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Serpentinization as a source of energy at the origin of life

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ABSTRACT

For life to have emerged from CO_2, rocks, and water on the early Earth, a sustained source of chemically transducible energy was essential. The serpentinization process is emerging as an increasingly likely source of that energy. Serpentinization of ultramafic crust would have continuously supplied hydrogen, methane, minor formate, and ammonia, as well as calcium and traces of acetate, molybdenum and tungsten, to off-ridge alkaline hydrothermal springs that interfaced with the metal-rich carbonic Hadean Ocean. Silica and bisulfide were also delivered to these springs where cherts and sulfides were intersected by the alkaline solutions. The proton and redox gradients so generated represent a rich source of naturally produced chemiosmotic energy, stemming from geochemistry that merely had to be tapped, rather than induced, by the earliest biochemical systems. Hydrothermal mounds accumulating at similar sites in today's oceans offer conceptual and experimental models for the chemistry germane to the emergence of life, although the ubiquity of microbial communities at such sites in addition to our oxygenated atmosphere preclude an exact analogy.

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> 'the chain of life is…a continuous one, from the mineral at one end to the most complicated organism at the other'.
>
> Leduc (1911, p. xv)

INTRODUCTION

The process of serpentinization is central to a hypothesis positing that life emerged at an alkaline hydrothermal vent (Russell *et al*., 1989, 1994; Früh-Green *et al*., 2004; Holm *et al*., 2006; Schulte *et al*., 2006; Martin & Russell, 2007). In some modern hydrothermal systems, serpentinization generates hydrogen that can reduce carbon dioxide to methane (Proskurowski *et al*., 2008) in a reaction that does a similar, although less efficient, job as does the overall metabolic core reaction of methanogenesis (Martin *et al*., 2008). The Lost City hydrothermal site is particularly exciting in this respect. It was discovered in 2000, 15 km away from the Mid Atlantic Ridge – just the distance modeled by Shock for such an off-ridge system (Shock, 1992; fig. 18; Kelley *et al*., 2001). And, as expected (Russell *et al*., 1989), the solutions are alkaline and do carry hydrogen. Direct sampling of Lost City hydrothermal exhalations (Proskurowski *et al*., 2006, 2008; Konn *et al*., 2009; Lang *et al*., 2010) and experimental simulation of vent conditions (McCollom & Seewald, 2003a,b, 2007; Seyfried *et al*., 2007) reveal that serpentinite-hosted hydrothermal systems can and do produce methane, short hydrocarbons and minor concentrations of formate and traces of acetate, although at least some of the latter may be a microbial by-product (Lang *et al*., 2010). These developments are important in the context of the origin of life, not only because they point to ways in which organic molecules might have been synthesized on the early Earth, but also because they identify a specific geochemical setting in which the abiotic reduction of carbon dioxide demonstrably takes place in nature.

During serpentinization, hydrogen is generated through the reduction of water by ferrous iron in what Bach *et al*. (2006) have shown to be complex reactions requiring aqueous silica (McCollom & Bach, 2009). Carbon dioxide may be introduced to the serpentinizing system either in downdrafts of ocean water, or from the mantle beneath, into an ultramafic/komatiitic crust where it is reduced by hydrogen to produce formate and methanol in aqueous phase (Seewald *et al*., 2006). Further reduction to methane probably involves iron–nickel alloys as catalysts (Horita & Berndt, 1999). Iron–nickel alloys could then also facilitate the reduction of primordial CO_2 carbon in the oceanic crust to C2 to C4 hydrocarbons through Fischer–Tropsch-type reactions (Proskurowski *et al*., 2008).

Here, we consider how reactions of molecular hydrogen, produced by serpentinization, with carbon dioxide of volcanic origin dissolved in the Hadean Ocean, progress toward the sustained synthesis of reduced organic compounds under alkaline hydrothermal conditions (Russell *et al.*, 1998; Schoonen *et al.*, 1999; Maden, 2000; Seewald *et al.*, 2006). We point out the similarities and differences between the chemical reactions that take place in serpentinizing hydrothermal systems and some of the core chemical reactions that drive energy metabolism during acetogenesis and methanogenesis, which have been suggested to be the most ancient forms of microbial metabolism (Martin & Russell, 2007). Moreover, in addition to the H_2O- and CO_2-reducing capabilities of serpentinization, the alkaline nature of the effluent appears to be a vital property when it comes to the search for analogies between naturally occurring geochemical process and the processes of life, both modern and ancestral.

INITIAL CONDITIONS

The Earth formed by accretion around 4.57 Ga (Halliday, 2004). Soon afterwards, and partly as a result of melting through the moon-producing impact of the relatively oxidized and volatile-rich protoplanet Theia, the Earth's mantle was drained of the native iron by rapid gravitation to the Earth's core (Delano, 2001; Boyet & Carlson, 2005; Wood & Halliday, 2005; Touboul *et al.*, 2007; Berry *et al.*, 2008). Thus, notwithstanding the suggestion of Schaefer & Fegley (2007) who assume a quartz–fayalite–*iron* (QFI) buffered mantle and thereby an early methane atmosphere, we follow the arguments of Wood *et al.* (1990, 2006) and Frost *et al.* (2004) who infer the Earth's mantle to have rapidly achieved an oxygen fugacity ~0.9 log units below that of the quartz–fayalite–*magnetite* (QFM) buffer, and thus to have been in equilibrium with CO_2 (and see Shock, 1992; fig. 17). In this view, the Hadean atmosphere was dominated by carbon dioxide and nitrogen (in much the same ratio as in the present day atmospheres of Venus and Mars) but with some NO, CO, P_4O_{10}, SO_2 and native sulfur (e.g. S_8) or, to borrow a phrase from Robert Boyle (1685, p. 276, cited in Keele, 1974), an atmosphere 'ascending out of the lower parts and as it were, bowels of the terraqueous globe' (Walker, 1985; Walker & Brimblecombe, 1985; Yamagata *et al.*, 1991; Kasting *et al.*, 1993; Delano, 2001; Pavlov & Kasting, 2002; Halevy *et al.*, 2007; Martin *et al.*, 2007). These gases could have accumulated in the atmosphere because volcanic eruptions were between 10 and 100 times more prolific in the Hadean than today (Martin *et al.*, 2007; but see Korenaga, 2008 for a contrary view).

An ocean had probably enveloped the Earth's surface by 4.4 Ga and may have had twice the present volume (Bounama *et al.*, 2001; Wilde *et al.*, 2001; Valley *et al.*, 2002, 2006; Korenaga, 2008) probably delivered by chondritic meteorites after the planet Theia's impact (Marty & Yokochi, 2006; Albarède, 2009). The ferrous iron silicates in the mafic and komatiitic lavas, minor pyroclastics, ultramafic and serpentinite intrusions and chemical precipitates comprising the oceanic crust would have partially reduced the circulating ocean water to hydrogen by ferrous iron in olivine and pyroxene during serpentinization. Hydrogen still emerges today at concentrations approaching 15 mmol kg^{-1} from hydrothermal fluid that results from serpentinization (Russell *et al.*, 1989; Charlou *et al.*, 2002; Proskurowski *et al.*, 2006, 2008; McCollom & Bach, 2009) and still today is the source of electrons fueling many forms of microbial metabolism (Wolin, 1982; Shock *et al.*, 1998; Morita, 2000; Amend & Shock, 2001; Takai *et al.*, 2004; Spear *et al.*, 2005).

The effect of both mantle and aqueous convective transfer of the early Earth's heat was to generate a geochemical disequilibrium (Shock, 1990) partially resolved by the reduction of carbon dioxide to organic molecules in a process that we think led to the emergence of life. The tension between the volatisphere comprising $H_2O > CO_2 > N_2 > SO_2 > CO > NO > P_4O_{10}/H_2PO_4^- > S_8$ and the reduced solid Earth was best focused and discharged at submarine alkaline springs where they interfaced with an acidulous ocean. A CO_2 atmosphere of between one and 10 bars is variously estimated to have imposed a pH of between 5.1 and ~6 on the carbonic Hadean ocean (Macleod *et al.*, 1994; Morse & Mackenzie, 1998) although the pH may have been locally lower where acidic high temperature (~400 °C) hydrothermal springs – then producing ~10 times the present volume of effluent – were particularly active or when volcanic exhalations of SO_2 were particularly vigorous (Lowell & Keller, 2003; Halevy *et al.*, 2007; and see Sigurdsson *et al.*, 1987). A CO_2-dominated atmosphere might be expected to lead to greenhouse temperatures anywhere between ~25 and, at the extreme, ~100 °C (Schwartzman and Lineweaver, 2005; Knauth, 2005; Zahnle *et al.*, 2007). However, cold spells induced by interstellar or impact-generated dust clouds (Pavlov *et al.*, 2005) are likely to have cooled the planet intermittently and given ample opportunity for off-ridge convection, and hence low-temperature (<150 °C) serpentinization, to occur at similar rates to those obtaining today. The alkaline fluids resulting from Hadean off-ridge, relatively low-temperature serpentinization processes, thus discharged into a carbonic ocean. At the same time, the myriad of very hot, *acidic* and low-sulfide springs at Hadean oceanic spreading centers, thermostated just above 400 °C by the thermodynamic properties of salt water, emitted micromolar concentrations of Fe, Zn, Mn, Co, Ni and Cu to the ocean (Jupp & Schultz, 2000; Douville *et al.*, 2002; Kump & Seyfried, 2005; Zerkle *et al.*, 2005; Konhauser *et al.*, 2009). Phosphate – another obligatory entity for emerging life – would have been emitted from volcanoes and rained into, and dissolved, in the carbonic ocean as orthophosphate at a concentration of between 6 and 9 mmol kg^{-1} (Yamagata *et al.*, 1991; Macleod *et al.*, 1994; Hagan *et al.*, 2007). Although we maintain that millimolar concentrations of ferrous iron were present in the Hadean Ocean, given that it is likely to have had a pH below 6 carries the implication that phosphate would have remained soluble as $FePH_2PO_4^+$ (Russell & Hall, 1997). We note in passing that iron(II) phosphate can catalyze pyrophosphate formation, from acetyl phosphate as the activated phosphoryl donor (de Zwart *et al.*, 2004).

Thus, the Hadean Ocean was a reservoir of the inorganic elements required of the earliest catalysts of organic reactions and, ultimately, enzymes. The acidulous Hadean Ocean was also a reservoir of potential free energy in the form of protons. It is important to recall that temperatures above 150 °C are less conducive to the formation of reduced organic compounds (Shock, 1990, 1992), a prerequisite for the origin of life. In this respect, the moderate temperature and alkaline nature of serpentinizing off-ridge hydrothermal convective systems would have offered conditions – on their interaction with CO_2-bearing mildly acidic ocean water – favoring the carbon, amine, thiolate and phosphate reactions and interactions that are essential to the chemistry of life (Rabinowitz *et al.*, 1969; Bonomi *et al.*, 1985; Huber & Wächtershäuser, 1997, 2003; de Zwart *et al.*, 2004; Gao *et al.*, 2008; Amend & McCollom, 2009; Lang *et al.*, 2010).

SERPENTINIZATION IN OFF-RIDGE HYDROTHERMAL SYSTEMS

While uniquely instructive as a modern example, the serpentinizing system that produced the chambered carbonate chimneys at the Lost City Hydrothermal Field is not completely homologous to the system that we posit to have fed emergent life over 4 billion years ago because (i) the Hadean Ocean was in equilibrium with a carbon dioxide atmosphere of up to 10 bars, was oxygen-free and harbored metals, phosphate and silica in the micro- to millimolar range contributed by ~400 °C hot spring plumes and volcanoes (Walker, 1985; Kasting, 1993; Lowell & Keller, 2003; cf. Sigurdsson *et al.*, 1987); (ii) ultramafic intrusions and/or komatiitic flows would have been more frequent in the early crust and may have hosted some hydrothermal systems (Nisbet, 1985); (iii) appreciable bisulfide (HS^-) activities in the alkaline hydrothermal fluid could have resulted where sulfide stockworks, previously generated in the ridge-crest komatiites by high temperature fluids or as magmatic sulfide flows (cf. Lambert *et al.*, 1998; Charlou *et al.*, 2002), were altered to green rust or magnetite, and (iv) carbonates in the mound would have been ephemeral as they dissolved at depth and high pressure in the acidic ocean, leaving serpentinite minerals, sepiolite and brucite as the main precipitates decorated with nickel–cobalt–iron sulfides and molybdenum and tungsten sulfide/oxide clusters (Figs 1 and 2) (Russell & Hall, 2006).

Thus the resulting bisulfide was free to react with transition metals, mainly ferrous iron but also nickel and cobalt, in the Hadean ocean, especially where the alkaline spring and its associated mound lay down-current from the kind of iron-rich hydrothermal plume that exhales at a high temperature of the kind encountered at the Rainbow field today (Douville *et al.*, 2002). In such a case, iron monosulfide precipitates bearing these other metals as well as phosphate would be expected to contribute to barriers forming spontaneously between the acidulous carbonic ocean and the alkaline hydrothermal solution, and produce a complex of naturally forming, semiconducting compartments with partially permeable catalytic inorganic walls (Russell & Hall, 1997; cf. Ferris *et al.*, 1992).

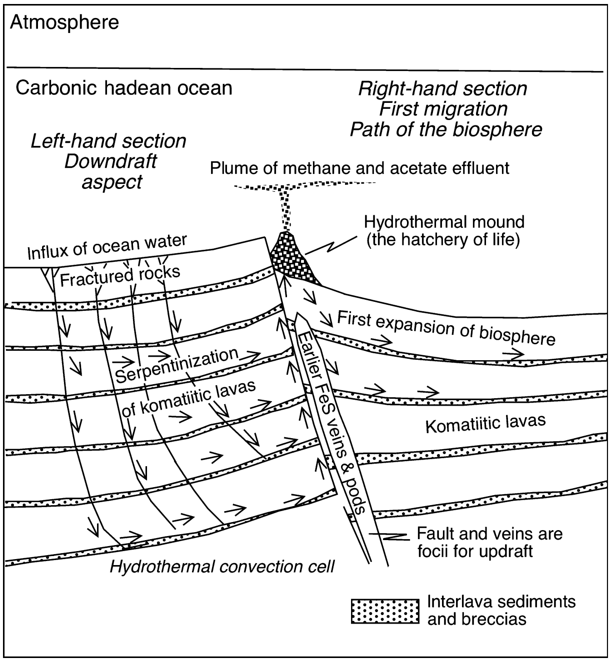

Fig. 1 A 4-billion-year-old off-ridge submarine mound forms above a serpentinizing hydrothermal convection cell in komatiitic lavas. The left-hand section illustrates how ocean water percolates through the ocean-floor crust and returns, heated, generally guided by fractures. The right-hand section shows possible colonization by the first prokaryotes of the komatiitic flows and ultramafic intrusives comprising the Hadean ocean floor (i.e. methanogenic archaea, acetogenic bacteria, subsequent heterotrophs and sulfate-reducing archaea and bacteria). Figure recast from Russell & Martin (2004) and Russell & Arndt (2005).

The chemical nature, in particular the pH values, of hydrothermal solutions coming from serpentinization of ultramafic crust depends largely on temperature: magma-driven systems are hot (>~250 °C) and acidic ($pH < 5$), while systems driven by residual heat are cooler and alkaline. When a magmatic thermal drive appears to be absent in serpentinized crust, direct measurements of submarine hydrothermal convective effluent have yet to exceed the 91 °C recorded at Lost City (Proskurowski *et al.*, 2006). While the high pH of up to 11 at Lost City is as expected for such a low temperature of serpentinization of ultramafic crust (Macleod *et al.*, 1994; fig. 6), the temperature of fluid-rock interactions responsible for Lost City effluent is controversial. Proskurowski *et al.* (2006; fig. 7) calculate temperatures of fluid-rock interactions to be between 110 and 150 °C from water-hydrogen isotope measurements

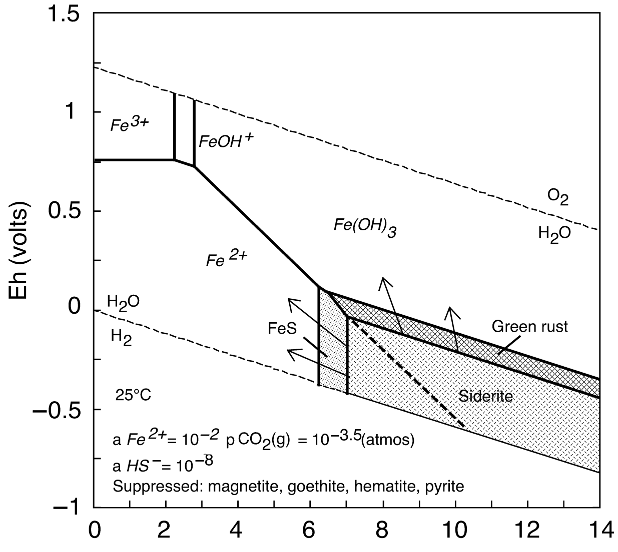

Fig. 2 Pourbaix (Eh/pH) diagram illustrating the stabilities of siderite ($FeCO_3$), mackinawite (as FeS) and green rust [$Fe^{II}_4Fe^{III}_2(OH)_{12}.CO_3.2H_2O$, cf. fougèrite, Blaß *et al.*, 1997; http://www.mindat.org/min-27543.html] pertinent to the contribution of various iron minerals to the hydrothermal mound. At higher pCO_2, the siderite field would expand as indicated by arrows at the expense of FeS and green rust. Release of HS^- from deeper and earlier FeS deposits to the hydrothermal solution would cause the re-precipitation of a FeS front or outer wall on meeting Fe^{2+} at the margins of the growing mound. Minerals are suppressed to reveal relationships. Initial activities, which are dimensionless, are equivalent here to molality. Calculated using Geochemist's Workbench (Bethke, 1996) with green rust data added from Rahman (2002).

at Lost City. These values, measured on the effluent, are broadly in agreement with those based on oxygen isotope studies in other serpentinites by Wenner & Taylor (1971). If anything, these temperatures are a little higher than those estimated for convective systems in subaerial Alpine peridotites and serpentinites (Fallick *et al.*, 1991; Zedef *et al.*, 2000). In contrast, Foustoukos *et al.* (2008) claim, on the basis of their oxygen isotope studies of vent fluids and their estimation that water-rock ratios were high during alteration beneath Lost City from boron isotopes, that circulating fluids reached temperatures exceeding 250 °C, and that extensive conductive heat loss accounted for the low exhalation temperatures. Allen & Seyfried's (2004) estimates on the basis of calcium sulfate concentrations are only a little lower at 200 ± 50 °C. However, water-rock ratios are likely to have been low because once an ultramafic rock has been hydrated and thereby softened, and fractures filled with carbonate, further flow and serpentinization are inhibited (cf. Barnes & O'Neil, 1969; Escartín *et al.*, 2001). Moreover, it is noteworthy that serpentinite has a thermal conductivity of only around 2.3 W m^{-1}·K^{-1} (Diment, 1964). That the convective system at Lost City has been operating in steady-state for at least 100 000 years (Ludwig *et al.*, 2005) in such well-insulated flow channels suggests to us that conductive heat loss could not lead to a drop in temperature of >150 °C in the updraft. Instead, these observations support the view that at least some of the hydrothermal convection cells operating in ultramafic lavas and intrusions away from spreading centers in the Hadean, as today, could have been thermostated at around 130 °C by rheological softening and expansion during serpentinization (Fig. 1) (Barnes & O'Neil, 1978; Fallick *et al.*, 1991; Adams, 1998; Zedef *et al.*, 2000; Amend & Shock, 2001; Escartín *et al.*, 2001; Russell & Hall, 2006; Baaske *et al.*, 2007).

Such moderate temperature submarine serpentinization of ultramafic rock could generate a combined thermal output sufficient for 100 000 years or so of stable, downward-excavating, convective hydrothermal flow driven by residual crustal heat, exothermic reactions and short range conduction (Russell, 1978; Macleod *et al.*, 1994; Lowell & Rona, 2002; Allen & Seyfried, 2004; Kelley *et al.*, 2005; Ludwig *et al.*, 2005; Emmanuel & Berkowitz, 2006; Vance *et al.*, 2007). Given some ambient heat loss as the hydrothermal updraft approached and occupied the mound, then life would have emerged here unthreatened by the kind of temperatures met in submarine hydrothermal fluids exhaling at oceanic spreading centers. At these moderate temperatures, serpentine and ferrobrucite are typical products from two-stage serpentinization of Mg-rich olivine (Bach *et al.*, 2006; McCollom & Bach, 2009):

$$2\underset{\text{olivine}}{Mg_{1.8}Fe_{0.2}SiO_4} + 3H_2O \rightarrow \underset{\text{serpentine}}{Mg_{2.85}Fe_{0.15}Si_2O_5(OH)_4} + \underset{\text{ferrobrucite}}{Mg_{0.75}Fe_{0.25}(OH)_2} \quad (1)$$

At the same time, as there are no feldspars in these ultramafic rocks and therefore no aluminum, these solutions can become alkaline as calcium and, in the lower temperature examples, magnesium (metals M in eqn 2) dissolve from pyroxene and olivine to release the hydroxide ion to maintain charge balance. (Although at lower concentrations than at present, magnesium ions would have been available in the Hadean Ocean and at the mound, supplied from cool submarine springs and seepages and bicarbonate spring waters (Fig. 3) (Barnes & O'Neil, 1969; Palandri & Reed, 2004; Hopkinson *et al.*, 2004; Foustoukis *et al.*, 2008):

$$(MO)_{\text{pyroxene}} + H_2O \rightarrow M^{2+} + 2OH^- \quad (2)$$

Although free silica is rendered extremely soluble as $H_2SiO_4^{2-}$ and $H_3SiO_4^-$ at pH >10 ($pK_a \sim 9$ at 120 °C, Fig. 4) (Kehew, 2001), aqueous silica from orthopyroxene would tend to react with ferrobrucite in the convective updrafts to produce further serpentine, magnetite and also hydrogen (Figs 4–6) (Bach *et al.*, 2006; Frost & Beard, 2007):

$$\begin{aligned} &14.25Mg_{0.75}Fe_{0.25}(OH)_2 + 7.5SiO_2(aq) \\ &\quad \rightarrow 3.75Mg_{2.85}Fe_{0.15}Si_2O_5(OH)_4 + 5.75H_2O \\ &\qquad + Fe_3O_4 + H_2\uparrow \end{aligned} \quad (3)$$

There is some controversy with respect to the carrying capacity of alkaline springs for magnesium and silica, especially

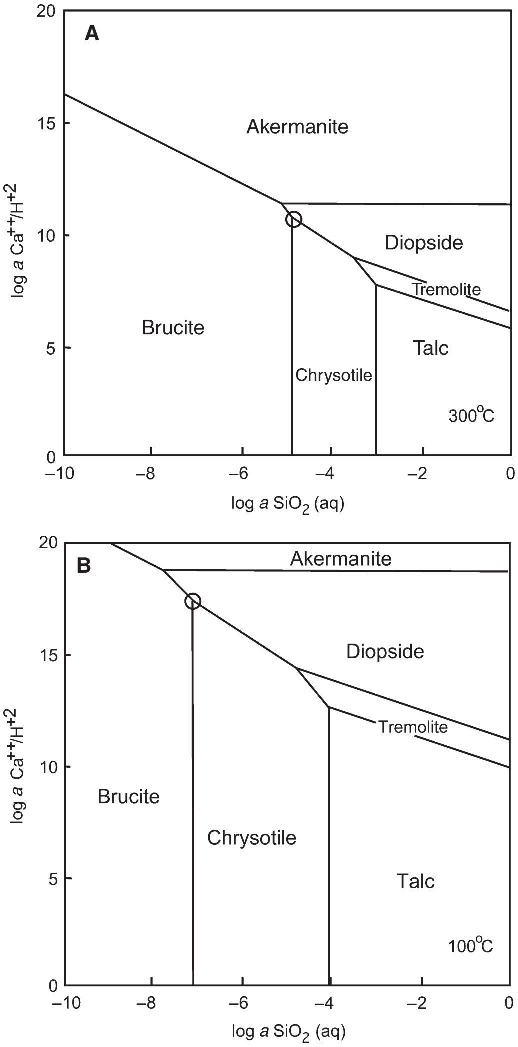

Fig. 3 Activity diagram for MgO–CaO–SiO_2–H_2O system demonstrating how the $aSiO_{2(aq)}$ and $aCa^{++}/a2H^+$ ratios can be controlled by the chrysotile–diopside–brucite invariant triple point, during the hydrothermal alteration of ultramafic rocks. Suppressed: antigorite, merwinite and monticellite. (A) At T = 300 °C and P = 85.81 bars the log $aCa^{++}/a2H^+$ is relatively low compared to the same ratio at (B) T = 100 °C, P = 1.013 bars, reflecting the differences of pH calculated to be 8.2 at 300 °C and 10.3 at 100 °C (Macleod *et al.*, 1994; fig. 6). Calculated using Geochemist's Workbench (Bethke, 1996), and to be compared with Foustoukos *et al.*, 2008, fig. 1.

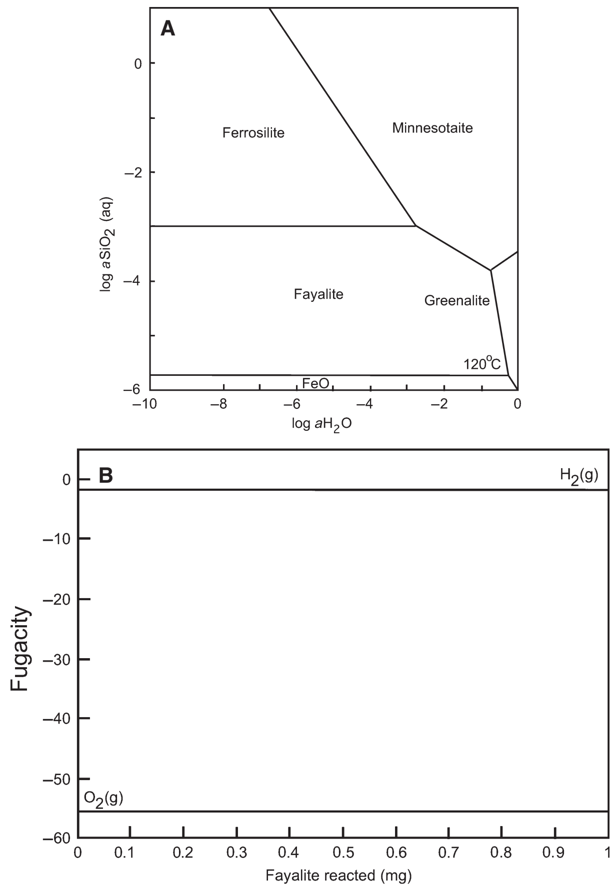

Fig. 4 (A) Activity diagram for log $aSiO_2(aq)$ versus aH_2O at 120 °C generated using Geochemist's Workbench (Bethke, 1996). The diagram demonstrates that on serpentinization, fayalite (Fe_2SiO_4) would be hydrated to greenalite $[Fe^{2+}_{4.5}Fe^{3+}_{1}Si_4O_{10}(OH)_8]$, but only at low SiO_2 activity, whereas minnesotaite $[Mg_{2.5}Fe_{0.5}Si_4O_{10}(OH)_2]$ is produced at a high activity of SiO_2. Ferrosilite ($FeSiO_3$ in orthopyroxene) could contribute to the higher SiO_2. In ultramafic rocks, fayalite would be present as solid-solution in forsterite, i.e. olivine. (B) Geochemist's Workbench 'React' subprogram (Bethke, 1996) result for model fayalite reaction with water at 120 °C. This demonstrates the high fugacity of hydrogen that can result from the overall oxidation of the Fe^{++} in fayalite to magnetite (Fig. 5). Only 1 mg of fayalite was reacted to represent the small amount in solid-solution in olivine.

as these two entities appear to be in very low concentration in the Lost City fluids (Kelley *et al.*, 2001). However, magnesite deposits, often with silica cavity fillings and pronounced chalcedony, opal and/or quartz hanging walls (silica caps) are a feature of low to moderate temperature hydrothermal deposits in the Alpine and other serpentinites (Dabitzias, 1980; Fallick *et al.*, 1991; Zedef *et al.*, 2000; Ilich & Toshovich, 2002).

Although the partial pressure of carbon dioxide was high in the Hadean, so was the hydrostatic pressure at and below the ocean floor. Thus, carbon dioxide was readily available for reactions with hydrogen, ammonia, sulfhydryl ions, and transition metals, both in the ocean crust and in the margins of the hydrothermal mound.

ORGANIC SYNTHESIS AND SERPENTINIZATION

Theoretical (Shock, 1992; Shock & Schulte, 1998; Amend & McCollom, 2009) and experimental work (McCollom & Seewald, 2003a,b; McCollom & Seewald, 2007) on the reduction of CO_2 and the partitioning of carbon species in simulated hydrothermal vents had suggested that organic synthesis should be occurring in serpentinizing systems at moderate temperature. The recent finding by Proskurowski

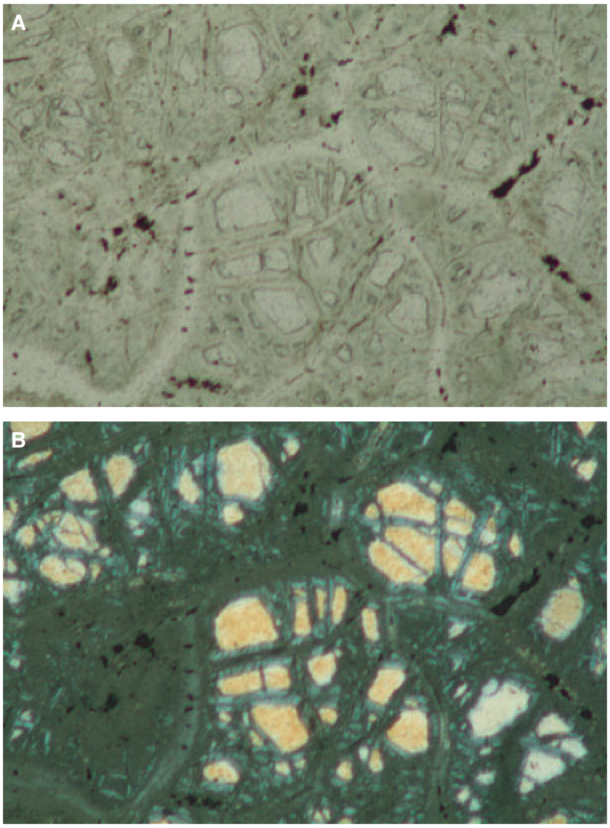

Fig. 5 Magnetite (black, opaque) crystallites in serpentinized olivine from Troodos dunite. Relict olivine, with cloudy serpentine, has high relief in plane-polarized light (A) and distinctive interference colors in cross-polars (B). The section demonstrates that magnetite, hence hydrogen can form on serpentinization of olivine-rich ultramafic rock. Field ~2 mm across. (Thin section supplied by Hunterian Museum, University of Glasgow.)

et al. (2008) that Lost City effluent contains 1–2 mmol kg^{-1} methane, nearly commensurate ethane and lower concentrations of other short (C3 and C4) hydrocarbons of likely abiogenic origin, can be readily understood in this context. That brings the CO_2 reducing capacity of serpentinization into focus and prompts further investigation of the specific geochemical mechanisms involved in the generation of H_2 (Fig. 4) (Neal & Stanger, 1983, 1984; Coveney *et al.*, 1987; Abrajano *et al.*, 1990; Russell *et al.*, 1994; Russell & Hall, 1997, 2006). Hydrogen as is released during serpentinization (eqn 3; Fig. 4B), reacts in the laboratory, between 175 and 260 °C and 350 atm, with aqueous CO_2 waters to produce formate ($HCOO^-$) (McCollom & Seewald, 2003a,b):

$$HCO_3^- + H_2 \rightarrow HCOO^- + H_2O \qquad (4)$$

This reaction can be seen as the transition from inorganic to organic chemistry.

Up to 158 μmol kg^{-1} of abiotic formate has been recorded in the Lost City (Lang *et al.*, 2010; cf. Haggerty & Fisher, 1992). The literature on biological formate synthesis (e.g. Volbeda & Fontecilla-Camps, 2006) suggests a possible hydrogenation mechanism involving a hydrogen molecule bridging a Ni–Fe site – broadly comparable to such a site in awaruite (Ni_3Fe) – that reacts with CO_2 or $HCO_3{}^-$ transiently bonded to either metal atom. A maximum of 34 μmol kg^{-1} of acetate is also contained in the effluent of Lost City (Lang *et al.*, 2010). While much of this acetate may be a microbial by-product, a case could be made for a few μmol kg^{-1} being produced abiologically (Lang *et al.*, 2010; fig. 3b and table 2) with a net stoichiometry:

$$2HCO_3^- + 4H_2 \rightarrow CH_3.COO^- + OH^- + 3H_2O \qquad (5)$$

A reaction to be expected from the laboratory studies of He *et al.* (2010) and the thermodynamic calculations of Shock & Schulte (1998). However, as we have seen, the main abiotic reduced carbon compound is methane which occurs at up to 2 mmol kg^{-1} (Proskurowski *et al.*, 2008) although even here some small portion of the CH_4 is likely to have a biological origin (Bradley *et al.*, 2008). This serpentinization-derived methane at Lost City is produced through a net reaction of

$$HCO_3^- + 4H_2 \rightarrow CH_4 + OH^- + 2H_2O \qquad (6)$$

The synthesis of H_2 would thus appear to be an imperative for the emergence and early evolution of life. But the molecules of life typically contain nitrogen, hence the reduction of N_2 to its chemically more reactive form NH_3 is equally important in this context. Smirnov *et al.* (2008) showed that in simulated hydrothermal conditions, 1–7 μm kg^{-1} ammonia is produced by the hydrogenation of nitrogen catalyzed by native iron (Fe^0) at 70 °C at pH 6–7, whereby native iron and iron–nickel alloy filaments are an expected component of serpentinizing systems (Krishnarao, 1964; Chamberlain *et al.*, 1965; McCollom & Bach, 2009). These metal catalysts are generated by the action of reduced fluid on pre-existing metal sulfides which lose their sulfur to the hot convecting fluids in the form of sulfide or bisulfide ions (Frost, 1985; Russell *et al.*, 1989, 1994; Macleod *et al.*, 1994; Delacour *et al.*, 2008; Proskurowski *et al.*, 2008; Klein & Bach, 2009). Using FeS as the catalyst and H_2S as the electron source, Dörr *et al.* (2003) reported modest rates of N_2 conversion to NH_3, albeit under acidic conditions (pH 3–4) at 80 °C. These initial reports indicate that N_2 reduction can, in principle, occur under hydrothermal conditions at moderate temperatures, although abiogenic ammonium in Lost City effluent has not been reported. Sulfur is also an essential constituent of biological molecules (Beinert *et al.*, 1997; Beinert, 2000); it may be supplied as bisulfide by alkaline hydrothermal systems (Fig. 1) (Barnes & Czamanske, 1967; Macleod *et al.*, 1994; Seward & Barnes, 1997; Russell & Hall, 2006) and is present in minor amounts in the Lost City effluent (Kelley *et al.*, 2001). Molybdenum and tungsten, known to occur occasionally as stratabound enrichments in Archaean mafic and ultramafic sequences, could also have been supplied in the alkaline hydrothermal solution, complexed as mixed valence sulfide

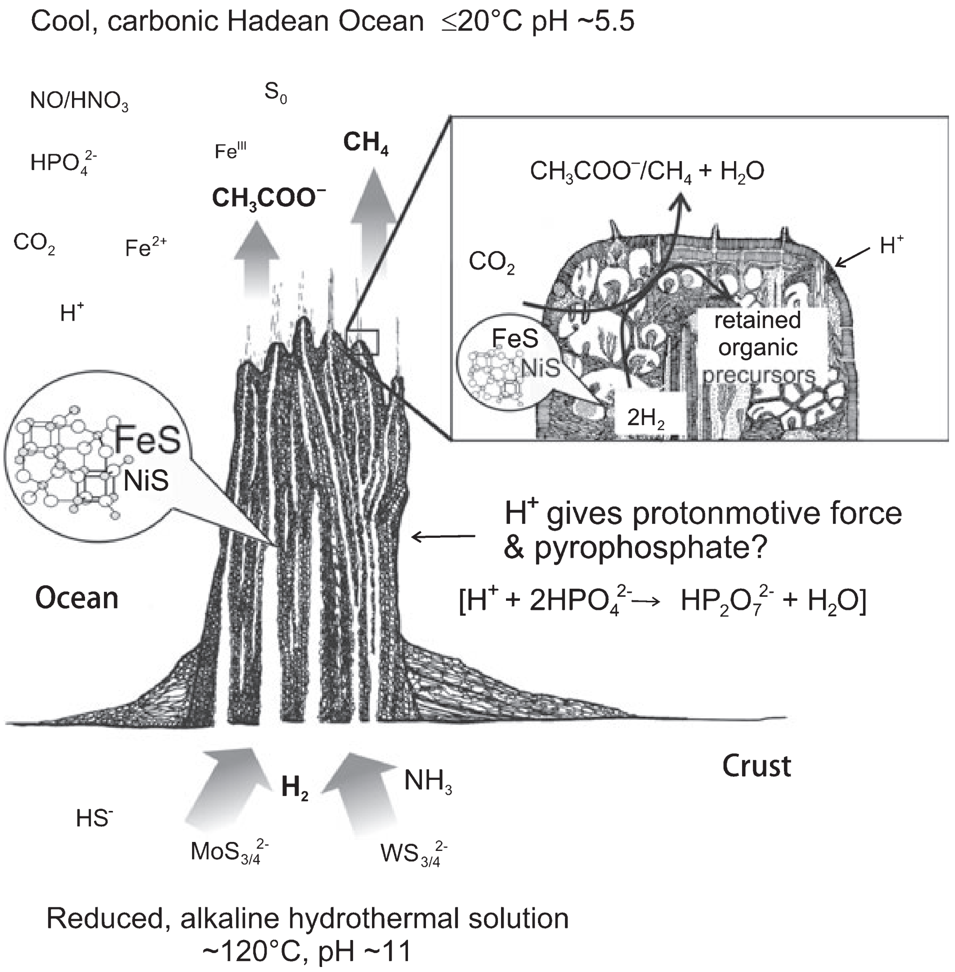

Fig. 6 The hydrothermal mound depicted as a methane and acetate generator. The detailed cross-section of the surface illustrates the sites where organic ions that have the potential to facilitate the generation of these two effluents are produced, retained, react together and self-organize to emerge as protolife (after Russell & Martin, 2004; Martin & Russell, 2007).

and selenide and/or oxide ions (Nekrasov *et al.,* 1982; Appel, 1994; Seward & Barnes, 1997; Russell & Hall, 1997; Russell & Hall 2006; Srinivasan, 2004; Arnórsson & Óskarsson, 2007). They are indispensible elements for overcoming the initial steps – those requiring high activation energies – along the mesothermal and hyperthermal tracks of the acetyl coenzyme-A pathway respectively (Adams, 1998; Schulzke, 2005; Zerkle *et al.*, 2005). Such molybdenum and tungsten complexes might have precipitated in clusters, some of them large, as pH dropped on meeting with acidulous ocean water percolating the hydrothermal mound (Helz *et al.*, 1996; Erickson & Helz, 2000).

Further reactions between hydrogen, carbon dioxide, reduced C1 compounds, ammonia and sulfhydryl ions in the hydrothermal mound precipitating above, and partly capping, the discharge site of these same fluids (Fig. 6) constitute a central prediction of hydrothermal theories for the origin of life, but detailed characterization of such reactions in laboratory simulations is still rare. In this respect, there is a small amount of confusion in the literature, because some biologically relevant reactions are readily catalyzed by transition metal sulfides, as predicted by theories positing a hydrothermal origin of life, while the results themselves are generally interpreted as specifically supporting an alternative theory based on 'pyrite-pulled' reactions in a volcanic environment. Thus, a brief distinction seems in order.

The pyrite-pulled theory of Wächtershäuser (1988a, 1993) posits that the prime source of energy underpinning the abiotic synthesis of organic precursors to life stems from the synthesis of pyrite (FeS$_2$) from iron monosulfide (FeS) and H$_2$S, which is an exergonic reaction ($\Delta G^0 = -38.4$ kJ mol^{-1}) involving the oxidation of sulfur. Our suggestion for the prime source of energy differs in that we suggest the prime exergonic reaction underpinning the synthesis of organic molecules to have been the reduction of CO$_2$ itself with electrons stemming from H$_2$, with the products of the central overall exergonic reaction being organic compounds such as methane and acetate (Russell & Martin, 2004; Martin & Russell, 2007), whereby the H_2 driving CO_2 reduction stems in turn from serpentinization (eqns 1–3). However, the fixation of CO_2 in the mound to formate and formyl, along the acetyl coenzyme-A pathway (Maden, 2000) also requires energy, which could have been readily supplied by H_2 itself, augmented by an ambient chemiosmotic gradient acting across the inorganic membrane and/or the catalytic coupling of exergonic redox reactions to those yielding formate/formyl via suitable variable valence metal catalysts such as Mo and W (Nitschke & Russell, 2009; Lane *et al.*, 2010).

Both theories draw upon the known properties of transition metal sulfides to catalyze organic reactions, and both theories posit that transition metal sulfide centers of modern proteins mimic the inorganically formed catalysts present at the origin of life. In that respect, several FeS-catalyzed reactions have been reported in the literature, such as the synthesis of CH_3SH from CO_2 and H_2S (Heinen & Lauwers, 1996), the synthesis of alpha ketoacids (Cody *et al.*, 2004), the synthesis of amino acids from ammonium compounds and alpha ketoacids (Huber & Wächtershäuser, 2003) and the synthesis of the thioester, acetyl methylsulfide, from CO and CH_3SH (Huber & Wächtershäuser, 1997). FeS also inhibits the hydrolysis of pyrophosphate (de Zwart *et al.*, 2004). Although it is sometimes stated that such results specifically favor the pyrite-pulled theory (Wächtershäuser, 1988a, 1993, 2006), if we look at the matter openly, they lend support to both theories, both of which can be seen as more specific formulations of the earlier suggestion (Corliss *et al.*, 1981; Baross & Hoffman, 1985) that life arose at hydrothermal vents, an idea that emerged almost concomitantly with their discovery on oceanic ridges in the Eastern Pacific (Corliss *et al.*, 1979; Hekinian *et al.*, 1980; Spiess *et al.*, 1980), although Harvey had hinted as much in 1924 from his studies of a prokaryote at Yellowstone National Park.

That said, the non-specialist might wonder what the differences between the two theories actually are. To name a few, Wächtershäuser, in his retrodictive approach, maintains that life arose on surfaces in two dimensions first and that the transition to three dimensions came later by a yet poorly explicated mechanism termed lipophilization (Wächtershäuser, 1988a,b, 2006). In contrast, approaching the issue geologically, we maintain the natural pores comprising the mounds forming at hydrothermal vents (Russell *et al.*, 1994; Kelley *et al.*, 2001; Marteinsson *et al.*, 2001; Baaske *et al.*, 2007) served as catalytically walled (three dimensional) compartments to concentrate the products of hydrothermal organic synthesis at the vent-ocean interface, and hence functionally served as the geologically formed inorganic forerunners of biologically formed cell membranes and walls (Russell *et al.*, 1989, 1994; Russell & Hall, 1997; Martin & Russell, 2003). Moreover, the form of the oxidized sulfides are also viewed differently – pyrite (FeS_2) in the Wächtershäuser model, greigite ($NiFe_5S_8$) in ours (Russell & Hall, 2006; Martin & Russell, 2007). In a later addition to his theory, Wächtershäuser (2006) maintains that volcanic conditions gave rise to life. However, volcanic conditions are inherently acidic, very high temperature, violent and episodic. In contrast, we maintain that stable, lower temperatures and alkaline conditions were crucial to the formation of organic molecules (Russell & Hall, 1997). Wächtershäuser maintains that the source of energy at the origin of life involved pyrite formation. In contrast, we maintain that the sources of potential energy to be dissipated at the origin of life were CO_2 reduction by H_2 that stemmed from serpentinization, and the steep proton gradient across the inorganic precipitate membranes toward the alkaline interiors of the compartments comprising the mound (Russell *et al.*, 1989, 1993).

Put another way, Wächtershäuser's various explications have transition metal catalysis in common, but otherwise draw upon geochemical process acting at different places, under different conditions, whereby the homology to an observable, modern microbial core energetic process is nowhere evident, and chemiosmosis is an afterthought that does not fit his geological scenario (Lane *et al.*, 2010). In our theory, transition metal catalysis is also central, but the geochemical setting (naturally chemiosmotic hydrogen-bearing alkaline hydrothermal vents) is fully congruent with the three-dimensional nature of the reproducing (although not replicating) inorganic compartments supporting the first forms of *chemical* selection from which cells ultimately arose (Russell & Hall, 1997), and all are furthermore fully congruent with the inferred homology to modern core metabolic processes – acetogenesis and methanogenesis (Martin & Russell, 2007) – geochemically afforded by the serpentinization process underlying such vents. The serpentinization process has been ongoing ever since there was water on Earth and is still observable today (e.g. at Lost City), albeit in a changed oceanic environment now unsuitable for life's renewed emergence.

THE CAPPING MOUND

We have seen that moderate temperature serpentinization itself produces fluids bearing hydrogen, formate, methane, ethane and other short hydrocarbons and perhaps trace amounts of acetate from the initial ingredients: carbon dioxide and hydrogen. Although it appears that the serpentinizing hydrothermal system only produces very little if any acetate, this may relate to the particular conditions at Lost City, for it can be produced readily enough in the laboratory below 130 °C from CO_2 and H_2 under pressure with powdered iron as reducing agent and catalyst (Tian *et al.*, 2007).

The autotrophic prokaryotes also produce a few of these carbon-bearing chemicals as effluent from the same reactants – some archaebacteria evolve methane while some bacteria generate acetate (Proskurowski *et al.*, 2008; Gaidos *et al.*, 2009; Konn *et al.*, 2009; Lang *et al.*, 2010). They do so by way of the acetyl co-A pathway – the simplest and cheapest (in terms of ATP) of all metabolic pathways and cycles (Fig. 7) (Fuchs, 1989). This pathway actually comprises two tributaries, one reducing CO_2 to a carbonyl group and the other to a methyl group. They meet where the methyl group combines with the carbonyl group on the active Ni–Fe sulfide center to acetyl coenzyme-A synthase (Fig. 7) (Ferry, 1995; Ragsdale, 2004; Volbeda & Fontecilla-Camps, 2006). This biochemical pathway produces either acetate or methane. Given what we know of geochemical reductions, the simplest path might appear to be the serial progression of abiotic hydrogenations of carbon dioxide to methane (Fig. 7) (Fuchs, 1989; Seewald *et al.*, 2006). However, for energy to be produced this way for biosynthesis is a lot more complicated (Grabarse *et al.*, 2001; Russell & Kanik, 2010). The biochemical path to acetate production is much simpler (Fig. 7) (Fuchs, 1989). Given that the path to methane goes by way of activated acetate it is not surprising that archaebacteria that generate ethane and propane can also live off acetate and hydrogen (Hinrichs *et al.*, 2006).

Modern, and geologically young, hydrothermal mounds are typically quite porous (Russell *et al.*, 1989; Kelley *et al.*, 2001; Marteinsson *et al.*, 2001). Indications that compartment walls should have formed in a Hadean environment is afforded by what appear to be hollow but contiguous iron sulfide bubbles found at the 350 Myr old Tynagh metal sulfide deposit in Ireland, although generated under different geological conditions (Russell & Hall, 1997, 2006) from those existing in the Hadean. The Hadean hydrothermal mounds accumulating at the vent-ocean interface central to our considerations would have consisted of porous precipitates of amorphous silica, palygorskite, sepiolite, smectite, saponite, brucite, green rust, siderite, ephemeral calcite and aragonite as well as colloidal metal sulfides that gelled on precipitation and then slowly crystallized to nickel-bearing nanocrysts of mackinawite and greigite (Bonatti *et al.*, 1983; Russell *et al.*, 1989; Russell & Hall, 2006; Kelley *et al.*, 2001; Marteinsson *et al.*, 2001; Geptner *et al.*, 2002; Wolthers *et al.*, 2003; Rickard & Luther, 2007) (Fig. 6). Molybdenum and tungsten, somewhat soluble in the alkaline hydrothermal solution, would precipitate as mixed valence (IV and/or VI) sulfides/oxides or be adsorbed onto clays or greenrust (Goldberg *et al.*, 1998).

The Hadean mounds would have formed over the exhalative site of a serpentinizing, off-axis alkaline hydrothermal system of moderate temperature. Within such a mound the production of reduced C1 compounds and ultimately methane, as observed at Lost City (Kelley *et al.*, 2001; Proskurowski *et al.*, 2008), and already generated slowly during

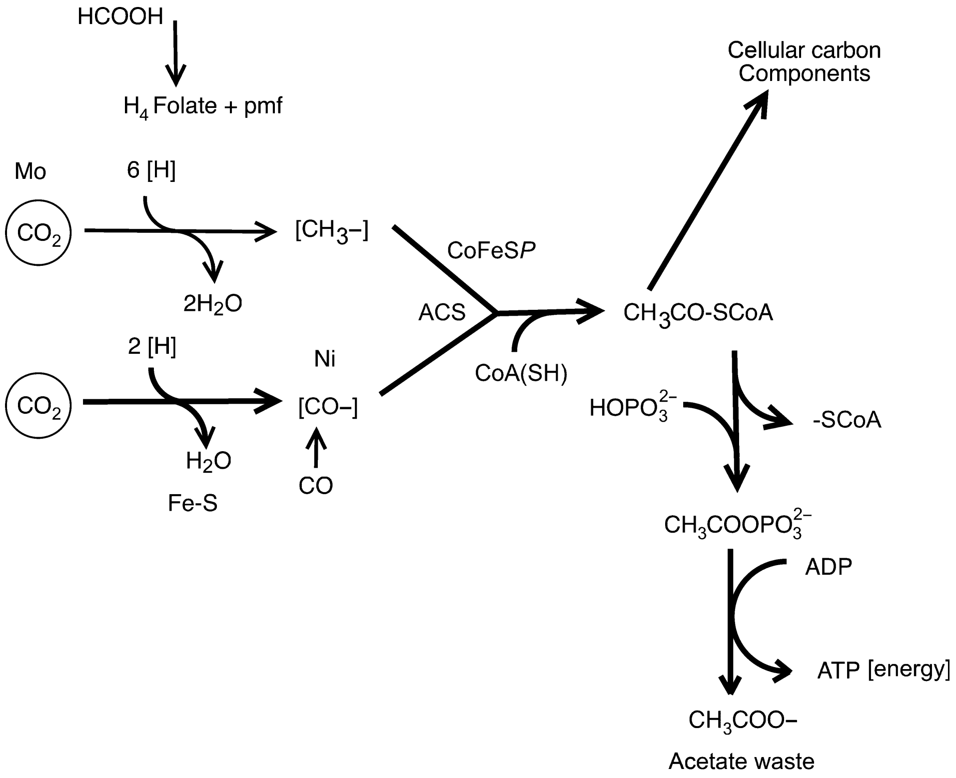

Fig. 7 The acetyl coenzyme-A pathway is shown as employed by the acetogens (Fuchs, 1989). Note that hydrothermal formic acid can feed into the cycle in prokaryotes ahead of carbon dioxide by exothermic disproportionation to CO_2 and H_2. Carbon monoxide dehydrogenase/acetyl coenzyme-A synthase (CODH/ACS) is the bifunctional enzyme wherein one nickel is involved in the reduction of CO_2 and another nickel is involved in synthesizing the acetyl group (Volbeda & Fontecilla-Camps, 2006). Based on Fuchs (1989).

serpentinization, is expected to have quickened where the submarine exhalations from these serpentinizing convection cells were capped by the porous mineral precipitates. Here, CO_2 in the relatively oxidized ocean could be directly entrained into the exhalative fluid through the permeable foundation of the developing hydrothermal mound (Fig. 6). Inhibition of flow, partial containment, catalytic surfaces and the augmenting effects of ionic gradients across the precipitated FeS-bearing walls of the mound provided a highly reactive chemical environment.

Important reactions from the standpoint of forging the transition from geochemistry to biochemistry would have involved reactions between reduced carbon, nitrogen, and sulfur species, occurring both in solution and on surfaces. These would have been promoted by the catalytic properties of the transition metals and their sulfide precipitates that partially comprised the naturally arising micro-compartments within which reaction products would have been restrained from free diffusion to the ocean. Results of chemical syntheses from flow-through reactors simulating the vent-ocean interface have not been reported so far, but results from steady-state reactions simulating these conditions suggest that compounds such as methyl sulfide (Heinen & Lauwers, 1996; Schulte & Rogers, 2004), acetyl thioesters (Huber & Wächtershäuser, 1997), formate, methanol (McCollom & Seewald, 2003a; Seewald *et al.*, 2006) and methane (Horita & Berndt, 1999; Seewald *et al.*, 2006) would be among the likely reaction products. With the exception of small amounts of pyruvate obtained at albeit very high temperatures (Cody *et al.*, 2000), so far the syntheses of 2-oxoacids has not been shown to occur easily under these moderate conditions (Cody *et al.*, 2004), although the FeS-catalyzed reductive aminations to amino acids, essential components of life, do occur readily (Huber *et al.*, 2003).

Noting the possibility that native iron and nickel–iron alloys can be generated through the serpentinization process opens the door to considering different kinds of moderate temperature chemical reductions achieved in the laboratory. He *et al.* (2010) have produced formate and acetate in millimolar amounts on reaction of aqueous CO_2 with nanoparticulate iron at temperatures up to 200 °C and pressures up to 14 bars. Acetate is favored below 130 °C while formate production increases markedly at higher temperatures. Similarly intriguing is the report by Tian *et al.* (2007), who synthesized phenols from sodium bicarbonate in water at 200 °C in the presence of powdered native iron. These authors note that phenol is a moiety of tyrosine, and suggest that such reactions could contribute to the roots of prebiotic chemistry. Because aromatics were obtained, such reactions in the presence of a suitable source of nitrogen would be of particular interest.

The nature, possible further reactions and possible biological significance of the first reduced organic compounds so formed has been discussed elsewhere (Martin & Russell, 2003, 2007; Milner-White & Russell, 2008). Synthesis of sugar-like or base-like constituents of RNA has not been reported so far under *these* conditions, and this remains an important challenge and area of endeavor for laboratory simulations of geochemical reactions driven by serpentinization and catalyzed by metal sulfides, because RNA is a currently indispensable component of concepts relating to the nature of early self-replication (Joyce, 2002; Koonin & Martin, 2005).

FROM SERPENTINIZATION TO CHEMIOSMOSIS

CO_2 reduction with H_2 from serpentinization is not the only striking similarity between modern microbes and a Hadean alkaline vent. This is because both acetogens and methanogens cannot grow on H_2 and CO_2 as energy sources without the participation of chemiosmosis (Fuchs, 1989; Ljungdahl, 1994; Thauer *et al.*, 2008). Chemiosmosis is the mechanism by which life as we know it converts environmentally available redox couples into (bio)chemical energy in the currency of ATP (adenosine triphosphate). In the main, chemiosmosis involves the pumping of protons from the inside of the cell to the outside of the cell, thereby generating across the plasma membrane a pH gradient (a proton gradient) that is harnessed by the cell via a class of proteins called ATPases that catalyze the synthesis of ATP from ADP and phosphate in a reaction mechanism that is driven by the re-entry of protons into the more alkaline interior of the cell through a specific channel in the ATPase (Mitchell, 1967; Walker, 1998). Acetogens and methanogens pump their protons to the outside of the cell (Müller, 2003; Thauer *et al.*, 2008) with the help of energy released during the process of CO_2 reduction, but there are a myriad of redox reactions other than CO_2 reduction that microbes can couple to such vectorial proton pumping (Amend & Shock, 2001).

Of course, serpentinization also produces H_2 that can in turn reduce CO_2 through purely geochemical means to methane in an overall exergonic reaction that is observed in the Lost City effluents (Proskurowski *et al.*, 2008). It is an exciting prospect that the geochemical production of methane is the chemical forerunner of biological methane production (Martin & Russell, 2007; Martin *et al.*, 2008), that is, that as the first genes and enzymes arose (which they did, somewhere, somehow) they came to promote energy releasing reactions that occur spontaneously in suitable geochemical settings (Shock & Schulte, 1998; Amend & McCollom, 2009). In that view, the first energy-harnessing biochemical pathways underpinning microbial growth were not invented by microbes, but were instead biologically catalyzed versions of pre-existing exergonic, although likely sluggish, geochemical processes generating methane and/or acetate (Russell & Martin, 2004; Lang *et al.*, 2010). Indeed, there are enough chemical and catalytic similarities between the core H_2- and CO_2-dependent energy producing pathways of methanogens and acetogens on the one hand and serpentinization-driven CO_2 reduction in alkaline hydrothermal systems on the other, to argue the case that the acetyl coenzyme-A pathway is not only energetically the most favorable, simplest and the most primitive pathway of microbial energy metabolism (Fuchs, 1989; Ljungdahl, 2009), but is also 'merely' a biologically portable manifestation of pre-existing geochemical reactions that existed on the early Earth (Martin & Russell, 2003, 2007; Seewald *et al.*, 2006).

Generally speaking, chemiosmosis is as universal among known life forms as the genetic code, hence its origin must be ancient. How ancient? We think that the geochemically formed pH gradient at alkaline hydrothermal vents is the naturally pre-existing forerunner of the proton gradient that cells generate by themselves today. That is, we think that cells had the *energy-harnessing* tools with which to convert a geochemically formed proton gradient into useable chemical energy before they evolved the *energy consuming* tools with which to generate proton gradients. In that sense, it is the naturally chemiosmotic nature of the vent-ocean interface that, for reasons of thermodynamics, might have been a bona fide prerequisite for the origin of free-living cells that gain their energy from the reduction of CO_2 with H_2 (Martin & Russell, 2007). At the very least, it provides an answer to a deeply profound, but too-seldom posed, question central to the origin of life: How, and from what, did the biological process of chemiosmosis arise (Lane, 2009; Nitschke & Russell, 2009)? For conditions at the vent-ocean interface – the redox gradient between the reduced (H_2-containing) and alkaline (pH $\sim$10–11) effluent from serpentization and the more oxidized (CO_2) and slightly acidic (pH 5–6) Hadean Ocean – provided an overall geochemically formed electrical potential that has been estimated to $\leq$850 mV, a value that has been corroborated in laboratory simulations (Russell & Hall, 2002, 2006; Filtness *et al.*, 2003). Such a potential at the interface would have led to CO_2 reduction and, we infer, massively increased reaction rates at the mound relative to the deeper hydrothermal system (Milner-White & Russell, 2010).

For proponents of organic soup or RNA-centric theories, the origin and universality of chemiosmosis in modern life-forms is generally not an issue and is not considered (Bada, 2004; Orgel, 2008). For proponents of the pyrite-pulled theory, the origin of chemiosmosis entails a sequence of events starting with an ancestral state of proton accumulation on the inside of the membrane, converse to the situation found in modern cells, hence requiring a series of complicated (and bioenergetically tenuous) corollary narratives to bring the theory into agreement with the chemistry of biological systems (*pace* Wächtershäuser, 2006), while patently overlooking the earlier, and far simpler, proposal offered by serpentinite-related processes (Russell *et al.*, 1993, 1994), which requires no such corollaries. Indeed, many of the most relevant FeS-catalyzed chemical reactions reported by proponents of the pyrite theory generally work better, or at all, under alkaline conditions (Huber & Wächtershäuser, 1997, 2003; Huber *et al.*, 2003; Russell, 2003) which we find significant.

Early formulations of the idea that life arose at hydrothermal vents stressed the role of the rich multiplicity of chemical gradients that can be found in such environments (Baross & Hoffman, 1985) but without specifically addressing the origin of chemiosmosis. Proponents of the idea that life arose in mounds specifically at alkaline hydrothermal vents have long stressed the role of serpentinization as the geochemical mechanism underlying the naturally chemiosmotic nature of the vent-ocean interface, and furthermore have stressed that the naturally existing proton and redox gradients represent a rich source of naturally produced energy stemming from geochemistry that merely had to be tapped by primitive biochemical systems (Russell *et al.*, 1993, 1994; Macleod *et al.*, 1994; Russell & Hall, 1997; Martin & Russell, 2007; Ducluzeau *et al.*, 2009; Nitschke & Russell, 2009), by inference as a thermodynamic *conditio sine qua non* to the transition to the free-living state (Martin & Russell, 2007). Satisfyingly from the standpoint of both geology and biology, the orientation of the proton gradient generated by serpentinite-related exhalative systems is identical to that found in modern cells (alkaline inside). This, coupled with the overall similarity of the chemical reactions going on at Lost City to biological CO_2 reduction in methanogens and acetogens, bring serpentinization more into focus than ever before in the investigation of life's origin.

CONCLUSION

The process of moderate temperature ocean-floor serpentinization has a variety of properties that increasingly point to its likely importance in the origin of life (Russell *et al.*, 1989, 1994). It can reduce CO_2 and supply a steady source of hydrogen in an alkaline solution and, judging from Lost City, it can proceed continuously and without significant variation for 100 000 years or more (Ludwig *et al.*, 2005; Proskurowski *et al.*, 2008). Its geochemistry involves abundant H_2 in the presence of transition metals and transition metal sulfides, which are among the most versatile hydrogenation and redox catalysts known in biological systems, rendering it salient and germane to all theories for the origin of life that posit a role of such catalysts at biochemical origins (Eck & Dayhoff, 1966; Hall *et al.*, 1974). The alkaline nature of hydrothermal effluent in serpentinizing systems creates naturally formed pH and redox gradients across the precipitate at the vent-ocean interface, which could readily have served as the geochemical template upon which biological chemiosmotic harnessing evolved (Russell *et al.*, 1993). More generally, hydrothermal vent precipitates provide natural three-dimensional microcompartments within which the products of serpentinization-driven organic synthesis could have been retained, so that the path to chemical complexity would not be faced with otherwise insurmountable problems of diffusion to the ocean (Baaske *et al.*, 2007; Budin *et al.*, 2009). These conditions that forced life into being here on Earth may well have obtained on other terraqueous globes such as Mars and Europa (Russell & Hall, 1999; Hand *et al.*, 2007; Russell & Kanik, 2010). Serpentinization clearly holds the key to understanding the early chemical evolution of the Earth's crust, and it may well hold the key to understanding the most ancient evolution of things biological too, both here and elsewhere in the Universe.

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