

# HYDROTHERMAL AND OCEANIC pH CONDITIONS OF POSSIBLE RELEVANCE TO THE ORIGIN OF LIFE

GORDON MACLEOD\*, CHRISTOPHER MCKEOWN, ALLAN J. HALL and  
MICHAEL J. RUSSELL

*Department of Geology & Applied Geology, University of Glasgow, Glasgow, G12 8QQ, Scotland, U.K.*

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**Abstract.** Because of the continuous focusing of thermal and chemical energy, ancient submarine hot springs are contenders as sites for the origin of life. But it is generally assumed that these would be of the acid and high-temperature 'black smoker' variety (Corliss *et al.*, 1981). In fact today the greater part of the ocean circulates through off-ridge springs where it issues after modification at temperatures of around 40 °C or so but with the potential to reach 200 °C. Such off-ridge or ridge-flank springs remind us that there are other candidate sites for the origin of life. Although there is no firm indication of the pH of these off-ridge springs we have argued that the solutions are likely to be alkaline rather than acid.

We test the feasibility of this idea using EQ geochemical water-rock interaction modelling codes (Wolery 1983) and find that for a range of possible initial chemistries of Hadean seawater, the pH of issuing solutions at around 200 °C is around one or more units alkaline. Such pH values hold for interaction with both basaltic and komatiitic crust. The robustness of this result suggests to us that alkaline submarine springs of moderate temperature, carrying many hundreds of ppm HS<sup>-</sup> to the ocean basins, are also serious contenders as sites for the origin of life, particularly as Hadean seawater was probably slightly acid, with a dissolved iron concentration approaching 100 ppm. On mixing of these solutions, supersaturation, especially of iron sulphide, would lead to the precipitation of colloidal gels. In our view iron sulphide was the likely substance of, or contributor to, the first vesicle membranes which led to life, as the supply of organic molecules would have been limited in the Hadean. Such a membrane would have had catalytic properties, expansivity, and would have maintained the natural chemiosmotic gradient, a consequence of the acid ocean and the alkaline interior to the vesicles.

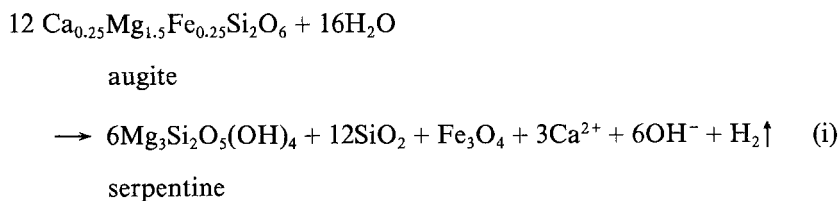
## Introduction

There are many conflicting ideas, factions and schools of thought regarding life's origins. Conflict like this arises when there is a dearth of data. But what data should we be attempting to collect? As geologists and geochemists we consider that the initial conditions for life's origins are of first importance and attempt here to define these theoretically for our favoured model. We have argued that as organics (particularly lipids) on the early Earth were likely to be in short supply, life's precursors developed from iron sulphide vesicles around long-lived medium temperature alkaline springs on the Hadean ocean floor away from spreading centres (Russell *et al.*, 1988, 1989, Cairns-Smith *et al.*, 1992). Such a site is also well protected from the effects of impacts of extra-terrestrial objects (Maher and Stevenson

\* Present address NRG Drummond Building, University of Newcastle, Newcastle upon Tyne, NE1 TRU, England.

1988). Although Miller and Bada (1988) have attempted to counter the suggestion of Corliss and his co-workers (1981) that life began at black smokers, on the grounds of the instability of organic complexes at high temperatures, the same reasoning does not apply to the medium temperature hot springs that we might expect on the deep ocean floor away from spreading centres and mantle plumes (Russell *et al.*, 1989). These springs would have been derived from the natural convection of seawater within the oceanic crust. As no vestige of Hadean ocean crust survives, its composition is the subject of debate (Kröner and Layer 1992): Nisbet (1985) argues for magnesium-rich lavas or komatiites, whereas Bickle (1986) considers typical mid-ocean basalts the more likely. We assume that upper mantle convection cells with aspect ratios of around 2 produced ocean basalts, and that the crust spread radially to be added to by komatiitic dykes and lavas generated at depth in the slow moving centres of the cells (Fig. 1a). This is the polygonal tectonics of Smith (1981). According to Abbott and Hoffman (1984) komatiite and basalt lavas would also have featured above the buoyant subduction zones (Fig. 1b). The shape of the zones were probably more symmetrical than today's, and the formation of eclogite at depth may have aided downwelling (Davies 1992).

Submarine springs at black smoker temperatures (350–400 °C) and pH (3–4) (see Seyfried *et al.*, 1991) would have issued above the mantle updraft and downwelling zones as well as above magma chambers feeding volcanoes on the ocean floor. However, as the heat flow would have been generally high 4 or so billion years ago (Smith 1981), other natural hydrothermal convection cells would have been common, issuing onto the ocean floor, away from volcanoes, and with a spacing of five to ten kilometres. Such springs we consider the more likely contenders for the site of life's origins. A high pH of the solutions would have been imparted by the dissolution of alkali and alkali earth elements particularly calcium, as shown notionally in Equation i.



As ocean floor spreading was probably approximately radial then tension in the ocean floor would have encouraged these free hydrothermal convection cells to deepen with time, while keeping the same temperature (200 °C approx.) and chemistry, and to hold their approximate position steady with respect to the spreading centre and subduction zones, allowing some spring systems to last millions of years (Fig. 1b).

Alkaline, medium temperature (ca 200 °C) hydrothermal solutions have the capacity to carry reduced sulphur and some transition elements, though not iron, in solution (Barnes and Czamanske 1967, Crerar *et al.*, 1978). Moreover, of special

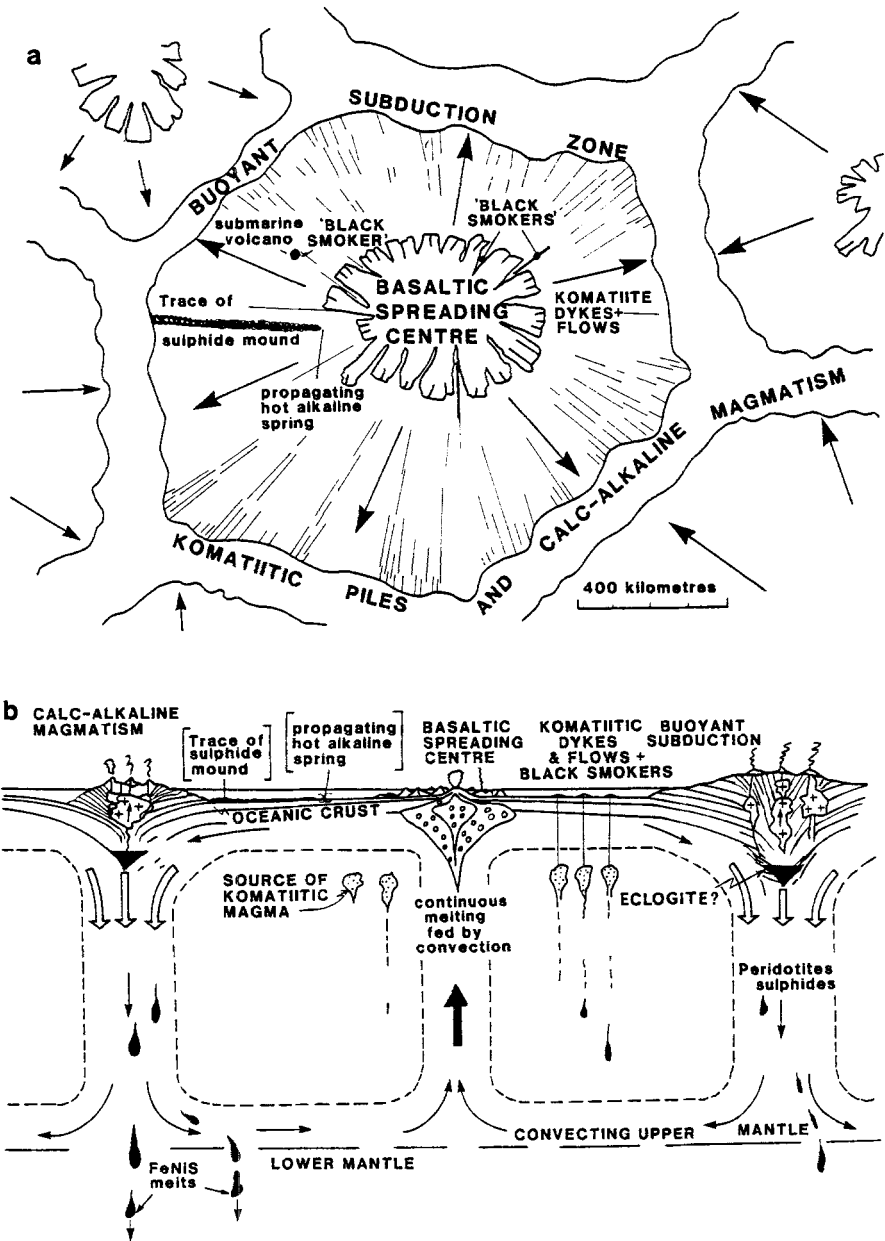


Fig. 1 Model for polygonal tectonics from Smith (1981) but with consideration of Abbott and Hoffman (1984), Bickle (1986) and Davies (1992). **a**, Plan view of a single convection cell involving the upper mantle and crust. Note the trace of the sulphide mound produced by one of many off-centre alkaline hot springs. The spring can outlive the oceanic crust by propagating towards the epicentre of the mantle convection cell as the ocean floor spreads towards the boundary zones. Black smokers also occur driven by shallow magma chambers. **b**, Cross-section of mantle convection cell to approximately the same scale.

significance to the origin of life is the possible reduction of dissolved  $\text{CO}_2$  to organics in conditions where hot water traverses reduced, pyrrhotite bearing, rock (cf. French 1964, Neal and Stanger 1983, Hall 1986, Shock 1990, 1992). Hall (1986) has recorded geological evidence which supports Wächtershäuser's (1988) idea that carbon dioxide may be fixed when pyrrhotite ( $\text{FeS}$ ) is oxidized to pyrite at about  $200^\circ\text{C}$  and 2 kb. Modern day conditions favouring the formation of abiogenic organics have been remarked on by Neal and Stanger (1983). They report the generation of hydrogen gas from mantle source rocks in Oman (see Equation i). Hydrogen is generated by the oxidation of silicate  $\text{Fe(II)}$  by ground waters and they draw attention to the similarities with conditions in the early Precambrian and suggest that hydrogenation of crustal carbon could have taken place where water circulated to depth in deep crustal faults. The fine-grained nickel-iron alloys (e.g. awaruite  $\text{FeNi}_3$ ) commonly produced during open-system serpentinization (Ulrich 1890, Krishnarao 1964) could have catalyzed such hydrogenation reactions.

In contrast to these medium temperature submarine springs, we assume that the Hadean ocean was somewhat acidic and therefore contained a significant concentration of reduced iron which, in the absence of continents (Moorbath 1985) was presumably derived from high temperature hydrothermal systems and micro-meteorites. The acidity was imparted to the oceans by a high partial pressure of atmospheric carbon dioxide. Whether there was some free oxygen derived from the photolysis of atmospheric water is unknown, but unlikely according to Kasting and Ackerman (1986). However, a portion of the iron would have been oxidised to the ferric species photochemically once the atmosphere became transparent (Braterman *et al.*, 1983).

The rapid drop in pH and temperature of these hydrothermal solutions concomitant upon interfacing with mildly acidic ocean water would bring about supersaturation and thereby the precipitation of  $\text{FeS}$ -rich colloidal gel membranes. Such non-equilibrium conditions are conducive to the kind of complex chemical interactions that may have been involved in the processes of the earliest life. In this hypothesis of the beginnings of life these supposed initial conditions are all-important. As the putative iron sulphide membrane separates an alkaline interior to the vesicles from an acid exterior then there is, in place, a proton-motive (chemiosmotic) force to drive the transport of sparse organic molecules onto, and into, the vesicle (Russell *et al.*, 1993). Because of the adsorption of organics the vesicle could, for a time, remain insulating and flexible. The membrane would also have catalytic properties, a forerunner to the iron-sulphur coenzymes.

The purpose of this paper is to explore the feasibility of these supposed initial conditions by further mass-balance and thermodynamic calculations. We are aware of the risks of this approach in that the calculations require geochemical parameters to be strictly defined and as Keynes remarked in other circumstances, we "prefer to be approximately right than precisely wrong", so we have used the calculations to test our postulated geochemical model rather than quantify its geochemical nature.

### Off-ridge medium temperature hydrothermal solutions

Medium temperature (150°–200 °C) hot springs away from spreading centres and discharging in one place can last for one million years or so (Russell 1978, Fehn and Cathles 1986). If the tectonics were polygonal in the Hadean as suggested by Smith (1981) then such springs may have migrated as radial tensional fractures propagated towards the spreading centre, effectively holding their position with respect to the ocean floor margins, and so endure for many millions of years (Fig. 1b). Anderson *et al.* (1977) have shown that in the Indian Ocean today, low to medium temperature hydrothermal plumes have spacings of about 7 km and it has been estimated that at least twenty times more seawater circulates through off-axis hydrothermal systems than through the ridge systems (COSOD II 1987). From calculations based on typical 'free' convection aspect ratios (cf. Combarous and Bories 1975) the hydrothermal systems will have initially plumbed depths of about 3km, successful systems probably deepening in time to 8 or 10km (cf. Russell 1978). We assume that chemical equilibrium is reached within these medium temperature cells given the long residence time of the fluids, estimated as at least 100 years (Cathles 1990) and that similar aspect ratios and residence times obtained 4 billion years ago.

Such large-scale long-lived off-spreading centre hydrothermal convection would have been encouraged by high horizontal stress ratios (Russell and Skauli 1991). Four billion years ago or so our planet was generating about five times the heat that it does today (Lambert 1976) and the near surface geothermal profile would have been about three times the present day slope (Smith 1981). The 'excess' heat was probably dissipated through faster spreading rates and many mantle updrafts (Smith 1981). Moreover the oceanic crust may have been at least three times its present thickness (Sleep and Windley 1982) and it is likely the ocean basins were highly fractured (Fig. 1a). This tectonic scenario is consistent with high horizontal stress ratios leading to high fracture permeabilities and the hydrothermal convection that we imagine. We now investigate the chemistry of these systems.

### Modelling methods

Hydrothermal chemistry is modelled using EQ3NR/EQ6, SOLMINEQ88 and SUPCRT92 computer codes.

The EQ3NR/EQ6 software package was developed to model geochemical and mineralogical reactions in aqueous geochemical systems. The package consists of EQ3NR, a speciation solubility code that uses a Newton Raphson iterative technique, EQ6 a reaction path modelling code, and EQLIB a supporting library and thermodynamic data base over the temperature range 0 °C–300 °C. The EQ package has been applied to many geochemical studies including water/rock interaction. A particular example is the successful modelling of alteration processes caused by magmatic fluids (Destringneville *et al.*, 1991). The package has been distributed globally to

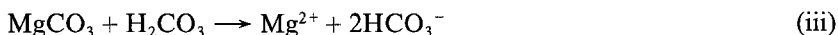
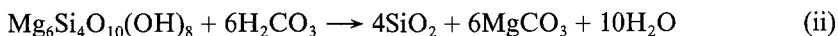
the scientific community. For details of the package and its capabilities readers are referred to the package guidebooks (Wolery 1983, 1989) and a review of the current status of the package by the code authors (Wolery *et al.*, 1990).

SOLMINEQ88 (SOLution MINeral EQUilibria88) is a geochemical code that has the capability of theoretically mixing fluids and titrating gases. Readers are again referred to the code handbook for details of the code (Kharaka *et al.*, 1989) and to a review of the code by its authors (Perkins *et al.*, 1990).

As iron and sulphur are critical to our ideas on the origin of life we address their respective solubilities in the conditions envisaged using SUPCRT92 (Johnson *et al.*, 1992) which also allows us to illustrate controls on oxygen and sulphur fugacities in the hydrothermal system.

### Oceanic water chemistry

The chemistry of Hadean ocean water is not known but of particular concern for us is its pH (because of the 'natural' proton-motive force), oxidation state (one pole to the energy potential) and concentration of iron (one of the contributors to the membrane). Present day ocean chemistry is highly evolved and greatly influenced by marine life, present-day oxic weathering and hydrothermal processes related to modern plate tectonics. What then would have controlled the chemistry of Hadean ocean water? The pH of fresh water is a function of the partial pressure of carbon dioxide (Garrels and Christ 1965) and we know that the pH of fresh water in equilibrium with present day atmospheric carbon dioxide is 5.7 (i.e. the pH of present day rain water) (Fig. 2). Hart (1978) and Owen *et al.* (1979) (and see Nisbet 1987) have argued that the partial pressure of carbon dioxide 4 billion years ago was probably between 100 and 1000 times today's values while Walker (1985) and Kasting and Ackerman (1986) consider the CO<sub>2</sub> pressure to have been 10 bars or more taking into account today's crustal, hydrospheric and atmospheric reservoirs of carbon. Such high partial pressures of CO<sub>2</sub> would have inevitably led to acidic rain water, and ocean waters too would also probably have been acidic. Clearly early ocean water would not have been pure. Weathering of subaerial volcanics and hydrothermal interaction with the crust at both medium (150 °C approx.) and high (400 °C approx.) temperatures would have introduced significant concentrations of solutes; especially magnesium and bisulphide ions and silica in the off-ridge springs, and calcium, potassium, sodium and some iron from the high temperature springs. The pH of the oceans would therefore have been greater than that of pure water (Fig. 2) as it moved to equilibrate at low temperature with mafic igneous rocks, notionally through:



Present day near surface ocean waters have reached a pH of about 8.4 which is the

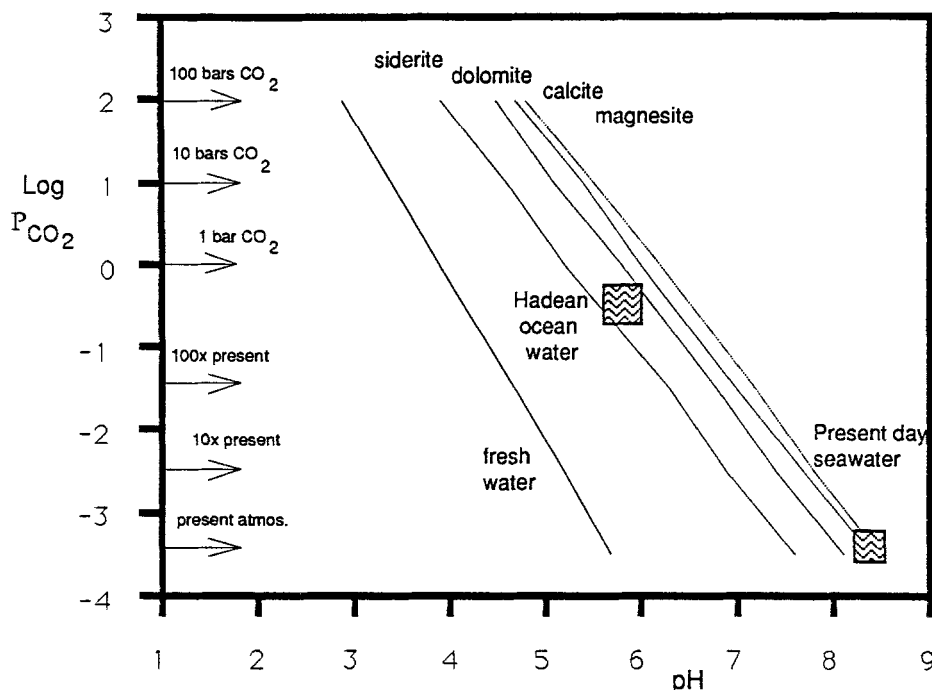


Fig. 2 A simple model for predicting ocean water pH values using a plot of  $\text{Log } P_{\text{CO}_2}$  and pH showing pure water and carbonate equilibria. Calculated following the method (see text) given in Garrels and Christ (1965). The theoretical pH of water in equilibrium with partial pressures of carbon dioxide from present day value to 100 bars provides minimum pH values for Hadean seawater. It is probable (see text) that within a few hundred million years, seawater would have become saturated in siderite and pH would have increased with decreasing  $P_{\text{CO}_2}$  to be buffered by dolomite. Present day upper ocean water is buffered to a pH of about 8.4 by biogenic calcite precipitation.

equilibrium value for calcite saturation (Garrels and Christ 1965) at present-day atmospheric  $P_{\text{CO}_2}$  (Fig. 2). This pH is attained by  $\text{CaCO}_3$  production by marine algae but the deep ocean waters below the carbonate compensation depth have a lower pH, about 7.9, indicative of the buffering capacity of the oceanic carbonate system.

A general equation derived from Garrels and Christ (1965) for calculating the pH of water saturated in carbonate minerals, as a function of the partial pressure of  $\text{CO}_2$  is:

$$10^{k+18.2+0.3-x}[\text{H}^+]^4 + [\text{H}^+]^3 - 10^{-7.9+x}[\text{H}^+] - 10^{-14}[\text{H}^+] = 10^{-17.9+x} \quad (\text{iv})$$

Where the equilibrium constant,  $K_{\text{carbonate}} = 10^k$  and  $P_{\text{CO}_2} = 10^x$ .

This has been used to construct the carbonate equilibria shown in Fig. 2. Thus, if bicarbonate had been the dominant species and the ocean was anoxic, high iron solubility would have been only possibly up to pH values defined by the siderite line (Fig. 2). In fact calcium is dissolved from mafic rocks to a disproportionate degree (e.g. Von Damm *et al.*, 1985) so for the EQ3 computation we make the

TABLE I

An estimated present day seawater chemistry (after Nordstrom *et al.* 1979). The pH and Eh are 8.22 and 0.5 respectively. Figures quoted have been rounded to two significant figures.

Species	Molal concentration
Ag <sup>+</sup>	$0.37 \times 10^{-10}$
Al <sup>3+</sup>	$0.74 \times 10^{-07}$
B(OH) <sub>3</sub> (aq)	$0.43 \times 10^{-03}$
Ba <sup>2+</sup>	$0.15 \times 10^{-06}$
Br <sup>-</sup>	$0.84 \times 10^{-03}$
Ca <sup>2+</sup>	$0.10 \times 10^{-01}$
Cd <sup>2+</sup>	$0.89 \times 10^{-09}$
Cl <sup>-</sup>	$0.55 \times 10^{+00}$
Co <sup>2+</sup>	$0.85 \times 10^{-09}$
CrO <sub>4</sub> <sup>2-</sup>	$0.58 \times 10^{-08}$
Cs <sup>+</sup>	$0.30 \times 10^{-08}$
Cu <sup>2+</sup>	$0.11 \times 10^{-07}$
F <sup>-</sup>	$0.73 \times 10^{-04}$
Fe <sup>2+</sup>	$0.36 \times 10^{-07}$
H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup>	$0.53 \times 10^{-07}$
HCO <sub>3</sub> <sup>-</sup>	$0.20 \times 10^{-02}$
Hg <sup>2+</sup>	$0.15 \times 10^{-09}$
HPO <sub>4</sub> <sup>2-</sup>	$0.66 \times 10^{-06}$
I <sup>-</sup>	$0.49 \times 10^{-06}$
K <sup>+</sup>	$0.10 \times 10^{-01}$
Li <sup>+</sup>	$0.26 \times 10^{-04}$
Mg <sup>2+</sup>	$0.53 \times 10^{-01}$
Mn <sup>2+</sup>	$0.36 \times 10^{-08}$
MoO <sub>4</sub> <sup>2-</sup>	$0.52 \times 10^{-07}$
Na <sup>+</sup>	$0.47 \times 10^{+00}$
Ni <sup>2+</sup>	$0.29 \times 10^{-07}$
NO <sub>3</sub> <sup>-</sup>	$0.47 \times 10^{-05}$
Pb <sup>2+</sup>	$0.24 \times 10^{-09}$
Rb <sup>2+</sup>	$0.13 \times 10^{-05}$
SiO <sub>2</sub> (aq)	$0.71 \times 10^{-04}$
SO <sub>4</sub> <sup>2-</sup>	$0.29 \times 10^{-01}$
Sr <sup>2+</sup>	$0.93 \times 10^{-04}$
Ti(OH) <sub>4</sub> (aq)	$0.86 \times 10^{-22}$
Zn <sup>2+</sup>	$0.75 \times 10^{-07}$

assumption here that evaporitic dolomite buffered the oceans in the Hadean and iron solubility would have been at a maximum defined by siderite solubility. However, the solubility of iron is not well constrained in this putative ocean, particularly at pressures of around 350 bars, equivalent to a depth of 3500 m, but as the carbonate complex it may have reached 100ppm (cf. Millero 1982, Bruno *et al.*, 1992). The composition used for modern seawater in the computations is taken from Nordstrom *et al.* (1979).

TABLE II

Mineralogical composition of komatiite prepared for computer program input for water-rock reactions.

Mineral	Moles
Magnetite	46.2
Albite	17.6
Anorthite	76.9
Diopside	309.0
Hypersthene ( $\text{En}_{0.8}\text{Fs}_{0.2}$ )	136.3
Olivine ( $\text{Fo}_{100}$ )	969.0
Arsenopyrite	$1.64 \times 10^{-3}$
Pyrrhotite	11.4

TABLE III

Mineralogical composition of basalt prepared for computer program input for water-rock reactions.

Mineral	Moles
Plagioclase ( $\text{An}_{0.2}\text{Ab}_{0.8}$ )	489.16
Diopside	194.34
Hypersthene ( $\text{En}_{0.8}\text{Fs}_{0.2}$ )	316.42
Olivine ( $\text{Fo}_{0.8}\text{Fa}_{0.2}$ )	23.21
K-feldspar	9.74
Ilmenite	40.87
Magnetite	$1.84 \times 10^{-2}$
Hydroxyapatite	$5.33 \times 10^{-4}$

### Oceanic crust composition

There is no consensus regarding the composition of Hadean oceanic crust but we prefer the possibility that the crust away from spreading centres was dominated by ultramafic lithologies. Nevertheless for the computations we have used the compositions of typical komatiite (Table II) and basalt (Table III), the latter being the consensus view of the makeup of the oceanic crust.

### Hadean hydrothermal chemistry

Hydrothermal fluid chemistry depends on the nature of the source water reservoir, the mineralogy of the host rocks, the temperature and pressure attained and the degree of water-rock interaction and equilibration. The computations outlined in the following sections focus on determining iron and sulphur concentrations as well as pH and Eh in hydrothermal solution.

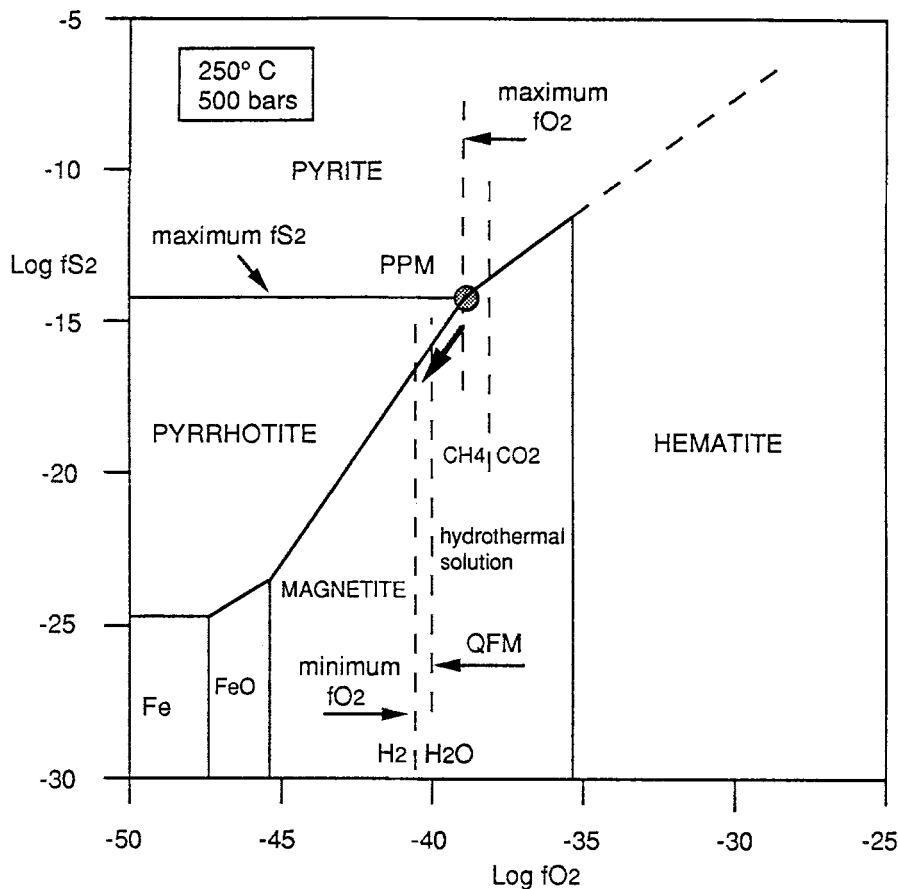


Fig. 3 Seawater – ultramafic hydrothermal system oxygen and sulphur fugacities calculated using SUPCRT92 (Johnson *et al.*, 1992) using method of Ripley and Ohmoto (1977). The arrow indicates the path of the hydrothermal solution towards the minimum oxygen fugacity represented by the reduction of water to hydrogen on serpentinisation. QFM is the quartz + fayalite + magnetite buffer for reference. Note also that the solution would be in the stability field of methane rather than carbon dioxide which implies the possibility of organic synthesis by hydrothermal anabolism\* (see Russell 1992).

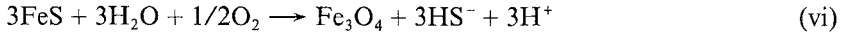
### Fugacity relationships determined using SUPCRT92

To determine the S:Fe ratio in the hydrothermal solution a method outlined by Ripley and Ohmoto (1979) was followed, but using the SUPCRT92 code of Johnson *et al.* (1992) for calculation of equilibrium constants. Ripley and Ohmoto (1977) explain how the likely maximum oxygen fugacity of a hydrothermal solution can be calculated by using appropriate buffers which are: the pyrite + pyrrhotite + magnetite (PPM) buffer for maximum fugacity; and the breakdown of water to hydrogen ( $H_2O/H_2$ ) for the minimum. The maximum sulphur fugacity is also given by the PPM buffer while the minimum can be calculated for coexisting pyrrhotite + magnetite at the minimum oxygen fugacity. Our computed relationships with some additional boundaries are given in Figure 3.

Since equilibrium conditions are considered to be achieved for the calculations, the mineralogical nature of the original rock is of little importance in theory. However, such assemblages for fugacity control are particularly appropriate for our hydrothermal model where serpentinisation of a pyrrhotite-bearing ultramafic lithology by an anoxic fluid is envisaged, and both magnetite and pyrrhotite would be stable phases. Thus it is the case of the minimum fugacities that is appropriate for our calculation of Fe and S solubilities.

The boundary of the  $\text{H}_2\text{S}$  and  $\text{HS}^-$  fields of predominance at 250 °C and 500 bars is 6.8 (SUPCRT92). At pH values significantly above 6.8 therefore, the activity (fugacity) of total sulphur is taken to be equal to that of  $\text{HS}^-$ .

Given the calculated gas fugacities for 250 °C and 500 bars, and considering a solution of 3 pH units above neutral (see next section), the sulphur and iron activities can be calculated from the following:

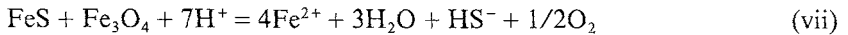


$$\text{Now, } K_{(\text{vi})} = \frac{a_{\text{HS}^-} \cdot a_{\text{H}^+}}{a_{\text{H}_2\text{O}} \cdot (f\text{O}_2)^{1/2}} \quad \text{and, } a_{\text{H}_2\text{O}} = 1$$

$$\text{thus, } 3\log a_{\text{HS}^-} = \log K_{(\text{vi})} + 1/2(\log f\text{O}_2) - 3\log a_{\text{H}^+} \quad (\text{note pH} = -\log a_{\text{H}^+})$$

Using SUPCRT92,  $\log K_1$  (250 °C, 500 bars) = -10.32, and  $\log f\text{O}_2 = -40.25$ , and the activity of  $\text{HS}^-$  as  $\log a_{\text{HS}^-}$  can be obtained for 3 pH units above neutral (5.6) and is -1.55 or about 930 ppm.

A similar procedure may be followed for calculating the activity of iron in the alkaline hydrothermal solution:



At 250 °C  $\log K_{(\text{vii})} = -11.46$  (SUPCRT92), and since,

$$4\log a_{\text{Fe}^{2+}} = \log K_{(\text{vii})} - \log a_{\text{HS}^-} - 1/2\log f\text{O}_2 - 7\text{pH} \quad (\text{viii})$$

thus,  $\log a_{\text{Fe}^{2+}} = -15$  (at  $f\text{O}_2$  of  $\text{H}_2\text{O}/\text{H}_2$  and pH 8.6) *i.e.* it is negligible.

Accepting that calculations of the true molar concentrations of sulphur and iron would require consideration of activity coefficients and ionic strengths of the solutions (Crerar *et al.*, 1978), we conclude that the SUPCRT92 calculations are indicative of a moderate sulphur solubility but very low iron solubility in the off-centre hydrothermal solution envisaged for the origin-of-life model considered here.

Support for increasing sulphur solubility for pH values above the pH of the  $\text{H}_2\text{S}/\text{HS}^-$  predominance boundary (calculated to be 6.8 at 250 °C and 500 bars using SUPCRT92) is evident from the calculations and diagrams of Barnes and Kullerud (1961). Also, the equation of Garrels and Christ (1965, p222) indicates that within the stability field of pyrrhotite, the higher the  $\text{HS}^-$  concentration and pH value, the lower the concentration of Fe:



$$\text{hence, } \log [\text{Fe}^{2+}] = \log K_{(\text{ix})} - \text{pH} - \log a_{\text{HS}^-}$$

Calculations of Fe and S solubility in present day mid-ocean ridge hydrothermal systems (Seyfried *et al.*, 1991) also give a relatively high S:Fe ratio especially at lower temperatures. Although these calculations are mainly concerned with higher temperatures, for fluid in equilibrium with PPM, plagioclase and epidote at 250 °C, 500 bars, pH = 5.2 and for 0.59 moles/kg Cl<sup>-</sup>, the calculations give log fO<sub>2</sub> = -38.08 and log fS<sub>2</sub> = -13.39 while the concentrations in mmol/kg are H<sub>2</sub>S = 0.36, and Fe = 0.05 (or H<sub>2</sub>S = 13 ppm, and Fe = 2.8 ppm), much lower than at higher pH.

### Rock:water interactions modelled using EQ3NR/EQ6

Although the speciation and solubility code EQ3NR and the aqueous geochemical reaction path modelling code EQ6 are powerful, great care must be taken in the use of the output data. Firstly, in the 'real world', complex geochemical kinetics will affect the precipitation of phases, but the thermodynamic prediction of saturation and supersaturation may involve metastable phases and the thermodynamic data base of the codes, although large, does not encompass every mineral phase. Yet the codes can be used successfully to determine trends in the bulk fluid chemistry in equilibrium situations.

As we are uncertain of Hadean ocean chemistry, pH and oxidation state, we start our simulation with the composition of modern seawater in EQ3NR, which is taken from Nordstrom *et al.* (1979) (Table I). We then investigate a number of pH conditions and amend the seawater file using chlorine to balance the overall charge. We simulate water:rock interactions with typical komatiite (Table II) and basalt (Table III). The calculated composition of the komatiite input to the EQ6 reaction file for reaction with 1kg of the seawater assumes a komatiite porosity of 1%.

Reacting present day seawater (at 25 °C) with komatiite produced an alkaline, reducing fluid at all temperatures from well over four pH units alkaline at 50 °C down to 2 units at 200 °C (Fig. 4). We then lowered the pH of present day seawater and carried out three further investigatory runs. The fluid remained invariably alkaline and reducing in all the runs. Similar reaction of present day seawater with basalt also produced alkaline fluids though the pH values are less extreme (Fig. 5).

The first model Hadean seawater composition estimated from Walker (1985) entered into the EQ3NR code is listed in Table IV. The code was instructed to hold the bicarbonate composition of the seawater in equilibrium with dolomite. The fluid was supersaturated with respect to aragonite and calcite, and saturated with respect to ordered dolomite, and monohydrocalcite. The code was set to maintain electrical neutrality by altering the concentration of Cl<sup>-</sup>. The pH of the fluid at each temperature was also set to neutrality. This solution was then entered into the EQ6 reaction path modelling code, to be reacted to equilibrium with a

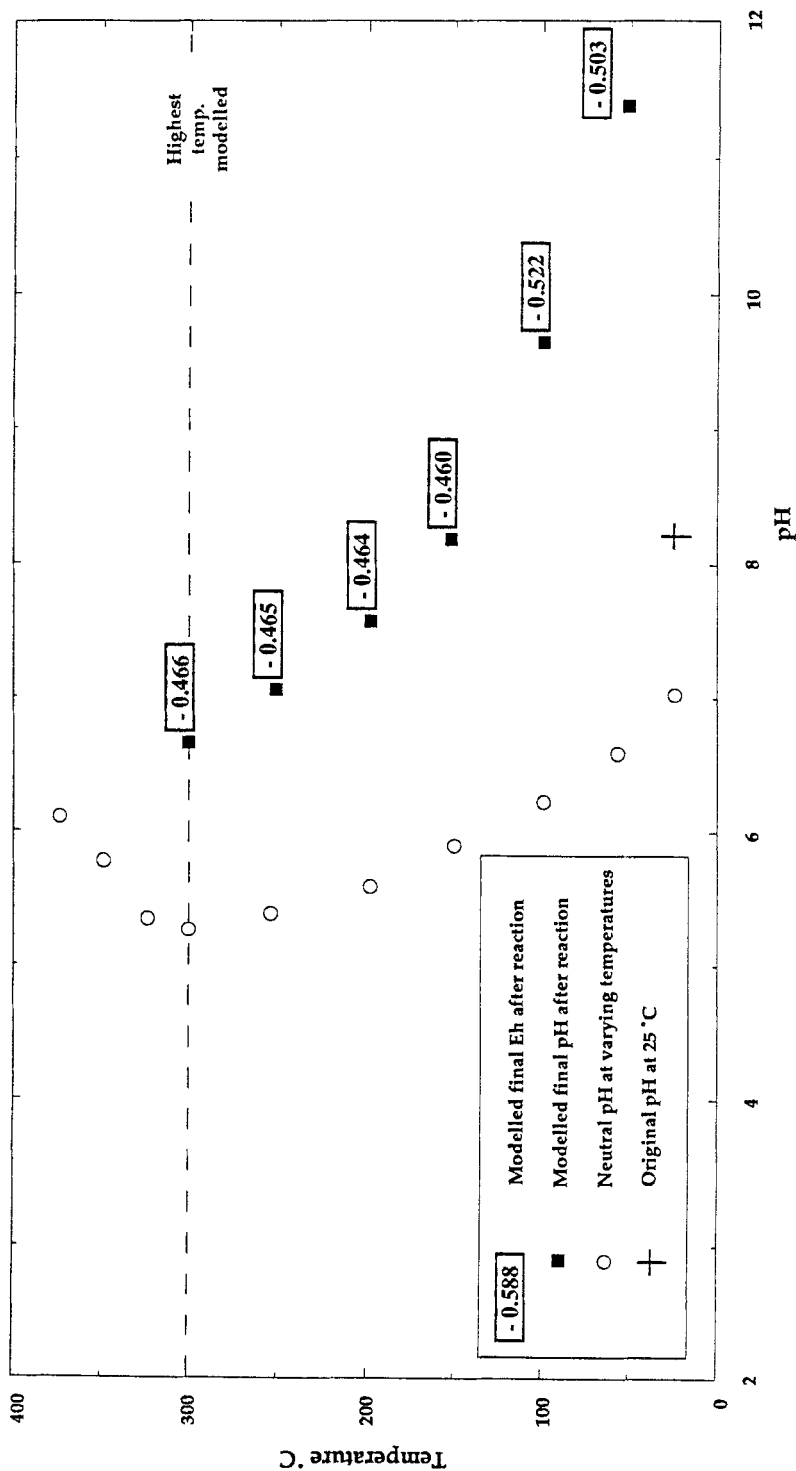


Fig. 4 A plot of pH and Eh for the final solution after reacting present day seawater (Table I) with komatiite (Table II) from 50–300 °C. The initial temperature of the solution was 25 °C.

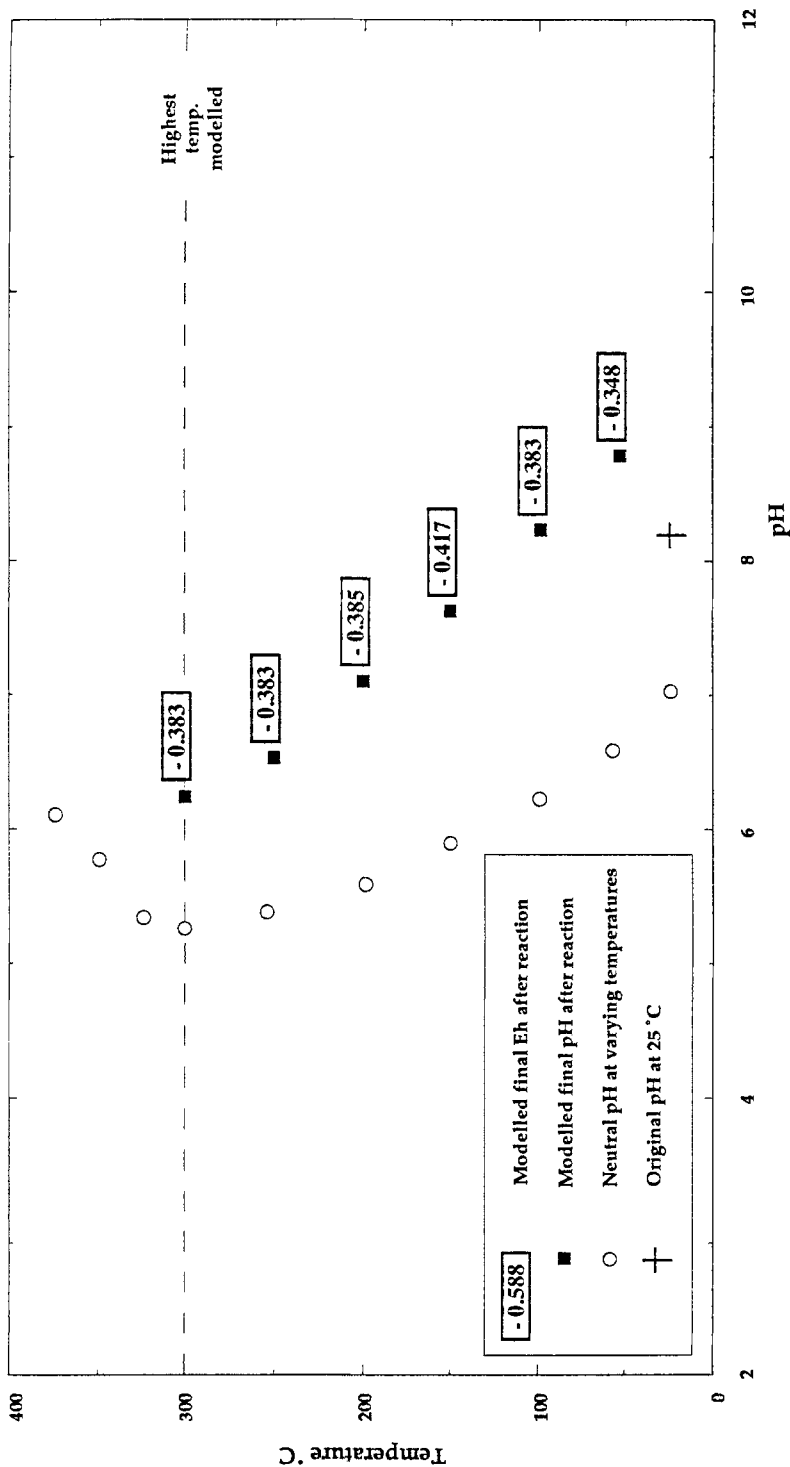


Fig. 5 A plot of pH and Eh for the final solution after reacting present day seawater (Table I) with basalt (Table III) from 50–300 °C. The initial temperature of the solution was 25 °C.

TABLE IV

An estimated Hadean seawater chemistry (after Walker 1985). The pH and Eh are 6.00 and 0.3 respectively. Figures quoted have been rounded to two significant places.

Species	Molal concentration
Al <sup>3+</sup>	$0.37 \times 10^{-21}$
B(OH) <sub>3</sub> (aq)	$0.16 \times 10^{-21}$
Ca <sup>2+</sup>	$0.31 \times 10^{-01}$
Cl <sup>-</sup>	$0.55 \times 10^{+00}$
Fe <sup>2+</sup>	$0.18 \times 10^{-02}$
H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup>	$0.71 \times 10^{-22}$
HCO <sub>3</sub> <sup>-</sup>	$0.20 \times 10^{+00}$
HPO <sub>4</sub> <sup>2-</sup>	$0.10 \times 10^{-21}$
K <sup>+</sup>	$0.51 \times 10^{-01}$
Mg <sup>2+</sup>	$0.59 \times 10^{-02}$
Na <sup>+</sup>	$0.27 \times 10^{+01}$
SiO <sub>2</sub> (aq)	$0.17 \times 10^{-21}$
SO <sub>4</sub> <sup>2-</sup>	$0.56 \times 10^{-02}$
Ti(OH) <sub>4</sub> (aq)	$0.86 \times 10^{-22}$

komatiite in a closed system. The saturated mineral phases and final fluid pH and Eh of this moderated seawater at temperatures between 25 °C and 300 °C, after reaction to equilibrium with the komatiite, are calculated via the EQ6 code. A graphical representation of the final equilibrated fluid pH values in relation to neutrality (Fig. 6), shows that the final fluid is alkaline from over four units at 50 °C, to two pH units at 200 °C. We note that Eh is much lower after fluid reaction with komatiite, a strong contrast with the results of seawater basalt interactions.

The same seawater composition was then reacted with basalt. In this case the equilibrated fluid was somewhat less alkaline but still exceeded neutrality by three pH units at 50 °C and one and a half pH units at 200 °C (Fig. 7). A number of other runs were calculated for, using a variety of initial water chemistries. Although not reported here they are available from the authors. The resulting fluid was invariably alkaline and reducing.

The composition of the Hadean seawater is speculative, yet we see that over a wide range of pH, Eh and hypothetical initial seawater chemistries, the final hydrothermal fluid between 100 and 250 °C is always alkaline and reducing. This robustness of results given us confidence in our predictions of reactions at offridge hydrothermal springs. Indeed using modern seawater as a comparison the results were remarkably similar. The pH and Eh of standard seawater reacting with basalt at 25 °C were 11.1 and 0.444, and for seawater with komatiite the values were 11.03 and 0.454. Our results are consistent with what is known of the pH of ground waters in equilibrium with mafic rocks (Barnes and O'Neil 1969).

The EQ3NR/EQ6 code is more sophisticated than SUPCRT92 and offers the

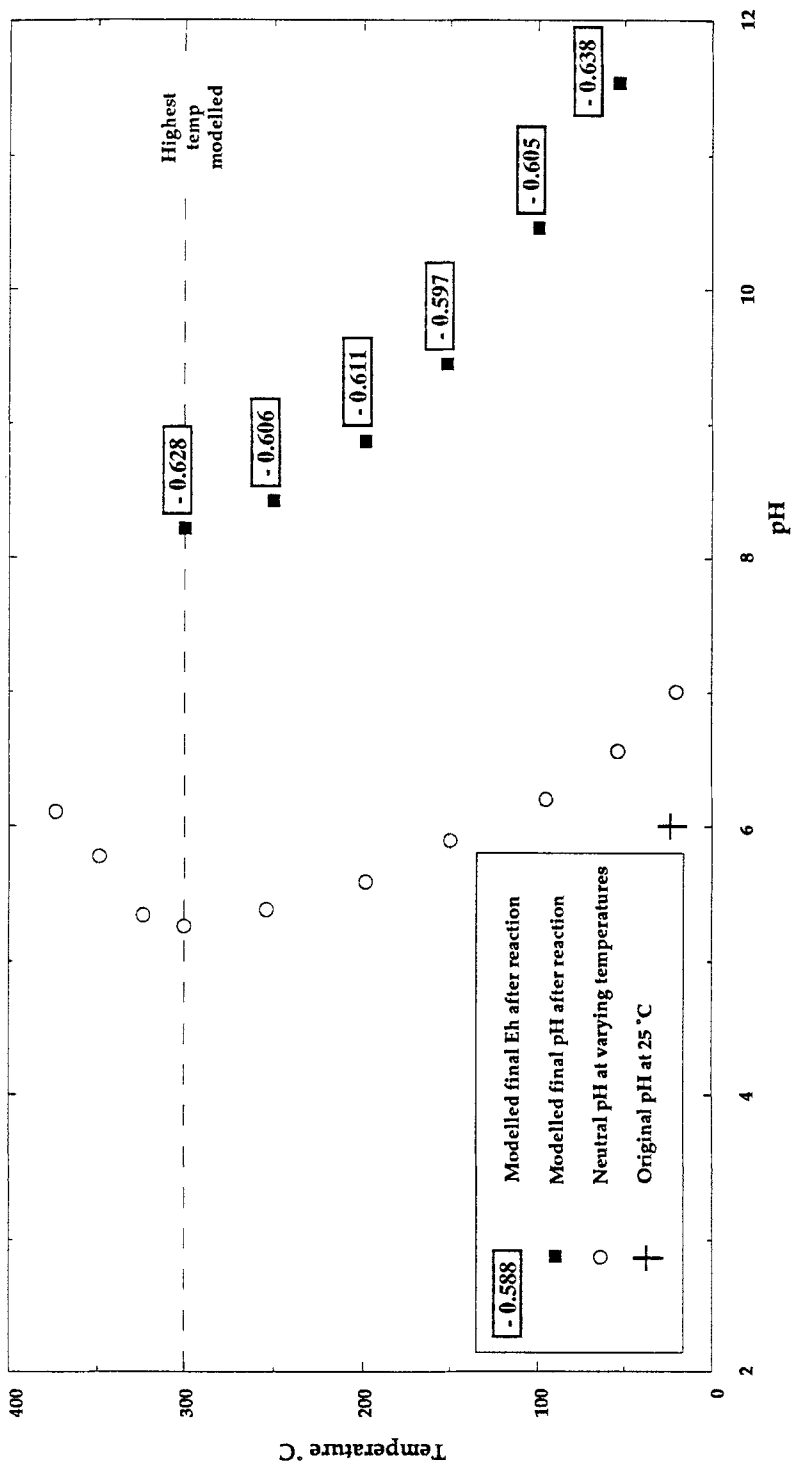


Fig. 6 A plot of pH and Eh for the final solution after reacting Hadean seawater (Table IV) with komatiite (Table I) from 50–300 °C. The initial temperature of the solution was 25 °C.

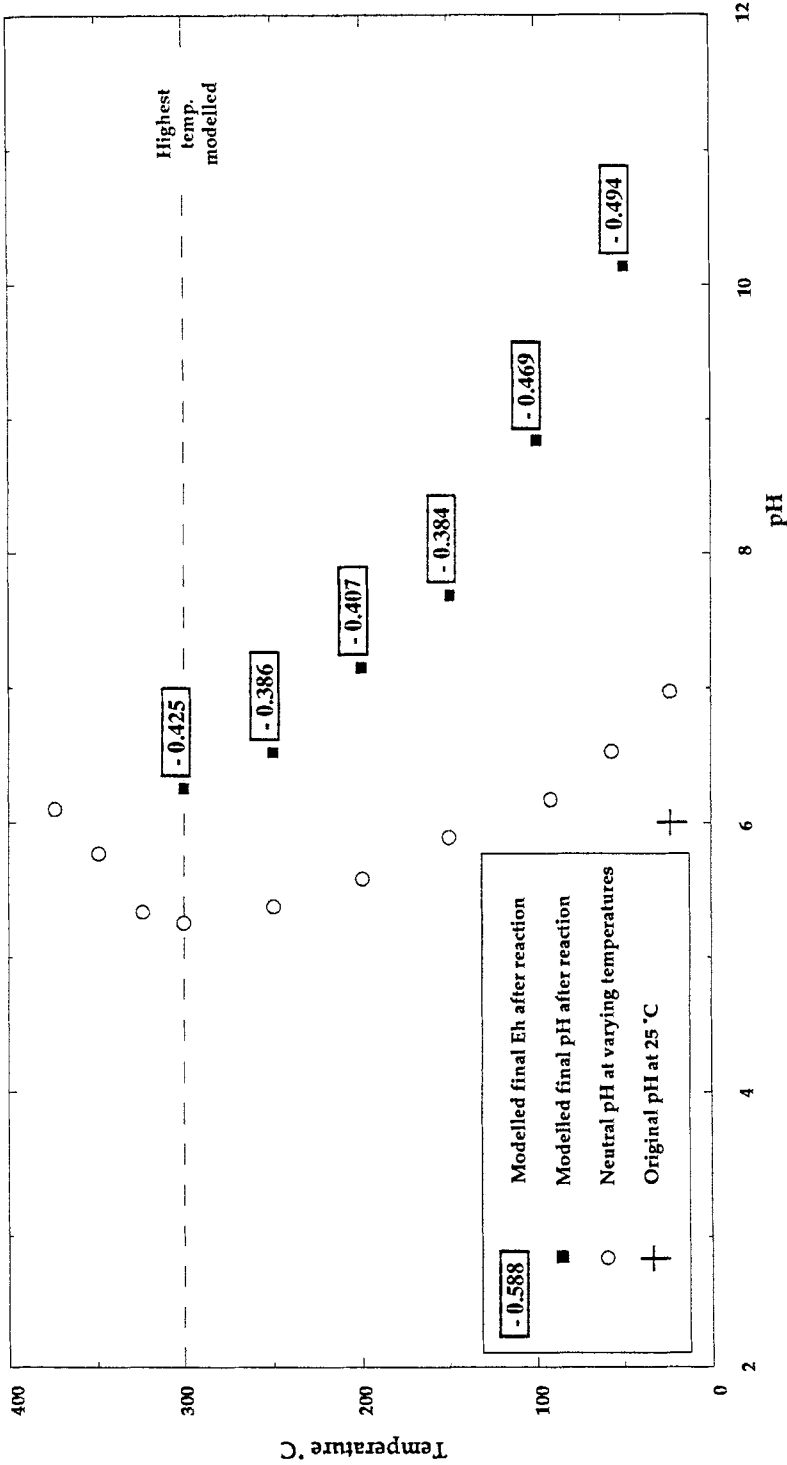


Fig. 7 A plot of pH and Eh for the final solution after reacting a Hadean seawater (Table II) with basalt (Table III) from 50–300 °C. The initial temperature of the solution was 25 °C.

possibility of obtaining calculated concentrations for the given conditions although it is more difficult to appreciate controls. In the case of sulphur and iron, for 250 °C and 500 bars the calculated molal concentrations are  $S = 2.37 \times 10^{-2}$  and  $Fe = 9.65 \times 10^{-9}$  for Hadean seawater reacted with komatiite, again supportive of a high S:Fe ratio, i.e. dissolved sulphur as  $HS^- = 780$  ppm whereas the tenor of dissolved iron is vanishingly small.

### Mixing of the hydrothermal springs and oceanwater

Iron monosulphide may be expected to precipitate rapidly at the interface between the sulphur-rich alkaline hydrothermal solutions and the iron-rich acid Hadean seawater to form membranous vesicles judging from our laboratory studies (Russell *et al.*, 1989).

In the real world, deposition from springs away from spreading centres would probably have occurred when the hydrothermal fluid, rich in acquired soluble species, reaches the sea floor, the pressure lowered and the fluids mixed. The computer code SOLMINEQ88 (Kaharaka, *et al.*, 1989) was used to model the mixing of some of the emergent hydrothermal fluids with the putative Hadean seawater from which it was derived. The fluids were mixed at a ratio of 50/50, approximately what we would expect at a membranous interface, although an exact ratio as to the volume of each fluid involved in the mixing zone at a vent is indeterminable and ever changing. As expected, mixing the set of hydrothermal fluids with the seawaters indicated a high degree of supersaturation with respect to clays, carbonates and iron sulphides.

A tentative Eh-pH diagram illustrating the concept of an iron-sulphide membrane forming between hydrothermal solution and seawater is given in Figure 8. Although calculated for 25 °C, this demonstrates the essential phase relationships and how such a membrane would provide an electro-chemical (chemiosmotic) gradient for focusing energy transitions as the first steps towards the initiation of life's metabolic processes (Russell *et al.*, 1993).

### Discussion

In this paper we have mainly attempted to establish the likely pH of medium temperature submarine springs away from volcanoes four or so billion years ago. We have taken a uniformitarian approach using both komatiite and basalt as idealised end-member compositions of oceanic crust, but this could well have led us to underestimating the contents of iron, nickel and sulphur in the crust at 4.4 to 4.0 Ga, with important implications for our modelling. At that time iron-nickel-sulphide droplets and minerals could have been present in the upper mantle. Even as late as about 2.9 Ga seemingly juvenile iron-nickel-sulphur magmas were intruding or extruding along with immiscible komatiitic magmas in Australia (Gresham and Loftus-Hills 1981). Crust with layers of iron-nickel-sulphides may have provided

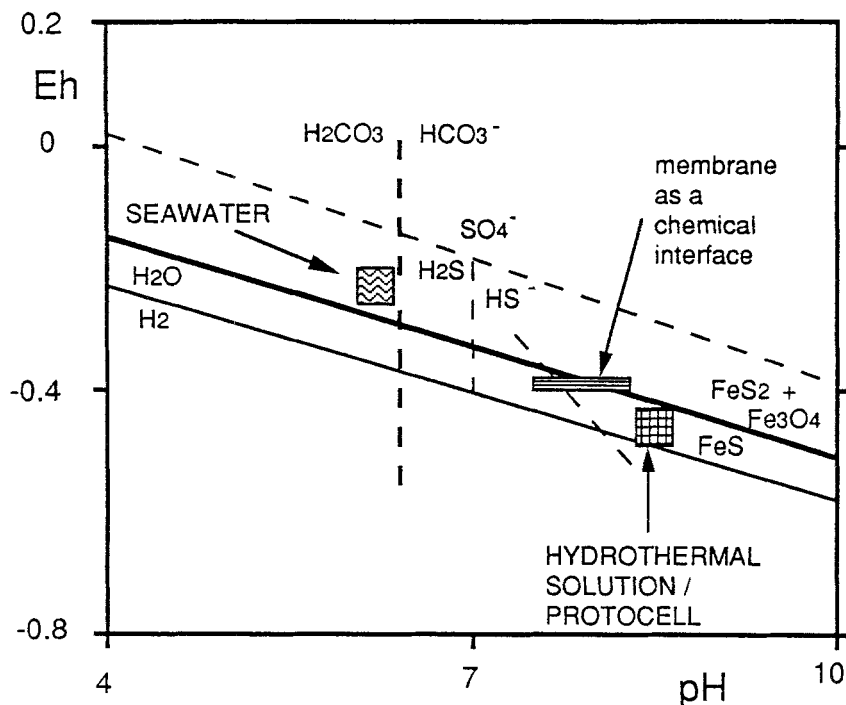


Fig. 8. Tentative Eh-pH diagram indicating electro-chemical gradient between early seawater and hydrothermal solution across the Fe(III,II) sulphide membrane. The thicker sloping solid line indicates the upper stability of FeS (co-existing with pyrite) calculated for the  $fS_2$  of the  $FeS + FeS_2 + Fe_3O_4$  (PPM) buffer at 25 °C, 1 bar. This represents the maximum Eh of the hydrothermal solution. The maximum Eh of the membrane is represented by a horizontal band just below the intersection of the PPM line and the aqueous Fe(II) / ferric oxide-hydroxide line (dashed). The Eh contrast between the seawater and hydrothermal solution would have provided at least 0.2V potential to initiate and drive catabolic processes. The protocell membrane exists at a low Eh and  $fS_2$  within the stability field of mixed-valence ferrous/ferric sulphides which could have evolved to ferredoxins.

higher concentrations of iron, and locally nickel, to very high temperature springs, and sulphur to medium temperature discharges.

We have also entertained the ideas of Henderson-Sellers and Henderson-Sellers (1988) in assuming a cool early Archaean ocean. In contrast Costa *et al.* (1980) and also Kasting and Ackerman (1986) have suggested a hot early ocean, an hypothesis supported by the isotopic studies of Karhu and Epstein (1986) although their results are apparently at variance with evidence of large scale glaciations back to at least 2.3Ga (Barron 1992). A hot Hadean ocean would require some reconsideration of the arguments and results presented in this paper. Open system hydrothermal convection would have been less vigorous because of a lower buoyancy contrast. Nevertheless the qualitative contrast between the pH of the medium temperature springs with that of the oceans would have been maintained.

### Conclusions

The concept that life may have started at the site of a long-lived non-volcanogenic medium temperature alkaline hydrothermal spring debouching into mildly acid, iron-bearing ocean water survives feasibility tests involving thermodynamic calculations and computer code interactions. An alkaline solution feeding the first protocellular colonies has much to commend it because supersaturation of iron sulphide ensues upon mixing with seawater to provide an Eh/pH barrier (Fig. 8). Hydrophobic colloidal iron sulphide membranes may form, perhaps in association with hydrothermal organosulphur molecules. Such a membrane represents the culmination and telescoping of the redox/pH front. So we have in place a naturally occurring proton-motive (chemiosmotic) force which would drive the sparse organics present in the acid Hadean ocean onto and through the membrane. This membrane would then be flexible and expansive, although aging would lead to vesicle rupture. But in this event the two fluids are administered directly to the break, and new membrane would be deposited contiguously with the old to encapsulate a daughter vesicle. Also the membrane would have catalytic properties so that, in time, vesicle growth and reproduction would rely more on osmosis concomitant with a developing metabolism and less on direct hydrothermal inflation (Russell *et al.*, 1989, 1993).

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