The Potential for Low-Temperature Abiotic Hydrogen Generation and a Hydrogen-Driven Deep Biosphere

Helge Hellevang,¹ Shanshan Huang,² and Ingunn H. Thorseth²

Abstract

The release and oxidation of ferrous iron during aqueous alteration of the mineral olivine is known to reduce aqueous solutions to such extent that molecular hydrogen, H₂, forms. H₂ is an efficient energy carrier and is considered basal to the deep subsurface biosphere. Knowledge of the potential for H₂ generation is therefore vital to understanding the deep biosphere on Earth and on extraterrestrial bodies.

Here, we provide a review of factors that may reduce the potential for H₂ generation with a focus on systems in the core temperature region for thermophilic to hyperthermophilic microbial life. We show that aqueous sulfate may inhibit the formation of H₂, whereas redox-sensitive compounds of carbon and nitrogen are unlikely to have significant effect at low temperatures. In addition, we suggest that the rate of H₂ generation is proportional to the dissolution rate of olivine and, hence, limited by factors such as reactive surface areas and the access of water to fresh surfaces. We furthermore suggest that the availability of water and pore/fracture space are the most important factors that limit the generation of H₂. Our study implies that, because of large heat flows, abundant olivine-bearing rocks, large thermodynamic gradients, and reduced atmospheres, young Earth and Mars probably offered abundant systems where microbial life could possibly have emerged. **Key Words:** Serpentinization—Olivine—Hydrogen—Deep biosphere—Water—Mars. *Astrobiology* 11, 711–724.

1. Introduction

HYDROUS ALTERATION of the mineral olivine (Mg_{2(1-x)}Fe_xSiO₄) is believed to be a key subsurface source for abiotic molecular hydrogen (H₂) generation (*e.g.*, Sleep *et al.*, 2004; Seyfried *et al.*, 2007; Klein *et al.*, 2009; McCollom and Bach, 2009). Olivine is the main mineral component in ultramafic rocks such as peridotite and dunite, which are abundant in the mantle, in seafloor crustal accumulates, and in ophiolites which represent sections of oceanic lithosphere obducted onto the continental crust (*e.g.*, Rossman *et al.*, 1989; Albrechtsen *et al.*, 1991; Dick *et al.*, 2000; Nicolas and Boudier, 2000; Iyer *et al.*, 2008). Moreover, olivine is abundant in the martian crust in ultramafic accumulates and in picritic ultramafic lavas (Hoefen *et al.*, 2003; Christensen *et al.*, 2005; Mustard *et al.*, 2005). As olivine alters and releases ferrous iron (Fe²⁺), molecular oxygen (O₂) acts as the main electron acceptor in the generation of ferric iron (Fe³⁺) and is consumed. This removal of molecular oxygen (O₂) from groundwaters ultimately leads to reduction of water into H₂ (*e.g.*, Neal and Stanger, 1983; Oze and Sharma, 2007; Hellevang, 2008; McCollom and Bach, 2009).

Molecular hydrogen is observed to seep out in gas mixtures in ophiolites (*e.g.*, Neal and Stanger, 1983; Abrajano

et al., 1988, 1990), in hydrothermal vent fluids hosted in ultramafic rocks at and near slow-spreading mid-ocean ridges (*e.g.*, Kelley *et al.*, 2001, 2005; Charlou *et al.*, 2002), and in continental groundwater and hydrothermal fluids (Stevens and McKinley, 1995; Spear *et al.*, 2005). H₂ forms at these settings by alteration reactions where mafic and ultramafic minerals dissolve and are replaced by hydrated mineral assemblages (Moody, 1976; Kelley *et al.*, 2002, 2004; Früh-Green *et al.*, 2004; Bach *et al.*, 2006; Schulte *et al.*, 2006; Oze and Sharma, 2007; Bach and Früh-Green, 2010).

Knowledge of the alteration of olivine and its potential to generate H₂ is important to the understanding of topics such as the emergence and evolution of microbial life (Sleep *et al.*, 2004; Russell, 2007; Milner-White and Russell, 2008; Sleep and Bird, 2008; Russell *et al.*, 2010), the use of H₂ and H₂-derived species as possible tracers for ongoing water-rock interactions in environments such as the martian surface (*e.g.*, Atreya *et al.*, 2007; Mumma *et al.*, 2009; Parnell *et al.*, 2010), and the deep subsurface biosphere driven by hydrogen or hydrogen-derived species (*e.g.*, Gold, 1992; Stevens and McKinley, 1995; Pedersen, 1997; Chapelle *et al.*, 2002; Kelley *et al.*, 2004; Takai *et al.*, 2004; Nealson *et al.*, 2005; Spear *et al.*, 2005). Microbes in the deep biosphere encompass a

¹Department of Geosciences, University of Oslo, Oslo, Norway.

²Department of Earth Science and Center for Geobiology, University of Bergen, Bergen, Norway.

wide range of energy metabolisms (*e.g.*, Kaplan *et al.*, 1963; Claypool and Kaplan, 1974; Teske *et al.*, 2003; Takai *et al.*, 2004; Schippers *et al.*, 2005; Schippers and Neretin, 2006; Wortmann *et al.*, 2007; Adhikari and Kallmeyer, 2010), in which H₂ is an integral part (*e.g.*, Morita, 2000; Spear *et al.*, 2005). The basal nature of H₂ in these systems suggests that, to some extent, the deep biosphere is dependent on the generation rate of H₂ or H₂-derived species (*e.g.*, Hellevang, 2008).

It has been recognized that the potential for H₂ generation is dependent on the partitioning of ferrous iron between mineral phases, the abundance of unaltered olivine, and temperature (*e.g.*, Sleep *et al.*, 2004; Seyfried *et al.*, 2007; Klein *et al.*, 2009; McCollom and Bach, 2009). The aim of our study was to evaluate additional factors that may potentially reduce the rate and amount of H₂ production in subsurface systems. Because a large part of seafloor and ophiolite alteration occurs in low-temperature systems, and the upper temperatures of microbial growth have been recorded to 121–122°C (Kashefi and Lovley, 2003; Takai *et al.*, 2008), we limited this review to relatively cold systems. For thermodynamic calculations, we used 80°C, which is a core temperature for thermophilic to hyperthermophilic microorganisms (Brock, 1985; Kashefi and Lovley, 2003; Roussel *et al.*, 2008; Torsvik and Øvreås, 2008). The factors that are covered are related to the effect of aqueous redox reactions in the nitrogen, carbon, and sulfur systems on mineral reaction rates and hydrodynamic conditions; and a brief section on the constraint of H₂ formation on the availability of water is given. Finally, the implication of inorganic hydrogen generation on the emergence of life on Earth and on the potential for hydrogen production and life on extraterrestrial planets is discussed. The results are organized by presenting factors that limit H₂ generation, together with numerical simulations.

2. Methods

All thermodynamic calculations were performed by using the geochemical code PHREEQC-v2 (Parkhurst and Appelo, 1999). The standard state employed was unit activity for pure minerals and H₂O at any temperature and pressure. For aqueous species other than H₂O, the standard state was unit activity of the species in a hypothetical 1 molal solution referenced to infinite dilution at any temperature and pressure. For gases, the standard state was unit fugacity of a hypothetical ideal gas at 1 bar of pressure.

We used the thermodynamic data for the minerals and aqueous species listed in the phreeqc.dat database with the following modifications: thermodynamic data for the minerals brucite (Mg(OH)₂), magnetite (Fe₃O₄), fayalite (Fe₂SiO₄), and forsterite (Mg₂SiO₄), were copied from the phreeqc.llnl.dat database file, as was the aqueous redox speciation of Fe. Activities of charged aqueous species were calculated according to the WATEQ Debye-Hückel equation (Truesdell and Jones, 1974). The olivine composition used in the calculations is Fo90, which represents a solid-solution mix between the forsterite (90%) and fayalite (10%) end members. The numerical simulations were done at 80°C and 1 bar pressure. For the sulfur and carbon systems, an initial gas phase was defined to consist of molecular nitrogen (N₂) and O₂, corresponding to the present-day atmosphere. The initial

aqueous solution had a NaCl content that closely corresponded to present-day seawater (Table 1).

3. Results

The potential for H₂ generation is dependent on the amount of ferrous iron supplied to the aqueous solution from olivine, the subsequent oxidation of the ferrous iron to ferric iron, and the precipitation of ferric iron into minerals such as magnetite (Fe₃O₄). The maximum potential for H₂ generation is given if magnetite is the only secondary mineral (*e.g.*, Seyfried *et al.*, 2007; Hellevang, 2008; McCollom and Bach, 2009). However, the potential is reduced if ferrous iron is removed from the aqueous solution without oxidation. This happens when ferrous iron is incorporated into other secondary minerals like solid solutions of ferrous brucite (Mg_{1-x}Fe_x(OH)₂) and Fe-serpentine (MgFe(II)Fe(III))₃Si₂O₅(OH)₄ (Seyfried *et al.*, 2007). The extent of iron substitution and the effect on H₂ generation was treated in detail by Seyfried *et al.* (2007) and will not be repeated here. We examine below three additional factors that associate this process for the potential for H₂ generation: (a) the dissolution rate of olivine and hence the supply rate of ferrous iron to the aqueous solutions; (b) the presence of other aqueous redox couples that directly or indirectly affects the aqueous activities of O₂ and hence H₂; and (c) pore space and the availability of water.

3.1. The olivine dissolution rate

The amount of ferrous iron supplied to the water from olivine within a given time interval is given by the amount of the mineral that dissolves multiplied with the stoichiometric moles of iron per mole olivine. For a typical seafloor olivine (Fo90 = Mg_{1.8}Fe_{0.2}SiO₄), this corresponds to

$$\frac{dn_{\text{Fe}^{2+}}}{dt} = v \frac{dn_{\text{Fo90}}}{dt} \quad (1)$$

where n denotes moles, t time, and v the stoichiometric coefficient ($v=0.2$ for Fo90). Data of far-from-equilibrium olivine dissolution rates are available from several reports for a

TABLE 1. DEFINITION OF THE INITIAL CONDITIONS FOR THE PHREEQC SIMULATIONS AND POSSIBLE SECONDARY PHASES THAT PRECIPITATED TO EQUILIBRIUM

Properties	Initial values
V_{aq}	82 mL
V_{g}	168 mL
m_{Fo90}	180 g
<i>Aqueous species</i>	
Na ⁺	0.5237 mol/kgw
Cl ⁻	0.5200 mol/kgw
Fe _{tot}	0.001 mol/kgw
O ₂	Eq. with atm ($P=0.21$ atm)
pH	5
<i>Secondary mineral phases (initial moles)</i>	
Magnetite	0
Hematite	0
Chrysotile	0
Talc	0
Quartz	0
Brucite	0
Pyrite	0

range of conditions (e.g., Grandstaff, 1978; Pokrovsky and Schott, 2000; Rosso and Rimstidt, 2000; Oelkers, 2001; Golubev *et al.*, 2005). The laboratory experiments suggest that the dissolution rate has a 0.5 order dependence on proton activity at acidic conditions (Pokrovsky and Schott, 2000; Rosso and Rimstidt, 2000; Oelkers, 2001), whereas the rates appear to become pH independent at $\text{pH} > 9$ (Pokrovsky and Schott, 2000). The dissolution rate can therefore be written as

$$\frac{dn_{\text{Fo90}}}{dt} = \bar{S}(k_{+,1}a_{\text{H}^+}^{0.5} + k_{+,2}) \quad (2)$$

where $\bar{S}$ is the average reactive surface area expressed in square meters, $a_{\text{H}^+}^{0.5}$ is the H^+ activity, and the 25°C dissolution rate coefficients $k_{+,1}$ and $k_{+,2}$ can be expressed as (Pokrovsky and Schott, 2000)

$$k_{+,1} = \frac{[\text{>Si}_2\text{O}-\text{H}^+]}{2.2 \times 10^{-5} K_{\text{ads}}^*} \cdot \left(1 + K_{\text{ads}}^* a_{\text{H}^+}^{0.5} + \frac{a_{\text{Mg}^{2+}}^2}{K_{\text{ex}} a_{\text{H}^+}^4} \right) \quad (3)$$

and

$$k_{+,2} = 1.62 \times 10^{-10} [\text{>MgOH}_2^+] \quad (4)$$

where $[\]$ denotes concentration, $\text{>}i$ are surface complexes, K_{ads}^* and K_{ex} are the apparent equilibrium constants for the surface adsorption and exchange reactions, respectively. The implications for olivine dissolution rates and H_2 generation are that any adsorbents that compete for olivine surface sites may affect the rates. The temperature dependence of the dissolution rate has been found to follow an apparent activation energy of 63.8 kJ/mol, which at low temperatures corresponds to an increase of approximately 1 order of magnitude per 30°C increase (Oelkers, 2001).

A simplified model for the temporal evolution of H_2 formation in seafloor hydrodynamic systems can be represented by a moving water mass as a closed-system package that is not mixed with other aqueous solutions but reacted with olivine according to a kinetic rate law. The time needed for waters to alter olivine and generate H_2 in a hydrothermal system can then be estimated. We simulated such a package represented by a saline aqueous solution in contact with Fo90 at 80°C. The kinetic coefficients were estimated from Oelkers (2001) and Pokrovsky and Schott (2000). Ten moles of Fo90 were initially defined to react with 1 kg of solution. No dependence was made between the reactive surface area and the mass of Fo90 present, and the rate was hence independent of the mass until all Fo90 was dissolved and the reaction stopped. As the average reactive surface area of olivine is likely to vary by orders of magnitude because of differences in grain size and degree of exposure (pore space versus fracture), we varied $\bar{S}$ from 0.1 to 10 m^2 .

The temporal evolution of H_2 generation for various average reactive surface areas is shown in Fig. 1. For a solution with a reactive surface area of 10 square meters per kilogram of water (m^2/kgw), H_2 at a millimolar concentration and higher was reached after only 6 years of Fo90 alteration. At 1 m^2/kgw , the time needed to reduce the solution and form H_2 increased to about 60 years. Because the rate of Fo90 dissolution was nearly constant during the simulated times, the time t needed to generate millimolar concentration of H_2 followed $t = \alpha/\bar{S}$, that is, increased inversely proportional to the

FIG. 1. The temporal evolution of the amount of H_2 that can form from a water package reacting with olivine of different reactive surface areas (S) varying from 0.1 to 10 m^2/kgw . For the highest average reactive surface area, high millimolar concentrations are reached after 6 years. The time needed to reach millimolar concentrations increases inversely proportional to the reactive surface area, that is, at 0.1 m^2/kgw it takes 600 years to reach the same high millimolar concentrations.

reactive surface area. However, as key factors such as average reactive surface area and temperature are likely to vary with time as a water package travels in a circulating system, such simple linear predictions are not applicable to natural systems.

Another factor that may affect the dissolution rate of olivine is surface passivation by secondary coatings or modifications of the surface morphology. From laboratory experiments, Béarat *et al.* (2006) observed that a layer of secondary minerals formed on dissolving olivine and explained this formation by a combination of non-stoichiometric dissolution leaving a silica-rich leached layer and the precipitation of amorphous silica. The progress of olivine alteration has been explained partly by exfoliation and partly by diffusive transport of ions through the surface layer (Kim *et al.*, 2005; Béarat *et al.*, 2006). Welch and Banfield (2002) found that the reactivity of olivine in acid solution in the presence of *Acidithiobacillus ferrooxidans* was passivated by catalyzed surface oxidation and adsorption of Fe^{3+} . At present, the extent of passivation is still not well understood. We thus conclude that, in natural systems where secondary coatings are formed and affected by microbial activities and passivating layers grow in a confined environment without exfoliation, diffusion-controlled dissolution with progressively lower release rates with time may reduce the potential for H_2 generation.

3.2. The effect of aqueous redox couples

Nitrogen, sulfur, and carbon occur in a range of redox states in natural waters. These compounds may affect the degree aqueous solutions can be reduced and, hence, the effect on the potential for H_2 formation.

Nitrogen occurs from the most-reduced cyanide (CN^-) and ammonium (NH_4^+), with N valence states of -5 and -3 ,

respectively, to the oxidized nitrate (NO_3^-) where nitrogen is in a N(+5) valence state. Molecular nitrogen (N_2) is in an intermediate redox state with N(+0). In redox reaction sequences, NO_3^- is second after O_2 and followed by oxidized manganese and iron. This means that the thermodynamic potential for NO_3^- to oxidize other compounds such as ferrous iron is second after O_2 . The present-day deep seawater has a N_2 concentration of *ca.* 16 ppm (Craig *et al.*, 1967), whereas dissolved NO_3^- is below 2.5 ppm (Johnson *et al.*, 1989). At low temperatures and without catalysts, the formation of N_2 from the reduction of NO_3^- and NO_2^- (nitrite) and the oxidation of NH_4^+ is irreversible because of the strong triple-bonded nitrogen atoms in N_2 . However, in the presence of catalysts such as metallic Fe and Ni and Fe-Ni alloys, and at reducing conditions, nitrogen has been shown to be further reduced to ammonium even down to low temperatures (Smirnov *et al.*, 2008). The reduction of NO_3^- to N_2 can be written in two steps through the unstable intermediate nitrite:

where the double arrow indicates equilibrium and the right arrow indicates an irreversible reaction in the forward direction. Assuming equilibrium between NO_3^- and N_2 , the aqueous O_2 activity in a system containing NO_3^- and N_2 can be found from

$$a_{\text{O}_{2,\text{aq}}} = 1.25 \sqrt{\frac{K_{(5)} a_{\text{H}^+}}{a_{\text{H}_2\text{O}}}} \cdot \frac{a_{\text{NO}_3^-}}{\sqrt{a_{\text{N}_{2,\text{aq}}}}} \quad (6)$$

where $K_{(5)}$ is the equilibrium constant for reduction of NO_3^- to N_2 . As oxidation of ferrous iron consumes O_2 , NO_2^- is irreversibly decomposed to N_2 and O_2 , and NO_3^- is correspondingly consumed according to the equilibrium in Reaction 5. Because present-day deep seawater contains less than 2.5 ppm NO_3^- , we conclude that, even at the extreme case where $\text{NO}_3^-/\text{N}_{2,\text{aq}}$ equilibrium is assumed, NO_3^- does not interfere with H_2 generation.

As for nitrogen, sulfur occurs in a range of redox states from the oxidized sulfate (SO_4^{2-}) with S(+6) to the reduced H_2S or HS^- with S(-2). The reduction of SO_4^{2-} to HS^- can be written in a series of aqueous equilibrium reactions according to

If equilibrium between SO_4^{2-} and all intermediates in the reduction series (7) are assumed, the direct reduction of SO_4^{2-} to HS^- can be written as

Then from the law of mass action, the activity of O_2 is

$$a_{\text{O}_{2,\text{aq}}} = \sqrt{\frac{K_{(8)} a_{\text{H}^+}}{a_{\text{HS}^-}}} \cdot \frac{a_{\text{SO}_4^{2-}}}{a_{\text{HS}^-}} \quad (9)$$

where $K_{(8)}$ is the equilibrium constant for Reaction 8. This expression suggests that, given thermodynamic equilibrium

in the aqueous sulfur system, the activity of O_2 is constrained by the activity ratio of SO_4^{2-} over HS^- . As reduced conditions favor the stability and growth of sulfide minerals and elemental sulfur, the total amount of sulfur in the aqueous solution will be reduced by the mineral growth, and the SO_4^{2-} activity will be correspondingly reduced.

To estimate the effect of SO_4^{2-} on the potential for H_2 generation, we performed numerical simulations of Fo90 alteration with initial SO_4^{2-} concentrations of 0.029 mol/kgw, which corresponds to that of seawater (Nordstrom *et al.*, 1979), and compared to simulations without initial SO_4^{2-} (Fig. 2). The mineral pyrite (FeS_2) was selected as proxy to illustrate the effect of secondary sulfide mineral growth on the aqueous sulfur activity. Examples of other sulfide-containing minerals that are likely to form in these systems and would have a similar effect are pyrrhotite (Fe_{1-x}S) and mackinawite ($(\text{Fe,Ni})_{1+x}\text{S}$). The simulations show that, when Fo90 reacts in a sulfate-containing solution, SO_4^{2-} is reduced to HS^- and H_2S as O_2 is consumed by the oxidation of the ferrous iron (Fig. 2a). As the reaction proceeds, pyrite precipitates, which reduces the amount of sulfur in the water-gas system (Fig. 2b). Eventually, after *ca.* 0.08 mol of Fo90 have dissolved (11.76 g in 82 mL of water), SO_4^{2-} drops to $<10^{-15}$ mol/kgw, and H_2 is produced to high concentrations (Fig. 2c, 2d). A comparison between the effect of Fo90 alteration on the aqueous O_2 activity and the amount of gas-phase H_2 with and without sulfur is shown in Fig. 3. The simulations suggest that the O_2 activity drops rapidly to $<10^{-67}$ (Fig. 3a), and H_2 is correspondingly produced at percent levels (Fig. 3b) in a system without oxidized sulfur compounds. On the other hand, in a system that contains seawater level of SO_4^{2-} , the O_2 activity remains above 10^{-64} (Fig. 3a), and the H_2 in the gas phase is only at part-per-million levels until 0.08 mol of Fo90 is reacted (see Fig. 2c). At high Fo90/water ratios, however, the time required to dissolve 0.08 mol/kgw of Fo90 is likely short, and the effect of SO_4^{2-} is hence limited.

Natural waters contain dissolved inorganic and organic carbon, and particulate inorganic and organic carbon, with the carbon valence states from the most oxidized CO_2 species with C(+4) to reduced species such as methane (CH_4) with C(-4). Ocean water in contact with an atmosphere exchanges CO_2 and approaches thermodynamic equilibrium with the gas. The dissolved CO_2 reacts with water and forms carbonic acid, H_2CO_3 , which dissociates to form bicarbonate and carbonate ions:

At progressively more reducing conditions, the C(+4) carbon in dissolved CO_2 is thermodynamically favored to be reduced in a series of steps to CH_4

Assuming equilibrium among all intermediates in Reaction 11 or the direct reaction of CO_2 with water to form CH_4 , the redox equilibrium between aqueous CO_2 and CH_4 can be expressed by

FIG. 2. The effect of sulfur on the generation of H_2 . (a) SO_4^{2-} is transformed to HS^- and H_2S before the aqueous solution is reduced enough to generate significant amounts of H_2 ; (b) the formation of pyrite (or other comparable sulfide minerals) reduces the amount of sulfur in the aqueous-gaseous system; (c) H_2 forms also at the presence of SO_4^{2-} , but the amount is limited; and (d) water and N_2 dominates the gas phase. At the latest stage H_2 clearly appears, whereas H_2S is a minor component.

FIG. 3. (a) The log activity of O_2 in the aqueous phase and (b) the fraction of H_2 in the gas phase at zero initial SO_4^{2-} and an initial SO_4^{2-} concentration that corresponds to average seawater (2.9×10^{-2} molar). It is clear that for the initial stage of olivine alteration SO_4^{2-} -rich solutions do not reach those low-oxygen activities needed to produce large amounts of H_2 . The required amount of Fo90 dissolved per kilogram aqueous solution to reduce the SO_4^{2-} sufficiently to allow significant H_2 production is, however, small (0.08 mol $\sim$ 11 g).

The O_2 activity is then fixed at equilibrium between $CO_{2,aq}$ and $CH_{4,aq}$ by

$$a_{O_{2,aq}} = \sqrt{K_{(12)} a_{H_2O}^2 \frac{a_{CO_{2,aq}}}{a_{CH_{4,aq}}}} \quad (13)$$

where $K_{(12)}$ is the equilibrium constant for Reaction 12. In closed systems, a constraint on the upper aqueous CO_2 activity is given by carbonate minerals as they are stabilized at increasing CO_2 contents and precipitate out (Griffith and Shock, 1995).

We simulated the effect of carbon on the potential for H_2 generation at various initial amounts of dissolved CO_2 and conditions as given in Table 1. Figure 4 shows the aqueous activity of H_2 and CH_4 as Fo90 is dissolved in the aqueous solution. Initial aqueous inorganic carbon concentrations were varied from 0.0012 to 0.12 M. At the lowest carbon content, the aqueous solution is rapidly reduced and forms significant amounts of H_2 (Fig. 4). As the carbon content increases by 1 order of magnitude to 0.012 M, more Fo90 is required to react before high levels of H_2 are reached. Finally, upon further increasing carbon by 1 order of magnitude, the H_2 activity does not reach values higher than 10^{-9} for the added Fo90. In simulations shown in Fig. 4, the amount of carbon is constant, but the CO_2 pressures vary. As the aqueous solutions are reduced, aqueous CO_2 may be inorganically or biologically converted to CH_4 , and the CO_2 pressure drops. This allows the O_2 activity, expressed in Eq. 13, to drop sufficiently to allow significant H_2 formation. In open systems with constant CO_2 pressure, the CO_2 aqueous activity is fixed by the corresponding CO_2 fugacity, and the potential for H_2 generation is likely to be more limited.

3.3. Pore space and water availability as limiting factors

The alteration of ultramafic or mafic rocks and minerals leads to the consumption of water into less dense hydrous minerals. The consequence of this is volume expansion, reduction of the pore space, and a consumption of pore-space water. The closed-system isochemical alteration of olivine corresponds to the type 1 rock-dominated alteration as defined by Beard *et al.* (2009), where pre-existing voids and fractures are the sources of water and the alteration is observed to be limited.

FIG. 4. The effect of dissolved carbon on the generation of H_2 . The figure shows log activity of CH_4 (solid lines) and H_2 (dashed lines) as a function of moles of Fo90 added to the aqueous solution defined in Table 1. Initial total inorganic carbon concentrations from 0.0012 to 0.12 N (mol/kgw) were simulated.

The first factor that limits the olivine alteration in a closed system is the amount of water available. For a given amount of water, a maximum alteration potential is given from the stoichiometric amount of water incorporated into the hydrous phases. For example, the alkaline isochemical alteration of Fo90 into pure Mg-serpentine and Mg-brucite, magnetite, and H_2 can be written as

Each mole of Fo90 altered produces 0.5 mol of serpentine, 0.3 mol of brucite, and hence consumes 41/30 mol of water. This means that approximately 24.63 g of water is consumed for every 147 g of Fo90 altered, or *ca.* 24.63 mL water is consumed for every 43.49 mL Fo90 altered. Any lower water content will only lead to partial alteration, until more water is gained access to the fresh olivine.

The second factor is the volume expansion of the solid phases that reduces the pore volume of the rock. The volume changes following olivine hydration include both the volume changes of the pore space and the aqueous phase. The total change in mineral volume ΔV_{min} can be estimated by the difference in reduced volume following olivine dissolution and the added volume of the secondary phases:

$$\Delta V_{min} = (-\Delta V_{ol} + \sum_i \Delta V_i) \Delta \xi \quad (15)$$

where ξ is the reaction progress given as moles of olivine released to the aqueous solution, V is volume, and subscripts i and ol denote secondary phases and olivine, respectively. Because of the lower densities of the secondary phases compared to olivine, the mineral volume changes are always positive. For a water-saturated closed system, the volume change of the aqueous solution corresponds to the pore-volume change, leading to changes in the specific volume of the aqueous phase and corresponding pressure changes. The specific volume is given by

$$V_\phi = \frac{V_{aq}}{n_{aq}} \quad (16)$$

where V is the specific volume, and V and n denote volume and moles of the aqueous phase, respectively. The pressure can be estimated by using a proper equation of state for water such as defined by Mao and Duan (2008). Equations 15–16 show that if the volume of aqueous solution consumed is greater than the reduction in pore space volume, the pore pressure will decrease, whereas if the volume of aqueous solution suffers a smaller reduction than the pore volume, then the internal pressure will increase.

Because olivine alteration consumes water, a maximum degree of alteration for a closed system can be estimated for a given porosity. We estimated the maximum extent of olivine alteration in an isochemical closed system as a function of pore-volume fraction, assuming a fully water-saturated pore space and no lower limit for the water activity to stop the process. The initial conditions and the secondary phases were the same as in Table 1, except that no gas phase was defined. Figure 5 shows the maximum percentage of olivine that can be

FIG. 5. The maximum possible percentage of olivine altered as a function of initial water content illustrated as pore- or fracture-volume fraction. Because water is consumed in the alteration, the maximum extent of alteration is given by the volume of water available per volume olivine. The simulations suggest that, for a complete conversion of Fo90 to secondary minerals, *ca.* 36% water-saturated pore/fracture volume is required.

hydrated as a function of rock/water content given as initial pore volume fraction. The simulations suggest that, for a complete conversion of Fo90 to secondary minerals, *ca.* 36% water-saturated pore/fracture volume is required. Therefore, in a closed system at low water contents, because of either the presence of a gas phase reducing the water saturation or limited pore space, olivine can only be partly altered (Fig. 5).

We simulated the same system as in the previous paragraph and estimated the volume changes of the solid and aqueous phases and the maximum potential for olivine alteration as a function of initial pore-volume fraction. In this case, we also limited the alteration potential by including proper activity calculations for the water phase, using the PHREEQC code. The total volume of the system was constant, but pressure changes following the alteration were not estimated. Densities of olivine, the secondary mineral phases, and the aqueous phase used for the calculations are listed in Table 2. Figure 6 shows the volume changes of the aqueous phase and the pore space and the maximum percentage of Fo90 that can be hydrated. The simulations suggest that the volume change of the pore space is less than that of the aqueous phase and that the maximum alteration potential therefore is given by the amount of water present (Fig. 6a). In such a closed system, the hypothetical expansion of the water phase into the pore space would lead to lower pressures, which would promote fluid flow into the system or rheological collapse. For higher-temperature systems with lower water densities, the difference between the volume changes would be larger. Because the reduced water activities limited complete hydration in this simulation, the maximum alteration potential was lower (Fig. 6b) than for the previous simulation (Fig. 5).

TABLE 2. DENSITIES OF MINERAL PHASES AND THE AQUEOUS SOLUTION USED TO ESTIMATE VOLUME CHANGES FOLLOWING OLIVINE ALTERATION

Phase	Density (g/cm ³)
Fo90	3.38
Chrysotile	2.53
Brucite	2.39
Hematite	5.15
Magnetite	5.30
Aq (H ₂ O + salts)	1.00

4. Discussion

4.1. Factors constraining the potential for H₂ generation

We have demonstrated that SO₄²⁻ may postpone generation of H₂ and reduce the aqueous concentration of H₂ by increasing the aqueous O₂ activity. The effect was, however, suggested to be small, as SO₄²⁻ was rapidly reduced at modest amounts of olivine dissolved (<0.1 mol Fo90/kgw). NO₃⁻ was shown to be irreversibly reduced to N₂ and should have little or no effect on the H₂ generation. When it comes to the carbon species, aqueous Fischer-Tropsch-type reactions, such as Reactions 12 and 13, have served to explain hydrocarbon plumes from hydrothermal sources such as the Lost City and Rainbow hydrothermal fields where CH₄ coexists with H₂ (*e.g.*, Holm and Charlou, 2001; Proskurowski *et al.*, 2008). The reduction of CO₂ or CO to CH₄, however, is known to only occur at elevated temperatures and in the presence of catalysts, such as magnetite (*e.g.*, Berndt *et al.*, 1996). At high temperatures and in the presence of metal-bearing catalysts such as magnetite, awaruite, native Fe, and Ni-Fe compounds, H₂ generation may be affected by the presence of CO₂ in two ways: (1) CH₄ formation from CO₂ consumes H₂ and drives the dissociation of water into H₂ and O₂ forward and (2) more ferrous iron needs to be oxidized as O₂ is supplied from CO₂. At low temperatures and without any bioactivity, the formation of CH₄ from CO₂ is likely to be limited (*e.g.*, McCollom and Bach, 2009), and CO₂ and CH₄ will most likely coexist in metastable equilibria. If this is the case, the O₂ activity given by Eq. 13 is no longer dependent on the activity ratio of CO₂ and CH₄, and the potential for H₂ production may be unaffected by CO₂. The effect of aqueous carbon, sulfur, and nitrogen on the potential for hydrogen generation is hence suggested to be minor. The other factors treated here are the dissolution rates and water availability to fresh surfaces in closed systems. It was shown that the fraction of pore or fracture volume and the amount of water determine the maximum amount of olivine altered in such systems. Because these constraints are only valid for closed systems, we show in the next section that the impact on the emergence of life is likely to be minimal, as one of the key assumptions for the emergence of life is serpentinization in open alkaline systems (*e.g.*, Martin and Russell, 2007; Russell, 2007; Russell *et al.*, 2010).

4.2. Potential for H₂ generation and the emergence of life

During the first millions of years after the accretion of Earth in the Hadean Eon, the surface of Earth was hot and

FIG. 6. Volume changes in pore/fracture space and aqueous solution following isochemical (closed system) and isovolumetric (constant volume) hydration of Fo90. (a) volume of pore space and aqueous solution as a function of percentage of Fo90 dissolved and (b) the maximum percentage of Fo90 dissolved for various initial pore- or fracture-volume fractions. It is evident that the volume of aqueous solution decreases faster than the volume of pore space. This would either result in a decrease of the pore pressure, leading to migration of external water into the pore space, or to a collapse of the pore space.

hostile. After 200–400 million years, however, detrital zircons formed, which indicates liquid surface waters and surface temperatures below the boiling point of water (Mojzsis *et al.*, 2001; Wilde *et al.*, 2001; Watson and Harrison, 2005). Moreover, inversion tectonics (Cooper and Williams, 1989) or early plate tectonics (*e.g.*, Harrison *et al.*, 2005) were active and refreshed the rock surfaces in contact with liquid water. Earth was then heavily bombarded, which heated up the thin lithospheric shell at least locally. The Hadean ended after the Late Heavy Bombardment at 3.9–3.8 Ga (Tera *et al.*, 1974). Trace evidence of putative microbial life from shortly after the Late Heavy Bombardment indicates that life had already emerged (*e.g.*, Mojzsis *et al.*, 1996; Furnes *et al.*, 2004).

The tectonics during Hadean Earth reworked crustal material, and mantle convection depressurized and partially melted the hot mantle at greater depths and higher pressures than modern analogues. This led to high-magnesium melts that formed extensive ultramafic intrusives and komatiitic lavas (Nisbet and Sleep, 2001). Komatiitic lavas resemble ultramafic minerals such as olivine, with high magnesium contents, low silica, and Fe^{2+} iron of *ca.* 10% (Smith *et al.*, 1980). Indeed they are largely composed of olivine, often with spinifex texture. The global potential for H_2 generation in the Hadean can thus be compared to the present potential by assuming that the ultramafic lavas and intrusives chemically corresponded to modern olivine-bearing ultramafic rocks. At present, ultramafic mantle rocks are mainly exposed to seawater along amagmatic sections of slow- to ultraslow-spreading mid-ocean ridges (Dick *et al.*, 2003) and at faster-spreading ridges where deep conductive extensional faults and fractures occur (Baker *et al.*, 1994). If we assume that plate tectonics operated during the Hadean Eon, the higher heat flow from the warmer mantle would likely have increased the partial melting of the mantle and led to extensive eruption of komatiitic lavas. It is therefore likely that, on a global scale, more ultramafic material was exposed to liquid water in the Hadean than at the present time.

The evolution of the atmospheric O_2 level has strongly influenced the oxidation level of seawater. During the Hadean and Archean eons, the atmosphere was likely to have been moderately oxidized and dominated by CO_2 and N_2 with low levels of O_2 (Shaw, 2008). Sometime between 2.45 and 2.22 billion years ago, the atmospheric O_2 rose from the low levels to higher than 10^{-5} times the present atmospheric level (Bekker *et al.*, 2004) and thereafter with a stepwise increase to the present level due to the advent of microbial photosynthetic activity. Because of the low O_2 levels before 2.45–2.22 billion years ago, ocean SO_4^{2-} was low with concentrations $< 200 \mu\text{M}$, with maximum values of 2–3 orders of magnitude lower than present-day seawater (Bekker *et al.*, 2004). Thus, based on the previous sections on the effect of initial SO_4^{2-} and O_2 on the rate of H_2 generation, we conclude that the Hadean and Archean atmospheres together with water chemistry promoted enhanced H_2 generation compared to the present time.

Alkaline springs analog to the present-day Lost City hydrothermal field (Kelley *et al.*, 2005) have been suggested as potential sites for the emergence of life (Martin and Russell, 2007; Russell, 2007; Russell *et al.*, 2010). Such systems are driven by serpentinization where H_2 and possibly light hydrocarbons form (Kelley *et al.*, 2001, 2004, 2005; Fröh-Green *et al.*, 2004; Proskurowski *et al.*, 2008). In these systems, hot alkaline fluids from deep underground meet cold acidic surface waters where stable steep thermodynamic gradients form. These thermodynamic gradients, combined with the availability of building blocks of life, are hypothesized to have provided favorable conditions for the emergence of chemolithoautotrophic microbial life (Russell *et al.*, 1989, 2010; Kelley *et al.*, 2002; Russell, 2007; Martin and Russell, 2007).

We further suggest that the availability of water and pore/fracture space are the most important factors that limit the dissolution of olivine and generation of H_2 . This has implications for the colonization and spreading of microbial life on early Earth and on other habitable planets and moons. From constraints on pore space and water volumes, we suggest that

the bulk H_2 generation should be in open systems such as permeable ultramafic sediments and fracture or fault zones, where fresh aqueous solutions can react for sufficient time to produce H_2 . From the olivine-bearing cumulates or lavas, H_2 and H_2 -derived aqueous species can then migrate as diffuse flows through overlying permeable units to the seafloor (Fig. 7). Once formed, the microbial communities could slowly develop and colonize the permeable seafloor, and the colonies could be carried along by plate tectonics (Russell, 2007, and references therein). Alternatively, microbial communities protected in low-density biofilms could detach from the mounds and be carried further by ocean currents (Fig. 7). Finally, because of the larger heat flow, more abundant ultramafic rocks, larger thermodynamic gradients offered by the CO_2 -rich atmosphere, and more-reduced oceans, the young Earth probably offered more systems similar to the Lost City field where life could possibly have emerged.

4.3. Potential for H_2 generation and life on extraterrestrial bodies

Although recently questioned by Zahnle *et al.* (2010), it is generally accepted that CH₄ is released in large quantities from regions on Mars (Formisano *et al.*, 2004; Mumma *et al.*, 2009). One indication of the source of the methane is given by recent numerical simulations that suggest CH₄ is released in pulses a short time before observation and from a broad

source region rather than from point sources (Mischna *et al.*, 2011). One of the potential causes for CH₄ formation on a regional scale is serpentinization that occurs beneath the surface of the planet (Oze and Sharma, 2005). The discovery of serpentine minerals has confirmed that hydration of olivine occurs, or has occurred, on Mars (Ehlmann *et al.*, 2010). Indeed, Mars houses olivine minerals (Hoefen *et al.*, 2003; Koeppen and Hamilton, 2008) and liquid water (Malin and Edgett, 2000) where possible hydrothermal processes (Marzo *et al.*, 2010; Morris *et al.*, 2010) may have provided the thermodynamic conditions for serpentinization to take place (Oze and Sharma, 2007; Quesnel *et al.*, 2009). These geological settings are likely not unique to Earth and Mars and may be common to the other terrestrial bodies in the Universe.

Water, a requisite for H_2 generation, is probably one of the most abundant molecules in the Universe (Kotwicki, 1991). It has been detected on a number of terrestrial planets and natural satellites, for example, Venus (Svedhem *et al.*, 2007), Mercury (Zurbuchen *et al.*, 2008), Titan (Griffith *et al.*, 2003), and Earth's moon (Feldman *et al.*, 1998), although mainly in the form of ice. Evidence of the existence of liquid water, which is essential for serpentinization and life on Earth, has been reported on Mars, Europa (Carr *et al.*, 1998), Enceladus (Waite *et al.*, 2009), and Titan (O'Brien *et al.*, 2005). Furthermore, liquid water is proposed to have existed on many extraterrestrial bodies at certain periods of their evolutionary history (Kasting, 1988; Baker *et al.*, 2005).

FIG. 7. Sketch illustrating H₂ generation and implications for the emergence and spreading of microbial life on early Earth. (1) The bulk H₂ generation occurred in open conductive ultramafic rock systems where availability of water and pore space were not limiting factors and where fresh solutions had sufficient time to be reduced; (2) Generated H₂ migrated from the ultramafic rocks and through overlying stratigraphic units such as pillow lavas and sediments and gave rise to microbial colonization in these units (e.g., Furnes *et al.*, 2006); (3) at the interface between seawater and reduced alkaline solutions, emitted from the ultramafic rocks, sharp thermodynamic gradients formed, providing favorable conditions for the emergence of microbial life (e.g., Russell, 2007); (4) from such systems, the microbial colonization of the seafloor occurred within permeable sediments or lavas and was carried along by plate tectonics (Russell, 2007, and references therein), or alternatively by the detachment of low-density protective biofilms or mats from the mounds carried along the seafloor by ocean currents. Color images available online at www.liebertonline.com/ast

Olivine and its high-pressure equivalents are believed to be the major mineral components of the mantles of all Earth-like planets and moons (Sohl *et al.*, 2002). The main constituent of pallasite, a differentiated meteorite whose composition reflects the interiors of parent bodies, is olivine (Buseck, 1977). Olivine has been identified, for example, on Mars (Papike *et al.*, 2009), Mercury (Sprague *et al.*, 2009) and Earth's moon (Lucy, 2004). Driven by the heat transfer from the mantle to the surface during the cooling of the Earth-like planets and satellites, hydrothermal processes are likely to operate when water is present (Vance *et al.*, 2007). Analysis of carbonate minerals in a meteorite from ancient Mars has indicated that this process happened on early Mars (Treiman *et al.*, 2002). Based on the differential structure that consists of a hot rocky core and a water shell, and the observation of its active region on the south pole, Glein *et al.* (2008) asserted that such a cooling-induced hydrothermal process also occurred on early Enceladus. In addition, impact-induced hydrothermal activity is an important process in our Solar System (Koeberl and Reimold, 2004; Abramov and Kring, 2005).

Based on the availability of liquid water, olivine, and local hydrothermal activity, we conclude that H₂ generation and possible conditions suitable for the emergence of life may be, or may have been, present on Mars and other Earth-like planets and moons. H₂ is the strongest electron donor possible to provide energy for microorganisms on Earth. Here, we have provided model calculations to demonstrate that, with suitable rocks and conditions, subsurface H₂ production is possible elsewhere. Furthermore, the discovery of hydrogen peroxide (H₂O₂) on the surface and in the atmosphere of Mars (Clancy *et al.*, 2004; Encrenaz *et al.*, 2004) suggests that the most habitable environment on Mars would be deep in the subsurface where the activity of H₂O₂ is zero. There, the potential for H₂ generation through serpentinization of olivine in low-temperature systems will be limited by the same factors as reviewed in this paper.

5. Summary

As H₂ is a key ingredient in the emergence of life and a basal part of the deep biosphere, knowledge of the potential for H₂ generation from water-rock interactions has received considerable attention. Here, we have provided a review of factors that may reduce the potential for the generation of H₂ with focus on low-temperature systems. We have shown that sulfate may affect the potential for H₂ generation as it potentially constrains the aqueous O₂ at levels higher than required to achieve high H₂ concentrations. Redox-sensitive compounds of carbon and nitrogen, on the other hand, are unlikely to have significant effect at low temperatures. We further suggest that the availability of water and pore/fracture space are the most important factors that limit the dissolution of olivine and generation of H₂. Finally, our study implies that, because of large heat flows, abundant olivine-bearing rocks, large thermodynamic gradients, and reduced atmospheres, the young Earth and Mars probably offered abundant systems where microorganisms could possibly have emerged.

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Abbreviation

kgw, kilogram of water.

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References

- Abrajano, T.A., Sturchio, N.C., Bohlke, J.K., Lyon, G.L., Poreda, R.J., and Stevens, C.M. (1988) Methane-hydrogen gas seeps, Zambales ophiolite, Philippines: deep or shallow origin? *Chem Geol* 71:211–222.
- Abrajano, T.A., Sturchio, N.C., Kennedy, B.M., Lyon, G.L., Muehlenbachs, K., and Bohlke, J.K. (1990) Geochemistry of reduced gas related to serpentinization of the Zambales ophiolite, Philippines. *Appl Geochem* 5:625–630.
- Abramov, O. and Kring, D.A. (2005) Impact-induced hydrothermal activity on early Mars. *J Geophys Res* 110:1–19.
- Adhikari, R.R. and Kallmeyer, J. (2010) Detection and quantification of microbial activity in the subsurface. *Chem Erde* 70:135–143.
- Albrechtsen, B.A., Furnes, H., and Pedersen, R.B. (1991) Formation of dunites in mantle tectonites, Leka Ophiolite Complex, Norway. *Journal of Geodynamics* 13:205–220.
- Atreya, S.K., Mahaffy, P.R., and Wong, A.-S. (2007) Methane and related trace species on Mars: origin, loss, implications for life, and habitability. *Planet Space Sci* 55:358–369.
- Bach, W. and Früh-Green, G.L. (2010) Alteration of the oceanic lithosphere and implications for seafloor processes. *Elements* 6:173–178.
- Bach, W., Paulick, H., Garrido, C.J., Ildefonse, B., Meurer, W.P., and Humphris, S.E. (2006) Unraveling the sequence of serpentinization reactions: petrography, mineral chemistry, and petrophysics of serpentinites from MAR 15°N (ODP Leg 209, Site 1274). *Geophys Res Lett* 33:1–4.
- Baker, E.T., Feely, R.A., Mottl, M.J., Sansone, F.T., Wheat, C.G., Resing, J.A., and Lupton, J.E. (1994) Hydrothermal plumes along the East Pacific Rise, 8°40' to 11°50'N: plume distribution and relationship to the apparent magmatic budget. *Earth Planet Sci Lett* 128:1–17.
- Baker, V.R., Dohm, J.M., Fairén, A.G., Ferré, T.P.A., Ferris, J.C., Miyamoto, H., and Schulze-Makuch, D. (2005) Extraterrestrial hydrogeology. *Hydrogeology Journal* 13:51–68.
- Béarat, H., McKelvy, M.J., Chizmeshya, A.V.G., Gormley, D., Nunez, R., Carpenter, R.W., Squires, K., and Wolf, G.H. (2006) Carbon sequestration via aqueous olivine mineral carbonation: role of passivating layer formation. *Environ Sci Technol* 40:4802–4808.
- Beard, J.S., Frost, B.R., Fryer, P., McCaig, A., Searle, R., Ildefonse, B., Zinin, P., and Sharma, S.K. (2009) Onset and progression of serpentinization and magnetite formation in olivine-rich troctolite from IODP Hole U1309D. *Journal of Petrology* 50:387–403.
- Bekker, A., Holland, H.D., Wang, P.-L., Rumble, D., III, Stein, H.J., Hannah, J.L., Coetzee, L.L., and Beukes, N.J. (2004) Dating the rise of atmospheric oxygen. *Nature* 427:117–120.

- Berndt, M.E., Allen, D.E., and Seyfried, W.E., Jr. (1996) Reduction of CO₂ during serpentinization of olivine at 300 °C and 500 bar. *Geology* 24:351–354.
- Brock, T.D. (1985) Life at high temperatures. *Science* 230: 132–138.
- Buseck, P.R. (1977) Pallasite meteorites—mineralogy, petrology and geochemistry. *Geochim Cosmochim Acta* 41:711–721.
- Carr, M.H., Belton, M.J.S., Chapman, C.R., Davies, A.S., Geissler, P., Greenberg, R., McEwen, A.S., Tufts, B.R., Greeley, R., Sullivan, R., Head, J.W., Pappalardo, R.T., Klaasen, K.P., Johnson, T.V., Kaufman, J., Senske, D., Moore, J., Neukum, G., Schubert, G., Burns, J.A., Thomas, P., and Veverka, J. (1998) Evidence for a subsurface ocean on Europa. *Nature* 391: 363–365.
- Chapelle, F.H., O'Neil, K., Bradley, P.M., Methe, B.A., Ciufo, S.A., Knobel, L.L., and Lovley, D.R. (2002) A hydrogen-based subsurface microbial community dominated by methanogens. *Nature* 415:312–315.
- Charlou, J.L., Donval, J.P., Fouquet, Y., Jean-Baptiste, P., and Holm, N. (2002) Geochemistry of high H₂ and CH₄ vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36°14'N, MAR). *Chem Geol* 191:345–359.
- Christensen, P.R., McSween, H.Y., Jr., Bandfield, J.L., Ruff, S.W., Rogers, A.D., Hamilton, V.E., Gorelick, N., Wyatt, M.B., Jakosky, B.M., Kieffer, H.H., Malin, M.C., and Moersch, J.E. (2005) Evidence for magmatic evolution and diversity on Mars from infrared observations. *Nature* 436:504–509.
- Clancy, R.T., Sandor, B.J., and Moriarty-Schieven, G.H. (2004) A measurement of the 362 GHz absorption line of Mars atmospheric H₂O₂. *Icarus* 168:116–121.
- Claypool, G.E. and Kaplan, L.R. (1974) The origin and distribution of methane in marine sediments. In *Natural Gases in Marine Sediments*, edited by L.R. Kaplan, Plenum Press, New York, pp 94–139.
- Cooper, M.A. and Williams, G.D., editors. (1989) *Inversion Tectonics*, Geological Society Special Publication No. 44, Blackwell Scientific Publications, Oxford.
- Craig, H., Weiss, R., and Clark, W. (1967). Dissolved gases in the equatorial and south Pacific Ocean. *J Geophys Res* 72: 6165–6181.
- Dick, H.J.B., Natland, J.H., Alt, J.C., Bach, W., Bideau, D., Gee, J.S., Haggas, S., Hertogen, J.G.H., Hirth, G., Holm, P.M., Ildefonse, B., Iturrino, G.J., John, B.E., Kelley, D.S., Kikawa, E., Kingdom, A., LeRoux, P.J., Maeda, J., Meyer, P.S., Miller, D.J., Naslund, H.R., Niu, Y.-L., Robinson, P.T., Snow, J., Stephen, R.A., Trimby, P.W., Worm, H.-U., and Yoshinobu, A. (2000) A long *in situ* section of the lower ocean crust: results of ODP Leg 176 drilling at the Southwest Indian Ridge. *Earth Planet Sci Lett* 179:31–51.
- Dick, H.J.B., Lin, J., and Schouten, H. (2003) An ultraslow-spreading class of ocean ridge. *Nature* 426:405–412.
- Ehlmann, B.L., Mustard, J.F., and Murchie, S.L. (2010) Geologic setting of serpentine deposits on Mars. *Geophys Res Lett* 37:1–5.
- Encrenaz, Th., Bézard, B., Greathouse, T.K., Richter, M.J., Lacy, J.H., Atreya, S.K., Wong, A.S., Lebonnois, S., Lefèvre, F., and Forget, F. (2004) Hydrogen peroxide on Mars: evidence for spatial and seasonal variations. *Icarus* 170:424–429.
- Feldman, W.C., Maurice, S., Binder, A.B., Barraclough, B.L., Elphic, R.C., and Lawrence, D.J. (1998) Fluxes of fast and epithermal neutrons from lunar prospector: evidence for water ice at the lunar poles. *Science* 281:1496–1500.
- Formisano, V., Atreya, S., Encrenaz, T., Ignatiev, N., and Giuranna, M. (2004) Detection of methane in the atmosphere of Mars. *Science* 306:1758–1761.
- Früh-Green, G.L., Connolly, J.A.D., Kelley, D.S., and Grobéty, B. (2004). Serpentinization of oceanic peridotites: implications for geochemical cycles and biological activity. In *The Subseafloor Biosphere at Mid-Ocean Ridges*, edited by W.S.D. Wilcock, E.F. DeLong, D.S. Kelley, J.A. Baross, and S.C. Cary, AGU Geophysical Monograph 144, American Geophysical Union, Washington DC, pp 119–136.
- Furnes, H., Banerjee, N.R., Muehlenbachs, K., Staudigel, H., and de Wit, M. (2004) Early life recorded in Archean pillow lavas. *Science* 304:578–581.
- Furnes, H., Dilek, Y., Muehlenbachs, K., and Banerjee, N.R. (2006) Tectonic control of bioalteration in modern and ancient oceanic crust as evidenced by carbon isotopes. *Island Arc* 15:143–155.
- Glein, C.R., Zolotov, M.Y., and Shock, E.L. (2008) The oxidation state of hydrothermal systems on early Enceladus. *Icarus* 197:157–163.
- Gold, T. (1992) The deep hot biosphere. *Proc Natl Acad Sci USA* 89:6045–6049.
- Golubev, S.V., Pokrovsky, O.S., and Schott, J. (2005) Experimental determination of the effect of dissolved CO₂ on the dissolution kinetics of Mg and Ca silicates at 25°C. *Chem Geol* 217:227–238.
- Grandstaff, D.E. (1978). Changes in surface area and morphology and the mechanism of forsterite dissolution. *Geochim Cosmochim Acta* 42:1899–1901.
- Griffith, C.A., Owen, T., Geballe, T.R., Rayner, J., and Rannou, P. (2003) Evidence for the exposure of water ice on Titan's surface. *Science* 300:628–630.
- Griffith, L.L. and Shock, E.L. (1995) A geochemical model for the formation of hydrothermal carbonates on Mars. *Nature* 377:406–408.
- Harrison, T.M., Blichert-Toft, J., Müller, W., Albarede, F., Holden, P., and Mojzsis, S.J. (2005) Heterogeneous Hadean hafnium: evidence of continental crust at 4.4 to 4.5 Ga. *Science* 310:1947–1950.
- Hellevang, H. (2008) On the forcing mechanism of the H₂-driven deep biosphere. *International Journal of Astrobiology* 7:157–167.
- Hoefen, T.M., Clark, R.N., Bandfield, J.L., Smith, M.D., Pearl, J.C., and Christensen, P.R. (2003) Discovery of olivine in the Nili Fossae region of Mars. *Science* 302:627–630.
- Holm, N.G. and Charlou, J.L. (2001) Initial indications of abiotic formation of hydrocarbons in the Rainbow ultramafic hydrothermal system, Mid-Atlantic Ridge. *Earth Planet Sci Lett* 191:1–8.
- Iyer, K., Austrheim, H., John, T., and Jamtveit, B. (2008) Serpentinization of the oceanic lithosphere and some geochemical consequences: constraints from the Leka Ophiolite complex, Norway. *Chem Geol* 249:66–90.
- Johnson, K.S., Sakamoto-Arnold, C.M., and Beehler, C.L. (1989) Continuous determination of nitrate concentrations *in situ*. *Deep Sea Res A* 36:1407–1413.
- Kaplan, I.R., Emery, K., and Rittenberg, S. (1963) The distribution and isotopic abundance of sulfur in recent marine sediments off Southern California. *Geochim Cosmochim Acta* 27:297–331.
- Kashefi, K. and Lovley, D.R. (2003) Extending the upper temperature limit for life. *Science* 301:934.
- Kasting, J.F. (1988) Runaway and moist greenhouse atmospheres and the evolution of Earth and Venus. *Icarus* 74:472–494.
- Kelley, D.S., Karson, J.A., Blackman, D.K., Früh-Green, G.L., Butterfield, D.A., Lilley, M.D., Olson, E.J., Schrenk, M.O., Roe, K.K., Lebon, G.T., Rivizzigno, P., and the AT3-60 shipboard party. (2001) An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30°N. *Nature* 412:145–149.

- Kelley, D.S., Baross, J.A., and Delaney, J.R. (2002) Volcanoes, fluids, and life at mid-ocean ridge spreading centers. *Annu Rev Earth Planet Sci* 30:385–491.
- Kelley, D.S., Lilley, M.D., and Fröh-Green, G.L. (2004) Volatiles in submarine environments: food for life. In *The Subseafloor Biosphere at Mid-Ocean Ridges*, edited by W.S.D. Wilcock, E.F. DeLong, D.S. Kelley, J.A. Baross, and S.C. Cary, AGU Geophysical Monograph 144, American Geophysical Union, Washington DC, pp 167–189.
- Kelley, D.S., Karson, J.A., Fröh-Green, G.L., Yoerger, D.R., Shank, T.M., Butterfield, D.A., Hayes, J.M., Schrenk, M.O., Olson, E.J., Proskurowski, G., Jakuba, M., Brandley, A., Larson, B., Ludwig, K., Glickson, D., Buckman, K., Bradley, A.S., Brazelton, W.J., Roe, K.K., Elend, M.D., Delacour, A., Bernasconi, S.M., Lilley, M.D., Baross, J.A., Summons, R.E., and Sylva, S.P. (2005) A serpentinite-hosted ecosystem: the Lost City hydrothermal field. *Science* 307:1428–1434.
- Kim, Y., Nunez, R., Carpenter, R.W., Chizmeshya, A.V.G., and McKelvy, M.J. (2005) The nanoscale mechanism for San Carlos olivine carbonation. *Microsc Microanal* 11:1530–1531.
- Klein, F., Bach, W., Jöns, N., McCollom, T., Moskowitz, B., and Berquó, T. (2009) Iron partitioning and hydrogen generation during serpentinization of abyssal peridotites from 15°N on the Mid-Atlantic ridge. *Geochim Cosmochim Acta* 73:6868–6893.
- Koeberl, C. and Reimold, W.U. (2004) Post-impact hydrothermal activity in meteorite impact craters and potential opportunities for life. In *Bioastronomy 2002: Life among the Stars*, edited by R.P. Norris and F.H. Stootmans, Astronomical Society of the Pacific, San Francisco, pp 299–304.
- Koeppen, W.C. and Hamilton, V.E. (2008) Global distribution, composition, and abundance of olivine on the surface of Mars from thermal infrared data. *J Geophys Res* 113, doi:10.1029/2007JE002984.
- Kotwicki, V. (1991) Water in the Universe. *Hydrological Sciences Journal* 36:49–66.
- Lucey, P.G. (2004) Mineral maps of the Moon. *Geophys Res Lett* 31, doi:10.1029/2003GL019406.
- Malin, M.C. and Edgett, K.S. (2000) Evidence for recent groundwater seepage and surface runoff on Mars. *Science* 288:2330–2335.
- Mao, S. and Duan, Z. (2008) The P, V, T,x properties of binary aqueous chloride solutions up to T=573 K and 100 MPa. *J Chem Thermodyn* 40:1046–1063.
- Martin, W. and Russell, M.J. (2007) On the origin of biochemistry at an alkaline hydrothermal vent. *Philos Trans R Soc Lond B Biol Sci* 362:1887–1926.
- Marzo, G.A., Davila, A.F., Tornabene, L.L., Dohm, J.M., Fairen, A.G., Gross, C., Kneissl, T., Bishop, J.L., Roush, T.L., and McKay, C.P. (2010) Evidence for Hesperian impact-induced hydrothermalism on Mars. *Icarus* 208:667–683.
- McCollom, T.M. and Bach, W. (2009) Thermodynamic constraints on hydrogen generation during serpentinization of ultramafic rocks. *Geochim Cosmochim Acta* 73:856–875.
- Milner-White, E.J. and Russell, M.J. (2008) Predicting the conformations of peptides and proteins in early evolution. *Biol Direct* 3, doi:10.1186/1745-6150-3-3.
- Mischna, M.A., Allen, M., Richardson, M.I., Newman, C.E., and Toigo, A.D. (2011) Atmospheric modeling of Mars methane surface releases. *Planet Space Sci* 59:227–237.
- Mojzsis, S.J., Arrhenius, G., McKeegan, K.D., Harrison, T.M., Nutman, A.P., and Friend, C.R.L. (1996) Evidence for life on Earth before 3,800 million years ago. *Nature* 384:55–59.
- Mojzsis, S.J., Harrison, T.M., and Pidgeon, R.T. (2001) Oxygen-isotope evidence from ancient zircons for liquid water at the Earth's surface 4,300 Myr ago. *Nature* 409:178–181.
- Moody, J.B. (1976) Serpentinization: a review. *Lithos* 9:125–138.
- Morita, R.Y. (2000) Is H₂ the universal energy source for long-term survival? *Microb Ecol* 38:307–320.
- Morris, R.V., Ruff, S.W., Gellert, R., Ming, D.W., Arvidson, R.E., Clark, B.C., Golden, D.C., Siebach, K., Klingelhofer, G., Schröder, C., Fleischer, I., Yen, A.S., and Squyres, S.W. (2010) Identification of carbonate-rich outcrops on Mars by the Spirit Rover. *Science* 329:421–424.
- Mumma, M.J., Villanueva, G.L., Novak, R.E., Hewagama, T., Bonev, B.P., DiSanti, M.A., Mandell, A.M., and Smith, M.D. (2009) Strong release of methane on Mars in northern summer 2003. *Science* 323:1041–1045.
- Mustard, J.F., Poulet, F., Gendrin, A., Bibring, J.-P., Langevin, Y., Gondet, B., Mangold, N., Bellucci, G., and Altieri, F. (2005) Olivine and pyroxene diversity in the crust of Mars. *Science* 307:1594–1597.
- Neal, C. and Stanger, G. (1983) Hydrogen generation from mantle source rocks in Oman. *Earth Planet Sci Lett* 66:315–320.
- Nealson, K.H., Inagaki, F., and Takai, K. (2005) Hydrogen-driven subsurface lithoautotrophic microbial ecosystems (SLIMES): do they exist and why should we care? *Trends Microbiol* 13:405–410.
- Nicolas, A. and Boudier, F. (2000) Large mantle upwellings and related variations in crustal thickness in the Oman ophiolite. In *Ophiolites and Oceanic Crust: New Insights from Field Studies and the Ocean Drilling Program*, GSA Special Paper 349, edited by Y. Dilek, E. Moores, D. Elthon, and A. Nicolas, Geological Society of America, Boulder, CO, pp 67–74.
- Nisbet, E.G. and Sleep, N.H. (2001) The habitat and nature of early life. *Nature* 409:1083–1091.
- Nordstrom, D.K., Plummer, L.N., Wigley, T.M.L., Wolery, T.J., Ball, J.W., Jenne, E.A., Bassett, R.L., Crerar, D.A., Florence, T.M., Fritz, B., Hoffman, M., Holdren, G.R., Lafon, G.M., Mattigod, S.V., McDuff, R.E., Morel, F., Reddy, M.M., Sposito, G., and Thraillkill, J. (1979) A comparison of computerized chemical models for equilibrium calculations in aqueous systems. In *Chemical Modeling in Aqueous Systems, Speciation, Sorption, Solubility, and Kinetics*, ACS Symposium Series Vol. 93, edited by E.A. Jenne, American Chemical Society, Washington DC, pp 857–892.
- O'Brien, D.P., Lorenz, R.D., and Lunine, J.I. (2005) Numerical calculations of the longevity of impact oases on Titan. *Icarus* 173:243–253.
- Oelkers, E.H. (2001) An experimental study of forsterite dissolution rates as a function of temperature and aqueous Mg and Si concentrations. *Chem Geol* 175:485–494.
- Oze, C. and Sharma, M. (2005) Have olivine, will gas: serpentinization and the abiogenic production of methane on Mars. *Geophys Res Lett* 32, doi:10.1029/2005GL022691.
- Oze, C. and Sharma, M. (2007) Serpentinization and the inorganic synthesis of H₂ in planetary surfaces. *Icarus* 186:557–561.
- Papike, J.J., Karner, J.M., Shearer, C.K., and Burger, P.V. (2009) Silicate mineralogy of martian meteorites. *Geochim Cosmochim Acta* 73:7443–7485.
- Parkhurst, D.L. and Appelo, C.A.J. (1999) User's guide to PHREEQC (version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water-Resources Investigations Report 99-4259, U.S. Geological Survey, Denver, CO.
- Parnell, J., Boyce, A.J., and Blamey, N.J.F. (2010) Follow the methane: the search for a deep biosphere, and the case of sampling serpentinites, on Mars. *International Journal of Astrobiology* 9:193–200.
- Pedersen, K. (1997) Microbial life in deep granitic rock. *FEMS Microbiol Rev* 20:399–414.

- Pokrovsky, O.S. and Schott, J. (2000) Kinetics and mechanism of forsterite dissolution at 25°C and pH from 1 to 12. *Geochim Cosmochim Acta* 64:3313–3325.
- Proskurowski, G., Lilley, M.D., Seewald, J.S., Früh-Green, G.L., Olson, E.J., Lupton, J.E., Sylva, S.P., and Kelley, D.S. (2008) Abiogenic hydrocarbon production at Lost City hydrothermal field. *Science* 319:604–607.
- Quesnel, Y., Sotin, C., Langlais, B., Costin, S., Manda, M., Gottschalk, M., and Dymont, J. (2009) Serpentinization of the martian crust during Noachian. *Earth Planet Sci Lett* 277:184–193.
- Rossmann, D.L., Castañeda, G.C., and Bacuta, G.C. (1989) Geology of the Zambales ophiolite, Luzon, Philippines. *Tectonophysics* 168:7–22.
- Rosso, J.J. and Rimstidt, J.D. (2000) A high resolution study of forsterite dissolution rates. *Geochim Cosmochim Acta* 64:797–811.
- Roussel, E.G., Cambon Bonavita, M.-A., Querellou, J., Cragg, B.A., Webster, G., Prieur, D., and John Parkes, R. (2008) Extending the sub-sea-floor biosphere. *Science* 320:1046.
- Russell, M.J. (2007) The alkaline solution to the emergence of life: energy, entropy and early evolution. *Acta Biotheor* 55:133–179.
- Russell, M.J., Hall, A.J., and Turner, D. (1989) *In vitro* growth of iron sulphide chimneys: possible culture chambers of origin-of-life experiments. *Terra Nova* 1:238–241.
- Russell, M.J., Hall, A.J., and Martin, W. (2010) Serpentinization as a source of energy at the origin of life. *Geobiology* 8:355–371.
- Schippers, A. and Neretin, L.N. (2006) Quantification of microbial communities in near-surface and deeply buried marine sediments on the Peru continental margin using real-time PCR. *Environ Microbiol* 8:1251–1260.
- Schippers, A., Neretin, L.N., Kallmeyer, J., Ferdelman, T.G., Cragg, B.A., Parkes, J.R., and Jørgensen, B.B. (2005) Prokaryotic cells of the deep sub-sea-floor biosphere identified as living bacteria. *Nature* 433:861–864.
- Schulte, M., Blake, D., Hoehler, T., and McCollom, T. (2006) Serpentinization and its implications for life on the early Earth and Mars. *Astrobiology* 6:364–376.
- Seyfried, W.E., Jr., Foustoukos, D.I., and Fu, Q. (2007) Redox evolution and mass transfer during serpentinization: an experimental and theoretical study at 200°C and 500 bar with implications for ultramafic-hosted hydrothermal systems. *Geochim Cosmochim Acta* 71:3872–3886.
- Shaw, G.H. (2008) Earth's atmosphere—Hadean to early Proterozoic. *Chem Erde* 68:235–264.
- Sleep, N.H. and Bird, D.K. (2008) Evolutionary ecology during the rise of oxygen in the Earth's atmosphere. *Philos Trans R Soc Lond B Biol Sci* 363:2651–2664.
- Sleep, N.H., Meibom, A., Fridriksson, Th., Coleman, R.G., and Bird, D.K. (2004) H₂-rich fluids from serpentinization: geochemical and biotic implications. *Proc Natl Acad Sci USA* 101:12818–12823.
- Smirnov, A., Hausner, D., Laffers, R., Strongin, D.R., and Schoonen, M.A.A. (2008) Abiotic ammonium formation in the presence of Ni-Fe metals and alloys and its implications for the Hadean nitrogen cycle. *Geochem Trans* 9, doi:10.1186/1467-4866-9-5.
- Smith, H.S., Erlank, A.J., and Duncan, A.R. (1980) Geochemistry of some ultramafic komatiite lava flows from the Barberton mountain land, South Africa. *Precambrian Res* 11:399–415.
- Sohl, F., Spohn, T., Breuer, D., and Nagel, K. (2002) Implications from Galileo observations on the interior structure and chemistry of the Galilean satellites. *Icarus* 157:104–119.
- Spear, J.R., Walker, J.J., McCollom, T.M., and Pace, N.R. (2005) Hydrogen and bioenergetics in the Yellowstone geothermal ecosystem. *Proc Natl Acad Sci USA* 102:2555–2560.
- Sprague, A.L., Hanna, K.L.D., Kozlowski, R.W.H., Helbert, J., Maturilli, A., Warell, J.B., and Hora, J.L. (2009) Spectral emissivity measurements of Mercury's surface indicate Mg- and Ca-rich mineralogy, K-spar, Na-rich plagioclase, rutile, with possible perovskite, and garnet. *Planet Space Sci* 57:364–383.
- Stevens, T.O. and McKinley, J.P. (1995) Lithoautotrophic microbial ecosystems in deep basalt aquifers. *Science* 270:450–454.
- Svedhem, H., Titov, D.V., Taylor, F.W., and Witasse, O. (2007) Venus as a more Earth-like planet. *Nature* 450:629–632.
- Takai, K., Gamo, T., Tsunogai, U., Nakayama, N., Hirayama, H., Nealson, K.H., and 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.
- Takai, K., Nakamura, K., Toki, T., Tsunogai, U., Miyazaki, M., Miyazaki, J., Hirayama, H., Nakagawa, S., Nunoura, T., and Horikoshi, K. (2008) Cell proliferation at 122°C and isotopically heavy CH₄ production by a hyperthermophilic methanogen under high-pressure cultivation. *Proc Natl Acad Sci USA* 105:10949–10954.
- Tera, F., Papanastassiou, D., and Wasserburg, G. (1974) The lunar time scale and a summary of isotopic evidence for a terminal lunar cataclysm [abstract 1289]. In *Abstracts of the Fifth Lunar Science Conference*, Lunar and Planetary Institute, Houston.
- Teske, A., Ashita, D., and Sogin, M.L. (2003) Genomic markers of ancient anaerobic microbial pathways: sulfate reduction, methanogenesis, and methane oxidation. *Biol Bull* 204:186–191.
- Torsvik, V. and Øvreås, L. (2008) Microbial diversity, life strategies, and adaption to life in extreme soils. *Soil Biology* 13:15–43.
- Treiman, A.H., Amundsen, H.E.F., Blake, D.F., and Bunch, T. (2002) Hydrothermal origin for carbonate globules in martian meteorite ALH84001: a terrestrial analogue from Spitsbergen (Norway). *Earth Planet Sci Lett* 204:323–332.
- Truesdell, A.H. and Jones, B.F. (1974) WATEQ, a computer program for calculating chemical equilibria of natural waters. *U.S. Geological Survey, Journal of Research* 2:233–274.
- Vance, S., Harnmeijer, J., Kimura, J., Hussmann, H., Demartin, B., and Brown, J.M. (2007) Hydrothermal systems in small ocean planets. *Astrobiology* 7:987–1005.
- Waite, J.H., Lewis, W.S., Magee, B.A., Lunine, J.I., McKinnon, W.B., Glein, C.R., Mousis, O., Young, D.T., Brockwell, T., Westlake, J., Nguyen, M.-J., Teolis, B.D., Niemann, H.B., McNutt, R.L., Jr., Perry, M., and Ip, W.-H. (2009) Liquid water on Enceladus from observations of ammonia and Ar-40 in the plume. *Nature* 460:487–490.
- Watson, E.B. and Harrison, T.M. (2005) Zircon thermometer reveals minimum melting conditions on earliest Earth. *Science* 308:841–844.
- Welch, S.A. and Banfield, J.F. (2002) Modification of olivine surface morphology and reactivity by microbial activity during chemical weathering. *Geochim Cosmochim Acta* 66:213–221.
- Wilde, S.A., Valley, J.W., Peck, W.H., and Graham, C.M. (2001) Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature* 409:175–178.

- Wortmann, U.G., Chernyavsky, B., Bernasconi, S.M., Brunner, B., Böttcher, M.E., and Swart, P.K. (2007) Oxygen isotope biogeochemistry of pore water sulfate in the deep biosphere: dominance of isotope exchange reactions with ambient water during microbial sulfate reduction (ODP Site 1130). *Geochim Cosmochim Acta* 71:4221–4232.
- Zahnle, K., Freedman, R.S., and Catling, D.C. (2010) Is there methane on Mars? *Icarus* 212:493–503.
- Zurbuchen, T.H., Raines, J.M., Gloeckler, G., Krimigis, S.M., Slavin, J.A., Koehn, P.L., Killen, R.M., Sprague, A.L., McNutt, R.L., and Solomon, S.C. (2008) MESSENGER observations of the composition of Mercury's ionised exosphere and plasma environment. *Science* 321:90–92.

Address correspondence to:
Helge Hellevang
Department of Geosciences
University of Oslo
Pb. 1047
Blindern
Oslo
Norway

E-mail: helghe@geo.uio.no

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