

An hypothesis concerning the relationship between submarine hot springs and the origin of life on Earth

Archean fossils
Submarine hydrothermal systems
Origin of life
Mid-ocean ridges

Fossiles archéens
Sources hydrothermales sous-marines
Origine de la vie
Dorsales mid-océaniques

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ABSTRACT

A diverse set of observations from Archaean fossil-bearing rocks, modern submarine hydrothermal systems, experimental and theoretical work on the abiotic synthesis of organic molecules and primitive organized structures, and on water-rock interactions suggests that submarine hot springs were the site for the synthesis of organic compounds leading to the first living organisms on earth. These systems are characterized by high fluxes of thermal energy, highly reducing conditions, abundant and appropriate catalytic surface areas (Fe-Mg clay minerals), significant concentrations of CH_4 , NH_3 , H_2 , metals, etc., and a continuous convective flow which removes products from the site of reaction upward through a mixing gradient of temperature and composition. We hypothesize that the sequence of reactions CH_4 , NH_3 , $\text{H}_2 \rightarrow$ amino acids \rightarrow proteins \rightarrow complex polymers \rightarrow metabolizing organized structures \rightarrow living organisms could occur within and/or adjacent to these systems. Microorganisms found in carefully preserved samples of sulfide chimneys from the East Pacific Rise may be modern counterparts of Archaean fossil organisms. This hypothesis suggests a number of critical observations to be made, both in laboratory experimental systems and on active submarine systems.

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RÉSUMÉ

Une hypothèse portant sur la relation entre les sources hydrothermales sous-marines et l'origine de la vie sur terre.

Une série très variée d'observations faites sur les roches fossilifères d'âge Archéen et sur les sources hydrothermales sous-marines contemporaines, à l'occasion de travaux expérimentaux et théoriques concernant la synthèse abiotique de molécules organiques et structures organisées primitives, et les réactions roches-eaux, indique que les sources hydrothermales sous-marines ont pu être les sites de la synthèse de composés organiques qui donnèrent naissance aux premiers organismes vivants de la terre. Ces systèmes sous-marins sont caractérisés par de hauts flux d'énergie thermique, de conditions fortement réductrices, des surfaces catalytiques abondantes et appropriées (argiles de Fe et Mg), d'importantes concentrations de CH_4 , NH_3 , H_2 , métaux, etc., aussi bien que par un courant continu de convection qui déplace les produits de leur site de réaction vers le haut, par l'intermédiaire d'un gradient continu de température et de composés chimiques en état perpétuel de mélange. Nous proposons que la chaîne de réactions CH_4 , NH_3 , $\text{H}_2 \rightarrow$ acides aminés \rightarrow protéines \rightarrow polymères complexes \rightarrow structures ordonnées et métabolisantes \rightarrow organismes vivants, ait pu prendre place à l'intérieur ou au voisinage de ces systèmes sous-marins. Les micro-organismes trouvés dans les échantillons soigneusement préservés des cheminées de sulfures provenant de la Dorsale Est-Pacifique, pourraient bien être les représentants

modernes d'organismes fossiles trouvés dans les roches de l'Archéen. Cette hypothèse suggère un nombre très important d'observations, qui pourraient être effectuées à la fois en laboratoire et sur les systèmes hydrothermaux sous-marins contemporains.

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INTRODUCTION

We propose that submarine hot springs recently discovered and explored along mid-oceanic rift systems (Corliss *et al.*, 1979 *a*) provide all of the conditions necessary for the creation of life on Earth. There is a parallel between the conditions in the vents and the conditions used in the experimental abiotic synthesis of high molecular weight organic polymers and primitive organized structures (Fox, 1971 ; Yanagawa *et al.*, 1980) with many of the characteristics of primitive living organisms. It appears from analysis of the events of early Earth history that hydrothermal activity connected with seafloor volcanism commenced simultaneously with the formation of the primeval oceans and that this followed soon after the final accretion of the Earth ~ 3.9 billion years ago. In examining the earliest Precambrian rock and fossil record it is notable that cell-like structures and simple organisms have been found in rock units from 3.5 to 3.8 billion years old which we and others interpret as submarine hydrothermal assemblages. In this paper, we synthesize the evidence from experimental biochemistry, micropaleontology, microbiology, planetology, marine geology, and chemistry to present a unified model for the origin of life on Earth. Our argument is presented in the following order :

- 1) early Earth history and the origin of the atmosphere, oceans, and crust ;
- 2) the history and results of abiotic synthesis experiments ;
- 3) a description of submarine hydrothermal processes and a discussion of their potential as sites for the abiotic synthesis of complex organic molecules and cell-like structures ;
- 4) the rock and fossil record of the earliest Precambrian ;
- 5) the evaluation of the hydrothermal vent hypothesis in comparison with other hypotheses for the origin of life ;
- 6) a description of the postulated first organisms.

We are aware of two papers which have previously proposed significant parts of the model proposed here : Ingmanson and Dowler (1977) and Degens (1979).

EARLY EARTH HISTORY

It is generally accepted that the Earth and the other terrestrial planets accreted roughly 4.5 BYBP. The process of accretion led to the differentiation of the core from the mantle. This stage of accretion and core-formation proceeded from roughly 4.6 to 4.2 BYBP (Smith, 1979 ; Ringwood, 1975 ; Hartmann, 1978 ; Goodwin, 1976).

Evidence from the Moon indicates that the inner Solar System was bombarded by large planetesimal objects (10-100 km in diameter) from 4.2 until about 3.9 BYBP (Tera *et al.*, 1974 ; Wasserburg *et al.*, 1977 ; Kaula, 1979). The impact of as many as 10^3 to 10^4 of these objects onto the Earth would have led to major volcanic activity as well as

contributing significant mass to the early Earth. It is possible that as much as one-fifth of the earth's mass was acquired in this period of giant impacting (Smith, 1976).

The enormous energies released through the processes of giant impacting and the decay of short-lived radionuclides would be sufficient to melt the surface of the planet, covering it with a hot silicate magma (Shaw, 1976). The magma would be convecting vigorously, degassing volatiles to form a primeval secondary atmosphere (Fanale, 1971) and radiating heat into that atmosphere. The atmosphere itself would be convecting and radiating heat into space.

As impacts diminished over time and as heat radiated into space, the surface of the planet eventually would have cooled sufficiently to permit thin crustal fragments to form. With continued cooling, rafts of solid silicates would coalesce to form a continuous, though thin and brittle shell, insulating the atmosphere from the magma. Continued cooling by radiation into space would then allow liquid water to condense from the atmosphere, and rains would begin on the primitive Earth (Walker, 1976).

Shaw (1976) proposes that lateral inhomogeneities in the composition of this early crust would be produced by magmatic differentiation and convection. The less dense, isostatically higher protocrust would form the primitive continental areas while ocean basins would form in areas of denser, isostatically lower protocrust. The thin suboceanic crust would be subjected to both tidal and isostatic body forces and to surface drag from the underlying convecting magma, leading it to fracture, resulting in submarine volcanism analogous to that at present day spreading centers. Once ocean waters came into contact with ocean floor volcanism, be it through individual volcanic centers or through rift zone processes, hydrothermal activity would commence. These hydrothermal systems extract both the heat and dissolved gases from the magma and transport them into the oceans ; the flux of both was presumably significantly greater in the first oceans.

The critical point for our model is that eruption of magma into the oceans and the cooling of this magma by hydrothermal circulation is the process required for the origin of life on Earth, and that this process has been a prominent feature of the oceans since they first formed.

ABIOTIC SYNTHESIS EXPERIMENTS

Early research on the origin of life was initially done by chemists and biochemists as experiments in closed laboratory systems (Calvin, 1969). The goal was synthesis of simple organic compounds, such as amino acids, from inorganic compounds under conditions considered to exist on the early Earth. The typical procedure involved confining a mixture of gases believed to be present in a primeval Earth atmosphere in some sort of distilling container, providing an energy input, and analyzing the resulting reaction products. It has been argued, e.g. Holland (1962),

that the early atmosphere which resulted from volcanic outgassing was a reducing one. The gases thought to have been present, and often observed as the products of volcanic outgassing, are H_2 , H_2O , CO_2 , H_2S , S , CH_4 , NH_3 , and/or SO_2 . Various combinations of these gases have been used in abiotic synthesis experiments.

There were at least five different sources of energy available on a primitive Earth: high energy particles from radioactive decay, solar radiation (UV and visible), electrical discharges from the atmosphere, shock waves from planetesimal impacts, and thermal energy from volcanism. Miller (1955) first demonstrated the abiotic synthesis of amino acids in a presumed early Earth environment by spark discharge in a continuously recycled low temperature mixture of reduced gases and water (CH_4 , NH_3 , H_2 , H_2O), simulating lightning discharge in a primitive atmosphere. Subsequent experiments have shown that these reactions can be driven by a variety of energy sources (Calvin, 1969).

The next steps in the abiotic synthesis sequence are the condensation reactions such as those necessary to polymerize amino acids to form complex proteins by extraction of water and formation of peptide bonds. Ultimately, the process must lead to the formation of individual entities which can carry out the processes which define a living organism: the ability to metabolize, reproduce identically, and adapt. Fox and his colleagues pioneered the use of thermal energy for abiotic synthesis, and developed a model sequence of events: primordial gases \rightarrow amino acids \rightarrow primitive protein \rightarrow a primitive organized structure. They used heat to drive off water and produce condensation reactions, forming "proteinoid" mixtures, which, on addition of water, produced "protocells" which had "a cellular type of ultrastructure, double layers, abilities to metabolize, to grow in size, to proliferate, to undergo selection, to bind polynucleotides, and to retain some macromolecules selectively" (Fox, 1971).

It is important to point out that these condensation reactions have been shown to occur, without drying, in aqueous solutions such as those in hydrothermal systems, if the reactions are coupled with the hydrolysis of condensing agents such as cyanamide or cyanoacetylene derived from hydrogen cyanide. HCN should be readily synthesized under hydrothermal conditions, thiocyanate presumably derived from HCN and H_2S , has been detected in the hydrothermally produced Red Sea brines (Dowler, Ingman, 1979). Montmorillonite clays, abundant in hydrothermal systems, have also been shown to catalyze these condensation reactions, serving as templates for protein synthesis (Degens, 1979; Lahav, Chang, 1976; Paecht-Horowitz, 1970; 1978). Recently, Yanagami *et al.* (1980) have succeeded in synthesizing "Fox-like" protocell structures by holding a mixture of amino acids in modified sea water (with added Fe, Mn, Zn, Ni, Co and Mo) under warm, acid conditions ($105^\circ C$, pH 5.2). Polymers containing peptide bonds, with molecular weights from 1,800 to 82,000 daltons, were produced in the interiors of these structures.

The physical and chemical conditions of those experiments are found in a natural environment which has been present in the oceans since they first formed, in hot springs associated with submarine volcanism.

SUBMARINE HYDROTHERMAL SYSTEMS

The quenching of newly injected crust on the sea floor by circulating seawater, which we believe is clearly recorded in

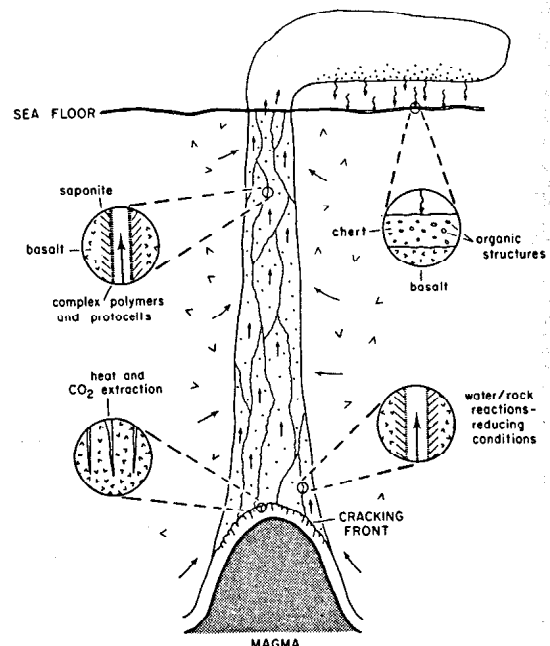
the Earth's oldest rocks (see below), continues today. The first direct observations of these hydrothermal systems along mid-oceanic spreading centers was carried out in early 1977 along the Galapagos Rift (Corliss *et al.*, 1979 *a*) using the deep diving submersible, Alvin. Research on the extensive set of data and samples collected on this expedition has allowed us to characterize the behavior of the interaction of seawater with newly erupted crust in great detail. More recent observations from the East Pacific Rise at $21^\circ N$ provide additional significant information (Spiess *et al.*, 1980; Hekinian *et al.*, 1980).

Sites of submarine volcanism bring together in a single system a unique combination of rocks, gases, heat, and water. The relevant features of a hydrothermal system are summarized in Figure 1. These sites of eruption occur when crustal plates are spreading apart, allowing magma to rise in the crust, approaching closer to the sea floor and producing a strong thermal gradient across the layer of previously erupted and cooled rock. This layer of rock has undergone thermal contraction and fracturing and is subject to tensional cracking resulting from the spreading of crustal plates. As a result, the crust is permeable and becomes saturated with seawater.

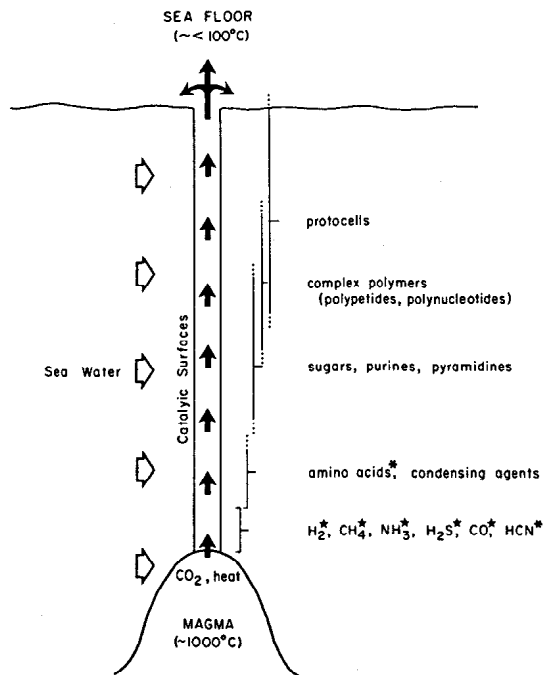
"Active" hydrothermal circulation is driven by the rapid transfer of heat from the magma to the water at the "cracking front" (Lister, 1974). The water which saturates

Figure 1

Hypothetical model of the submarine hydrothermal system as a continuous flow, and mixing gradient packed-bed reactor for the abiotic synthesis of living organisms or their immediate precursors.



a. Heat and CO_2 are extracted from the magma at the cracking front; the reduced gases, reduced transition metals and other appropriate components are introduced during the water/rock interactions. These low density, low viscosity fluids, rise rapidly through an anastomosing fracture system, lined by appropriate catalytic surfaces, entraining and mixing with the cool sea water saturating the surrounding cold rocks. As the fluids reach the sea floor and mix rapidly with bottom water, the supersaturated components of the fluids which are saturated in the bottom water precipitate, forming chemical sediments around the vents.



b. The proposed sequence of chemical and biochemical events leading to the formation and development of "protocells" would occur along the thermal and the chemical substrate concentration gradients which exist within the upwelling fluids of these hydrothermal vents. Amino acids and other reactive compounds such as hydrogen cyanide and its derivatives and formaldehyde could be synthesized from the dissolved gases, initially at high temperatures. At lower temperatures additional amino acids and peptides could be synthesized, catalyzed by reactive compounds and clay minerals. "Protocell" formation could occur within this gradient under the appropriate temperature, pH and other chemical and physical conditions (for example, Yanagawa *et al.*, 1980). These "protocells" provide a protected microenvironment bathed in cooling hydrothermal fluids and/or bottom waters containing reduced transition metals, dissolved reactive gases and other components which have been shown to be appropriate for the abiotic synthesis of polypeptides and polynucleotides. The "protocells" could be deposited along with silica precipitated from the supersaturated hydrothermal fluids to form carbonaceous cherts, containing organized organic structures such as found in the *Isua* rocks. The asterisk components have been detected in modern hydrothermal systems (Gordon, Lilley, *pers. comm.*), the starred components have been reported in Red Sea brines (Ingmanson, Dowler, 1979; and Dowler, Ingmanson, 1980).

the cold, permeable rock "attacks" the magma body in a continuous cycle:

cooling → crack propagation → water penetration → convection → cooling.

Within the magma body, removal of heat from the upper surface leads to plating of the crystallizing mineral phases onto the roof of the magma chamber, forming a zone of crystalline mush which grades upward into solid rock. Heat from the magma is conducted across this interface up to the "cracking front" where it is extracted by circulating water.

This interface is the site where a significant fraction of the cooling and degassing of the Earth has occurred. Gordon and Lilley (*pers. comm.*) have shown that significant quantities of CO_2 , NH_3 , and H_2 are present in the hydrothermal fluids at the Galapagos Rift. O'Neil (*pers. comm.*) has analyzed the carbon isotope composition of CO_2 in these samples and found $\delta^{13}\text{C}$ values of -5.1 to -5.3 , establishing it as primordial carbon. Primordial He^3 is also present in the Galapagos fluids (Jenkins *et al.*, 1978). The constancy of the

He^3 /heat ratio in several individual vents suggests that the gases and heat are extracted from the rock in the same process (Corliss *et al.*, 1979 *b*). In addition to these gases, the magma contains all of the naturally occurring elements.

As the magma crystallizes, the gases and the "incompatible" elements (those not entering the growing crystal lattices) are fractionated into the intercrystalline fluid, and when crystallization is complete, they occupy the intergranular spaces. As the rock cools below the solidus, the differential thermal contraction of the individual grains will tend to open an interconnecting network. As a fracture propagates into the vicinity, it introduces water into the network. The water extracts both the gases and "incompatible" elements in the intergranular spaces, and reacts with solid phases altering them and extracting additional elements, including transition metals.

It is difficult to estimate the maximum temperatures this water can attain. The magma solidifies at $\sim 980^\circ\text{C}$. Lachenbruch (1962) has suggested that such fractures, once initiated, could propagate past the solidus boundary into the area where residual fluids are not entirely crystallized. It is not unreasonable to believe that water could attain temperatures close to the solidus temperature of the magma. Evidence from the Galapagos Rift and the East Pacific Rise indicates that the water reaches temperatures greater than 350°C (Spiess *et al.*, 1980). Water at these temperatures and sea floor depths has low density and viscosity, leading to very rapid convection and the ability to readily penetrate into the rocks. As the fluids rise, they enter an anastomosing and expanding set of fractures and fissures, all the while incorporating cooler water which is drawn into the rising plume from the adjacent cool, permeable rocks. Hot seawater interacts with the basalt, forming saponite, a magnesium-rich smectite clay which incorporates magnesium from the seawater. This process lowers the pH of the seawater by removing OH^- and lowers the Eh by oxidizing ferrous iron in the rocks through the reduction of SO_4^- and/or oxygen from the dissociation of water (Bischoff, Dickson, 1975; Hajash, 1975; Seyfried *et al.*, 1978; Seyfried, Bischoff, 1977). The fluids emerging out of the sea floor from vents on the Galapagos Rift and from most vents on the East Pacific Rise (21°N) had temperatures in the range of $10\text{-}30^\circ\text{C}$ as a result of the mixing process. However, at some of the 21°N vents, water emerged at temperatures of $\sim 350^\circ\text{C}$. Presumably, there was a direct vertical channel to some depth in the rock. These high-temperature vents precipitate dissolved metals forming large sulfide chimneys (Hekinian *et al.*, 1980).

It appears to us that submarine hydrothermal systems are ideal reactors for abiotic synthesis. The stages of the process which we are proposing are shown in Figure 1 *b*. The raw materials are extracted from the magma in the vicinity of the cracking front. Low molecular weight organic compounds could be synthesized at high temperatures and then rapidly moved upward along a gradient of continuously decreasing temperature and concentration. The exposed surface area in the fractures and interstices is coated with alteration minerals, dominantly saponite, a Mg-montmorillonite. Montmorillonites have been demonstrated to be effective catalysts for abiotic synthesis reactions. Through clay catalysis and condensing agents the low molecular weight organic compounds could be polymerized into more complex compounds and plate out onto the walls of the fractures, eventually forming protocells. These interiors of these protocells form a protected microenvironment in which further abiotic synthesis could proceed. The rising

fluids would wash the protocells off the surfaces and transport them upward, depositing them in cooler environments in the vent system or on the adjacent sea floor. Continuous supply in a limited area could result in significant accumulations of these protocells.

EVIDENCE FROM THE OLDEST ROCKS

The evidence for this statement can be found in the three oldest dated series of rocks on the Earth (Table 1). They are Archaean greenstone belts containing sequences of rock that have all the major characteristics of modern sea floor hydrothermal environments and/or of preserved sea floor hydrothermal environments found throughout the geological record younger than the Archaean. They contain sequences of hydrothermally metamorphosed tholeiitic mafic and ultramafic rocks including pillow basalt sequences, overlain by and overlying bedded sediments (silicate, carbonate, sulfide, oxide and reduced carbon facies). Ridler (1970 ; 1976) has named these hydrothermal chemical sediments, common in Archaean greenstone belts, the "exhalite" facies.

The Onverwacht Series is a 3.5 billion year old (Hamilton *et al.*, 1979) rock assemblage in the Barberton Mountain land of South Africa. The Onverwacht Series forms the base of the Swaziland System. Directly above the Onverwacht Series is the Fig Tree Series. A synthesis and review of the earlier field work in this area was presented by Anhaeusser *et al.* (1968). Recently, de Wit *et al.* (1980) have reinterpreted the entire Swaziland System in light of present-day knowledge of submarine hydrothermal processes.

Anhaeusser *et al.* described a sequence of metamorphosed basic lavas with interlayered siliceous sediments, occasional thin carbonaceous chert horizons, and bands and lenses of serpentinized ultramafic rocks. De Wit and Stern noted the similarities in metamorphic textures and mineralogies to the sheeted dike complexes and flanking pillow lavas of Phanerozoic ophiolites. The extensive hydration of the Onverwacht minerals they feel is best explained by metamorphism at a spreading ridge. Evidence for this interpretation is also found in the presence of banded iron formation, rich metallogenic sediments, barite, carbonates, and cherts. Si, Ba, Ca, and Fe are dominant components of greenschist belt chemical sediments (Ridler, 1976) and submarine hydrothermal systems are a significant or dominant source of these elements into the ocean today (Corliss *et al.*, 1979 a ; Edmond *et al.*, 1979 a, b). Si, Ba and Ca are presently maintained near saturation by biological mediated precipitation. In the Archaean ocean, hydrothermal input must have saturated the oceans in these components, leading to rapid precipitation in areas of submarine volcanism. Vezeir (1979) describes chemical and isotopic data for Archaean sediments, all of which are consistent with a single assumption that the seawater-oceanic crust exchange was exceptionally high during the Archaean. Fe-oxides are the dominant component of metalliferous sediments associated with hydrothermal activity along modern mid-ocean ridges (Dymond, 1981).

It is a very intriguing fact that a number of workers have isolated fossil forms from the Onverwacht Series. Engel *et al.* (1968) "isolated both siliceous and carbonaceous particles and carbonaceous filaments" from cherts, argillites and carbonate beds in the Onverwacht. Furthermore, "the spheroids within the carbonaceous Onverwacht sedi-

Table 1
A comparison of Isua, Onverwacht, Warrawoona and Modern Mid-Ocean ridge environments

Age	ISUA ~ 3.8 b.y.n.p. [Moorbath, 1973]	ONVERWACHT ~ 3.5 b.y.b.p. [Jahn and Shih, 1974]	WARRAWOONA ~ 3.5 b.y.b.p. [Sangster and Brook, 1977 ; Pidgeon, 1977]	MODERN MID-OCEAN [RIDGE]
Igneous and Metamorphic Petrology	— amphibolites (layered, massive and dikes) (Bridgewater, 1973) ; — metabasalts with major element distribution in good accord with... modern ocean-ridge basalts (Appel, 1979).	— ophiolite complex consisting of sheeted feeder dike complex, extrusive units fed by dikes, magmatic cumulates spreading ridge metamorphism (deWit <i>et al.</i> , 1980).	— "basalt lavas, commonly pillowed with intercalated chert horizons" (Lipple, 1974).	— tholeiitic pillow basalts and intrusives, hydrothermally metamorphosed crust, greenschist and amphibolite facies.
Chemical Sediments	— cherts, banded iron formation, — "submarine exhalative sulfides in iron formations" (Appel, 1979).	— banded iron formation, manganese rich sediments, clastic and chemical cherts barite (deWit <i>et al.</i> , 1980), — carbonaceous cherts.	— concordant bedded chert-barite within a sequence of carbonated and silicified metabasalts (Dunlop <i>et al.</i> , 1978).	— metalliferous sediments, massive sulfides, biogenic silica and carbonate sediments, hydrothermal sulfides.
Organic Compounds, Structures and Fossils	— carbonized organic matter and esters in fossil cells (Pflug, Jaeschke-Boyer, 1979), — unicells, filaments, and cell colonies with laminar walls (Pflug, 1978), — "fluid inclusions" (Bridgewater <i>et al.</i> , 1981).	— kerogen beaving spheroids and filaments in carbonaceous chert (Engel <i>et al.</i> , 1968), — "fossil microorganisms arrested and preserved in the midst of biological activity" (Knoll Barghoorn, 1977).	— "microfossils with a wide range of morphologies, including solitary spheroids, spheroids with splits, paired spheroids and rare chains of spheroids" (Dunlop <i>et al.</i> , 1978), — stromatolitic fabric (Walter <i>et al.</i> , 1980).	— complex chemosynthetic bacteriological and animal communities (Corliss <i>et al.</i> , 1979 a ; Karl <i>et al.</i> , 1980), — filaments, organic debris, sulfide chimneys (Fig. 2 and 3).

ments not only have the morphologies of fossils, but also are intimately associated with the kerogen-bearing carbonaceous substances which appear to form parts of their walls and interiors. They are also closely associated with *kerogen-bearing, filamentous forms which have the appearance of microfossils*".

Knoll and Barghoorn (1977) have also described populations of organic walled microstructures from the Swartkoppie which they conclude are fossil organisms, in which "various stages of binary division are clearly recorded". They also conclude that the fossil-bearing cherts were deposited in shallow water, citing the presence of oolites, cross-bedding and flat-pebble conglomerates.

Engel *et al.* commented upon the difficulties of interpretation of the carbonaceous filaments, reporting that the filamentous layers in the carbonaceous argillic chert are of a diverse morphology and remarkably lifelike. They concluded that "many appear to be true fossils, although less well-preserved than those found in younger Precambrian sediments". There is an interesting correlation between these fossil descriptions from 3.5 billion years old hydrothermal sediments and the appearance of complex filamentous organic structures in scanning electronmicrographs of chimney rock samples from 21°N. One of these micrographs is reproduced here as Figure 2.

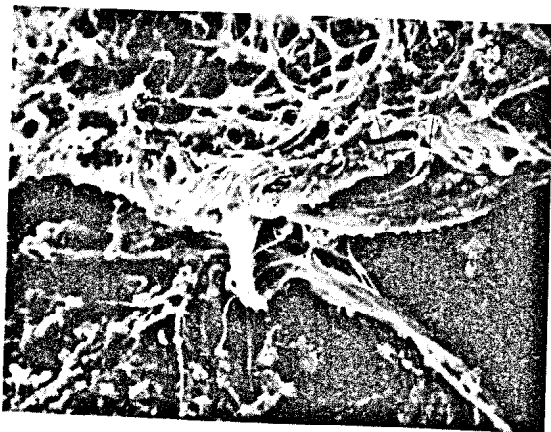


Figure 2
Scanning electronmicrograph showing thin unraveling strands of organic or possibly inorganic sheaths which were frequently found on hot chimney rock surfaces from 21°N. These structures resemble, to some extent, the fossil structures observed in ancient rocks (see text). Bar is 10 μ m. The samples were fixed in sterile artificial seawater containing 2% glutaraldehyde within minutes after the Alvin surfaced. Sterile techniques were used with all specimens. The fixed samples were dried by the critical method, then mounted on aluminum stubs and coated under a vacuum with a layer of gold 10-20 nm in thickness. The samples were viewed using an international scientific instruments mini-SEM, model MSM-2, scanning electron microscope.

Recently, a new suite of Archaean microfossils has been found in a 3.5 billion year old terrain in Western Australia, the Warrawoona Group of the eastern Pilbara Block (Dunlop *et al.*, 1978). The organisms were discovered in stromatolitic structures (Lowe, 1980; Walter *et al.*, 1980) which form a part of the North Pole dome, a major greenstone dome consisting of pillow basalts, cherts, and felsic volcanics (Hickman, 1972; Lipple, 1974). A remarkable similarity between the Onverwacht succession and the Warrawoona Group has already been noted (Barley *et al.*, 1979).

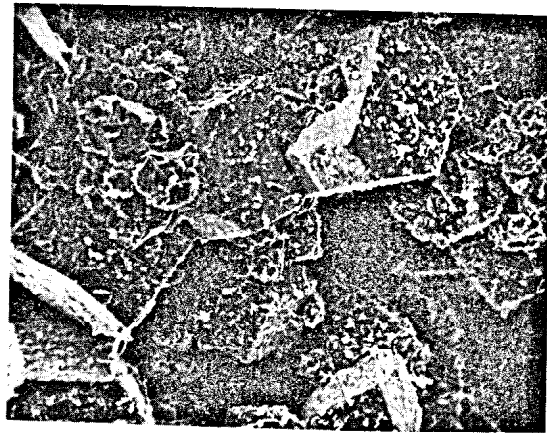


Figure 3
Scanning electronmicrograph showing the surfaces of inorganic crystals covered with deposits of organic debris and microorganisms which have been emitted from "black smoker" chimneys at 21°N and have settled on the surfaces of the chimneys and the surrounding rocks and animals. The samples were prepared as described in Figure 2. Photo magnified 400x.

Once again, there is a sequence of mafic and ultramafic extrusives, pillow basalts, cherts, and other volcanic rocks intercalated with pyroclastics and probable turbidite deposits, which indicates extensive submarine volcanism and consequent hydrothermal activity and evidence of a high energy depositional environment interpreted as indicative of shallow water.

Even more interesting in terms of our model is a group of rocks which outcrop in southwest Greenland at the edge of the Greenland ice cap. This is the Isua supracrustal succession, which includes the oldest sedimentary rocks yet dated. The stratigraphy and petrology of the Isua succession are described by Bridgwater *et al.* (1976) and Allaart (1976). The rocks are basic and ultrabasic greenschist, metamorphosed sediments and quartz feldspathic rocks with many similarities to younger greenschist belts. They have been metamorphosed to the amphibolite facies, and some units have retrogressed to the greenschist facies. The rocks form a layered series. Included in the succession is the Isua ironstone, a finely banded sequence of magnetite and quartz-rich layers. The ironstones have been dated by Pb-Pb at $3.76 \pm .07$ BYBP (Moorbath, 1973). Bridgwater *et al.* interpret these siliceous rocks as chemical sediments. They are interlayered with chlorite-rich basic rocks interpreted as sills. We interpret this sequence of rocks as submarine lava flows and related hydrothermally-derived silica and iron oxides.

Appel (1979) has noted that the major element distribution of the Isua metabasalts is in good accordance with the patterns of modern ocean ridge basalts and that the massive amphibolites in the Isua succession probably represent basaltic lava flows and intrusive sills. Appel concludes that "a submarine exhalitive source of the copper and iron seems... more plausible" because of the occurrence of the sulfides in distinct layers concordant with the banding of the iron formation and the layering of the amphibolites. Overall, the stratigraphic relationships of the sulfide layers to the ironstones and the amphibolites, Appel believes, exclude the possibility of a replacement process. We believe that Appel's observations suggest that the Isua sediments were precipitated from the hydrothermal solutions which cooled and metamorphosed the basaltic precursors of the amphibolites.

In the cherty layers of the Isua quartzite, Pflug (1978) found cell-like inclusions occurring as individual unicells, filaments, or cell colonies. He describes the structures as surrounded by multilaminar sheaths enclosing a more or less globular hollow partially filled with organic matter. Raman laser molecular microprobe analyses of these objects (Pflug, Jaeschke-Boyer, 1979) produced two kinds of spectra: the cell walls and fillings consist of carbonized and graphitized organic material while cell vacuoles contained esters and aliphatic hydrocarbons. They point out the similarities with Fox's protocells but assert that the Isua objects are fossils of living organisms.

Bridgwater *et al.* (1981) cite evidence that the rocks have been exposed to high temperatures in post-depositional metamorphic events which they suggest the fossils could not have survived. They also present the results of their microscopic studies of these objects and conclude that the Pflug microstructures are non-biogenic. They acknowledge the presence of graphitic carbonaceous matter in the Isua metasediments, but assert that "it remains to be established whether this is biogenic or abiogenic in nature and to what extent it may be post-depositional rather than solely syngenetic in origin".

Our model suggests that carbonaceous microstructures such as those described by Pflug could be readily produced abiogenically within the submarine hydrothermal systems which produced the silica in which these microstructures are found. In the Onverwacht and Warrawoona rocks, the carbonaceous microstructures, in what we interpret as hydrothermally deposited cherts, have been widely accepted as fossil living organisms. The question of the origin of the Isua microstructures requires further clarification.

A COMPARISON OF HYPOTHESES FOR THE ORIGIN OF LIFE

All of the other currently favored models for the origin of life lack one or many of the conditions necessary to make the transition from the synthesis of simple organic compounds to the formation of "protocell" structures and complex biopolymers. Table 2 offers a comparison of our model with the model of Oparin (1957; 1977), the theory of panspermia (Crick, Orgel, 1973). Many models, including Oparin's, picture an aquatic environment which contains high concentrations of organic compounds formed through

the input of UV radiation or lightning discharges which somehow react to form larger molecules. Eventually these larger molecules are formed into "coacervates" or "protocells" that acquire the capacity to "transport" organic compounds through a highly organized membrane and to carry on oxidation/reduction and synthetic reactions. These quasi-heterotrophs, as a result of continued exposure to ultraviolet light, develop other structures, including photon-absorbing porphyrins.

This "organic soup" hypothesis predicts that, before the formation of biochemically active "protocells", a proto-environment would have to be formed which contained a high concentration of amino acids and other organic compounds. If such an environment had existed, very ancient sediments should contain significant levels of these amino acids and organic compounds. This is not the case. Instead, in the oldest rocks known to exist, which formed shortly after the cessation of giant impacting, structures have been found which strongly resemble the budding "protocells" described as resulting from experiments using thermal energy. There is no detectable sedimentary evidence for a pre-existing "organic soup". It is also important to point out that, in an oceanic environment, the concentrations of organic compounds would be quite dilute except at the site of synthesis, and heterotrophic organisms could not survive under these conditions. Consequently, the suggestion that the first protist was heterotrophic does not seem to be supportable.

Another problem with the "organic soup" model is that it is known that the conditions necessary for the formation of amino acids and of low molecular weight reactive organic compounds are different from the conditions required for the formation of macromolecules and "protocells". The "organic soup" hypothesis has all these processes taking place in the same vat under the same conditions. However, in our model for the origin of life in submarine hydrothermal systems, the rapid and continuous upward flow of fluids creates gradients of temperature, pH, and chemical concentration in which all of the synthetic reactions needed for the creation of life could take place.

Many biochemically active macromolecules contain various metals, particularly iron, molybdenum, manganese, copper, etc., as part of their structure. Molybdenum, for example, is important in various biochemical processes including the fixation of nitrogen and the reduction of nitrate. It has been hypothesized that early in the evolution

Table 2

Comparison of the properties inherent in the various hypotheses for the origin of life.

Hypothesis	Early Atmosphere	Environment	Energy	Kinds of Gradients	Early Microorganism	Time to Evolve Active "Protocells"
Oparin model.	Reducing (gases).	"Terrestrial" soup.	UV, electric discharges.	None.	Anaerobic heterotrophs.	> 10 ⁹ year.
Panspermia.	"	Directed or non-directed cosmic source.	Moot.	T only.	Anaerobic heterotrophs or phototrophs.	Preformed.
Hydrothermal model.	Oxidizing.	Hydrothermal gradient in seawater.	Heat.	T, pH, chemical concentration.	Anaerobic chemototrophs.	~ instantaneous reaction from reduced gases to "protocells".

of cells or cell-like structures, metallo-proteins, including enzymes, were formed from simple polypeptides and that these early macromolecules were active, although inefficient when compared to present analogous compounds (Ochai, 1978; Egami, 1975). The importance of molybdenum in biochemical processes and the apparent scarcity of this metal in terrestrial environments has been used to support the hypothesis that the first microorganisms on Earth originated from an extraterrestrial source where molybdenum was abundant (Crick, Orgel, 1973). However, the concentrations of molybdenum and other biochemically active metals are not limiting in the present ocean, and it is generally accepted that this was also the case in the early ocean (Holland, 1962). Hydrothermal alteration of oceanic crust has been the primary source of these transition metals to both the ancient and the present oceans.

The synthesis of amino acids from gases by thermal energy has been repeatedly demonstrated in the laboratory (Lemmon, 1970). The fact that very high temperatures (800 to 1,000°C) are required to form amino acids has been a criticism of the hypothesis that life could have originated in high temperature environments. This is because the continued exposure of both low molecular weight organic compounds and polymers to high temperatures after formation leads to their rapid decomposition. It would take only minutes to denature complex protein structures at temperatures greater than 100°C. The temperature gradient of hydrothermal environments provides a natural solution to this problem.

It is also possible that many of the amino acids, particularly those with low molecular weights, are formed at much lower temperatures, given appropriate chemical conditions. It has been demonstrated, for example, that if, besides the presence of the usual gases, reactive compounds such as hydrogen cyanide and formaldehyde are available, amino acids can be synthesized at temperatures between 80° and 100°C (Lemmon, 1970). Amino acids have also been synthesized from formaldehyde and hydroxylamine at 105°C in seawater (Ochai, 1978). This process was found to be greatly influenced by the concentration of molybdenum in artificial seawater. In addition, as previously discussed, Yanagawa and Egami synthesized "protocell" structures in a "modified seawater" medium resembling hydrothermal fluids.

However, the synthesis of the high molecular weight amino acids, such as tyrosine and phenylalanine, from gases requires temperatures close to 1,000°C. High temperatures (600 to 950°C) are also required to form sulfur-containing amino acids from hydrogen sulfide (Raulin, 1978), which is one of the most abundant gases formed in hydrothermal vents. Although oceanic hydrothermal waters have not been analyzed in order to detect hydrogen cyanide and formaldehyde, Dowler and Ingmanson (1979) recently reported the discovery of thiocyanate in Red Sea brines.

In view of these experimental results, we believe that it is highly probable that amino acids are formed in hydrothermal environments over a wide temperature range, between roughly 100° and 1,000°C (see Fig. 1 b). These varying conditions exist in hydrothermal systems and the spatial distance of the hydrothermal temperature gradient is relatively short.

The formation of peptides and other organic polymers from low molecular weight intermediate compounds has also been shown to occur under varying conditions and at temperatures between roughly 150° and 200°C. At tempera-

tures lower than 100°C, the presence of polyphosphoric acid can initiate polymerization (Harada, Fox, 1964). In the Fox recipe for the formation of "protocells", amino acids must be heated to 200° or 300°C under dehydrating conditions. However, in addition to the dehydration reaction described by Fox, it is possible to effectively remove water from amino acids and form peptides through the use of various reactive compounds, such as cyanamides and carbodiimides (Ponnumperuma, 1978). These compounds have been shown to initiate the condensation of amino acids to peptides and of certain purines and pyrimidines to nucleotides. Although there are no published reports on the possible existence of condensing compounds in hydrothermal environments, the necessary reducing gases are present in the required concentrations in order for the synthesis of these compounds to readily take place.

THE FIRST ORGANISMS

Earlier in this paper we discussed how "protocells" containing hydrothermally-derived organic compounds could have formed in very high numbers within the vents and would have been carried out into cooler ocean waters by circulating hydrothermal fluids. In the present vents, the most abundant groups of chemoautotrophic bacteria isolated from both the Galapagos and 21°N have a temperature range for growth from a minimum of 10 to 20°C to over 70°C (the higher minimum and maximum growth temperatures are from bacteria isolated from 21°N samples) (Baross, unpublished results). Since the ambient water temperature around the vents is approximately 2°C these bacteria would be incapable of growth outside of the vents proper. The fact that a significant portion of the primary producers in these environments is found within the vents definitely underscores the efficiency of hydrothermal gradients in sustaining life.

In a hydrothermal system, it is highly probable that most of the amino acids and other organic compounds would be condensed into polymers and "protocells" shortly after their synthesis. Consequently, it does not seem likely that there would be an accumulation of soluble organics as in the Oparin model. Instead, within the newly-formed protocells, the synthesis of high molecular weight compounds would probably continue due to the inclusion of low molecular weight organic condensing compounds, reactive gases and reduced metals. Any high molecular weight substances internally synthesized would be unable to pass out of the early cells. This strongly implies that the first protocells and ultimately the first protists were *anaerobic chemoautotrophs*, organisms which could utilize the hydrothermally delivered gases such as CO₂, H₂, NH₃, H₂S (and perhaps sulfate or some other oxidized form of sulfur), and HCN with the reduced metals to carry out internal oxidation/reduction reactions. Eventually, biochemically active macromolecules and energy transforming compounds such as NAD and ATP could be formed.

The use of inorganic gases and metals as energy sources in these early organisms would solve one of the major problems in current research into the origin of life: explaining the formation of the complex membrane required by heterotrophic organisms for the transport of organic compounds. It would also explain how these early microorganisms would survive in an oceanic environment where organic compounds would be quite dilute and how they could perpetuate before evolving the complex macromolecules

needed for division by binary fission. It is possible that the earliest cells "reproduced" as a result of "swellings" in portions of the cell surface, a mechanism that would appear similar to budding and would result in the distribution of internally synthesized organic compounds. It is interesting that "protocells" synthesized in the laboratory were found to be capable of budding and forming chains of cells (Fox, 1971), and that Pflug and Jaeschke-Boyer (1979) and Knoll and Barghoorn (1977) found possible fossil evidence of budding cells in the Isua and Onverwacht rocks.

It is also quite conceivable that these early "protocells" were capable of reducing CO₂ and sulfate to methane and sulfides through the use of hydrogen. This implies that the earliest organisms were methanogens (Woese, 1977) and related "archaeobacteria". The molecular analyses of tRNAs, rRNAs, and cell wall components of various species of methanogens not only indicate that they are distinctly separate from most of the other procaryotes but also that, as a nutritional group, they are markedly heterogeneous (Balch *et al.*, 1979). They state that the apparent rate of change in the sequence of RNAs is more rapid in methanogens than in other groups of bacteria, such as the "eubacteria". A possible interpretation of these data, in keeping with our hypothesis for the origin of life, is that the methanogens developed somewhat different molecular structures and morphologies, because they evolved separately over some period of time in different hydrothermal environments. It is conceivable that the most common present-day group of procaryotes, the "eubacteria", could have evolved from just one of the separate groups of methane producers.

CONCLUSION

In this paper we have drawn together data from diverse scientific disciplines to assert that hydrothermal systems provide an ideal environment for the thermal abiotic synthesis of complex organic compounds and simple organisms. This hypothesis is compatible with the geology and paleontology of the Archaean and with the results of abiotic synthesis experiments. We are proposing that abiotic synthesis occurred as an integral part of the origin and evolution of the atmosphere, ocean, and crust.

There are three additional interesting considerations regarding this model:

- 1) A reducing atmosphere is not a prerequisite for the origin of life. An appropriate reducing environment, with sources for all of the required raw materials and which feeds into a packed-bed continuous flow gradient reactor lined with appropriate catalytic surfaces has been present on the floor of the oceans since they formed.
- 2) A long time interval between the appearance of a life sustaining environment (e.g. liquid water) and the appearance of the first living organism on earth may not be required. There seems to be no reason why protocell structures would not have been rapidly produced in these hot springs as soon as they formed in the Archaean oceans. The next step, the evolution of protocells to living organisms, is a function of probabilities, an improbable event becomes more probable with an increasing number of trials.

The ubiquitous nature of the process provided an extremely large number of trials.

- 3) It is not clear whether deep water hot springs are required for the process. The Onverwacht and Warrawoona fossils are found in rocks with evidence of a high energy depositional environment with evaporite minerals which has been interpreted as a shallow environment, but it is possible that a high energy environment and salt saturation could occur in deeper water in the Archaean oceans. Interesting questions include the effect on abiotic synthesis of boiling in shallow systems and high pressures in deep systems.

The early Earth was a complex, evolving system. The system was probably driven then, as it is now, by mantle convection through a mechanism of plate tectonics. Then, as now, new crust formed along submarine rift systems and was cooled, degassed and metamorphosed through reaction with seawater. We believe that we have convincingly demonstrated that living organisms could have been created as a result of this reaction.

One of the unavoidable conclusions to be drawn from our hypothesis is that the events leading to the formation of complex organic compounds and "protocell" structures may still be occurring in present-day oceanic hydrothermal systems. However, the complex communities of bacteria in modern oceanic environments would outcompete and consume any abiotically synthesized protocells, preventing their evolution into more organized entities. Future expeditions to oceanic hydrothermal environments will attempt to obtain evidence bearing upon our hypothesis.

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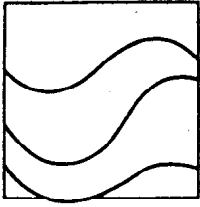
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REFERENCES

- Allaart J. H., 1975. The pre-3760 m.y. old supracrustal rocks of the Isua area, central West Greenland, and the associated occurrence of quartz-banded ironstone, in: *The Early history of the Earth*, edited by B. F. Windley, John Wiley and Sons.
- Annhaeuser C. A., Roering C., Viljoen M. J., Viljoen R. R., 1968. The Barberton Mountain land: a model of the elements and evolution of an Archaean fold belt, *Geol. Soc. South Africa Trans.*, **71**, 225-254.
- Appel P. W. U., 1979. Stratabound copper sulfides in a banded iron-formation and in basaltic tuffs in the early Precambrian Isua supracrustal belt, West Greenland, *Econ. Geol.*, **74**, 45-52.
- Balch W. E., Fox G. E., Magrum L. J., Woese C. R., Wolfe R. S., 1979. Methanogens — re-evaluation of a unique biological group, *Microbiol. Rev.*, **43**, 260.
- Barley M. E., Dunlop J. S. R., Glover J. E., Groves D. I., 1979. Sedimentary evidence for an Archaean shallow-water volcanic-sedimentary facies, Eastern Pilbara Block, Western Australia, *Earth Planet. Sci. Lett.*, **43**, 74-84.
- Bischoff J. L., Dickson F. W., 1975. Seawater-basalt interaction at 200°C and 500 bars: implications for origin of sea floor heavy-metal deposition and regulation of seawater chemistry, *Earth Planet. Sci. Lett.*, **25**, 385-397.
- Bridgewater D., Keto L., MacGregor V. R., Myers J. S., 1976. The Archaean gneiss complex of Greenland, in: *Geology of Greenland*, edited by A. Escher and W. S. Watts, Geological Survey of Greenland, 1976.
- Bridgewater D., Allaart J. H., Schopf J. W., Klein C., Walter M. R., Barghoorn E. S., Strother P., Knoll A. H., Gorman B. E., 1981. Microfossil-like objects from the Archaean of Greenland: a cautionary note, *Nature*, **289**, 51-53.
- Calvin M., 1969. *Chemical Evolution*, Oxford University Press.
- Corliss J. B., Dymond J., Gordon L. I., Edmond J. M., von Herzen R. P., Ballard R. D., Green K., Williams D., Bainbridge A., Crane K., van Andel T. H., 1979 a. Submarine thermal springs on the Galapagos Rift, *Science*, **203**, 1073-1083.
- Corliss J. B., Gordon L. I., Edmond J. M., 1979 b. Some implications of heat/mass ratios in Galapagos Rift hydrothermal fluids for models of seawater rock interaction and the formation of oceanic crust, in: *Deep Drilling Results in the Atlantic Ocean: ocean crust*, edited by M. Talwani *et al.*, *Am. Geophys. Union, Ewing Symposium*, **2**, 391-402.
- Crick F. H. C., Orgel L. E., 1973. Directed Panspermia, *Icarus*, **19**, 341-346.
- Degens E. T., 1979. Primordial synthesis of organic matter, in: *The global Carbon cycle*, edited by B. Bolin, E. T. Degens, S. Kemper and P. Kctma, John Wiley and Sons.
- de Wit M. J., Hart R., Stern C. R., Barton C. M., 1980. Metallogenesis related to seawater interaction with 3.5 b.y. oceanic crust, *Eos*, **61**, 386.
- Dowler M. J., Ingmanson D. E., 1979. Thiocyanate in Red Sea brine and its implications, *Nature*, **279**, 51-52.
- Dymond J., 1981. The geochemistry of Nazca Plate surface sediments; an evaluation of hydrothermal, biogenic, detrital and hydrogenous sources, in: *Studies of the Nazca Plate and Andean convergence zone*, edited by L. D. Kulm *et al.*, *Geol. Soc. Am.* (in press).
- Edmond J. M., Measures C., McDuff R. E., Chan L. H., Collier R., Grant B., Gordon L. I., Corliss J. B., 1979 a. Ridge crest hydrothermal activity Galapagos data, *Earth Planet. Sci. Lett.*, **46**, 19-30.
- Edmond J. M., Measures C., Mangum B., Grant B., Sclater F. R., Collier R., Hudson A., Gordon L. I., Corliss J. B., 1979 b. On the formation of metal rich deposits at ridge crests, *Earth Planet. Sci. Lett.*, **46**, 1-18.
- Egami F., 1975. Origin and early evolution of transition element enzymes, *J. Biochem.*, **77**, 1165.
- Engel A. E. J., Nagy B., Nagy L. A., Engel C. G., Kremp G. O. W., Drew C. M., 1968. Alga-like forms on Onverwacht series, South Africa: oldest recognized lifelike forms on earth, *Science*, **161**, 1005-1008.
- Fanale F. P., 1971. A case for catastrophic early degassing of the earth, *Chem. Geol.*, **8**, 79-105.
- Fox S. W., 1971. Self-assembly of the protocell from a self-ordered polymer, in: *Prebiotic and biochemical evolution*, edited by A. P. Kimball and J. Oro, North-Holland Publishing Company, Amsterdam.
- Goodwin A. M., 1975. Giant impacting and the development of continental crust, in: *The Early history of the Earth*, edited by B. F. Windley, John Wiley and Sons, London, 77-95.
- Hajash A., 1975. Hydrothermal processes along mid-ocean ridges: an experimental investigation, *Contrib. Miner. Pet.*, **53**, 205-226.
- Hamilton P. J. *ET AL.*, 1979. Sm-Nd dating of Onverwacht group volcanics southern Africa, *Nature*, **279**, 298.
- Harada K., Fox S. W., 1964. Thermal synthesis of natural amino acids from a postulated primitive terrestrial atmosphere, *Nature*, **201**, 335-336.
- Hartmann W. K., 1978. The planet-forming state: toward a modern theory, in: *Protostars and Protoplanets*, edited by T. Gehrels, Univ. Arizona Press, 58-73.
- Hekinian R. *et al.*, 1980. Sulfide deposits from the East Pacific Rise. near 21°N, *Science*, **207**, 1433.
- Hickman A. H., 1972. The North Pole barite deposits, Pilbara Goldfield. *Geol. Surv. Western Australia Annu. Rep.*
- Holland H. D., 1962. Model for the evolution of the earth's atmosphere, in: *Petrologic studies: a volume to honor A. F. Buddington*, edited by A. E. J. Engel, H. I. James and B. F. Leonard, 447-477.
- Ingmanson D. E., Dowler M. J., 1977. Chemical evolution and the evolution of the earth's crust, *Origins of Life*, **8**, 221-224.
- Ingmanson D. E., Dowler M. J., 1980. Unique amino acid composition of Red Sea brine, *Nature*, **286**, 51-52.
- Jahn B., Shih C.-Y., 1974. On the age of the Onverwacht Group, Swaziland Sequence, South Africa. *Geochim. Cosmochim. Acta*, **38**, 873-885.
- Jenkins W. J. *et al.*, 1978. Excess ³He and ⁴He in Galapagos submarine hydrothermal waters, *Nature*, **272**, 156.
- Karl D. M., Wirsén C. O., Jannasch H. W., 1980. Deep-sea primary production at the Galapagos hydrothermal vents, *Science*, **207**, 1345-1347.
- Kaula W. M., 1979. Thermal evolution of earth and moon growing by planetesimal impacts, *J. Geophys. Res.*, **84**, 999-1008.
- Knoll A. H., Barghoorn E. S., 1977. Archean microfossils showing cell division from the Swaziland system of South Africa, *Science*, **198**, 396-398.
- Lachenbruch A. M., 1962. Mechanics of thermal contraction cracks and ice wedge polygons in permafrost, *Geol. Soc. Am. Spec. Pap.*, **70**.
- Lahav N., Chang S., 1976. The possible role of solid surface area in condensation reactions during chemical evolution: re-evaluation, *J. Mol. Evol.*, **8**, 357-380.
- Lemmon R. M., 1970. Chemical evolution, *Chem. Rev.*, **70**, 95-109.
- Lipple S. L., 1974. Definitions of new and revised stratigraphic units of the eastern Pilbara region, *Geol. Surv. Western Australia Annu. Rep.*
- Lister C. R. B., 1974. On the penetration of water into hot rock, *Geophys. J. R. Astron. Soc.*, **39**, 465.
- Lowe D. R., 1980. Stromatolites 3.400 m.y.r. old from the Archaean of Western Australia, *Nature*, **284**, 441-443.
- Miller S. L., 1955. Production of some organic compounds under possible primitive earth conditions, *J. Am. Chem. Soc.*, **77**, 2351-2361.
- Moorbath S., O'Nions R. K., Pankhurst R. J., 1973. Early Archaean age for the Isua iron formation, West Greenland, *Nature*, **245**, 138-139.
- Ochai E. I., 1978. Principles in the selection of inorganic elements by organisms-application to molybdenum enzymes, *Biosystems*, **10**, 329-337.

- Ochiai T., Matanaka H., Ventilla M., Yanagawa H., Ogawa Y., Egami F., 1978. Experimental approach to the chemical evolution in the primeval sea: I. Formation of amino acids and amino acid polymers in modified sea mediums, in ; *Origin of Life*, edited by H. Noda, Jpn Sci. Soc. Press., 135-140.
- Oparin A. I., 1957. *The origin of life on Earth*, Academic Press.
- Oparin A. I., 1978. The nature and origin of life, in ; *Comparative planetology*, edited by C. Ponnampuruma, Academic Press, New York.
- Paecht-Horowitz M., 1978. The influence of various cations on the catalytic properties of clays, *J. Mol. Evol.*, **11**, 101-107.
- Paecht-Horowitz M., Berger J., Katchalsky A., 1970. Prebiotic synthesis of polypeptides by heterogeneous polycondensation of amino-acid adenylates, *Nature*, **228**, 636.
- Pflug H. D., 1978. Yeast-like microfossils detected in oldest sediments of the earth, *Naturwissenschaften*, **65**, 611-615.
- Pflug H. D., Jaeschke-Boyer H., 1979. Combined structural and chemical analysis of 3.800 m.y.r. old microfossils, *Nature*, **280**, 483-486.
- Pidgeon R. T., 1978. 3450-m.y-old volcanics in the Archean layered greenstone succession of the Pilbara Block, Western Australia, *Earth Planet. Sci. Lett.*, **37**, 421-428.
- Ponnampuruma C., 1978. Prebiotic molecular evolution, in ; *Origin of Life*, edited by H. Noda, Jpn Sci. Soc. Press, 67-81.
- Raulin F., 1978. Incorporation of sulfur in chemical evolution, in : *Origin of Life*, edited by H. Noda, Jpn Sci. Soc. Press, 177-196.
- Ridler R. M., 1970. Relationship of mineralization to volcanic stratigraphy in the Kirkland-Lander Lakes area, Ontario, *Proc. Geol. Assoc. Can.*, **21**, 33-42.
- Ridler R. M., 1976. Stratigraphic keys to the gold metallogeny of the Abitibi Belt, *Can. Min. J.*, **97**, 81-87.
- Ringwood A. E., 1975. *The composition and petrology of the Earth's mantle*, McGraw-Hill, New York.
- Sangster D. F., Brook W. A., 1977. Primitive lead in an Australian Zn-Pb-Ba deposit, *Nature*, **270**, 423.
- Seyfried W., Bischoff J. L., 1977. Hydrothermal transport of heavy metals by seawater: the role of seawater/basalt mass ration, *Earth Planet. Sci. Lett.*, **34**, 71-77.
- Seyfried W. E., Mottl M. J., Bischoff J. L., 1978. Seawater/basalt ratio effects on the chemistry and mineralogy of spilites from the ocean floor, *Nature*, **275**, 211-212.
- Shaw D. M., 1976. Development of the early continental crust. Part 2: Pre-archaeon, protoarchaeon and later eras, in : *The Early history of the Earth*, edited by B. F. Windley, John Wiley and Sons.
- Smith J. V., 1976. Development of the earth-moon system with implications for the geology of the early earth, in : *The Early history of the Earth*, edited by B. F. Windley, John Wiley and Sons, 3-20.
- Smith J. V., 1979. Mineralogy of the planets: a voyage in space and time, *Mineral. Mag.*, **43**, 1-89.
- Spieß F. M. et al., 1980. East Pacific Rise: hot springs and geophysical experiments, *Science*, **207**, 1421.
- Tera F., Papanastassiou D. A., Wasserburg G. J., 1974. Isotopic evidence for a terminal lunar cataclysm, *Earth Planet. Sci. Lett.*, **22**, 1-21.
- Veizer J., 1979. Chemistry of the early oceans: implications for crustal development, Australian National University, *Res. Sch. Earth Sci. Annu. Rep.*, 1979.
- Walker J. C. G., 1976. Implications for atmospheric evolution of the inhomogeneous accretion model of the origin of the earth, in : *The Early history of the Earth*, edited by B. F. Windley, John Wiley and Sons.
- Walter M. R., Buick R., Dunlop J. S. R., 1980. Stromatolites 3,400-3,500 m.y.r. old from the North Pole Area, western Australia, *Nature*, **284**, 443-445.
- Wasserburg G. J., Papanastassiou D. A., Tera, F., Huneke J. C., 1977. The accumulation and bulk composition of the moon. Outline of a lunar chronology, *Philos. Trans. R. Soc. London, Ser. A*, **285**, 7-22.
- Woese C. R., 1977. A comment on methanogenic bacteria and the primitive ecology, *J. Mol. Evol.*, **9**, 369-371.
- Yanagawa H., Kobayashi Y., Egami F., 1980. Characterization of marigranules and marisomes, organized particles and elastin-like structures, *J. Biochem.*, **87**, 855-869.



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