

# Serpentinization as a source of energy at the origin of life

M. J. RUSSELL,<sup>1</sup> A. J. HALL<sup>2</sup> AND W. MARTIN<sup>3</sup>

<sup>1</sup>*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*

<sup>2</sup>*Department of Archaeology, University of Glasgow, Glasgow, UK*

<sup>3</sup>*Institut für Botanik III, Heinrich-Heine Universität Düsseldorf, Düsseldorf, Germany*

## ABSTRACT

For life to have emerged from CO<sub>2</sub>, 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.

Received 17 November 2009; accepted 16 May 2010

Corresponding author: M. J. Russell. Tel.: +1 818 354 4985; fax: +1 818 393 4445; e-mail: mrussell@jpl.nasa.gov

‘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 hydro-

thermal 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<sub>2</sub> carbon in the oceanic crust to C<sub>2</sub> to C<sub>4</sub> 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<sub>2</sub>O- and CO<sub>2</sub>-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  $\sim 0.9$  log units below that of the quartz–fayalite–magnetite (QFM) buffer, and thus to have been in equilibrium with CO<sub>2</sub> (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<sub>4</sub>O<sub>10</sub>, SO<sub>2</sub> and native sulfur (e.g. S<sub>8</sub>) 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 serpentine 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<sup>-1</sup> 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<sub>2</sub>O > CO<sub>2</sub> > N<sub>2</sub> > SO<sub>2</sub> > CO > NO > P<sub>4</sub>O<sub>10</sub>/H<sub>2</sub>PO<sub>4</sub><sup>-</sup> > S<sub>8</sub> and the reduced solid Earth was best focused and discharged at submarine alkaline springs where they interfaced with an acidulous ocean. A CO<sub>2</sub> atmosphere of between one and 10 bars is variously estimated to have imposed a pH of between 5.1 and  $\sim 6$  on the carbonic Hadean ocean (Macleod *et al.*, 1994; Morse & Mackenzie, 1998) although the pH may have been locally lower where acidic high temperature ( $\sim 400$  °C) hydrothermal springs – then producing  $\sim 10$  times the present volume of effluent – were particularly active or when volcanic exhalations of SO<sub>2</sub> were particularly vigorous (Lowell & Keller, 2003; Halevy *et al.*, 2007; and see Sigurdsson *et al.*, 1987). A CO<sub>2</sub>-dominated atmosphere might be expected to lead to greenhouse temperatures anywhere between  $\sim 25$  and, at the extreme,  $\sim 100$  °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<sup>-1</sup> (Yamagata *et al.*, 1991; Macleod *et al.*, 1994; Hagan *et al.*, 2007). Although we maintain that millimolar

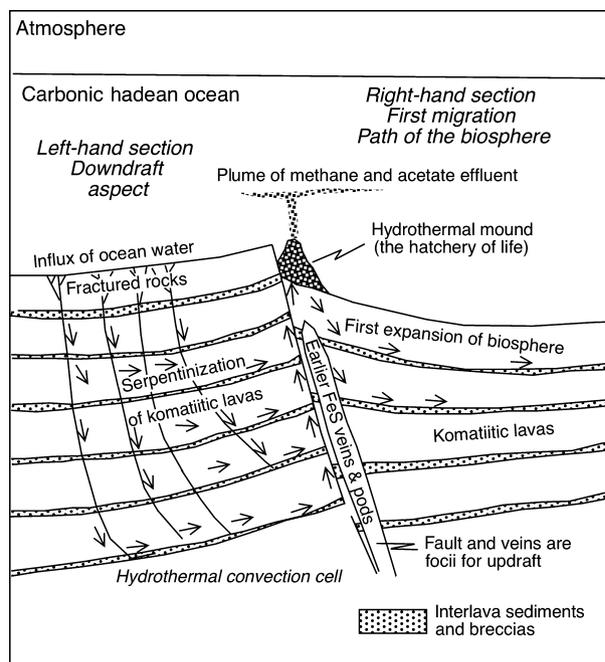
concentrations of ferrous iron were present in the Hadean Ocean, given that it is likely to have had a pH below 6 carries the implication that phosphate would have remained soluble as  $\text{FePH}_2\text{PO}_4^+$  (Russell & Hall, 1997). We note in passing that iron(II) phosphate can catalyze pyrophosphate 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  $\text{CO}_2$ -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 ( $\text{HS}^-$ ) 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

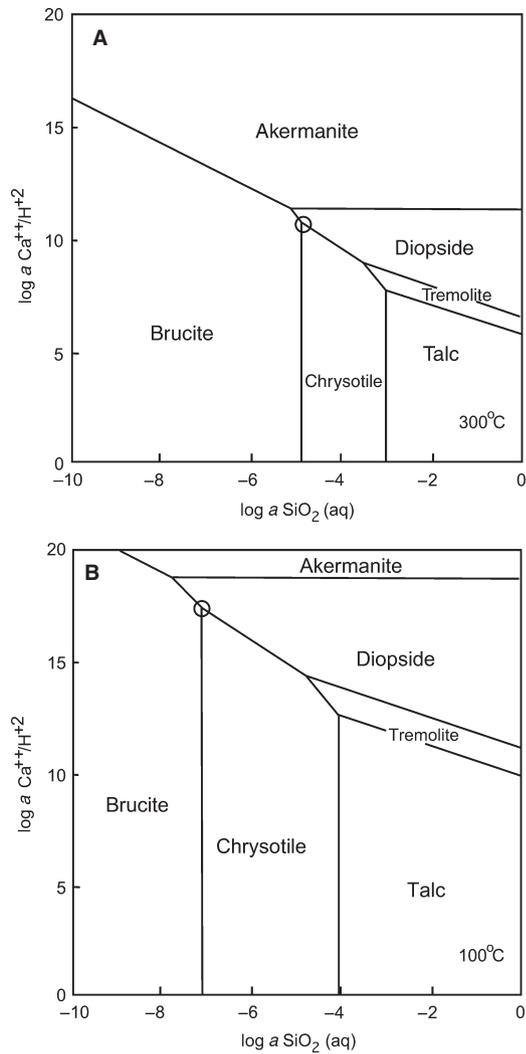


**Fig. 1** A 4-billion-year-old off-ridge submarine mound forms above a serpentinizing hydrothermal convection cell in komatiitic lavas. The left-hand section illustrates how ocean water percolates through the ocean-floor crust and returns, heated, generally guided by fractures. The right-hand section 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).

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).

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

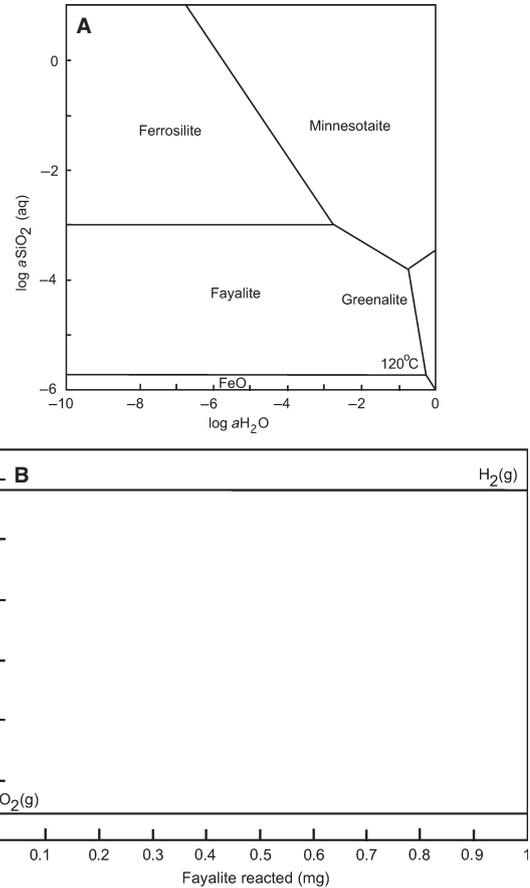




**Fig. 3** Activity diagram for MgO–CaO–SiO<sub>2</sub>–H<sub>2</sub>O system demonstrating how the  $a_{\text{SiO}_2(\text{aq})}$  and  $a_{\text{Ca}^{++}}/a_{2\text{H}^+}$  ratios can be controlled by the chrysotile–diopside–brucite invariant triple point, during the hydrothermal alteration of ultramafic rocks. Suppressed: antigorite, merwinite and monticellite. (A) At  $T = 300^\circ\text{C}$  and  $P = 85.81$  bars the  $\log a_{\text{Ca}^{++}}/a_{2\text{H}^+}$  is relatively low compared to the same ratio at (B)  $T = 100^\circ\text{C}$ ,  $P = 1.013$  bars, reflecting the differences of pH calculated to be 8.2 at  $300^\circ\text{C}$  and 10.3 at  $100^\circ\text{C}$  (Macleod *et al.*, 1994; fig. 6). Calculated using Geochemist's Workbench (Bethke, 1996), and to be compared with Foustoukos *et al.*, 2008, fig. 1.

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 chalcidony, 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

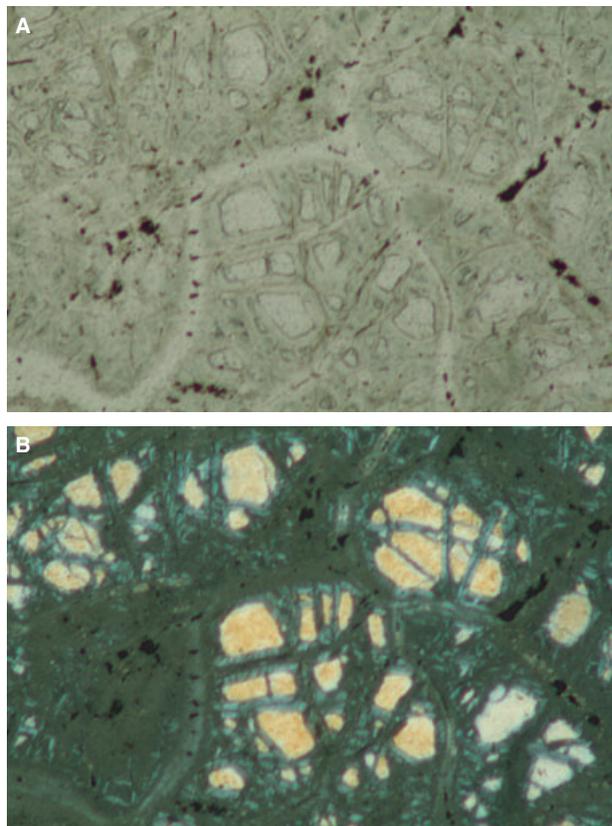


**Fig. 4** (A) Activity diagram for  $\log a_{\text{SiO}_2(\text{aq})}$  versus  $a_{\text{H}_2\text{O}}$  at  $120^\circ\text{C}$  generated using Geochemist's Workbench (Bethke, 1996). The diagram demonstrates that on serpentinization, fayalite ( $\text{Fe}_2\text{SiO}_4$ ) would be hydrated to greenalite [ $\text{Fe}^{2+}_{4.5}\text{Fe}^{3+}_1\text{Si}_4\text{O}_{10}(\text{OH})_2$ ], but only at low  $\text{SiO}_2$  activity, whereas minnesotaite [ $\text{Mg}_{2.5}\text{Fe}_{0.5}\text{Si}_4\text{O}_{10}(\text{OH})_2$ ] is produced at a high activity of  $\text{SiO}_2$ . 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  $120^\circ\text{C}$ . This demonstrates the high fugacity of hydrogen that can result from the overall oxidation of the  $\text{Fe}^{++}$  in fayalite to magnetite (Fig. 5). Only 1 mg of fayalite was reacted to represent the small amount in solid-solution in olivine.

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  $\text{CO}_2$  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  $\sim 2$  mm across. (Thin section supplied by Hunterian Museum, University of Glasgow.)

*et al.* (2008) that Lost City effluent contains 1–2 mmol kg<sup>-1</sup> 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<sub>2</sub> reducing capacity of serpentinization into focus and prompts further investigation of the specific geochemical mechanisms involved in the generation of H<sub>2</sub> (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<sub>2</sub> waters to produce formate (HCOO<sup>-</sup>) (McCollom & Seewald, 2003a,b):



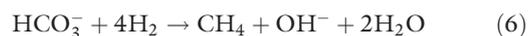
This reaction can be seen as the transition from inorganic to organic chemistry.

Up to 158 μmol kg<sup>-1</sup> 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

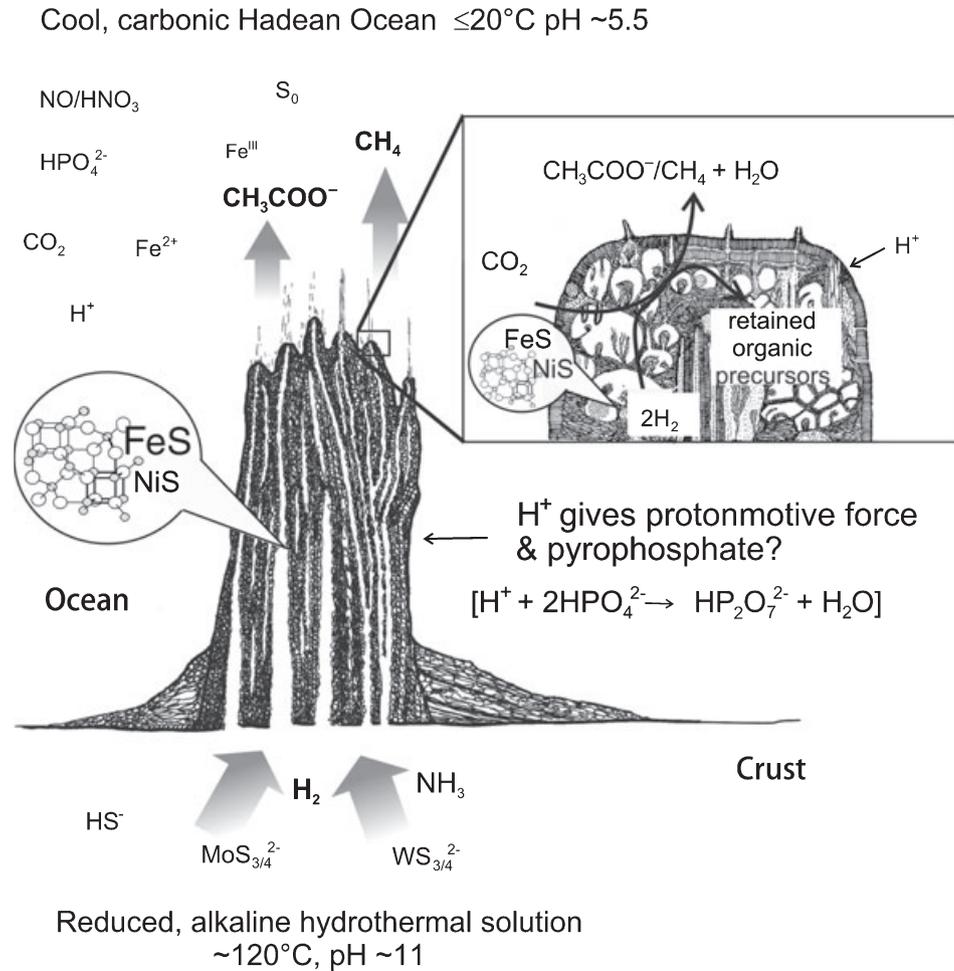
hydrogenation mechanism involving a hydrogen molecule bridging a Ni–Fe site – broadly comparable to such a site in awaruite (Ni<sub>3</sub>Fe) – that reacts with CO<sub>2</sub> or HCO<sub>3</sub><sup>-</sup> transiently bonded to either metal atom. A maximum of 34 μmol kg<sup>-1</sup> of acetate is also 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<sup>-1</sup> being produced abiologically (Lang *et al.*, 2010; fig. 3b and table 2) with a net stoichiometry:



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<sup>-1</sup> (Proskurowski *et al.*, 2008) although even here some small portion of the CH<sub>4</sub> 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



The synthesis of H<sub>2</sub> 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<sub>2</sub> to its chemically more reactive form NH<sub>3</sub> is equally important in this context. Smirnov *et al.* (2008) showed that in simulated hydrothermal conditions, 1–7 μmol kg<sup>-1</sup> ammonia is produced by the hydrogenation of nitrogen catalyzed by native iron (Fe<sup>0</sup>) 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<sub>2</sub>S as the electron source, Dörr *et al.* (2003) reported modest rates of N<sub>2</sub> conversion to NH<sub>3</sub>, albeit under acidic conditions (pH 3–4) at 80 °C. These initial reports indicate that N<sub>2</sub> 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 indispensable 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<sub>2</sub>) from iron monosulfide (FeS) and H<sub>2</sub>S, which is an exergonic reaction ( $\Delta G^0 = -38.4 \text{ kJ mol}^{-1}$ ) 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<sub>2</sub> itself with electrons stemming from H<sub>2</sub>, 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<sub>2</sub> driving CO<sub>2</sub> reduction stems in turn from serpentinization (eqns 1–3). However, the fixation of CO<sub>2</sub> 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<sub>2</sub> 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<sub>3</sub>SH from CO<sub>2</sub> and H<sub>2</sub>S (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<sub>3</sub>SH (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<sub>2</sub>) in the Wächtershäuser model, greigite (NiFe<sub>5</sub>S<sub>8</sub>) 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<sub>2</sub> reduction by H<sub>2</sub> 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<sub>2</sub> and H<sub>2</sub> under pressure with powdered iron as reducing agent and catalyst (Tian *et al.*, 2007).

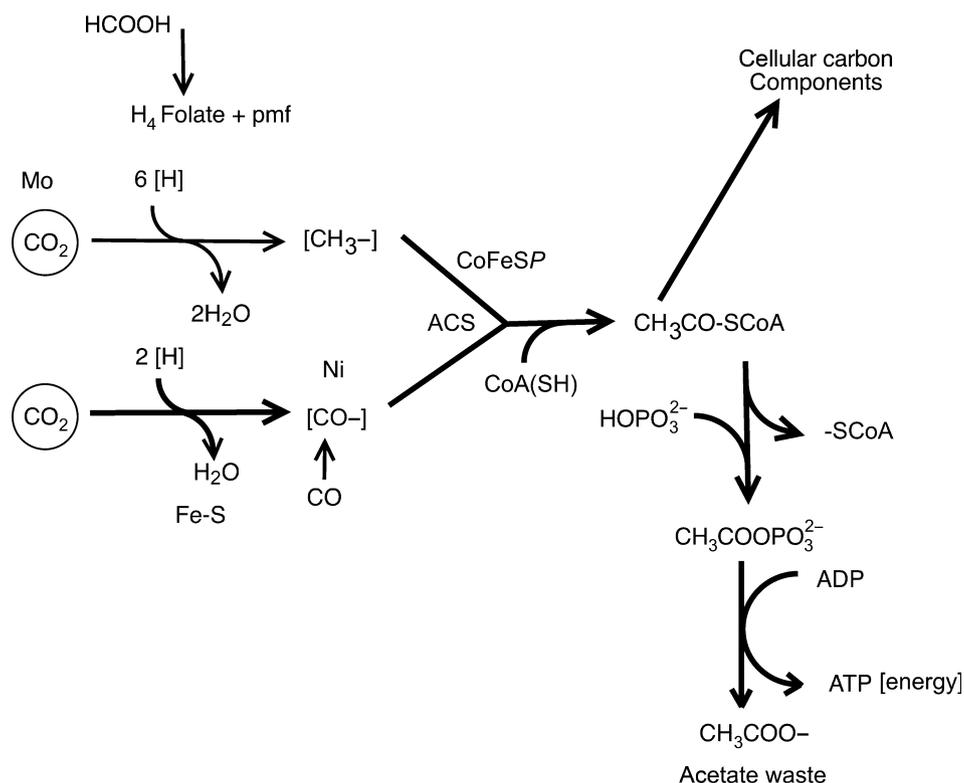
The autotrophic prokaryotes also produce a few of these carbon-bearing chemicals as effluent from the same reactants – some archaeobacteria evolve methane while some bacteria generate acetate (Proskurowski *et al.*, 2008; Gaidos *et al.*, 2009; Konn *et al.*, 2009; Lang *et al.*, 2010). They do so by 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  $\text{CO}_2$  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 archaeobacteria 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  $\text{CO}_2$  and  $\text{H}_2$ . Carbon monoxide dehydrogenase/acetyl coenzyme-A synthase (CODH/ACS) is the bifunctional enzyme wherein one nickel is involved in the reduction of  $\text{CO}_2$  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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> reduction with H<sub>2</sub> 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<sub>2</sub> and CO<sub>2</sub> 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<sub>2</sub> reduction, but there are a myriad of redox reactions other than CO<sub>2</sub> reduction that microbes can couple to such vectorial proton pumping (Amend & Shock, 2001).

Of course, serpentinization also produces H<sub>2</sub> that can in turn reduce CO<sub>2</sub> 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<sub>2</sub>- and CO<sub>2</sub>-dependent energy producing pathways of methanogens

and acetogens on the one hand and serpentinization-driven CO<sub>2</sub> 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<sub>2</sub> with H<sub>2</sub> (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<sub>2</sub>-containing) and alkaline (pH ~10–11) effluent from serpentinization and the more oxidized (CO<sub>2</sub>) and slightly acidic (pH 5–6) Hadean Ocean – provided an overall geochemically formed electrical potential that has been estimated to ≤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<sub>2</sub> 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; Ducluzau *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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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.

## ACKNOWLEDGMENTS

We thank Wolfgang Nitschke, Tony Fallick, Kevin Hand, Susan Lang, Isik Kanik, Shawn McGlynn, Randy Mielke, Victoria Orphan, Mark Skidmore and Steve Vance for discussions and support. Anonymous referees gave helpful critiques. M.J.R.'s research was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration for Astrobiology: Exobiology and Evolutionary Biology and supported by NASA's Astrobiology Institute (Icy Worlds). Copyright 2010 California Institute of Technology, Government sponsorship acknowledged. W.M.'s research is supported by grants from the European Research Council and the Deutsche Forschungsgemeinschaft.

## REFERENCES

- Abrajano TA, Sturchio NC, Kennedy BM, Lyon GL, Muehlenbachs K, Bohlke JK (1990) Geochemistry of reduced gas related to serpentinization of the Zambales ophiolite, Philippines. *Applied Geochemistry* **5**, 625–630.
- Adams MWW (1998) The evolutionary significance of the metabolism of tungsten by microorganisms growing at 100°C. In *Thermophiles: The Keys to Molecular Evolution and the Origin of Life?* (eds Wiegand J, Adams MW). Taylor and Francis, London/Philadelphia, pp. 325–338.
- Albarède F (2009) Volatile accretion history of the terrestrial planets and dynamic implications. *Nature* **461**, 1227–1233.
- Allen DE, Seyfried WE (2004) Serpentinization and heat generation: constraints from Lost City and Rainbow hydrothermal systems. *Geochimica et Cosmochimica Acta* **68**, 1347–1354.
- Amend JP, McCollom TM (2009) Energetics of biomolecule synthesis on early Earth. In *Chemical Evolution II: From the Origins of Life to Modern Society* (eds Zaikowski L, Friedrich JM, Seidel SR). American Chemical Society Symposium Series, Oxford University Press, New York, pp. 63–94.
- Amend JP, Shock EL (2001) Energetics of overall metabolic reactions of thermophilic and hyperthermophilic Archaea and Bacteria. *FEMS Microbiological Reviews* **25**, 175–243.
- Appel PWU (1994) Stratabound scheelite in altered Archean komatiites, West Greenland. *Mineralium Deposita* **29**, 341–352.
- Arnórsson S, Óskarsson N (2007) Molybdenum and tungsten in volcanic rocks and in surface and <100°C ground waters in Iceland. *Geochimica et Cosmochimica Acta* **71**, 284–304.
- Baaske P, Weinert F, Duhr S, Lemke K, Russell MJ, Braun D (2007) Extreme accumulation of nucleotides in simulated hydrothermal pore systems. *Proceedings of the National Academy of Sciences of the USA* **104**, 9346–9351.
- Bach W, Paulick H, Garrido CJ, Ildefonse B, Meurer WP, Humphris SE (2006) Unraveling the sequence of serpentinization reactions: petrography, mineral chemistry, and petrophysics of serpentinites from MAR 15°N (ODP Leg 209, Site 1274). *Geophysical Research Letters* **33**, L13306. doi:10.1029/2006GL025681.
- Bada JL (2004) How life began on Earth: a status report. *Earth and Planetary Science Letters* **226**, 1–15.
- Barnes HL, Czamanske GK (1967) Solubilities and transport of ore minerals. In *Geochemistry of Hydrothermal Ore Deposits* (ed. Barnes HL). Rinehart & Winston, New York, pp. 236–333.
- Barnes I, O'Neil JR (1969) The relationship between fluids in some fresh Alpine-type ultramafics and possible modern serpentinization, Western United States. *Bulletin of the Geological Society of America* **80**, 1947–1960.
- Barnes I, O'Neil JR (1978) Present day serpentinization in New Caledonia, Oman and Yugoslavia. *Geochimica et Cosmochimica Acta* **42**, 144–145.
- Baross JA, Hoffman SE (1985) Submarine hydrothermal vents and associated gradient environments as sites for the origin and evolution of life. *Origins of Life and Evolution of the Biosphere* **15**, 327–345.
- Beinert H (2000) A tribute to sulfur. *European Journal of Biochemistry* **267**, 5657–5674.
- Beinert H, Holm RH, Münck E (1997) Iron-sulfur clusters: nature's modular, multipurpose structures. *Science* **277**, 653–659.
- Berry AJ, Danyushevsky LV, O'Neil HStC, Newville M, Sutton SR (2008) Oxidation state of iron in komatiitic melt inclusions indicates an hot Archean mantle. *Nature* **455**, 960–963.
- Bethke C (1996) *Geochemical Reaction Modelling*. Oxford University Press, Oxford.
- Blaß G, Graf H-W, Pichler A (1997) Sekundäre Neubildungen in Schlacken von St Martin am Silberberg in Kärnten (2). *Mineralien-Welt* **8**, 54–55.
- Bonatti E, Simmons EC, Breger D, Hamlyn PR, Lawrence J (1983) Ultramafic rock/seawater interaction in the oceanic crust: Mg-silicate (sepiolite) deposit from the Indian Ocean floor. *Earth and Planetary Science Letters* **62**, 229–238.
- Bonomi F, Werth MT, Kurtz DM (1985) Assembly of FeSn(SR)<sub>2</sub> (n = 2,4) in aqueous media from iron salts, thiols and sulfur, sulfide, thiosulfide plus rhodanase. *Inorganic Chemistry* **24**, 4331–4335.
- Bounama C, Franck S, von Bloh W (2001) The fate of the Earth's ocean. *Hydrology and Earth System Sciences* **5**, 569–575.
- Boyet M, Carlson RW (2005) <sup>142</sup>Nd evidence for early (>4.53 Ga) global differentiation of the silicate Earth. *Science* **309**, 576–581.
- Boyle R (1685) Some unheeded causes of the insalubrity and salubrity of the air. In *Complete Works in Five Volumes*, Vol. 4 (ed. Birch T). A Millar, London, 1744 pp.
- Bradley AS, Hayes JM, Summons RE (2008) Extraordinary <sup>13</sup>C enrichment of diether lipids at the Lost City hydrothermal field suggests a carbon-limited system. *Geochimica et Cosmochimica Acta* **73**, 102–118.
- Budin I, Bruckner RJ, Szostak JW (2009) Formation of protocell-like vesicles in a thermal diffusion column. *Journal American Chemical Society* **131**, 9628–9629.
- Chamberlain JA, McLeod CR, Traill RJ, Lachance GR (1965) Native metals in the Muskox intrusion. *Canadian Journal of Earth Science* **2**, 188–215.
- Charlou JL, Donval JP, Fouquet Y, Jean-Baptiste P, Holm N (2002) Geochemistry of high H<sub>2</sub> and CH<sub>4</sub> vent fluids issuing from ultra-

- mafic rocks at the Rainbow hydrothermal field (36°14'). *Chemical Geology* **191**, 345–359.
- Cody GD, Boctor NZ, Filley TR, Hazen RM, Scott JH, Sharma A, Yoder HS (2000) Primordial carbonylated iron-sulfur compounds and the synthesis of pyruvate. *Science* **289**, 1337–1340.
- Cody GD, Boctor NZ, Brandes JA, Filley TR, Hazen RM, Yoder HS (2004) Assaying the catalytic potential of transition metal sulfides for abiotic carbon fixation. *Geochimica et Cosmochimica Acta* **68**, 2185–2196.
- Corliss JB, Dymond J, Gordon LI, Edmond JM, von Herzen RP, Ballard RD, Green K, Williams D, Bainbridge A, Crane K, van Andel TH (1979) Submarine thermal springs on the Galápagos Rift. *Science* **203**, 1073–1083.
- Corliss JB, Baross JA, Hoffman SE (1981) An hypothesis concerning the relationship between submarine hot springs and the origin of life on Earth. Proceedings 26th International Geological Congress, Geology of Oceans Symposium, Paris, July 7–17, 1980. *Oceanologica Acta No. SP*, pp. 59–69.
- Coveney RM, Goebel ED, Zeller EJ, Dreschhoff GAM, Angino EE (1987) Serpentinization and the origin of hydrogen gas in Kansas. *Bulletin of the American Association of Petroleum Geologists* **71**, 39–48.
- Dabitzias GS (1980) Petrology and genesis of Vavdos cryptocrystalline magnesite deposits, Chalkidiki Peninsula, northern Greece. *Economic Geology* **75**, 1138–1151.
- Delacour A, Früh-Green GL, Bernasconi SM (2008) Sulfur mineralogy and geochemistry of serpentinites and gabbros of the Atlantis Massif (IODP Site U1309). *Geochimica et Cosmochimica Acta* **72**, 5111–5127.
- Delano JW (2001) Redox history of the Earth's interior since 3900 Ma: implications for prebiotic molecules. *Origins of Life and Evolution of the Biosphere* **319**, 311–341.
- Diment WH (1964) Thermal conductivity of serpentinite from Mayaguez, Puerto Rico, and other localities. *National Academy of Sciences, National Research Council Publication* **1188**, 92–106.
- Dörr M, Käßbohrer J, Grunert R, Kreisel G, Brand WA, Werner RA, Geilmann H, Apfel C, Robl C, Weigand WA (2003) Possible prebiotic formation of ammonia from dinitrogen on iron sulfide surfaces. *Angewandte Chemie International Edition* **42**, 1540–1543.
- Douville E, Charlou JL, Oelkers EH, Bienvenu P, Colon CFJ, Donval JP, Fouquet Y, Prieur D, Appriou P (2002) The rainbow vent fluids (36°14'N, MAR): the influence of ultramafic rocks and phase separation on trace metal content in Mid-Atlantic Ridge hydrothermal fluids. *Chemical Geology* **184**, 37–48.
- Ducluzeau A-L, van Lis R, Duval S, Schoepp-Cothenet B, Russell MJ, Nitschke W (2009) Was nitric oxide the first strongly oxidizing terminal electron sink. *Trends in Biochemical Sciences* **34**, 9–15.
- Eck RV, Dayhoff MO (1966) Evolution of the structure of ferredoxin based on living relics of primitive amino acid sequences. *Science* **152**, 363–366.
- Emmanuel S, Berkowitz B (2006) Suppression and stimulation of seafloor hydrothermal convection by exothermic mineral hydration. *Earth and Planetary Science Letters* **243**, 657–668.
- Erickson BE, Helz GR (2000) Molybdenum (VI) speciation in sulfidic waters: stability and lability of thiomolybdates. *Geochimica et Cosmochimica Acta* **64**, 1149–1158.
- Escartín J, Hirth G, Evans B (2001) Strength of slightly serpentinized peridotites: implications of the tectonics of oceanic lithosphere. *Geology* **29**, 1023–1026.
- Fallick AE, Ilich M, Russell MJ (1991) A stable isotope study of the magnesite deposits associated with the Alpine-type ultramafic rocks of Yugoslavvia. *Economic Geology* **86**, 847–861.
- Ferris FG, Jack TR, Bramhill BJ (1992) Corrosion products associated with attached bacteria at an oil field water injection plant. *Canadian Journal of Microbiology* **38**, 1320–1324.
- Ferry JG (1995) CO dehydrogenase. *Annual Review of Microbiology* **49**, 305–333.
- Filtner MJ, Butler IB, Rickard D (2003) The origin of life: the properties of iron sulphide membranes. *Applied Earth Science (Transactions of the Institution of Mining and Metallurgy)* **112B**, 171–172.
- Foustoukos DI, Savov IP, Janecky DR (2008) Chemical and isotopic constraints on water/rock interactions at the Lost City hydrothermal field, 30°N Mid-Atlantic Ridge. *Geochimica et Cosmochimica Acta* **72**, 5457–5474.
- Frost BR (1985) On the stability of sulfides, oxides and native metals in serpentinite. *Journal of Petrology* **26**, 31–63.
- Frost BR, Beard JS (2007) On silica activity and serpentinization. *Journal of Petrology* **48**, 1351–1368.
- Frost DJ, Langenhorst F, McCammon CA, Trønnes RG, Rubie DC (2004) Experimental evidence for the existence of iron-rich metal in the Earth's lower mantle. *Nature* **428**, 409–412.
- Früh-Green GL, Connolly JAD, Kelley DS, Plas A, Grobety B (2004) Serpentinization of oceanic peridotites: implications for geochemical cycles and biological activity. *Subseafloor Biosphere at Mid-Ocean Ridges, AGU Geophysical Monograph* **144**, 119–136.
- Fuchs G (1989) Alternative pathways of autotrophic CO<sub>2</sub> fixation. In *Autotrophic Bacteria* (eds Schlegel HG, Bowen B). Science Technology, Madison, WI, pp. 365–382.
- Gaidos E, Marteinson T, Thorsteinsson T, Jóhannesson T, Rúnarson AR, Stefansson A, Glazer B, Lanoil B, Skidmore M, Han S, Miller M, Rusch A, Foo W (2009) An oligarchic microbial assemblage in the anoxic bottom waters of a volcanic subglacial lake. *The ISME Journal* **3**, 486–497.
- Gao X, Liu Y, Cai YM, Zhao YF (2008)  $\alpha$ -amino acid behaves differently from  $\beta$ - or  $\gamma$ -amino acids as treated by metaphosphate. *Amino Acids* **34**, 47–53.
- Geptner A, Kristmannsdóttir H, Kristjánsson JK, Marteinson VTh (2002) Biogenic saponite from an active submarine hot spring, Iceland. *Clays and Clay Minerals* **50**, 174–185.
- Goldberg S, Su C, Foster HS (1998) Sorption of molybdenum on oxides, clay minerals and soils: Mechanisms and models. In *Adsorption of Metals by Geomedia: Variables, Mechanisms, and Model Applications* (ed. Jenne EA). Academic Press, San Diego, pp. 401–426.
- Grabarse W, Mahlert F, Duin EC, Goubeaud M, Shima S, Thauer RK, Lamzin V, Ermler U (2001) On the mechanism of biological methane formation: structural evidence for conformational changes in methyl-coenzyme M reductase upon substrate binding. *Journal of Molecular Biology* **309**, 315–330.
- Hagan WJ, Parker A, Steuerwald A, Hathaway M (2007) Phosphate solubility and the cyanate-mediated synthesis of pyrophosphate. *Origins of Life and Evolution of the Biosphere* **37**, 113–122.
- Haggerty JA, Fisher JB (1992) Short-chain organic acids in interstitial waters from Mariana and Bonin forearc serpentines: Leg125. *Proceedings of the Ocean Drilling Program, Scientific Results* **125**, 387–395.
- Halevy I, Zuber MT, Schrag DP (2007) A sulfur dioxide climate feedback on early Mars. *Science* **318**, 1903–1907.
- Hall DO, Cammack R, Rao KK (1974) The iron-sulfur proteins: evolution of a ubiquitous protein from model systems to higher organisms. *Origins of Life and Evolution of the Biosphere* **5**, 363–386.
- Halliday AN (2004) Mixing, volatile loss and compositional change during impact-driven accretion of the Earth. *Nature* **427**, 505–509.
- Hand KP, Carlson RW, Chyba CF (2007) Energy, chemical disequilibrium, and geological constraints on Europa. *Astrobiology* **7**, 1006–1022.

- Harvey RB (1924) Enzymes of thermal algae. *Science* **50**, 481–482.
- He C, Tian G, Liu Z, Feng S (2010) A mild hydrothermal route to fix carbon dioxide to simple carboxylic acids. *Organic Letters* **12**, 649–651.
- Heinen W, Lauwers AM (1996) Organic sulfur compounds resulting from the interaction of iron sulfide, hydrogen sulfide and carbon dioxide in an anaerobic aqueous environment. *Origins of Life and Evolution of the Biosphere* **26**, 131–150.
- Hekinian R, Fevrier M, Bischoff JL, Picot P, Shanks WC (1980) Sulfide deposits from the East Pacific Rise near 21°N. *Science* **207**, 1433–1444.
- Helz GR, Miller CV, Charnock JM, Mosselmans JFW, Patrick RAD, Garner CD, Vaughan DJ (1996) Mechanism of molybdenum removal from the sea and its concentration in black shales. EXAFS evidence. *Geochimica et Cosmochimica Acta* **60**, 3631–3642.
- Hinrichs K-U, Hayes JM, Bach W, Spivak AJ, Hmelo LR, Holm NG, Johnson CG, Sylva SP (2006) Biological formation of ethane and propane in the deep marine subsurface. *Proceedings of the National Academy of Sciences of the USA* **103**, 14684–14689.
- Holm NG, Dumont M, Ivarsson M, Konn C (2006) Alkaline fluid circulation in ultramafic rocks and formation of nucleotide constituents: a hypothesis. *Geochemical Transactions* **7**, 7. doi:10.1186/1467-4866-7-7.
- Hopkinson L, Beard JS, Boulter CA (2004) The hydrothermal plumbing of a serpentinite-hosted detachment: evidence from the West Iberia non-volcanic rifted continental margin. *Marine Geology* **204**, 301–315.
- Horita J, Berndt ME (1999) Abiogenic methane formation and isotopic fractionation under hydrothermal conditions. *Science* **285**, 1055–1057.
- Huber C, Wächtershäuser G (1997) Activated acetic acid by carbon fixation on (Fe,Ni)S under primordial conditions. *Science* **276**, 245–247.
- Huber C, Wächtershäuser G (2003) Primordial reductive amination revisited. *Tetrahedron Letters* **44**, 1695–1697.
- Huber C, Eisenreich W, Hecht S, Wächtershäuser G (2003) A possible primordial peptide cycle. *Science* **301**, 938–940.
- Ilich M, Toshovich R (2002) Geology and origin of the Goleš vein magnesite deposit: a brief survey. Guide to Geological Excursions, Proceedings of XVII, Congress of Carpathian-Balkan Geological Association, Bratislava, September 1st–4th, 2002, 53 pp. Available at: [http://www.geologicacarpathica.sk/src/special\\_issue\\_vol53.php](http://www.geologicacarpathica.sk/src/special_issue_vol53.php).
- Joyce GF (2002) The antiquity of RNA-based evolution. *Nature* **418**, 214–221.
- Jupp T, Schultz A (2000) A thermodynamic explanation for black smoker temperatures. *Nature* **403**, 880–883.
- Kasting JF (1993) Earth's early atmosphere. *Science* **259**, 920–926.
- Kasting JF, Egger DH, Raeburn SP (1993) Mantle redox evolution and the oxidation state of the Archean atmosphere. *Journal of Geology* **101**, 245–257.
- Keele KD (1974) The Sydenham-Boyle theory of moribific particles. *Medical History* **18**, 240–248.
- Kehew AE (2001) *Applied Chemical Hydrogeology*. Prentice-Hall, Upper Saddle River, NJ.
- Kelley DS, Karson JA, Blackman DK, Früh-Green GL, Butterfield DA, Lilley MD, Olsen EJ, Schrenk MO, Roe KK, Lebon GT, Rivizzigno P, AT3-60 Shipboard Party (2001) An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30° N. *Nature* **412**, 145–149.
- Kelley DS, Karson JA, Früh-Green GL, Yoerger DR, Shank TM, Butterfield DA, Hayes JM, Schrenk MO, Olson EJ, Proskurowski G, Jakuba M, Bradley A, Larson B, Ludwig K, Glickson D, Buckman K, Bradley AS, Brazeton WJ, Roe K, Elend MJ, Delacour A, Bernasconi SM, Lilley MD, Baross JA, Summons RE, Sylva SP (2005) A serpentinite-hosted ecosystem: the Lost City hydrothermal field. *Science* **307**, 1428–1434.
- Klein F, Bach W (2009) Fe-Ni-Co-O-S Phase relations in peridotite-seawater interactions. *Journal of Petrology* **50**, 37–59.
- Knauth LP (2005) Temperature and salinity history of the Precambrian ocean: implications for the course of microbial evolution. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **219**, 53–69.
- Konhäuser KO, Pecoits E, Lalonde SV, Papineau D, Nisbet EG, Barley ME, Arndt NT, Zahnle K, Kamber BS (2009) Oceanic nickel depletion and a methanogen famine before the Great Oxidation Event. *Nature* **458**, 750–753.
- Konn C, Charlou JL, Donval JP, Holm NG, Dehairs F, Bouillon S (2009) Hydrocarbons and oxidized organic compounds in hydrothermal fluids from Rainbow and Lost City ultramafic-hosted vents. *Chemical Geology* **258**, 299–314.
- Koonin E, Martin W (2005) On the origin of genomes and cells within inorganic compartments. *Trends in Genetics* **21**, 647–654.
- Korenaga J (2008) Plate tectonics, flood basalts and the evolution of Earth's oceans. *Terra Nova* **20**, 419–439.
- Krishnarao JSR (1964) Native nickel-iron alloy, its mode of occurrence, distribution and origin. *Economic Geology* **59**, 443–448.
- Kump LR, Seyfried WE (2005) Hydrothermal Fe fluxes during the Precambrian: effect of low oceanic sulfate concentrations and low hydrostatic pressure on the composition of black smokers. *Earth and Planetary Science Letters* **235**, 654–662.
- Lambert DD, Foster JG, Frick LR, Ripley EM, Zientek ML (1998) Geodynamics of magmatic Cu-Ni-PGE sulfide deposits; new insights from the Re-Os isotope system. *Economic Geology* **93**, 121–136.
- Lane N (2009) The cradle of life. *New Scientist* **2730**, 38–42.
- Lane N, Allen JF, Martin W (2010) How did LUCA make a living? Chemiosmosis and the origin of life. *BioEssays* **32**, 271–280.
- Lang SQ, Butterfield DA, Schulte M, Kelley DS, Lilley MD (2010) Elevated concentrations of formate, acetate and dissolved organic carbon found at the Lost City hydrothermal field. *Geochimica et Cosmochimica Acta* **74**, 941–952.
- Leduc S (1911) *The Mechanism of Life*. Rebman Ltd, London.
- Ljungdahl LG (1994) The acetyl-CoA pathway and the chemiosmotic generation of ATP during acetogenesis. In *Acetogenesis* (ed. Drake HL). Chapman and Hall, New York, pp. 63–87.
- Ljungdahl LG (2009) A life with acetogens, thermophiles, and cellulolytic anaerobes. *Annual Review of Microbiology* **63**, 1–25.
- Lowell RP, Keller SM (2003) High temperature hydrothermal circulation over geological time and archean banded iron formations. *Geophysical Research Letters* **30**, doi:10.1029/2002GL016536.
- Lowell RP, Rona PA (2002) Seafloor hydrothermal systems driven by the serpentinization of peridotite. *Geophysical Research Letters* **29**, 1531. doi:10.1029/2001GL014411.
- Ludwig KA, Kelley DS, Shen C, Cheng H, Edwards RL (2005) U/Th geochronology of carbonate chimneys at the Lost City hydrothermal field. *EOS Transactions AGU* **86**, 1487.
- Macleod G, McKeown C, Hall AJ, Russell MJ (1994) Hydrothermal and oceanic pH conditions of possible relevance to the origin of life. *Origins of Life and Evolution of the Biosphere* **24**, 19–41.
- Maden BEH (2000) Tetrahydrofolate and tetrahydromethanopterin compared: functionally distinct carriers in C1 metabolism. *Biochemical Journal* **350**, 609–629.
- Marteinsson VTh, Kristjánsson JK, Kristmannsdóttir H, Dahlkvist M, Sæmundsson K, Hannington M, Pétursdóttir SK, Geptner A, Stoffers P (2001) Discovery of giant submarine smectite cones on the seafloor in Eyjafjörður, North Iceland, and a novel thermal

- microbial habitat. *Applied and Environmental Microbiology* **67**, 827–833.
- Martin W, Russell M (2003) On the origins of cells: a hypothesis for the evolutionary transitions from abiotic geochemistry to chemoautotrophic prokaryotes, and from prokaryotes to nucleated cells. *Philosophical Transactions of the Royal Society of London, Series B: Biological Sciences* **358**, 59–85.
- Martin W, Russell MJ (2007) On the origin of biochemistry at an alkaline hydrothermal vent. *Philosophical Transactions of the Royal Society of London, Series B: Biological Sciences* **362**, 1887–1925.
- Martin RS, Mather TA, Pyle DM (2007) Volcanic emissions and the early Earth atmosphere. *Geochimica et Cosmochimica Acta* **71**, 3673–3685.
- Martin W, Baross J, Kelley D, Russell MJ (2008) Hydrothermal vents and the origin of life. *Nature Reviews, Microbiology* **6**, 805–814.
- Marty B, Yokochi R (2006) Water in the early Earth. *Reviews in Mineralogy and Geochemistry* **62**, 421–450.
- McCollom T, Bach W (2009) Thermodynamic constraints on hydrogen generation during serpentinization of ultramafic rocks. *Geochimica et Cosmochimica Acta* **73**, 856–875.
- McCollom T, Seewald JS (2003a) Experimental constraints on the hydrothermal reactivity of organic acids and acid anions: I Formic acid and formate. *Geochimica et Cosmochimica Acta* **67**, 3625–3644.
- McCollom T, Seewald JS (2003b) Experimental study of the hydrothermal reactivity of organic acids and acid anions: II Acetic acid, acetate, and valeric acid. *Geochimica et Cosmochimica Acta* **67**, 3645–3664.
- McCollom T, Seewald JS (2007) Abiotic synthesis of organic compounds in deep-sea hydrothermal environments. *Chemical Reviews* **107**, 382–401.
- Milner-White EJ, Russell MJ (2008) Predicting the conformations of peptides and proteins in early evolution. *Biology Direct* **3**, 3. doi:10.1186/1745-6150-3-3.
- Milner-White EJ, Russell MJ (2010) Polyphosphate-peptide synergy and the organic takeover at the emergence of life. *Journal of Cosmology* **10** (in press).
- Mitchell P (1967) Proton-translocation phosphorylation in mitochondria, chloroplasts and bacteria: natural fuel cells and solar cells. *The FASEB Journal* **26**, 1370–1379.
- Morita RY (2000) Is H<sub>2</sub> the universal energy source for long-term survival? *Microbial Ecology* **38**, 307–320.
- Morse JW, Mackenzie FT (1998) Hadean ocean carbonate geochemistry. *Aquatic Geochemistry* **4**, 301–319.
- Müller V (2003) Energy conservation in acetogenic bacteria. *Applied and Environmental Microbiology* **69**, 6345–6353.
- Neal C, Stanger G (1983) Hydrogen generation from mantle source rocks in Oman. *Earth and Planetary Science Letters* **66**, 315–320.
- Neal C, Stanger G (1984) Calcium and magnesium hydroxide precipitation from alkaline groundwater in Oman, and their significance to the process of serpentinization. *Mineralogical Magazine* **48**, 237–241.
- Nekrasov IY-A, Konyushok AA (1982) The physicochemical conditions of tungstenite formation. *Mineralogicheskii Zhurnal* **4**, 33–40 (in Russian).
- Nisbet EG (1985) The geological setting of the earliest life forms. *Journal of Molecular Evolution* **21**, 289–298.
- Nitschke W, Russell MJ (2009) Hydrothermal focusing of chemical and chemiosmotic energy, supported by delivery of catalytic Fe, Ni, Mo/W, Co, S and Se, forced life to emerge. *Journal Molecular Evolution* **69**, 481–496.
- Orgel LE (2008) The implausibility of metabolic cycles on the prebiotic Earth. *Public Library of Science, Biology* **6**, e18.
- Palandri J, Reed MH (2004) Geochemical models of metasomatism in ultramafic systems: serpentinization, rodingitization, and sea floor carbonate chimney precipitation. *Geochimica et Cosmochimica Acta* **68**, 1115–1133.
- Pavlov AA, Kasting JF (2002) Mass-independent fractionation of sulfur isotopes in Archean sediments: strong evidence for an anoxic Archean atmosphere. *Astrobiology* **2**, 27–41.
- Pavlov AA, Toon OB, Pavlov AK, Bally J, Pollard D (2005) Passing through a giant molecular cloud: “Snowball” glaciations produced by interstellar dust. *Geophysical Research Letters* **32**, L03705.
- Proskurowski G, Lilley MD, Kelley DS, Olson EJ (2006) Low temperature volatile production at the Lost City hydrothermal field, evidence from a hydrogen stable isotope geothermometer. *Chemical Geology* **229**, 331–343.
- Proskurowski G, Lilley MD, Seewald JS, Früh-Green GL, Olson EJ, Lupton JE, Sylva SP, Kelley DS (2008) Abiogenic hydrocarbon production at Lost City hydrothermal field. *Science* **319**, 604–607.
- Rabinowitz J, Flores R, Krebsback R, Rogers G (1969) Peptide formation in the presence of linear or cyclic polyphosphates. *Nature* **224**, 795–796.
- Ragsdale SW (2004) Life with carbon monoxide. *Critical Reviews in Biochemistry and Molecular Biology* **39**, 165–195.
- Rahman L (2002) *The Geochemical Modelling of Emergent Life From Submarine Hydrothermal Environments*. Unpublished PhD thesis, University of Glasgow.
- Rickard D, Luther GW (2007) Chemistry of iron sulfides. *Chemical Reviews* **107**, 514–562.
- Russell MJ (1978) Downward-excavating hydrothermal cells and Irish-type ore deposits: importance of an underlying thick Caledonian Prism. *Transactions of the Institution of Mining and Metallurgy (Applied Earth Science Section B)* **89**, B168–B171.
- Russell MJ (2003) On the importance of being alkaline. *Science* **302**, 580–581.
- Russell MJ, Arndt NT (2005) Geodynamic and metabolic cycles in the Hadean. *Biogeosciences* **2**, 97–111.
- Russell MJ, Hall AJ (1997) The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front. *Journal of the Geological Society of London* **154**, 377–402.
- Russell MJ, Hall AJ (1999) On the inevitable emergence of life on Mars. In *Search for Life on Mars* (ed. Hiscox JA). Proceedings of the 1st UK Conference of the British Interplanetary Society, London, 11th November 1998, pp. 26–36.
- Russell MJ, Hall AJ (2002) From geochemistry to biochemistry: chemiosmotic coupling and transition element clusters in the onset of life and photosynthesis. *The Geochemical News* **113/October**, 6–12.
- Russell MJ, Hall AJ (2006) The onset and early evolution of life. In *Evolution of Early Earth's Atmosphere, Hydrosphere, and Biosphere—Constraints from Ore Deposits* (eds Kesler SE, Ohmoto H). Geological Society of America, Memoir 198, Boulder, Colorado, pp. 1–32.
- Russell MJ, Kanik I (2010) Why does life start, What Does It do, where might it be, how might we find it? *Journal of Cosmology* **5**, 1008–1039.
- Russell MJ, Martin W (2004) The rocky roots of the acetyl-CoA pathway. *Trends in Biochemical Science* **29**, 358–363.
- Russell MJ, Hall AJ, Turner D (1989) In vitro growth of iron sulphide chimneys: possible culture chambers for origin-of-life experiments. *Terra Nova* **1**, 238–241.
- Russell MJ, Daniel RM, Hall AJ (1993) On the emergence of life via catalytic iron-sulfide membranes. *Terra Nova* **5**, 343–347.
- Russell MJ, Daniel RM, Hall AJ, Sherringham J (1994) A hydrothermally precipitated catalytic iron sulphide membrane as a first step toward life. *Journal of Molecular Evolution* **39**, 231–243.

- Russell MJ, Daia DE, Hall AJ (1998) The emergence of life from FeS bubbles at alkaline hot springs in an acid ocean. In *Thermophiles: The Keys to the Molecular Evolution and the Origin of Life* (eds Wiegel J, Adams MWW). Taylor & Francis, Washington, DC, pp. 77–126.
- Schaefer L, Fegley B (2007) Outgassing of ordinary chondritic material and some of its implications for the chemistry of asteroids, planets, and satellites. *Icarus* **186**, 462–483.
- Schoonen MAA, Xu Y, Bebie J (1999) Energetics and kinetics of the prebiotic synthesis of simple organic and amino acids with the FeS-H<sub>2</sub>/FeS<sub>2</sub> redox couple as reductant. *Origins of Life and Evolution of the Biosphere* **29**, 5–32.
- Schulte MD, Rogers KL (2004) Thiols in hydrothermal solution: standard partial molar properties and their role in the organic geochemistry of hydrothermal environments. *Geochimica et Cosmochimica Acta* **68**, 1087–1097.
- Schulte MD, Blake DF, Hoehler TM, McCollom T (2006) Serpentinization and its implications for life on the early Earth and Mars. *Astrobiology* **6**, 364–376.
- Schulzke C (2005) Temperature dependent electrochemical investigations of molybdenum and tungsten oxobis(dithiolene) complexes. *Dalton Transactions* **2005**, 713–720.
- Schwartzman D, Lineweaver CH (2005) Temperature, biogenesis and biospheric self-organization. In *Non-equilibrium Thermodynamics and the Production of Entropy: Life, Earth and Beyond* (eds Kleidon A, Lorenz R). Springer Verlag, Heidelberg, pp. 207–217.
- Seewald JS, Zolotov MY, McCollom T (2006) Experimental investigation of single carbon compounds under hydrothermal conditions. *Geochimica et Cosmochimica Acta* **70**, 446–460.
- Seward TM, Barnes HL (1997) Metal transport in hydrothermal ore fluids. In *Geochemistry of Hydrothermal Ore Deposits* (ed. Barnes HL). Rinehart & Winston, New York, pp. 435–486.
- Seyfried WE, Foustoukos DI, Fu Q (2007) Redox evolution and mass transfer during serpentinization: an experimental and theoretical study at 200°C, 500 bar with implications for ultra-mafic hosted hydrothermal systems at Mid-Ocean Ridges. *Geochimica et Cosmochimica Acta* **71**, 3872–3886.
- Shock EL (1990) Geochemical constraints on the origin of organic compounds in hydrothermal systems. *Origins of Life and Evolution of the Biosphere* **20**, 331–367.
- Shock EL (1992) Chemical environments of submarine hydrothermal systems; marine hydrothermal systems and the origin of life. *Origins of Life and Evolution of the Biosphere* **22**, 67–107.
- Shock EL, Schulte MD (1998) Organic synthesis during fluid mixing in hydrothermal systems. *Journal of Geophysical Research* **103**, 28513–28527.
- Shock EL, McCollom T, Schulte MD (1998) The emergence of metabolism from within hydrothermal systems. In *Thermophiles: The Keys to Molecular Evolution and the Origin of Life* (eds Wiegel J, Adams MWW). Taylor and Francis, Washington, pp. 59–76.
- Sigurdsson H, Devine JD, Tchoua FM, Presser TS, Pringle MKW, Evans WC (1987) Origin of the lethal gas burst from Lake Monoun, Cameroon. *Journal of Volcanology and Geothermal Research* **31**, 1–16.
- Smirnov A, Hausner D, Laffers R, Strongin DR, Schoonen MAA (2008) Abiotic ammonium formation in the presence of Ni-Fe metals and alloys and its implications for the Hadean nitrogen cycle. *Geochimical Transactions* **9**, 5. doi:10.1186/1467-4866-9-5.
- Spear JR, Walker JJ, McCollom TM, Pace NR (2005) Hydrogen and bioenergetics in the Yellowstone geothermal ecosystem. *Proceedings of the National Academy of Sciences of the USA* **102**, 2555–2560.
- Spiess FN, Macdonald KC, Atwater T, Ballard R, Carranza A, Cordoba D, Cox C, Garcia VMD, Francheteau J, Guerrero J, Hawkins J, Haymon R, Hessler R, Juteau T, Kastner M, Larson R, Luyendyk B, Macdougall JD, Miller S, Normark W, Orcutt J, Rangin C (1980) East Pacific Rise: hot springs and geophysical experiments. *Science* **207**, 1421–1433.
- Srinivasan BR (2004) Does an all-sulphur analogue of heptamolybdate exist? *Journal of Chemical Science* **116**, 251–259.
- Takai K, Gamo T, Tsunogai U, Nakayama N, Hirayama H, Nealson KH, Horikoshi K (2004) Geochemical and microbiological evidence for a hydrogen-based, hyperthermophilic subsurface lithoautotrophic microbial ecosystem (HyperSLiME) beneath an active deep-sea hydrothermal field. *Extremophiles* **8**, 269–282.
- Thauer RK, Kaster A-K, Seedorf H, Buckel W, Hedderich R (2008) Methanogenic archaea: ecologically relevant differences in energy conservation. *Nature Reviews, Microbiology* **6**, 579–589.
- Tian G, Yuan H, Mu Y, He C, Feng S (2007) Hydrothermal Reactions from Sodium hydrogen Carbonate to Phenol. *Organic Letters* **9**, 2019–2021.
- Touboul M, Kleine T, Bourdon B, Palme H, Wieler R (2007) Late formation and prolonged differentiation of the Moon inferred from W isotopes. *Nature* **450**, 1206–1209.
- Valley JW, Cavosie AJ, Fu B, Peck WH, Wilde SA (2002) Comment of “heterogeneous Hadean hafnium: evidence of continental crust at 4.4 to 4.5 Ga”. *Science* **312**, 1139a.
- Valley JW, Peck WH, King EM, Wilde SA (2006) A cool early Earth. *Geology* **30**, 351–354.
- Vance S, Harmmeijer J, Kimura J, Hussmann H, Demartin B, Brown JM (2007) Hydrothermal systems in small ocean planets. *Astrobiology* **7**, 987–1005.
- Volbeda A, Fontecilla-Camps JC (2006) Catalytic nickel-iron-sulfur clusters: from minerals to enzymes. In *Topics in Organometallic Chemistry*, Vol. 17 (ed. Simmonneaux G). Springer, Berlin, Germany, pp. 57–82.
- Wächtershäuser G (1988a) Pyrite formation, the first energy source for life: a hypothesis. *Systematic Applied Microbiology* **10**, 207–210.
- Wächtershäuser G (1988b) Before enzymes and templates: theory of surface metabolism. *Microbiological Reviews* **52**, 452–484.
- Wächtershäuser G (1993) The cradle chemistry of life: on the origin of the natural products in pyrite-pulled chemo-autotrophic origin of life. *Pure and Applied Chemistry* **65**, 1343–1348.
- Wächtershäuser G (2006) From volcanic origins of chemoautotrophic life to Bacteria, Archaea and Eukarya. *Philosophical Transactions of the Royal Society of London, Series B: Biological Sciences* **B361**, 1787–1808.
- Walker JCG (1985) Carbon dioxide on the early Earth. *Origins of Life and Evolution of the Biosphere* **16**, 117–127.
- Walker JE (1998) ATP synthesis by rotary catalysis. *Angewandte Chemie International Edition* **37**, 2308–2319.
- Walker JCG, Brimblecombe P (1985) Iron and sulfur in the prebiological ocean. *Precambrian Research* **28**, 205–222.
- Wenner DB, Taylor HP (1971) Temperatures of serpentinization of ultramafic rocks based on <sup>18</sup>O/<sup>16</sup>O fractionation between coexisting serpentine and magnetite. *Contributions to Mineralogy and Petrology* **32**, 165–185.
- Wilde SA, Valley JW, Peck WH, Graham CM (2001) Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature* **409**, 175–178.
- Wolin MJ (1982) Hydrogen transfer in microbial communities. In *Microbial Interactions and Communities* (eds Bull AT, Slater JH). Academic Press, London, pp. 323–356.
- Wolthers M, Van der Gaast SJ, Rickard D (2003) The structure of disordered mackinawite. *American Mineralogist* **88**, 2007–2015.
- Wood BJ, Halliday AN (2005) Cooling of the Earth and core formation after the giant impact. *Nature* **437**, 1345–1348.

- Wood BJ, Bryndzia LT, Johnson KE (1990) Mantle oxidation state and its relation to tectonic environment and fluid speciation. *Science* **248**, 337–345.
- Wood BJ, Walter MJ, Wade J (2006) Accretion of the Earth and segregation of its core. *Nature* **441**, 825–833.
- Yamagata Y, Wanatabe H, Saitoh M, Namba T (1991) Volcanic production of polyphosphates and its relevance to prebiotic evolution. *Nature* **352**, 516–519.
- Zahnle K, Arndt N, Cockell C, Halliday A, Nisbet E, Selsis F, Sleep NH (2007) Emergence of a habitable planet. *Space Science Reviews* **129**, 35–78.
- Zedev V, Russell MJ, Hall AJ, Fallick AE (2000) Genesis of vein-stockwork and sedimentary magnesite and hydromagnesite deposits in the ultramafic terranes of southwestern Turkey: a stable isotope study. *Economic Geology* **95**, 429–446.
- Zerkle AL, House CH, Brantley SL (2005) Biogeochemical signatures through time as inferred from whole microbial genomes. *American Journal of Science* **305**, 467–502.
- de Zwart II, Meade SJ, Pratt AJ (2004) Biomimetic phosphoryl transfer catalysed by iron(II)-mineral precipitates. *Geochimica et Cosmochimica Acta* **68**, 4093–4098.