

# CHAPTER 1

## WHY ARE HYDROTHERMAL SYSTEMS PROPOSED AS PLAUSIBLE ENVIRONMENTS FOR THE ORIGIN OF LIFE?

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### 1. Introduction

The paradigm change in geology by the general acceptance of plate tectonics around two decades ago has brought about an increased interest in geothermal processes at plate boundaries. Thus the enhanced research activity at spreading centers led to the discovery of large spectacular submarine hydrothermal systems of global significance to ocean chemistry and geochemistry. Among the best known such areas are the Galapagos Ridge (Corliss *et al.*, 1979), the East Pacific Rise at 21°N (Francheteau *et al.*, 1979; Spiess *et al.*, 1980), and the Juan de Fuca Ridge (Chase *et al.*, 1985). Rona and coworkers (1983) have compiled the early landmark studies of hydrothermal processes at seafloor spreading centers. Recently Edmond (1991) also reviewed U.S. research on oceanic hydrothermal chemistry for the period 1987-1990. The spectacular nature of marine hydrothermal systems with features such as 'black smokers', 'white smokers' and peculiar ecosystems that are independent of sunlight as a source of reducing power has focused much interest on hydrothermal processes for the explanation of an array of geochemical processes and phenomena. Hydrothermal systems located at global plate spreading centers soon attracted the attention of geochemists as viable environments for chemical evolution and the origin of life (cf. Ingmanson and Dowler, 1981). However, the discovery of the deep-sea hydrothermal systems is only one of several reasons why in the last ten or fifteen years interest has been focused on hydrothermal systems in general as potential sites for life's origin. Some other aspects are listed below:

- 1) The most primitive organisms found in modern environments are thermophiles.
- 2) The view of the composition of the early atmosphere has changed. There is no longer a consensus on the prevalence of reducing conditions on the early Earth. Most scientists now envision a 'redox neutral' primitive atmosphere. There is, however, a possibility that the iron vapor and reduced carbon liberated from impacting objects like meteorites would leave the ocean reducing for a long period.
- 3) Hydrothermal systems and deep sediments are about the only environments where primitive life would have been protected against postulated meteorite impacts and partial vaporisation of the ocean.
- 4) The presence of supercritical fluids is known (CO<sub>2</sub>, H<sub>2</sub>O) or postulated (CH<sub>4</sub>) in hydrothermal systems. Supercritical fluids like water and carbon dioxide are excellent

solvents of organic compounds and would probably be of great potential for several of the chemical reactions eventually leading to the origin of life.

Hydrothermal cells are dynamic systems, which has been one of the main arguments for their potential as sites for abiotic organic geochemical processes in the lithosphere. One of the first to explore igneous activity in the context of chemical evolution was Oparin (1936). He did not support the idea, mainly because the proposed carbon source on the early Earth would have been volcanogenic CO<sub>2</sub>. Oparin rejected CO<sub>2</sub> as the carbon source for primitive life processes by citing Pflüger (1875): 'Carbon dioxide is not the beginning but the end of life'. Later on it was common to ignore igneous environments in conjunction with early life by the argument that the existence of volcanoes is too episodic in order to be of importance for chemical evolution. In a more recent paper Sylvester-Bradley (1976) discussed the hypothesis of life's origin as a result of igneous activity. He emphasized oscillation of chemical systems between different environments far removed from equilibrium as one of the main mechanisms for abiogenesis. Indeed, Mukhin and coworkers (Mukhin, 1974; Mukhin *et al.*, 1978) reported the occurrence of thiocyanates and soluble ferrocyanides in hydrothermal systems of volcanoes of the Kurile Islands and the Kamchatka Peninsula in the Far East of Asian Russia (for geographical names mentioned in text, see Fig. 1). This would indicate the primary formation of hydrogen cyanide, which is often considered a likely precursor of abiogenically formed amino acids and nucleotide bases.

## 2. Early Proposals

The first article that proposed connections between chemical evolution and plate margins was published by Ingmanson and Dowler (1977). They proposed that the hydrothermal brine pools in the deeps of the Red Sea rift valley, especially the Atlantis II Deep, would be fruitful sites for testing whether or not life could evolve in lithospheric environments. Their arguments were that: 1) the brines were reported sterile, 2) the environment is reducing, 3) there is no free oxygen, 4) there is much methane and ethane, 5) montmorillonite is present, 6) residual gases from the Earth's paleo-atmosphere appear to be present, and 7) the temperature is high (about 60°C in the Atlantis II Deep). Ingmanson's and Dowler's subsequent reports of the occurrence of thiocyanates (Dowler and Ingmanson, 1979) and anomalous concentrations of the amino acid glycine (Ingmanson and Dowler, 1980) in the hot brines of the Red Sea supported their ideas, although their conclusions were later questioned by Simoneit and coworkers (1987). However, the Red Sea does not represent the 'standard' type of oceanic plate spreading center. The Red Sea represents an early stage of opening of an ocean basin with restricted water circulation and thus resembles the Atlantic Ocean about 200 Ma (million years ago). This is probably a process that has occurred at regular intervals in Earth's history, but that type of environment can not be expected to have had the same longevity as the ones of the deep ocean spreading centers.

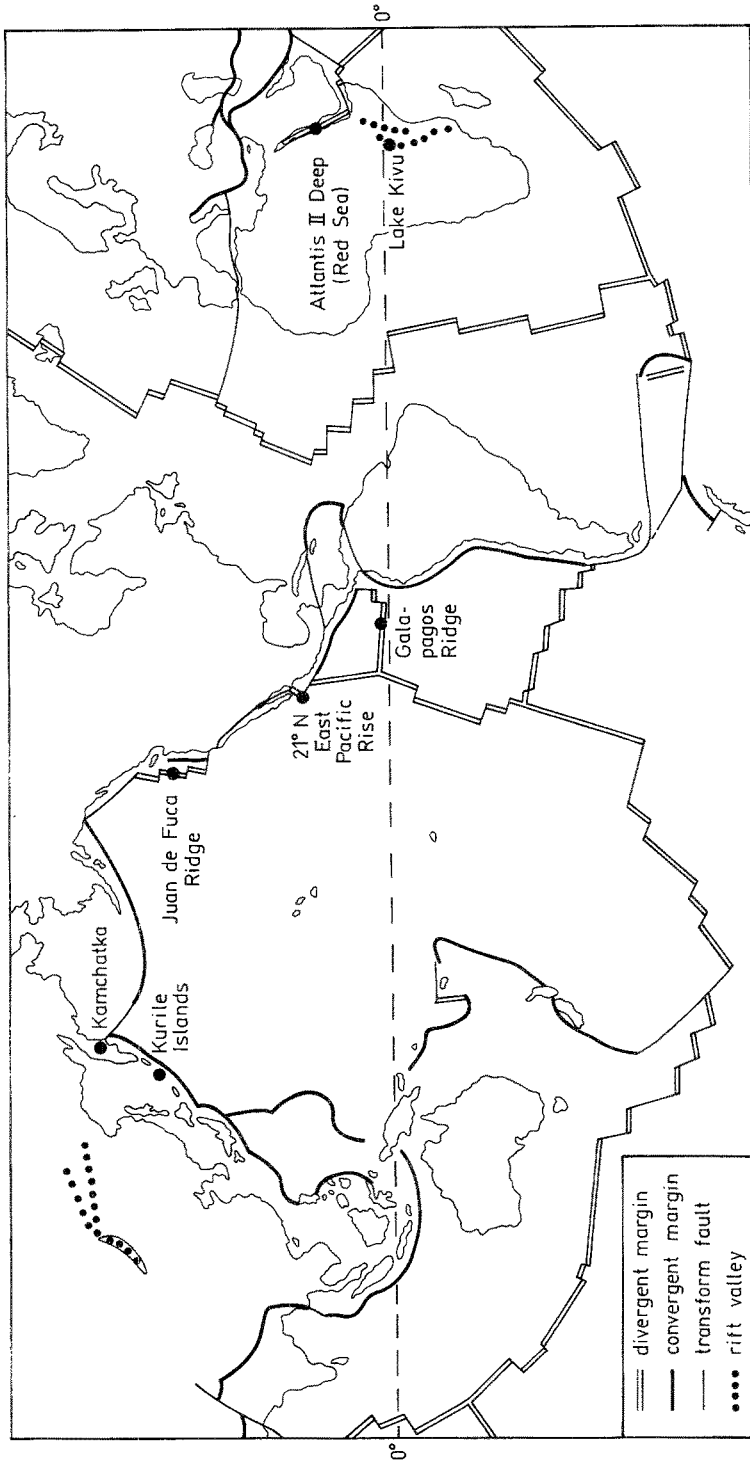


Fig. 1. Outline map showing the major plate tectonic boundaries of the earth's lithosphere and sites mentioned in the text.

The next paper that modelled life's origin in lithospheric hydrothermal systems at plate margins was published by Egon Degens (Degens, 1979). He and Johann Matheja had published articles about ten years earlier that treated the potential of life's origin in lithospheric environments (Degens and Matheja, 1968; Matheja and Degens, 1971). Degens hypothesized that hydrothermal systems, like the ones of Lake Kivu in the East African Great Rift Valley, would be perfect environments for primitive life forms to evolve. He considered three criteria necessary for any model on the origin of life. The system must: 1) be thermodynamically feasible, 2) have a high yield, and 3) allow for chemical evolution towards a primordial cell. Degens stated that biochemical molecules do not arise under equilibrium conditions, mainly because of the inability to separate the newly generated compounds in a quasi stationary phase. He also concluded that the number of non-equilibrium systems established in the lithosphere is great and that there is less occasion in either the hydrosphere or the atmosphere to maintain non-equilibrium conditions for extended periods of time. The East African Great Rift Valley is, however, like the Red Sea, not considered to be a plate spreading center in an ordinary sense. It represents instead the first stage of an 'aulacogen', i.e. a failed arm of a plate triple junction.

### 3. The Hydrothermal Model of Corliss, Baross and Hoffman

John Corliss led the first expedition that directly observed active submarine hydrothermal vents at an oceanic ridge (the Galapagos Spreading Center). He and his coworkers John Baross and Sarah Hoffman were also the ones who first identified the mid-oceanic rift sutures as likely sites for chemical evolution of organic compounds. The model was presented at the 26th International Geological Congress in Paris in 1980 and was published a year later (Corliss *et al.*, 1981). It has been further developed and presented in later publications (for example, Baross and Hoffman, 1985; Corliss, 1986, 1989, 1990). Corliss and coworkers claimed that the hot springs along the mid-oceanic rifts provided all the conditions necessary for the creation of life on Earth. The scope of the article was wide and had therefore a considerable impact on several disciplines of the natural sciences community. However, because of the wide scope it was also relatively easy for specialized scientists of biochemistry, microbiology, etc. to find weak spots of the model.

In the original hydrothermal origin of life model the dynamic vent systems are thought of as 'life reactors'. This is based on the gradients of temperature, pH and concentrations of various chemical components and the presence of mineral catalysts like montmorillonite clays, iron oxide hydroxides, manganates, sulfides, and zeolites. Water that circulates through the systems transports dissolved substances from the high temperature zone (about 350-400°C) to the intermediate/low temperature zone. Abiogenic organic monomers such as amino acids, sugars, purines, and pyrimidines are proposed to be produced in the high temperature zone from H<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>S, CO, HCN, etc. This first step of condensation of organic monomers from simple inorganic constituents is followed by transportation to the intermediate temperature zone and polymerization of the

monomers to poly-peptides and polynucleotides. Eventually lifelike 'protocells' are formed in a lower temperature window and are released to the deep-sea bottom water. Nisbet (1987, 1991) has elaborated on the hydrothermal origin of life model in his books 'The Young Earth' and 'Living Earth' and elsewhere (Nisbet, 1986). A report summarizing the state of the field was also published after a workshop in Prague, 1989, on 'Chemical Evolution and Neo-Abiogenesis in Marine Hydrothermal Systems' (Holm, 1990).

Why then would the concept of chemical evolution in hydrothermal systems be more attractive than other models? The dynamic characteristics of the hydrothermal 'life reactors' has already been mentioned. This means that non-equilibrium conditions are maintained and that a continuous flow of components connects different chemical environments with each other. Reactions requiring, for instance, quite different temperatures could be going on in the proximity of each other. Oscillations within the system would add to the overall instability and non-equilibrium characteristics. For geochemists one of the main advantages of having the origin of life in hydrothermal water is probably that such systems can be postulated to have existed through the entire length of Earth's history (confer Table I for the ages of the Earth). It is possible that the tectonic style of the Earth changed from 'micro-plate tectonics' to modern plate tectonics (see Chapter 2) during the transition from the Archean to the Proterozoic Eon 2.5 Ga (billion years ago). However, since heat production and heat flow from the planet's interior was much more intense on the young Earth, the hydrothermal activity can only have been more pronounced in the early Archean than now.

#### 4. Modified Models

The generally accepted theory of the redox state of the early Earth not too long ago was that the atmosphere and the oceans were reducing. Most biochemists are of the opinion that life must have originated in reducing environments since there is little evidence for any substantial recovery of reaction products in oxidizing abiotic simulation experiments. This led some geologists to comment that the majority of diagenetic environments are reducing and have always been so (cf. Clemmey and Badham, 1982). However, probably scientists working on problems in conjunction with life's origin are too much focused on the impact on chemistry at the Earth's surface redox conditions. As we shall see later in this chapter, changes in physical parameters of the Earth's interior may cause response by redox pairs that we are not quite used to at surface conditions.

Wächtershäuser (1988a,b; 1990a) and Russell and coworkers (1989) have emphasized the reduced minerals of hydrothermal systems as potential catalysts in chemical processes leading to the origin of life. Wächtershäuser proposed that energy for primitive chemoautotrophic carbon fixation in hydrothermal systems is provided by the redox process of converting ferrous ions and hydrogen sulfide into the mineral pyrite ( $\text{FeS}_2$ ). At the same time pyrite is postulated to serve as a kind of mineral template for the polymer-

TABLE I  
The ages of the Earth (modified from Ballard, 1983)

Eon	Era	Period	Epoch	Ma	
Phanerozoic	Cenozoic		Holocene	0.010	
		Quaternary	Pleistocene	2	
			Pliocene	5	
			Miocene	24	
			Oligocene	38	
			Eocene	55	
		Tertiary	Paleocene	63	
	Mesozoic		Cretaceous		138
			Jurassic		205
			Triassic		240
			Permian		290
	Paleozoic			Pennsylvanian	330
		Carboniferous	Mississippian		360
			Devonian		410
			Silurian		435
			Ordovician		500
			Cambrian		570
		Proterozoic			
	Archean	Precambrian time			3,800
Hadean				4,600	

ization of organic monomers to large structures. The main advantage with mineral surface processes is that slow lateral two-dimensional migration and growth of bonded organic compounds can occur. Small constituents that are weakly bonding will give way to stronger bonding large ones. On the basis of the solubility of salts of organic constituents Wächtershäuser (1988a) ruled out ionic bonding to negatively charged mineral surfaces, for instance clays, as processes of importance for chemical evolution, a statement for which there is little evidence in the literature. He argued that the mineral surfaces must have positive charges and that the organic constituents must be anionic. The most common minerals with positive surface charges at neutral pH in any environment are sulfides and oxides of the transition elements. Both groups of elements (as well as clays) are abundant in hydrothermal systems. However, in most modern marine hydrothermal systems not covered by sediments the pH is several units below neutrality, thus enabling positive surface charge also of the clay minerals.

Wächtershäuser concluded that the surface-bonding function is the oldest function of the phosphate groups. Therefore the insolubility of calcium phosphate and the concomitant low abundance of dissolved phosphate ions poses a major difficulty for all versions of the prebiotic 'broth theory'. In his surface-metabolic scenario, on the other hand, there is a simple solution to this problem if it is assumed that the surface metabolism is attached to a phosphate mineral or to a mineral with adsorbed phosphate ions. Fluids of hydrothermal systems and other geothermally active zones of the Earth's crust are among the few types of environments on our planet where phosphate is a relatively common constituent. Yamagata and coworkers (Yamanaka *et al.*, 1988, Yamagata *et al.*, 1991) have even detected pyrophosphate and tripolyphosphate in condensed water of volcanic gas. Accordingly, Nisbet (1987) has remarked: 'The critical role of phosphates both in the utilisation of energy and in the cell membrane is interesting and can be interpreted as eloquent testimony for a hydrothermal origin. On the Archean planet, perhaps only in such a setting would a non-negligible supply of phosphates be reliably present'.

## 5. Hydrothermal Systems as Protected Environments

Although Weyl (1968) did not discuss abiotic processes in hydrothermal systems he preferred deep water environments for modelling the origin of life. The reason for doing this was that newly formed organic aggregates would have been shielded from hazardous ultraviolet radiation at depth. Solar ultraviolet light is quenched by only a few meters of water. However, the necessity of a protective screen for early life from radiation and impacting objects from space has become a major argument lately in favour of the hydrothermal model. Maher and Stevenson (1988) proposed a deep marine hydrothermal setting for the origin of life on the basis of the calculated impact flux during the Hadean (pre-3.8 Ga) and Early Archean Eons (3.8-3.4 Ga) (Table I). They concluded that abiogenesis could have happened as early as 4.0 to 4.2 Ga in deep hydrothermal systems

without early life forms being totally destroyed by impacts. At the surface of the Earth, on the other hand, it could not have occurred earlier than between 3.7 and 4.0 Ga.

Sleep and coworkers (1989) argued in an independent study that the major way in which the Earth could have been sterilized was by evaporation of ocean water. Impact vaporization of the photic zone as late as 3.8 Ga is probable. Since life was unambiguously present on Earth at about 3.5 Ga, there is therefore a very narrow time window for it to have evolved on the Earth's surface. Ecosystems with chemoautotrophic primary producers in the deep ocean, especially those at hydrothermal vents, would have been much better protected. According to Sleep and coworkers (1989) the last impact that vaporized the ocean completely may have occurred as early as 4.44 Ga.

## 6. The Hydrothermal Models Challenged

It did not take long after Corliss and coworkers (1981) had published their original paper on the origin of life in hydrothermal systems until articles appeared that seemingly refuted their model. The first two were written by White (1984) and Bernhardt and coworkers (1984). Both articles primarily opposed the report by Baross and Deming (1983) that thermophilic marine bacteria isolated from vents had been grown at 265 bar and 250°C. Their arguments were, however, also applicable to the general ideas of the origin of life in hydrothermal systems. White determined decomposition rates for certain bonds of various biomolecules at 39 bar and 250°C. Bernhardt and coworkers did the same thing at the reported vent conditions, i.e. 265 bar and 250°C. Both articles concluded that organisms can not survive at such high temperatures if they are composed of biomolecules such as proteins and nucleic acids, due to the very rapid rate of decomposition of such molecules. On the other hand Yanagawa and Kojima (1985) and Yanagawa and coworkers (1988) reported the formation of stable silicate derivatives of microspheres from an amino acid mixture at 134 bar and 250-350°C. One of the obvious differences between their experiments and those of Bernhardt and coworkers and White is, first of all, that White worked at relatively low pressure. Another difference is that Yanagawa and coworkers used autoclave tubes made of glass at high pressure whereas Bernhardt and coworkers used nickel tubes. The great difference between the experiments, however, appears to be how and if the problem of presence of oxygen in the experimental systems has been tackled. New results achieved by Yanagawa and Kobayashi (1989) has added the recovery of silicate derivatives of simple amino acids (glycine, alanine, sarcosine) from pressurized  $\text{CH}_4$ ,  $\text{NH}_4^+$ ,  $\text{CO}_2$  and silica glass at 260-325°C.

Although the controversy about the existence of the extremely thermophilic bacteria also affected the general view of the Corliss-Baross-Hoffman model, it was not until Stanley Miller and Jeffrey Bada published a couple of articles that their ideas became severely challenged (Miller and Bada, 1988; Miller *et al.*, 1989). Miller's and Bada's main arguments can be divided into four groups: 1) The high temperature of the vents



(specified as 350°C) destroys rather than synthesizes organic compounds and polymers (references to Miller and Orgel, 1974; White, 1984; Miller *et al.*, 1976; and Bernhardt *et al.*, 1984); 2) the mere synthesis of polymers is not equivalent to synthesizing a living organism; 3) gradients do not exist near vents except from the mixing of 350°C water with cold sea water; 4) an important role for minerals and clays in prebiotic chemistry still remains to be demonstrated. The last argument would obviously be valid for any model on the origin of life that uses minerals as potential catalysts. Ferris and coworkers (cf. Ferris *et al.*, 1990) have, however, clearly demonstrated the catalytic activity of montmorillonite clays on, for instance, oligomerization reactions of deoxyribonucleotides. Argument no. 1 is not correct in the sense that hydrothermal waters in principle may have any temperature between 2 and 1,200°C; the observed interval in the upper lithosphere thus far is 2-400°C. Therefore vent waters of, for instance, 110°C, which is the maximum registered temperature so far of any living organism (Stetter, 1982), should also be described by the term 'hydrothermal'. Argument no. 3 is not at all true (see Chapter 2). In order to demonstrate further that biomolecules are very unstable at high temperatures and that their stability is not enhanced by high pressures, Miller and Bada carried out several experiments at 250°C, 265 bar and an initial pH that was neutral at room conditions. A mixture of equal molar amounts of aspartic acid, serine, alanine, and leucine was heated for up to 6 hours. All amino acids were decomposed quite rapidly, alanine less so than the others. Glycine, which was not present originally, was produced during the course of the heating experiment. This pattern is almost identical to the one observed for decomposition of L-amino acids by Bernhardt and coworkers (1984). The data presented by Miller and Bada (1988) was, however, used by Shock (1990a,b) in order to show that this type of experiment is normally performed out of equilibrium and that the redox state of the experimental systems is not controlled. Shock showed by simple thermodynamic calculations that Miller's and Bada's experiment probably was carried out somewhere in the predominance field of alanine and that a close approach to metastable equilibrium among leucine, glycine and alanine was attained in their system. Therefore it is not correct, Shock claimed, to use terms like 'instability' and 'decomposition' in this context, when the only thing that is happening is that the aqueous amino acids respond to the changes in external physico-chemical conditions and strive towards metastable equilibrium. The role of temperature is simply to overcome the kinetic barriers that prevent equilibrium or metastable equilibrium from being established.

Shock (1988, 1990a,b) has emphasized that it is the oxidized and metastable carbon and nitrogen compounds that are of special interest in hydrothermal vents rather than the reducing ones. He shares this view with Wächtershäuser (1990). CO<sub>2</sub> and N<sub>2</sub> may be in stable redox equilibrium with organic compounds such as amino and carboxylic acids in the Earth's interior, while CH<sub>4</sub> and perhaps NH<sub>3</sub> are not. This is explained by the fact that the oxidation states of the lithosphere are controlled by mineral buffer assemblages. Shock considered two mineral assemblages to be of primary importance in seawater-basalt systems: the fayalite-magnetite-quartz (FMQ) assemblage and the pyrite-

pyrrhotite-magnetite (PPM) assemblage. At great depths within the circulation systems of the oceanic crust the conditions would probably be buffered by the FMQ assemblage. Shallower than about 1.3 km the PPM assemblage is the prevailing redox buffer. This means that for temperatures beyond about 275°C CO<sub>2</sub> and N<sub>2</sub> are the dominant carbon and nitrogen species at stable equilibrium. As a hydrothermal solution cools below 275°C it may still be buffered by the PPM assemblage, although it passes into a stability field where CH<sub>4</sub> and NH<sub>3</sub> predominate. If there exist kinetic hindrances that prevent equilibrium conditions from being established, the organic chemistry of the hydrothermal solution will then be 'locked up' in metastable compounds. Shock has calculated that the activities of several classes of organic metastable compounds, like alkanes, alkylbenzenes, carboxylic acids, amines, and amino acids, are maximized in the temperature interval 150-250°C, i.e. in the intermediate temperature window. The abiotic synthesis of various amino acids at 150°C, under reducing hydrothermal conditions, has been demonstrated experimentally (Hennet *et al.*, 1992). These results are in agreement with the calculations proposed by Shock, as discussed above.

One of the objectives of SCOR Working Group 91 has been to summarize the state of knowledge of hydrothermal systems and the origin of life sciences and to identify research opportunities in the field. This document with its collection of contributions is an attempt to cope with that challenge and has the ambition to open up a scientific area for future research. The following chapters will give you the background to why hydrothermal systems are considered potential environments in the context of life's origin, what the input parameters and starting materials in such systems would be or would have been, what indicator compounds there might be to look for, and what experiments should be conducted in order to verify or falsify models for the origin of life in marine hydrothermal systems.