us to assume that the DNA of the genetic mechanism is a late comer. Since there is no reason why heredity could not be transmitted via RNA instead, and since the modern deoxyribose biosynthesis is a late step, being formed from ribose already combined, this assumption is hardly questioned.

But generation of a self-replicating RNA chain and of a protein translation mechanism are much more controversial. It is first necessary to have spon-

taneously formed monomers in the environment. This, itself, is problematical (above). Then, an RNA chain must be found to catalyze the synthesis of itself and/or another RNA as a polymerase using RNA as a template. It has been found that an (enzymatically formed) chain of poly-cytosine will catalyze the formation of the complementary chain of poly-guanosine, from activated monomers. The monomers were guanidine–monophosphate, on the phosphate of which was attached an imidazole, thereby activating it. However, the reverse of this synthesis did not work, making the origin of a positive feedback mechanism uncertain at best. (The pace of research may, of course, overtake this criticism.)

Although proteins have been downgraded in schemes of aboriginal genetics, Lee et al. (1996, 1997) have given examples of protein self-replication.

Another idea that has had extensive support is that mineral surfaces may catalyze the formation of important compounds. Cairns-Smith (1982, 1985) has concluded that organic mechanisms are too uncertain and has put forth a long proposal for the predominance of catalytic clay surfaces as the first genetic mechanism. Although clays are, on the average, rather monotonous, Cairns-Smith emphasizes that irregularities in the crystal structure are reproduced, layer by layer. Thus, accidental sites which have special catalytic properties would be amplified. If these became involved with organic reproduction, say of special RNAs or catalytic proteins, a connection between the clay ‘genes’ and organic ones would be established.

Clays are, of course, chemically reactive. The primordial ocean should have been full of clay (above). Their involvement in the origin of life was first suggested by J.D. Bernal, a half century ago (see also Bernal, 1967). Laszlo (1987), Negron-Mendoza et al. (1996) and Zubay (1996) have reviewed this topic. Cairns-Smith and Hartman (1986) have edited a volume devoted to various aspects of clays in the origin of life. A variety of processes have been observed to be catalyzed by clays, including amino acid formation and amino acid polymerization. Ferris (1993) observed the formation of RNA oligomers on montmorillonite. I tend to feel that this is important, if only because catalysis on

clay surfaces would be stereospecific, totally avoiding the necessity for any cosmic or primordial bias in the synthesis of chiral amino acids, etc.

According to Cairns-Smith, the inorganic genetic mechanism would be superseded by the RNA/DNA mechanism. As far as I am aware, this is, so far, only a speculation.

Following the assembly of the most primitive cell, i.e., one with a membrane and a genetic/protein-synthetic mechanism, Darwinian evolution could begin, gradually developing into the last common ancestor.

Since autotrophs (whether photosynthetic or chemolithotrophic) are the most independent, they have seemed, to some, ideal candidates for the first cells. The trouble with this idea is that autotrophs have the most complex internal requirements. The alternative, then, is that the first cells were the most complete heterotrophs, utilizing materials found in the environment, amino acids, purines, pyrimidines, vitamins, etc. But a primitive cell using light or chemical reactions as energy sources would not have ignored any environmental inputs. Thus, the energy source for the early heterotrophic system may have been light driven or based on inorganic reactions (Deamer, 1997).

A somewhat different hypothesis is that of Wächtershäuser (1994) and Huber and Wächtershäuser (1998). He discards the whole idea of a primordial soup in which the first organism was a heterotroph. Instead, he proposes a sequence of mineral catalysts which spontaneously form positive feedback syntheses involving both organic and inorganic compounds. He postulates the following reaction as the source of reductive energy for this process:



and the reductive citric acid cycle as the primary source of organic units. Most of his discussion is hypothetical, but no more so than some other authors. In concordance with the above discussion of clays, Wächtershäuser posits adsorption on pyrite crystal surfaces, or mineral bubbles. However, I have trouble accepting his energy source. Others have claimed that  $\text{H}_2\text{S}$  would be rare in the early ocean, being precipitated by an excess of iron; and the abundance of pyrrhotite (or troilite,  $\text{FeS}$ ) does not

seem to have been demonstrated. Huber and Wächtershäuser (1998) have shown the synthesis of peptides on a (NiFe)S surface.

## 9. The tree of life and the last common ancestor

We can try to determine how the first living thing may have arisen, but we can also work in the other direction. The idea is to sample ‘all’ of living things to find the characteristics common to all. Then we try to construct a family tree (phylogeny) to try to determine what the last common ancestor was like.

It must be emphasized, however, that this analysis does not identify the first cell type in the origin of life. There would necessarily be major developmental changes from such a first cell to the last common ancestor (Lazcano, 1994a, 1997; Oró, 1994). By the time the last common ancestor came to be, most, if not all, of the environmental foods would have disappeared, eaten up by organisms. We can only hope to fill the gap between the first cell and the last common ancestor speculatively, and a couple of examples will be given below (Section 10). But first, let us look for the last common ancestor.

It is now the method of choice, in determining biological relationships, to use protein or nucleic acid sequences. Of these, one method that carries us near to the common ancestor of all is the sequence of one or another of the RNAs in ribosomes (for the structure of ribosomes, see Frank, 1998). Ribosomes are found in all organisms, participating in protein synthesis, and so must be of ancient origin. It is from these analyses that Woese et al. first separated the Archaea from the Bacteria (Woese and Fox, 1977; Fox et al., 1980; Woese, 1981; Pace et al., 1986). In the meantime, more taxa have been analyzed, and methods have even been devised for the analysis of appropriate RNAs isolated directly from sediments without the necessity of culturing the organisms (Barns et al., 1996a,b; Hugenholtz et al., 1998). Three ‘domains’ have been generally recognized: Archaea (or Archaeobacteria), Bacteria (or Eubacteria), and Eukarya. The Archaea include hot spring organisms, methanogens, halophilic and acidophilic organisms, plus other organisms from cool habitats. The Bacterial domain includes all the ordinary bacte-

ria, including the Cyanobacteria and the anoxygenic photosynthetic bacteria, and the mitochondria and chloroplasts of the Eukarya, with their somewhat independent metabolism. The Eukarya include all the rest of us.

Stetter (1996) has addressed this subject from the point of view of ‘hyperthermophiles’, defined as having optimum growth temperatures above 80°C. He concludes: ‘‘hyperthermophiles occupy all the shortest and deepest branches closest to the root’’, including both Bacteria and Archaea. Many of these organisms are anaerobes, conducting their chemolithotrophic metabolism in the absence of molecular oxygen. Others, presumably more advanced, are aerobes, requiring O<sub>2</sub>. However, the situation is not simple. Barns et al. (1996a) and Hershberger et al. (1996) have described a number of new taxa (by RNA isolation) that fit into the section of Archaea called Crenarchaeota (see also Williams and Embley, 1996), previously thought to be entirely thermophiles. Some of these were isolated from Yellowstone hot springs, but others were from lake sediments, soil or marine sediments, i.e., cool places. Hugenholtz et al. (1998) using the same methods, but looking for Bacteria, found, in the same Yellowstone hot spring (Obsidian Pool), 54 different bacterial types. The majority were similar to known bacteria, but 12 were novel sequences, suggested to represent previously unknown major subdivisions of the Bacteria. Some of the identified clones are apparently chemolithotrophs, reducing sulfate or oxidizing hydrogen; some others are photosynthetic green sulfur bacteria.

It is clear that the situation is much more complex than many of us thought. It may be that thermophilic Archaea and Bacteria are the extant organisms closest to the last common ancestor. But the biochemical basis of high temperature resistance is not yet known. It may be easier to develop a mesophilic species from a thermophilic one than vice versa, but we do not know. One ancient protein is ferredoxin (an organic pyrite). Pfeil et al. (1997) found that the ferredoxin from a thermophile (*Thermotoga*) did not unfold until 125°C, in contrast to other ferredoxins.

One justification for the primacy of thermophiles, sometimes cited, is the thought that if massive impacts heated the oceans, any but thermophiles would have perished. Thus, it is said, hot spring organisms

would have repopulated the world. Even so, this does not necessarily mean that they represent the last common ancestor. The last common ancestor originated long before the thermophiles now extant. Over the millions of years of development (before the fossil record begins) there was time to diversify. And, subsequent to the moon-forming impact, we have no information on how hot things got. Some authors suggest that a number of sterilizing events occurred during the first half billion years of Earth history, but there is no direct evidence. The big Phanerozoic impacts did not boil the entire ocean. On the other hand, if the greenhouse effect did not keep the ocean from freezing, maybe the hot impacts were necessary to keep the ocean liquid (Bada et al., 1995), eliminating any need for thermophiles.

One problem is the root of the phylogenetic tree. In normal phylogenies, one has an outside group with which to compare and establish the root. But with the set of all organisms, there is no outgroup; one gets an unrooted tree (e.g., Hershberger et al., 1996). Kandler (1994) and Stetter (1994, 1996) insert a root between the Archaea and the Bacteria. Recently, the amino acid sequences of a pair of 'protein elongation factors', which are found in all three domains and are thought to have originated by gene duplication before the origin of the last common ancestor, have come into use, to establish a root. Barns et al. (1996a,b) reviewed the data, and put the root between the Bacteria and the divergence of the Eukarya from the Archaea. Baldauf et al. (1996), by increasing the sample size (for the elongation factors) among the Bacteria, Archaea and Eukarya, arrive at what they believe a more certain tree. They came up with a root between the Bacteria and the Archaea, but with the noteworthy addition that the Eukarya have a common origin with one branch (Crenarchaeota) of the Archaea (Fig. 4). So the last common ancestor may still be somewhere among the thermophiles; there are no thermophiles among the eukaryotes.

To further try to pin down the relationships between the three domains, Brown and Doolittle (1997) have examined the sequences of 60 different proteins. Discounting the ones (10 in all) where the differences were not statistically significant, they found that in 31 cases, the Archaea clustered with the Eukarya, in 18 cases the Archaea clustered with

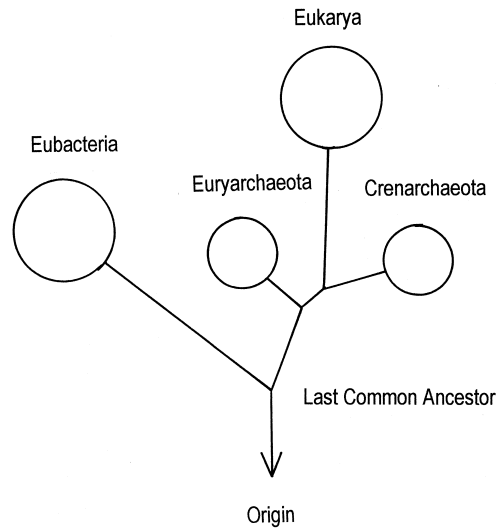


Fig. 4. A recently devised phylogenetic tree showing the early diversification. The lengths of the lines from the root (the last common ancestor) are proportional to the genetic distances to the oldest branch of each line, as given by Baldauf et al. (1996). The data are from amino acid sequencing of elongation factors (EF Tu and EF G) from 24 Eukarya, 13 Eubacteria and nine Archaea (Euryarchaeota + Crenarchaeota).

the Bacteria, and in only seven cases did the Bacteria cluster with the Eukarya. Some of these similarities could have been from horizontal gene transfer; so in general, the Eukarya do seem to be derived from the Archaea. The common ancestor remains between the Bacteria and the Archaea.

Pierson (1994) believes that the common ancestor of the Eubacteria could very well have been photosynthetic, but refrains from suggesting that the last common ancestor of Archaea could be photosynthetic as well. She is at pains to demonstrate that solar UV could be effectively screened out, permitting active growth in the light. Others have suggested very early involvement of light in energy transduction, perhaps with the involvement of ferrous iron (Pierson, 1994)

## 10. Development of metabolism: from soup to the common ancestor

The last common ancestor could not have been a primitive object; whether obtaining energy from light



or minerals, it had to have a complete set of metabolic capabilities. How did it accomplish that (Lazcano, 1994a, 1997; Oró, 1994)?

There are several interesting aspects of that development. But it must be remembered that nobody can say in what order these developments occurred, or even if they took place sequentially. Cell fusions, leading to what we would now call symbioses, surely occurred. The symbioses between Bacteria and Eukaryotes, leading to the modern mitochondria and chloroplasts, are well established.

One principle must be emphasized. That is, no complex system could develop instantaneously. There had to be a period of sequential development. Morowitz (1992) calls this the principle of continuity. Horowitz (1945) first enunciated this principle in connection with the development of synthetic metabolic pathways. He pointed out that since many intermediates in biosynthetic pathways have no other function, a pathway had to be developed in a direction inverse from the synthetic sequence. Otherwise, no positive selection could occur, and negative selection would eliminate the useless variants. This scenario assumes a genetic mechanism already in place.<sup>1</sup>

However logically imperative the Horowitz hypothesis (the retrograde hypothesis) may be, it must be recognized that at the early time that metabolism started, enzymes (whether RNA or protein based) could not have had the high specificity found today. In fact, metabolism must have started non-enzymatically, using as catalysts amino acids, small peptides, clays, and the same basic cofactors (or their analogs) used today: pyridoxal, nicotinamide, pyrophosphate, thiamin, folic acid, metal ions, etc. In a similar vein, Wächtershäuser (1994) and de Duve (1995) emphasized thiols (such as coenzyme A) and the importance of the coenzymes and their synthesis in primordial times. Some of the coenzymes have been found in prebiotic syntheses (such as nicotinamide) but others have not (Miller, 1992). Keefe et al. (1995) have reported the abiotic synthesis of the

thiol pantetheine, a portion of Coenzyme A, essential in the metabolism of carbohydrates and fats. Pyridoxal (and its variants), by itself, is known to take part in the same reactions as now catalyzed by pyridoxal with the help of enzymes. Subsequent biological progress has been in the increased enzyme specificity with respect to the substrate, a Darwinian process.

The aspect of molecular biology that has most interested those also interested in origins is the genetic code and its associated protein synthetic mechanism. Lacey and Mullins (1983) and Lacey et al. (1985) proposed that the code arose by a lipophilic/hydrophilic match between certain amino acids and nucleotides of the code itself, but using the anticodons (of the transfer RNAs) rather than the codons of the mRNAs. Hobish et al. (1995) have shown, using an NMR analysis, a direct association between amino acids and the nucleotides of the corresponding anticodons. (The codons are the triplets of the mRNA which code for the amino acids; the anticodons are the corresponding triplets of the tRNAs, carrying the amino acids.)

Carrying on the theme of gradualism, some authors have suggested that the early protein synthetic mechanism only coded for four amino acids and that the others were added later. On the contrary, this author (McClendon, 1987) has suggested that the early protein synthetic mechanism did not discriminate well between amino acids of similar hydrophobicity. Zubay (1996) elaborates on this theme. From this hypothesis, I concluded that the specificity of the coding system gradually increased until, by the time of the last common ancestor, it was fixed as we see it today. Although minor variations do occur, the present code could not be seriously altered without damaging most of the proteins of an organism. If other genetic codes once existed, they have disappeared.

Another theme I have elaborated (1987) builds on the Horowitz hypothesis with respect to the synthetic pathways of amino acid synthesis. Here, I give some examples.

The synthesis of lysine is carried out today by two different pathways; one in the higher fungi and Euglena (the AAA pathway), and the other (the DAP pathway) in all other organisms that do make lysine, i.e., all autotrophs and many bacterial heterotrophs.

<sup>1</sup> Horowitz (1965) later proposed a mechanism for the initiation of new enzymes which is not so plausible (Lazcano et al., 1995) but does not negate the general hypothesis.

The fungal mechanism (AAA) builds off the citric-acid-cycle; this latter is common to many bacteria and all higher organisms (even though they use the DAP pathway) as an essential part of their respiratory system. The DAP mechanism is much more exotic, using reactions and intermediates which occur there and nowhere else. The only reason I can think of for this situation is that at the time that lysine synthesis became critical (it is extremely scarce in primordial synthesis experiments, but essential for life as we know it), the citric acid cycle had not been developed and an alternative was improvised. (The fungal pathway could develop later, in a heterotroph utilizing exogenous lysine.) The immediate metabolic precursor of lysine (on the DAP pathway) is 2,6-diamino pimelate, which must be at least as rare as primordial lysine. However, pipercolic acid, the ring analog of lysine (as proline is the ring analog of ornithine), is found in spark syntheses and in the Murchison meteorite (Table 1). The last ordinary precursors of lysine in this pathway are aspartic acid and pyruvic acid, but several steps intervene between these and the pimelate.

On the other hand, the synthesis of several other amino acids do depend upon intermediates of the citric acid cycle. In this regard, it is necessary to note that some bacteria today do not have a complete citric acid cycle, using the part they do have only for amino acid synthesis. Some of these, and others, use the citric acid cycle in reverse, the reductive citric acid cycle, in their photosynthetic carbon fixation. Wächtershäuser (1994) and Russell and Hall (1997) include the reverse citric acid cycle in their very earliest proto-organisms, but this seems unlikely to me.

Thus, if we assume that the earliest organisms derived their amino acids from the environment, the capacity for their biosynthesis probably developed in the reverse order of their abundance in that environment.

Melendez Hevea et al. (1996) have considered the citric acid cycle from the point of view of its evolutionary development. They admit that it must have started as a means to generate amino acids. But they also came to the conclusion that it is the best possible sequence of reactions to oxidize acetate with a high yield of ATP. I conclude that it probably went through a period of Darwinian optimization.

Another example of the diversity of metabolism is the nature of the mechanisms by which photosynthetic and chemosynthetic organisms fix carbon dioxide. The dominant one today is the Calvin–Benson cycle, with Rubisco, found in all photosynthetic Eukarya and in the Cyanobacteria from which their chloroplasts arose. But Kandler (1994) points out that among the other Bacteria, three other mechanisms also exist: the reductive citric acid cycle, the reductive acetyl-CoA pathway, and the reductive malonyl-CoA pathway. Among the Euryarchaeota, only the reductive acetyl-CoA pathway has been found, while in the Crenarchaeota, the reductive citric acid cycle has been found.

The question that these examples are intended to illuminate is the possibility of elucidation of an order of development of all of internal metabolism. A thorough exposition of this is beyond the scope of this review, however.

## 11. Conclusions

The geological history of the Earth is in a mature phase as regards the early Archean and Hadean. The biological fossil record goes back as far as we can reasonably expect it. Perhaps, new discoveries will extend the record into the Hadean, but that seems unlikely. Unfortunately, this history apparently begins with metabolically advanced organisms which emit elemental oxygen. Thus, much of the origin of life is still hidden from us. Perhaps, exploration of Mars will give us more clues.

Likewise, the history of the formation of the solar system, and of the Earth in particular, seems to be pretty well settled. But the atmosphere and climate of the early Earth are not so well known and we need more information about the composition of short period comets and the deposition of organics on the early Earth.

There seems to be agreement that the water of the ocean came as comets. Theoretical models indicate that the ocean arose within a few million years of the origin of the Earth, accumulating after the massive impact that formed the moon. At the same time, plate tectonics began, with submarine hot springs and subduction zones. Since almost the whole litho-

spheric surface was ocean floor, evidence of Hadean events has been destroyed.

The original atmosphere probably contained much carbon dioxide, to generate the warming needed. On the other hand, perhaps the ocean was kept warm only by incoming bolides. The geochemical evidence indicates that the atmosphere was generally reducing or neutral until the Proterozoic. Microfossil and isotopic evidence has been interpreted to indicate that oxygen was being produced by Cyanobacteria as early as 3.8 Ga. This apparently was used up in the ocean by oxidizing iron and sulfur, without addition to the atmosphere.

Numerous possible sources of abiogenic organic compounds have been identified. Some were extraterrestrial (meteorites, comets, smaller debris). Others were terrestrial (impacts by meteorites in the atmosphere, lightning, submarine hot springs).

The synthetic organic chemistry of 'prebiotic' compounds has come to an impasse. Although many monomers have been shown to occur in simulations, nucleic acid-type polymers resist our efforts. Proteins of regular structure are likewise missing. Most of this work has involved chemistry in solution, attempting to simulate primordial conditions. But other approaches may yet yield fruit, such as the clay genes of Cairns-Smith (1982, 1985) and the primitive autotrophs of Wächtershäuser (1994). Catalysis on mineral surfaces may be needed to provide the stereospecific environment for biopolymer synthesis.

The projection backward of family trees has been very informative, suggesting that the 'last common ancestor' was somewhere between the Eubacteria and the Archaea. New is the suggestion that the origin of the Eukarya (which share some characters with the Archaea) is between two sections of the Archaea. Since modern thermophilic bacteria (both Archaea and Eubacteria) occur near the root of the phylogenetic tree, some authors suggest that the last common ancestor was a thermophile. But there is a long distance between any modern organism and the last common ancestor, and another long distance between the origin of life and the last common ancestor.

Attempts to fill the gap between the remote origin and the last common ancestor have been made. The 'RNA world' is a term given to the idea that the first genetic system was based on RNA rather than DNA.

But more than that, RNA is seen as the first enzymes, 'ribozymes', which acted upon themselves to make new copies. There is some experimental support for this idea, but limited. Nevertheless, the gap between simple monomers and RNA remains.

Other approaches have to do with deciphering the metabolic pathways of small molecule synthesis, to ascertain the order in which various systems became available. It seems incontrovertible that the synthesis of amino acids must have been devised early, as the supply in the environment ran out. Lysine, being one of the rarest of amino acids that was needed, must have had an early synthesis. Its synthetic pathway in most organisms is unique; in the higher fungi its synthesis branches off the common citric acid cycle. Consequently, it seems probable that the common pathway of lysine synthesis preceded the invention of the citric acid cycle. Other syntheses are not so clear, but the citric acid cycle, even today, is used for synthesis of amino acids, and not for respiration, in some bacteria. An effort to unify the development of metabolism is called for.

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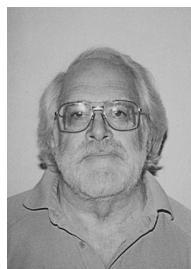
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