Research Paper

Serpentinization and Its Implications for Life on the Early Earth and Mars

MITCH SCHULTE,[1],* DAVID BLAKE,[1] TORI HOEHLER,[1] and THOMAS McCOLLOM[2]

ABSTRACT

Ophiolites, sections of ocean crust tectonically displaced onto land, offer significant potential to support chemolithoautotrophic life through the provision of energy and reducing power during aqueous alteration of their highly reduced mineralogies. There is substantial chemical disequilibrium between the primary olivine and pyroxene mineralogy of these ophiolites and the fluids circulating through them. This disequilibrium represents a potential source of chemical energy that could sustain life. Moreover, E_h–pH conditions resulting from rock–water interactions in ultrabasic rocks are conducive to important abiotic processes antecedent to the origin of life. Serpentinization—the reaction of olivine- and pyroxene-rich rocks with water—produces magnetite, hydroxide, and serpentine minerals, and liberates molecular hydrogen, a source of energy and electrons that can be readily utilized by a broad array of chemosynthetic organisms. These systems are viewed as important analogs for potential early ecosystems on both Earth and Mars, where highly reducing mineralogy was likely widespread in an undifferentiated crust. Secondary phases precipitated during serpentinization have the capability to preserve organic or mineral biosignatures. We describe the petrology and mineral chemistry of an ophiolite-hosted cold spring in northern California and propose criteria to aid in the identification of serpentinizing terranes on Mars that have the potential to harbor chemosynthetic life. Key Words: Serpentinization—Ophiolite—Habitability—Early Earth—Mars. Astrobiology 6, 364–376.

INTRODUCTION

PRIOR TO THE EVOLUTION of photosynthesis, organisms on the early Earth relied on chemical forms of metabolic energy ("chemosynthesis"). Similarly, the apparent lack of photosynthetic life on the surface of Mars indicates that, should life exist there today, any organisms must also rely on chemical forms of energy (Boston *et al.*, 1992; Shock,

1997; McCollom, 2006). Consequently, investigation of environments that support chemosynthesis on the modern Earth can enlighten our understanding of life on the early Earth and the situation that may have existed on Mars.

For an organism to derive chemical energy for metabolism from the natural environment (martian or terrestrial, modern or ancient), a state of thermodynamic disequilibrium must exist. The

[1]Exobiology Branch, NASA Ames Research Center, Moffett Field, California.
[2]Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, Colorado.
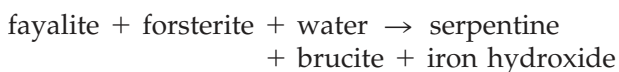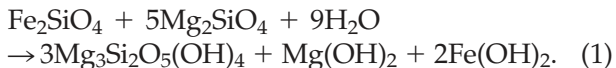*Present address: Department of Geological Sciences, University of Missouri, Columbia, Missouri.

single most widespread environment of *chemical disequilibrium* on present-day Earth results from the interaction of mafic and ultramafic rocks of the ocean crust with liquid water. Such environments make up three-quarters of the Earth's surface and potentially host a vast chemolithoautotrophic biosphere (Deming and Baross, 1995; McCollom and Shock, 1997). Fluid–rock interactions like those presently occurring in the shallow ocean crust were even more pervasive on the Archean Earth because of increased geothermal heat flow, the greater abundance of ultramafic rocks, and the absence of widespread continental crust formation (Nisbet, 1987; Nisbet and Sleep, 2001; Sleep *et al.*, 2004).

The mafic and ultramafic rocks that constitute the ocean crust (*i.e.*, basalts, gabbros, and peridotites) are dominated by the minerals olivine and orthopyroxene. Compositionally, the modern oceanic crust and upper mantle of the Earth are essentially the same as they were on the early Earth and Mars (Nisbet, 1987). Additionally, the crust and upper mantle of Mars also appear to be composed of mafic/ultramafic rocks largely similar to those of the ocean crust on Earth (Longhi *et al.*, 1992). It follows that a comprehensive understanding of the mineralogy, water–rock chemistry, and microbial ecology of Earth's oceanic crust could be of great value in devising a search strategy for evidence of past or present life on the early Earth and Mars.

Olivine and orthopyroxene are thermodynamically stable at the high temperatures and pressures present deep within the Earth (or within Mars), but they are thermodynamically unstable at the lower temperatures in the near-surface environments. As a consequence, when these minerals are exposed to surface or shallow environments, they readily react with water, which results in mineral alteration. Because the serpentine minerals (lizardite, chrysotile) are frequently the dominant alteration mineral formed, the process is commonly referred to as serpentinization. In addition to mineral alteration, serpentinization frequently generates fluids with high concentrations of H_2 and CH_4 (Neal and Stanger, 1983; Abrajano *et al.*, 1990; Charlou *et al.*, 1998; Wetzel and Shock, 2000; Kelley *et al.*, 2001a, 2005), and produces heat and an increase in volume (Allen and Seyfried, 2004; Früh-Green *et al.*, 2004). The amounts of H_2 generated during water–rock reactions of ultramafic rocks such as peridotites are substantially higher than those produced in basalt-hosted hydrothermal systems (Wetzel and Shock, 2000).

The process of serpentinization, through which olivine and pyroxene are altered into serpentine minerals, can be generally described by the reactions:

$$Fe_2SiO_4 + 5Mg_2SiO_4 + 9H_2O$$
$$\rightarrow 3Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 + 2Fe(OH)_2. \quad (1)$$

fayalite + forsterite + water → serpentine
                          + brucite + iron hydroxide

where fayalite and forsterite are the olivine solid-solution end-members, and

$$Mg_2SiO_4 + MgSiO_3 + 2H_2O$$
$$\rightarrow Mg_3Si_2O_5(OH)_4. \quad (2)$$

forsterite + pyroxene + water → serpentine
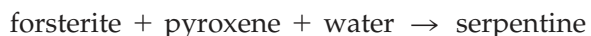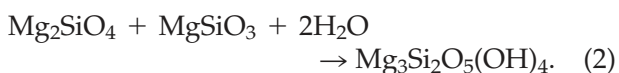
The reduced iron from the fayalite component of olivine (shown in Reaction 1) may then be oxidized to magnetite through the reduction of water to molecular hydrogen through the reaction

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2. \quad (3)$$

iron hydroxide → magnetite + water
                 + hydrogen
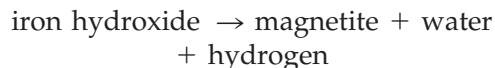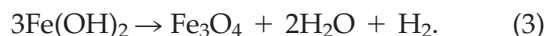
Reaction 3 represents a geochemical process that could serve as an energy source for biology through the production of H_2, the electron donor for a number of chemoautotrophic biochemical processes, including methanogenesis ($CO_2 + 4H_2 = CH_4 + 2H_2O$) (Brock and Madigan, 1991). The amount of olivine relative to pyroxene is an important consideration in these rocks, as the release of excess silica during water–rock reactions results in the formation of talc (Bach *et al.*, 2004). Because talc more readily incorporates Fe into its structure than do serpentine minerals, magnetite formation and the resulting production of H_2 are reduced in proportion to the amount of talc produced.

Because the igneous rocks of the modern ocean crust are only exposed in the deep sea, it is difficult to study directly the processes that support microbial communities in these environments. However, in some tectonic regimes, such as convergent plate boundaries, cross sections of lower oceanic crust and upper mantle are emplaced

onto the continental crust where they are more readily studied. Sections of former lower oceanic crust and upper mantle (often referred to as "ophiolite suites") are preserved and exposed on land throughout the state of California as a result of its location adjacent to active plate margins since the Jurassic (Bailey *et al.*, 1970). These mafic and ultramafic rocks are found in the Coast Range, Point Sal, Josephine, and the Trinity Ophiolite complexes and elsewhere. Outcrops of these complexes contain numerous springs from which water trapped in the rocks issues. The rocks are Jurassic-Cretaceous in age with formation dates as old as 160+ million years (Bailey *et al.*, 1970; Page, 1972; Harper *et al.*, 1994; Dickinson *et al.*, 1996; Coleman, 2000). Many of the numerous springs and seeps that emanate from these rocks are at temperatures less than ~50°C. Previous studies (Barnes *et al.*, 1972; Peters, 1993) have shown that the fluids from springs hosted by the Coast Range ophiolite are alkaline, with pH as high as 12 and high concentrations of the alkaline elements Na, K, and Ca. The composition of these fluids appears to be the result of the reaction of ancient seawater with the ultramafic rocks. Peters (1993) concluded, on the basis of oxygen and hydrogen isotopic data, that the primitive endmember component of water emanating from northern California ophiolite terranes is seawater of Cretaceous age that was trapped with the sediments and crust during emplacement onto the North American craton.

Despite the fact that the fluid compositions can vary, we note that these general geochemical processes, in which ultramafic rocks react with liquid water, are broadly similar in both the "continental" (or ophiolite) and ocean floor settings in that the products of the reaction (serpentine, brucite, magnetite) are the same for a wide range of temperatures, pressures, and fluid compositions. Because these terranes have been resident on the North American craton for tens to hundreds of millions of years, this study is relevant to present-day Mars, which lacks evidence for sustained plate tectonic processes, and even to an ancient Mars that may have never developed standing oceans or large-scale plate tectonics. Serpentinization is an exergonic process with a concomitant volume increase. While it does not appear that sufficient energy is released to attain high temperatures or induce large-scale hydrothermal circulation (Allen and Seyfried, 2004), the thermal energy released during this process may enhance further reaction and circulation driven by other forces (Kelley *et al.*, 2005). The discovery by the Mars Exploration Rovers of a rock record on Mars, however, indicates that the presence of significant amounts of crustal water furthers the possibilities of water–rock interactions.

MATERIALS AND METHODS

Hand samples of olivine-rich rocks (peridotites) were collected from actively dewatering outcrops in the Coast Range Ophiolite during field trips just to the north of the Indian Valley Reservoir in Lake County, California. Standard petrographic thin sections were prepared from the hand samples for detailed examination of the mineralogy, petrology, and alteration textures. The thin sections were examined by optical and scanning electron microscopy, and mineral compositions were determined by electron microprobe analysis and x-ray diffraction analysis. Electron microprobe analysis was conducted using the JEOL (Tokyo, Japan) JXA-733 Superprobe in the Department of Earth and Planetary Sciences, Washington University, St. Louis, MO. Data were collected using an accelerating voltage of 15 kV and a beam current of 20–30 nA. The beam spot size was 10 μm, and x-ray counts were collected generally for 20 s using wavelength dispersive analysis. Data were gathered for the major rock-forming elements (Mg, Al, Si, Ca, Ti, Mn, and Fe) and for trace elements Cr and Ni. Because of low counts and the potential for higher error, the alkali elements Na and K were not analyzed; however, these elements are generally present only at very low abundances in rocks of this composition. Natural and synthetic minerals, provided by the Electron Microprobe Facility at Washington University (reference standard numbers 203, 204, 206, 207, 210, 212, 220, 222, and 224), were used as calibration standards. The raw data were corrected using Probe for Windows® software (Advanced MicroBeam, Inc., Vienna, OH). X-ray diffraction analysis was carried out at NASA Ames Research Center (Moffett Field, CA) using the CheMin x-ray diffraction analysis/x-ray fluorescence instrument (InXitu, Inc., Mountain View, CA), and the data were reduced using commercial Jade™ software (Material Data, Inc., Livermore, CA).

RESULTS

Petrography

Hand samples of rocks collected from the Coast Range Ophiolite are peridotites, or rocks composed predominately of olivine. Based on examination of the proportions of remnant primary mineralogy, they are further subclassified as harzburgites (peridotites composed principally of olivine and pyroxene). Approximately 10% of the hand samples do, however, contain a high enough percentage of clinopyroxene to be classified as lherzolites. We estimated from hand sample and thin section inspection of the remnant primary (*i.e.*, unaltered) mineralogy that the modal proportions of minerals in the original rock were approximately 70% olivine, 20% orthopyroxene, 7% clinopyroxene, and 3% other minerals, including accessory and trace phases. This mineralogy falls within the range of mineralogies reported for sea floor serpentinites (Bach *et al.*, 2004).

Examination of petrographic thin sections by optical and scanning electron microscopy revealed that serpentinization reactions occurred within the peridotites of the Coast Range Ophio-
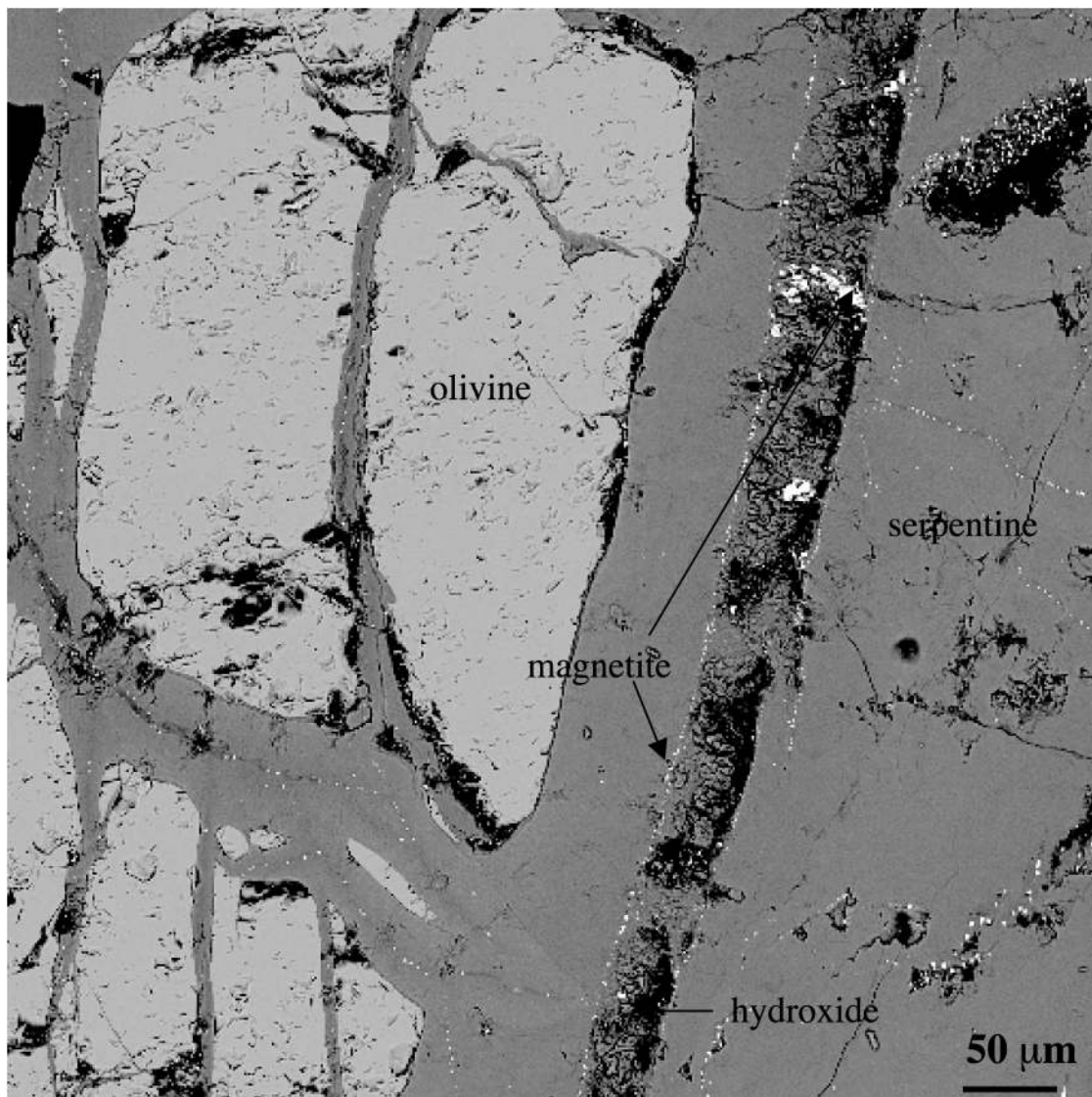

FIG. 1.   Backscattered electron micrograph of a thin section made from hand samples (NFG-10) of the Coast Range ophiolite peridotite collected near Clear Lake, CA. The large grain, an olivine, has been altered to serpentine. The very small, bright objects are magnetite grains that appear to define the extent of the olivine grain before alteration.

lite (Figs. 1 and 2). Active serpentinization was previously reported within California ophiolite complexes on the basis of geochemical data by Barnes *et al.* (1967) and Barnes and O'Neil (1969) in the form of high pH fluids issuing from the rocks. In cross-polarized light, the primary olivine and pyroxene were easily recognized and together accounted for roughly half of the mineralogy of the thin sections. Fine-grained groundmass constituted the bulk of the remaining mineralogy, and the cross-hatched "snake-skin" pattern of the serpentine was clearly visible and accounted for most of the groundmass. The ob-

served textures and optical properties are characteristic of the serpentine minerals lizardite and chrysotile (Robert Dymek, personal communication). X-ray diffraction analysis confirmed the presence of clinochlore, lizardite, chrysotile, olivine, pyroxene, magnetite, brucite, and anthophylite.

The serpentine also resides in veins that crosscut the olivine and pyroxene grains. Furthermore, several generations of alteration products were visible, and veins that contain alteration products cut across previously formed veins and alteration product ground mass. Opaque, micron-sized
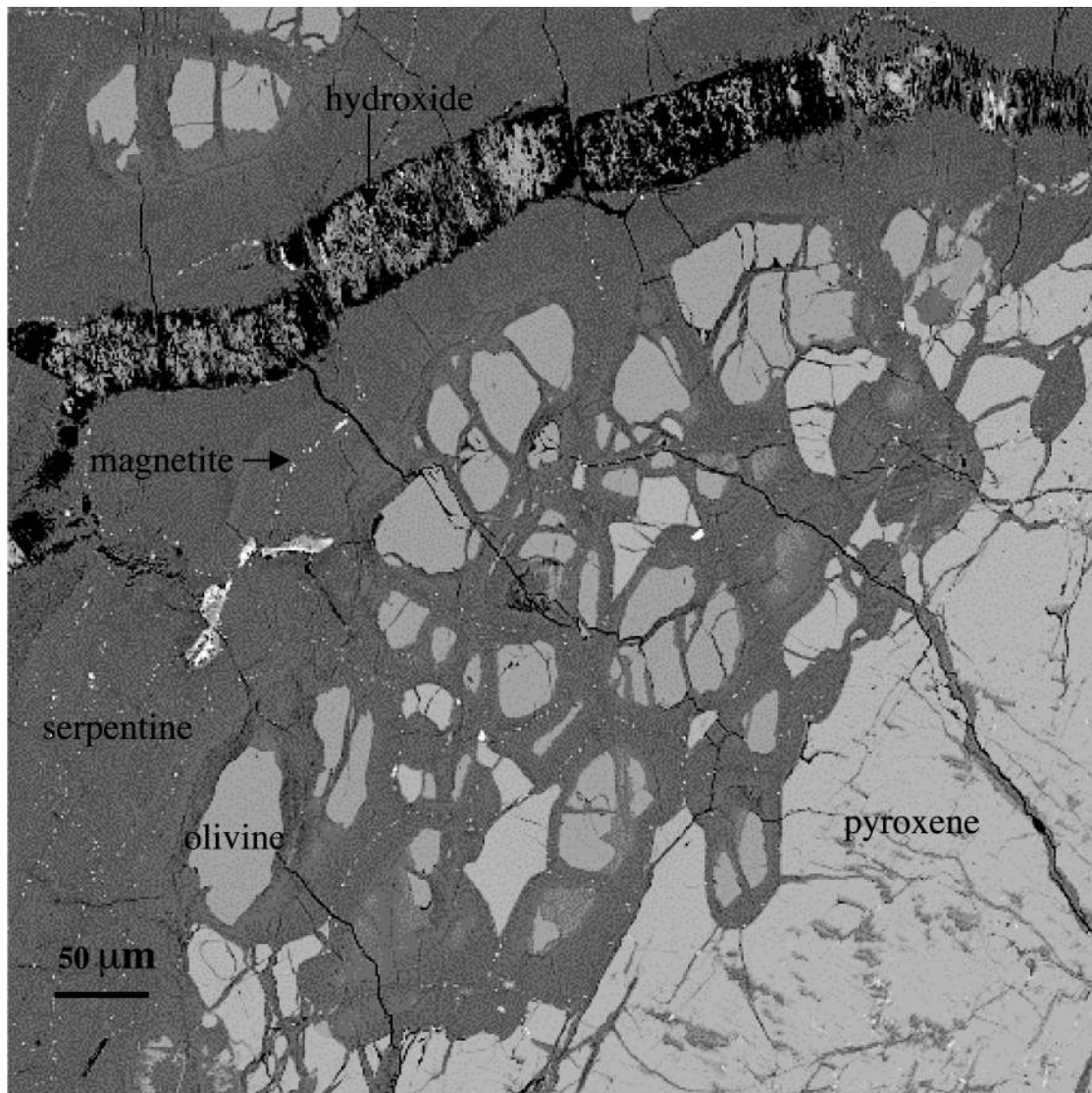

FIG. 2. Backscattered electron micrograph of a thin section made from a hand sample (NFG-10) of the Coast Range ophiolite peridotite collected near Clear Lake, CA. Primary minerals olivine and pyroxene are visible, and show clear signs of alteration. The ground mass consists primarily of serpentine, with numerous magnetite grains and a vein filled in large part with both serpentine and iron-rich brucite.

mineral grains line the veins that run throughout the thin sections, and opaque minerals also occurred as larger grains, making up the bulk of the accessory phases visible in thin section.

Note that all of the mineralogical components of Reactions 1 and 2, given above for generation of serpentine from olivine and pyroxene, are illustrated in Figs. 1 and 2. The involvement of liquid water was evidenced by the presence of veins and numerous fluid inclusions observed in optical microscopic examination of the thin sections (data not shown). On the basis of these observa-

tions, it follows that production of H_2 has also occurred and would have been (and may be) available for organisms that potentially inhabit these rocks.

Mineral chemistry

The olivines in the peridotite are quite homogeneous with an approximate composition of $Fo_{90}Fa_{10}$. The homogeneity of composition can be seen in Fig. 3A, in which the weight percent MgO was plotted as a function of weight percent SiO_2
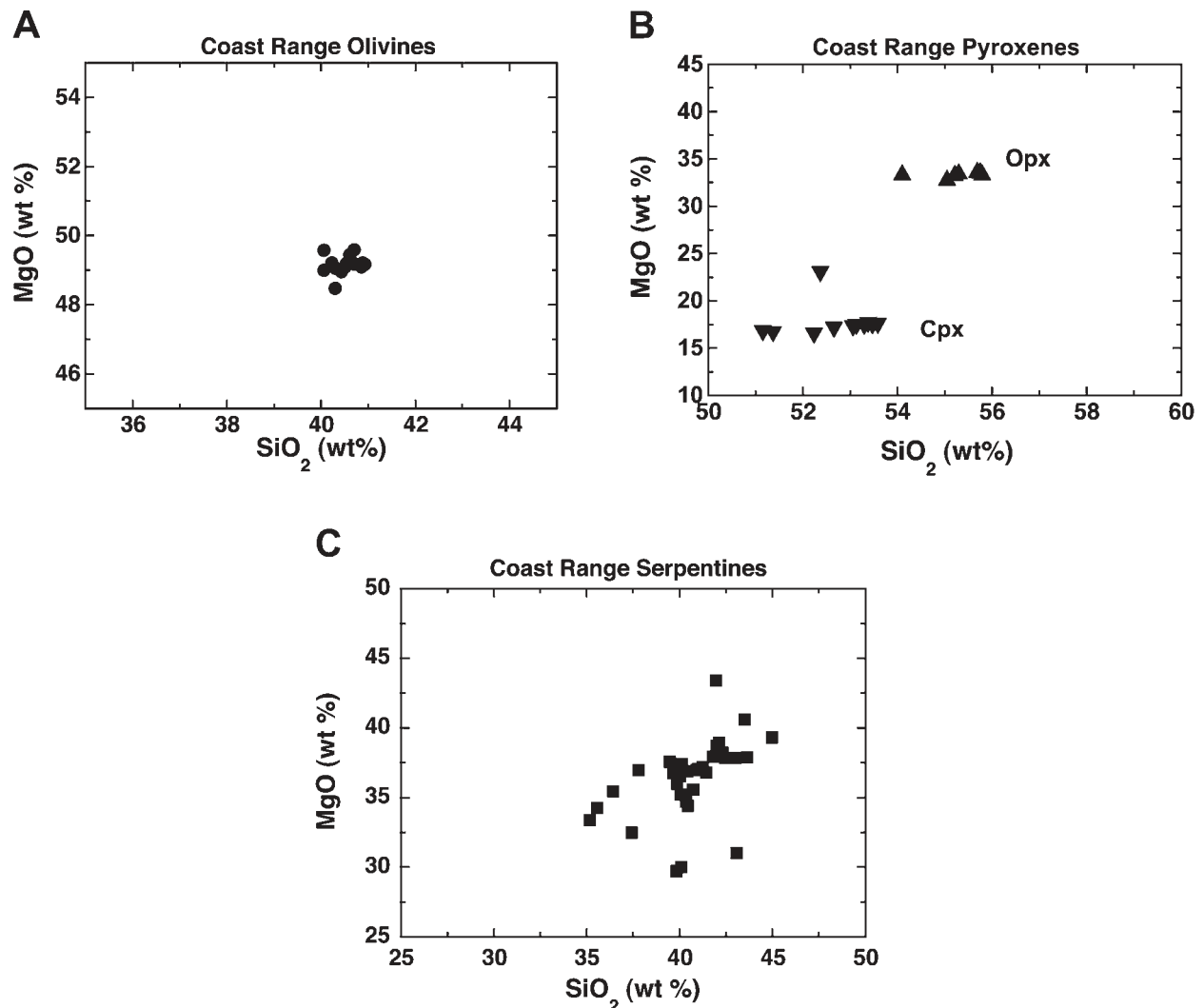

FIG. 3.   A: Compositions of olivine grains from rocks collected from the Coast Range ophiolite peridotite, represented by SiO$_2$ content in weight percent on the *x*-axis and MgO content in weight percent on the *y*-axis. Note the homogeneity in composition in the 30 or so individual analyses, corresponding to a composition of $Fo_{90}Fa_{10}$. B: Compositions of pyroxenes from rocks collected from the Coast Range ophiolite peridotite, represented by SiO$_2$ content in weight percent on the *x*-axis and MgO content in weight percent on the *y*-axis. Note the homogeneity in MgO composition of the orthopyroxenes (Opx, triangles) and the variability in MgO composition of the clinopyroxenes (Cpx, inverted triangles). **C:** Compositions of serpentines from rocks collected from the Coast Range ophiolite peridotite, represented by SiO$_2$ content in weight percent on the *x*-axis and MgO content in weight percent on the *y*-axis. Note the variability in compositions, reflecting differences in the parent mineralogy.

for the olivines. The composition of the orthopyroxenes is also relatively homogeneous with a molar composition of $En_{90}Fs_{10}$ (90% enstatite, $MgSiO_3$; 10% ferrosilite, $FeSiO_3$) with variation of only a few weight percent SiO_2 (see Fig. 3B). The clinopyroxenes are also fairly homogeneous in composition with approximately $En_{49}Wo_{48}Fs_{03}$ (49% enstatite, $MgSiO_3$; 48% wollastonite, $CaSiO_3$; 3% ferrosilite, $FeSiO_3$). The average compositions in oxide weight percent for the olivines, as well as for the pyroxenes and serpentines from these rocks, are given in Table 1.

The opaque minerals identified in thin section include magnetite and chromite, along with more chromium- and aluminum-rich spinels. The magnetite generally lines the veins in three dimensions and appears to correlate quite well with presumed aqueous fluid flow. The magnetite-lined veins contain not only serpentine, but also magnesium hydroxide, *i.e.*, brucite (with variable amounts of iron) and occasionally minor amounts of carbonates (calcium-, magnesium-, and iron-bearing). In addition to lining veins, magnetite occurs along relict grain boundaries and, in rare cases, interspersed within veins and groundmass. Chromite and other spinel occur as irregularly shaped grains surrounded by either serpentine/chlorite groundmass or the primary olivine and pyroxene. We also observed spinel grains that were fractured and the fractures were filled with magnetite.

The serpentines are predominantly composed of silica and magnesium, with minor and highly variable amounts of other cations (iron, manganese, aluminum, chromium, calcium, and nickel). A direct correlation was observed between the aluminum content of the serpentine and the precursor mineralogy. Aluminum content increased in serpentine when formed from altered clinopyroxene, and was low when the parent minerals are olivine or orthopyroxene. The variability in composition can be seen graphically in Fig. 3C.

Serpentines cannot incorporate all of the iron from the alteration of the olivines into their crystal structures (Deer *et al.*, 1992). This is demonstrated by the calculated $Fe/(Fe + Mg)$ ratios for the serpentines relative to the olivines. The $Fe/(Fe + Mg)$ ratio for the olivines from the Coast Range peridotite was, on average, 0.097. For the serpentines, this ratio dropped to much lower values, which ranged from 0.04 to 0.07. As a result, the excess iron is forced to go into the formation of magnetite, according to Reactions 1 and 3.

DISCUSSION

The geology of the early Earth and Mars is likely to be closely approximated by ultramafic remnants of terrestrial ocean lithosphere now exposed on land (Nisbet, 1987; Longhi *et al.*, 1992; Singer and McSween, 1993; Nisbet and Sleep, 2001; Sleep *et al.*, 2004). Though the compositions of seawater and hydrothermal fluids on the early Earth and those on Mars are largely unknown, the fluid compositions were likely controlled by interaction with rocks. Consequently, studies of water–rock interactions that occur within ophiolite terranes on present-day Earth should provide insight into such processes on the early Earth and Mars. The presence of similar environments on the early Earth would bolster arguments presented by Russell *et al*. (1998), Russell (2003), and Hanczyc *et al*. (2003), who have proposed that such alkaline fluids would be very conducive to chemistry that led to biochemistry.

In addition to finding remnant, primary mineralogy within the rocks (primarily olivine and pyroxene), examination of samples collected from these environments revealed evidence of exten-

TABLE 1. AVERAGE MAJOR ELEMENT COMPOSITION OF PREDOMINANT MINERAL GROUPS FOR COAST RANGE OPHIOLITE PERIDOTITES, IN WEIGHT PERCENT OF ELEMENT OXIDES

	SiO_2	MgO	FeO	Al_2O_3	CaO	Total
Olivine	40.52	49.18	9.32	<1	<1	99.02
Orthopyroxene	55.26	33.60	6.36	3.31	<1	98.53
Clinopyroxene	52.60	17.49	2.36	3.03	23.98	99.16
Serpentine	41.41	37.54	3.98	<1	<1	82.93

The total for serpentine does not include structural water. Note that the totals for the primary igneous minerals (olivine, orthopyroxene, and clinopyroxene) are close to 100%.

sive aqueous alteration. Generation of H_2 during serpentinization of mafic rocks has been shown theoretically (Wetzel and Shock, 2000), in field measurements (Neal and Stanger, 1983; Abrajano *et al.*, 1990), and experimentally (Janecky and Seyfried, 1986; Berndt *et al.*, 1996; McCollom and Seewald, 2001). High concentrations of H_2 [up to 13,000 μM (Kelley *et al.*, 2001a)] have also been observed at several sea floor hydrothermal vent sites including Lost City (in the Atlantis Fracture Zone of the Mid-Atlantic Ridge) and Rainbow (on the Mid-Atlantic Ridge), where the high H_2 abundances are believed to result from water–rock interaction with ultramafic rocks (Charlou *et al.*, 1998; Holm and Charlou, 2001; Kelley *et al.*, 2001a,b). While the temperatures in ultramafic-hosted sites like Lost City are much lower than those typical of "black smoker" hydrothermal vents, it has been suggested that life may have begun in relatively cold conditions (Forterre, 1996; Galtier *et al.*, 1999; Moulton *et al.*, 2000). Ultramafic rocks in the flanks of mid-ocean ridge systems, represented by ophiolite sections on continental cratons, could have provided the chemical energy necessary for metabolic functions to begin on the early Earth and on Mars. In addition, because there may be a substantial volume increase (Hostetler *et al.*, 1966) and generation of heat during the serpentinization process, the alteration is somewhat self-sustaining once it begins. Volume increases induce fracturing of the rocks, which allows further intrusion of fluids into fresh primary material that also reacts with the fluid. The temperature increase would obviate the need to some extent for a nearby volcanic heat source to drive fluid flow or induce hydrothermal circulation.

Mineralogical evidence from ophiolite-hosted spring samples indicates that, though the thermodynamic driving force for serpentinization is large, the approach to equilibrium is slow. Such a situation, in which a large free energy potential is only slowly relaxed by abiotic processes, provides an ideal mechanism for long-term support of chemotrophic organisms, given that those organisms can overcome kinetic barriers and catalyze the process themselves.

The potential amount of hydrogen that could be generated from serpentinization of the rocks examined from the Coast Range Ophiolite can be estimated based on petrographic observations of the alteration products. Since the primary mineralogy has been extensively altered, some as-

sumptions must be made, which renders these conclusions only tentative. However, examination of thin sections of the peridotite indicate that approximately 70% of the remaining primary mineralogy (by volume) is olivine. Assuming that all of the primary minerals alter in the same proportions [though, in general, olivine tends to react faster with water than does pyroxene at temperatures <250°C (Bach *et al.*, 2004)], we can estimate that the original rock contained approximately 70% olivine by volume. For 1 m^3 of peridotite composed of 70% olivine, for which one-half of the olivine component has been altered and contains 10 mol% iron-bearing olivine with a density of 4.4 g/cm^3, we calculate that 755 mol of fayalite (the iron end-member of olivine) would have been consumed. With a ratio of 3 mol of fayalite producing 2 mol of H_2 through the reaction

$$3Fe_2SiO_4 + 2H_2O = 2Fe_3O_4 + 3SiO_2 + 2H_2 \quad (4)$$

the maximum amount of hydrogen that could be generated is 500 mol. Furthermore, assuming that it took the entire ~150 million years to alter the rocks to the point seen today, this gives a hydrogen production of 8.6 nmol/day/m^3 of rock.

Hydrogen can be used as an electron donor and energy source by a wide variety of chemotrophic organisms (Schwarz and Friedrich, 2003). Methanogenic microorganisms, which combine H_2 with mantle-derived CO_2, are frequently envisioned as prospective inhabitants of rock-hosted systems, and some studies have provided evidence for the existence of such communities supported by H_2 resulting from water–rock reactions (Stevens and McKinley, 1995; Chapelle *et al.*, 2002). The potential for other metabolic strategies is dependent on the availability of suitable electron acceptors (such as CO_2, Fe^{3+}, or other metals) and other nutrients in these systems. Preliminary results indicate the presence of Archaea that have a 98% genetic match with known haloalkaliphiles in the ophiolite spring (authors' unpublished data). The presence of these organisms in the fluids indicates that metabolic function is feasible for these systems, and there is a hypothesized connection between the conditions of the fluids and the nature of the organism tentatively identified. Based on the calculations presented below, other nutrients such as nitrogen and phosphorus need only be present at the microgram per cubic meter level to support the amount of

biomass estimated to be supportable by the amount of hydrogen available.

The quantity of biomass that can be supported by a given chemical flux is determined by the maintenance energy requirement (Harder, 1997; Tijhuis *et al.*, 1993). The energy delivered by a flux of 8.6 nmol of H_2/day depends on the metabolic process in question and the aqueous activity of H_2 and other products and reactants. However, methanogenic metabolism will not occur at energy yields significantly less than 2.5 kJ/mol of H_2 (Hoehler *et al.*, 2001), and energy yields are maximally about 40 kJ/mol of H_2 when H_2 is present at millimolar levels. At these energy yields, the H_2 flux delivers 15–345 μJ/day/m^3 of rock (minimally). In laboratory culture studies, the required maintenance energy for anaerobic microorganisms is about 1,300 J/g of biomass (dry weight)/day at 15°C (Tijhuis *et al.*, 1993), but a variety of work suggests that the requirement for maintenance of populations in nature is about three orders of magnitude smaller (Morita, 1997; Price and Sowers, 2004). Adopting a maintenance energy value of 1.3 J/g of biomass (dry weight)/day, we calculated that each cubic meter of rock could potentially support 12–265 μg of biomass (dry weight). Whether the system can actually host such a biomass depends on additional biological energy requirements and whether the flow of energy is diffuse or concentrated (Hoehler, 2004). At the present time, it should be noted that there is insufficient information to make this assessment. However, the greater the volume of rock that is altered by a Coast Range Ophiolite spring during passage to its ultimate effluent, the greater the potential for H_2 generation and concentration, and the greater the potential for hosting life. Similarly, if the observed mineral alteration occurred over a shorter time period, say 1 million years, the amount of hydrogen produced would be 86 μmol/day (or 2.1×10^{-3} L at standard temperature and pressure), certainly enough to sustain primary productivity based on hydrogen.

The discovery of Archean ophiolites, including a complete sequence in northern China that is reported to be 2.505 billion years old (Kusky *et al.*, 2001), provides evidence that similar rocks have existed near the surface over a significant portion of Earth's history (Moores, 2002). Thus, there is the potential for ophiolites to have supported a biosphere in the Archean and for the present-day study of such areas to aid the search for evidence of early chemolithoautotrophic life on Earth. (In contrast, since the ocean's crust is nowhere older than about 180 million years as a result of crustal subduction, such studies are impossible in more conventional ocean floor terranes.) Recently, Furnes *et al.* (2004) described evidence for a chemosynthetic biota in 3.5-billion-year-old pillow lavas, which are the upper units of ophiolitic sequences. If similar evidence is found within other portions of ophiolites, this could represent a characteristic of the earliest chemosynthetic life on Earth that would prove useful in searching for evidence of biological activity in such rocks.

The crust of Mars may be much more like ophiolite terranes than previously appreciated. Lack of significant plate tectonic activity would limit the potential for widespread "ridge processes" (*e.g.*, hydrothermal vent formation) and concentrate hydrothermal activity into more narrowly focused areas with active fluid flow. The similarity of Mars' crust to ophiolite terranes as a whole (as evidenced by studies of the Mars meteorites, for example, which range in composition from basalts to dunites) suggests that serpentinization processes such as those occurring in the Coast Range Ophiolite must have occurred throughout Mars' history wherever subsurface water was present. If subsurface liquid water is extant on Mars, the serpentinization process may still be occurring in limited areas. Serpentinization will undoubtedly occur at depth wherever liquid water comes into contact with ultramafic rocks. Because the reactions proceed more rapidly at higher temperatures, it is quite possible that sources of H_2 occur beneath habitable zones within the martian crust. One could imagine that volume increases associated with serpentinization would provide pathways upward through the crust for H_2 and heated fluid, thereby providing reducing power at shallower depth, as well as anomalous heat. Ophiolites may be the best analog to environments on Mars where life might have existed in the past and may yet exist today.

Serpentinizing terranes within the Mars crust are (or were) habitable zones in which liquid water, energy, and reducing power have been in existence for extended periods of time. They are zones where abiotic organic synthesis can occur (Holm and Charlou, 2001; Sleep *et al.*, 2004) and protobiological structures can be formed as a result of the reducing and alkaline nature of the fluids within them (Hanczyc *et al.*, 2003; Russell, 2003). Serpentinizing terranes are volumes of

subsurface rock, where chemosynthetic life can flourish for extended periods of time in the absence of light and independent of harsh or changing surface conditions.

How does one locate serpentinized terranes on Mars? Mineralogical, chemical, and morphological data gathered from Mars orbit can provide clues. Serpentine minerals may be a significant source of the elevated hydrogen seen in some equatorial regions by the Odyssey spacecraft, with abundances up to 8–9 wt% water-equivalent present in areas where water ice should not be stable (Feldman *et al.*, 2003). It is possible that some of these regions of elevated hydrogen abundances correspond to serpentinized or serpentinizing bodies at, or immediately below, the Mars surface.

Olivine has been identified at the surface of Mars on the basis of Mars Global Surveyor Thermal Emission Spectrometer data (Hoefen *et al.*, 2003). It should be noted that the olivine from Mars has been reported to be much higher in iron content (McSween *et al.*, 2004) than typical upper mantle olivines on Earth. Higher iron content in the same rock types (peridotites) would likely lead to an increase in the amount of hydrogen that could be generated through serpentinization. Concentrations of olivine in the Nili Fossae region of Mars were proposed to be deep-seated, olivine-rich units exposed after the occurrence of impact-related faulting. Similar exposures could occur in the central peaks or walls of impact craters as a result of deep impact gardening of the crust. The presence of olivine on the Mars surface produces a dilemma in the sense that, if water were ever present over Mars history, these presumably ancient exposures would have been altered to serpentine. However, the kinetics of the serpentinization reaction are very sluggish at temperatures below 200°C (Wegner and Ernst, 1983), and experimental data extrapolated to present Mars surface temperatures may not provide accurate reaction rates.

Craters and impact-related structures are very interesting localities from the perspective of serpentinization. In a process that could be likened to tectonic uplift, deep impact gardening is capable of elevating deep-seated ultrabasic rocks such as dunites to the surface. The heating and fracturing resulting from the impact can generate short-lived (10^5–10^6-year time scale) hydrothermal systems (Arengi, 1977; Whitehead *et al.*, 1990; Bunch *et al.*, 1999) that could begin the serpentinization process in rocks, which would have been previously dry and inaccessible to subsurface or surface water. Once serpentinization is initiated, the volume increase to the reactions could help provide fresh mineral surfaces that, in turn, continue to serpentinize.

In the absence of cratering activity, other morphological clues may be present. On Earth, serpentinization with its attendant volume increase is recognized as a tectonic force. The Lost City Hydrothermal Field (Kelley *et al.*, 2001a,b; Früh-Green *et al.*, 2004), for example, lies on the Atlantis Massif, a 15–20-km-wide dome-like exposure of serpentinized peridotite near the Mid-Atlantic Ridge axis. The Atlantis Massif has a relief of nearly 4,000 m, much of which is the result of volume increase and faulting associated with the serpentinization process. Likewise, Mottl *et al.* (2003) have described serpentinite mud volcanoes that appear as domes on the sea floor overlying the subducting Pacific plate in the Mariana forearc. Similar, albeit smaller, features may be present on Mars. These features could be easily mistaken for volcanic domes.

Because serpentinization can generate heat and hydrothermal activity, other promising areas could be the source regions for ancient mass wasting and water drainage, where no obvious volcanic activity has been noted. As higher-resolution terrain maps become available, the style of faulting and tectonic uplift could be studied in detail to identify potential serpentinizing terrains.

Lastly, serpentinizing terrains quite commonly release hydrogen and methane as a consequence of inorganic reactions or methanogenesis. Recent reports from the ESA Mars Express spacecraft (see, for example, http://www.esa.int/SPECIALS/Mars_Express/SEML131XDYD_1.html) have described co-varying and anomalously high concentrations of water vapor and methane in the atmosphere above regions where the Odyssey spacecraft has observed a water ice layer immediately below the surface. Could these areas of water ice (or excess hydrogen) be the consequence of deep-seated serpentinizing terrains where methane and hydrogen are generated in a hydrothermal cell? One could imagine that hydrogen or methane, dissolved in the hydrothermal fluid, could rise to the point where the liquid froze in the shallow crust. Under such conditions, the methane could be incorporated into a solid methane clathrate hydrate phase,

which would have different (anomalously high) melting properties relative to pure water ice (Stern *et al.*, 1996).

Based on our observations of the petrology of peridotites from the Coast Range Ophiolite, we hypothesize that these terranes represent locations analogous to those where early life may have taken hold on the early Earth and on Mars. Given the nature of chemical weathering in these rocks, they seem likely to have provided the raw materials and energy for chemolithoautotrophic organisms adapted to conditions typical of these environments. We further suggest that, based on recent results from the flotilla of spacecraft currently at Mars, fruitful searches for life on the Red Planet should focus on areas similar to terrestrial ophiolites.

ACKNOWLEDGMENTS

REFERENCES

Abrajano, T.A., Sturchio, N.C., Kennedy, B.M., Lyon, G.L., Muehlenbachs, K., and Böhlke, J.K. (1990) Geochemistry of reduced gas related to serpentinization of the Zambales ophiolite, Phillipines. *Appl. Geochem.* 5, 625–630.

Allen, D.E. and Seyfried, W.E., Jr. (2004) Serpentinization and heat generation: constraints from Lost City and Rainbow hydrothermal systems. *Geochim. Cosmochim. Acta* 68, 1347–1354.

Arengi, J.T. (1977) Evolution of the Sudbury Basin [M.S. thesis], University of Toronto, Toronto, Canada.

Bach, W., Garrid, C.J., Paulick, H., Harvey, J., and Rosner, M. (2004) Seawater-peridotite interactions: first insights from ODP Leg 209, MAR 15° N. *Geochem. Geophys. Geosyst.* 5, Q09F26, doi:10.1029/2004GC000744.

Bailey, E.H., Blake, M.C., Jr., and Jones, D.L. (1970) Onland Mesozoic oceanic crust in California Coast Ranges. *U.S. Geol. Survey Prof. Paper* 700-C, C70–C81.

Barnes, I. and O'Neil, J.R. (1969) The relationship between fluids in some fresh Alpine-type ultramafics and possible modern serpentinization, western United States. *GSA Bull.* 80, 1947–1960.

Barnes, I., LaMarche, V.C., Jr., and Himmelberg, G. (1967) Geochemical evidence of present-day serpentinization. *Science* 156, 830–832.

Barnes, I., Rapp, J.B., O'Neil, J.R., Sheppard, R.A., and Gude, A.J., III (1972) Metamorphic assemblages and the direction of flow of metamorphic fluids in four instances of serpentinization. *Contrib. Mineral. Petrol.* 35, 263–276.

Berndt, M.E., Allen, D.E., and Seyfried, W.E. (1996) Reduction of CO_2 during serpentinization of olivine at 300°C and 500 bars. *Geology* 24, 351–354.

Boston, P.J., Ivanov, M.V., and McKay, C.P. (1992) On the possibility of chemosynthetic ecosystems in subsurface habitats on Mars. *Icarus* 95, 300–308.

Brock, T.D. and Madigan, M.T. (1991) *Biology of Microorganisms*, 6th ed., Prentice-Hall, Inc., Englewood Cliffs, NJ.

Bunch, T.E., Becker, L., Des Marais, D., Tharpe, A., Schultz, P.H., Wolbach, W., Glavin, D.P., Brinton, K.L., and Bada, J.L. (1999) Carbonaceous matter in the rocks of the Sudbury Basin, Ontario, Canada. In *Large Meteorite Impacts and Planetary Evolution II, Geological Society of America Special Paper 339*, edited by B.O. Dressler and V.L. Sharpton, Geological Society of America, Boulder, CO, pp. 331–344.

Chapelle, F.H., O'Neill, K., Bradley, P.M., Methé, B.A., Ciufo, S.A., Knobel, L.L., and Lovely, D.R. (2002) A hydrogen-based subsurface microbial community dominated by methanogens. *Nature* 415, 312–315.

Charlou, J.L., Fouquet, Y., Bougalt, H., Donval, J.P., Etoubleau, J., Jean-Baptiste, Ph., Dapoigny, A., Appriou, P., and Rona, P.S. (1998) Intense CH_4 plumes generated by serpentinization of ultramafic rocks at the intersection of the 15°20'N fracture zone and the Mid-Atlantic Ridge. *Geochim. Cosmochim. Acta* 62, 2323–2333.

Coleman, R.G. (2000) Prospecting for ophiolites along the California continental margin. In *Ophiolites and Oceanic Crust: New Insights from Field Studies and the Ocean Drilling Program, Geological Society of America Special Paper 349*, edited by Y. Dilek, E. Moores, D. Elthon, and A. Nicolas, Geological Society of America, Boulder, CO, pp. 351–364.

Deer, W.A., Howie, R.A., and Zussman, J. (1992) *An Introduction to the Rock-Forming Minerals*, 2nd ed., Longman, Essex, UK.

Deming, J.W. and Baross, J.A. (1995) Deep-sea smokers: windows to a subsurface biosphere? *Geochim. Cosmochim. Acta* 57, 3219–3230.

Dickinson, W.R., Hopson, C.A., and Saleeby, J.B. (1996) Alternate origins of the Coast Range Ophiolite (California): introduction and implications. *GSA Today* 6(2), 1–11.

Feldman, W.C., Prettyman, T.H., Boynton, W.V., Squyres, S.W., Bish, D.L., Elphic, R.C., Funsten, H.O., Lawrence, D.J., Maurice, S., Moore, K.R., Tokar, R.L., and Vaniman, D.T. (2003) The global distribution of near-surface hydrogen on Mars [abstract 3218]. In *Sixth International Conference on Mars* [CD-ROM], Lunar and Planetary Institute, Houston.

Forterre, P. (1996) A hot topic: the origin of hyperthermophiles. *Cell* 85, 789–792.

Früh-Green, G.L., Connolly, J.A.D., Plas, A., 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, Geophysical Monograph Series 144*, edited by W.S.D. Wilcock, E.F. DeLong, D.S. Kelley, J.A. Baross, and S.C. Cary, 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.

Galtier, N., Tourasse, N., and Gouy, M. (1999) A nonhyperthermophilic common ancestor to extant life forms. *Science* 283, 220–221.

Hanczyc, M.M., Fujikawa, S.M., and Szostak, J.W. (2003) Experimental models of primitive cellular compartments: encapsulation, growth and division. *Science* 302, 618–621.

Harder, J. (1997) Species-independent maintenance energy and natural population sizes. *FEMS Microbiol. Ecol.* 23, 39–44.

Harper, G.D., Saleeby, J.B., and Heizler, M. (1994) Formation and emplacement of the Josephine ophiolite and Nevadan orogeny in the Klamath Mountains, California-Oregon: U/Pb zircon and $^{40}Ar/^{39}Ar$ geochronology. *J. Geophys. Res.* 99, 4293–4321.

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.

Hoehler, T.M. (2004) Biological energy requirements as quantitative boundary conditions for life in the subsurface. *Geobiology* 2, 205–215.

Hoehler, T.M., Alperin, M.J., Albert, D.B., and Martens, C.S. (2001) Apparent minimum free energy requirements for methanogenic archaea and sulfate-reducing bacteria in an anoxic marine sediment. *FEMS Microbiol. Ecol.* 38, 33–41.

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.

Hostetler, P.B., Coleman, R.G., Mumpton, F.A., and Evans, B.W. (1966) Brucite in Alpine serpentinization. *Am. Mineral.* 51, 75–98.

Janecky, D.R. and Seyfried, W.E., Jr. (1986) Hydrothermal serpentinization of peridotite within the oceanic crust: experimental investigations of mineralogy and major element chemistry. *Geochim. Cosmochim. Acta* 50, 1357–1378.

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 (2001a) An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30°N. *Nature* 412, 145–149.

Kelley, D., Karson, J., Blackman, D., Früh-Green, G., Butterfield, D., Lilley, M., Schrenk, M., Olson, E., Roe, K., Lebon, J., and the Shipboard Scientific Party (2001b) Discovery of Lost City: an off-axis, peridotite hosted, hydrothermal field near 30°N on the Mid-Atlantic Ridge. *Ridge Events* 11(2), 3–9.

Kelley, D.S., Karson, J.A., Früh-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., Bradley, A., Larson, B., Ludwig, K., Glickson, D., Buckman, K., Bradley, A.S., Brazelton, W.J., Roe, K., Elend, M.J., 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.

Kusky, T.M., Li, J.-H., and Tucker, R.D. (2001) The Archean Dongwanzi ophiolite complex, North China craton: 2.505-billion-year-old oceanic crust and mantle. *Science* 292, 1142–1145.

Longhi, J., Knittle, E., Holloway, J.R., and Wänke, H. (1992) The bulk composition and internal structure of Mars. In *Mars*, edited by H.H. Kieffer, B.M. Jakosky, C.W. Snyder, and M.S. Matthews, University of Arizona Press, Tucson, pp. 184–208.

McCollom, T.M. (2006) The habitability of Mars: past and present. In *Solar System Update*, edited by P. Blondel and J. Mason, Springer, London (in press).

McCollom, T.M. and Seewald, J.S. (2001) A reassessment of the potential for reduction of dissolved CO_2 to hydrocarbons during serpentinization of olivine. *Geochim. Cosmochim. Acta* 65, 3769–3778.

McCollom, T.M. and Shock, E.L. (1997) Geochemical constraints on chemolithoautotrophic metabolism by microorganisms in seafloor hydrothermal systems. *Geochim. Cosmochim. Acta* 61, 4375–4391.

McSween, H.Y., Jr., Arvidson, R.E., Bell, J.F., III, Blaney, D., Cabrol, N.A., Christensen, P.R., Clark, B.C., Crisp, J.A., Crumpler, L.S., Des Marais, D.J., Farmer, J.D., Gellert, R., Ghosh, A., Gorevan, S., Graff, T., Grant, J., Haskin, L.A., Herkenhoff, K.E., Johnson, J.R., Jolliff, B.L., Klingelhoefer, G., Knudson, A.T., McLennan, S., Milam, K.A., Moersch, J.E., Morris, R.V., Rieder, R., Ruff, S.W., de Souza, P.A., Jr., Squyres, S.W., Wänke,

H., Wang, A., Wyatt, M.B., Yen, A., and Zipfel, J. (2004) Basaltic rocks analyzed by the Sprit Rover in Gusev Crater. *Science* 305, 842–845.

Moores, E.M. (2002) Pre-1 Ga (pre-Rodinian) ophiolites: their tectonic and environmental implications. *GSA Bull*. 114, 80–95.

Morita, R. (1997) *Bacteria in Oligotrophic Environments*, Chapman & Hall, New York.

Mottl, M.J., Komor, S.C., Fryer, P., and Moyer, C.L. (2003) Deep-slab fluids fuel extremophilic Archaea on a Mariana forearc serpentinite mud volcano: Ocean Drilling Program Leg 195. *Geochem. Geophys. Geosyst*. 4(11), 9009, doi:10.1029/2003GC000588.

Moulton, V., Gardner, P.P., Pointon, R.F., Creamer, L.K., Jameson, G.B., and Penny, D. (2000) RNA folding argues against a hot-start origin of life. *J. Mol. Evol*. 51, 416–421.

Neal, C. and Stanger, G. (1983) Hydrogen generation from mantle source rocks in Oman. *Earth Planet. Sci. Lett*. 91, 73–88.

Nisbet, E.G. (1987) *The Young Earth—An Introduction to Archaean Geology*, Allen & Unwin, Boston.

Nisbet, E.G. and Sleep, N.H. (2001) The habitat and nature of early life. *Nature* 409, 1083–1091.

Page, B.M. (1972) Oceanic crust and mantle fragment in subduction complex near San Luis Obispo, California. *GSA Bull*. 83, 957–972.

Peters, E.K. (1993) δ-^{18}O enriched waters of the Coast Range Mountains, northern California: connate and ore-forming fluids. *Geochim. Cosmochim. Acta* 57, 1093–1104.

Price, B. and Sowers, T. (2004) Temperature dependence of metabolic rates for microbial growth, maintenance, and survival. *Proc. Natl. Acad. Sci. USA* 101, 4631–4636.

Russell, M.J. (2003) The importance of being alkaline. *Science* 302, 580–581.

Russell, M.J., Daia, D.E., and Hall, A.J. (1998) The emergence of life from FeS bubbles at alkaline hot springs in an acid ocean. In *Thermophiles: The Keys to Molecular Evolution and the Origin of Life?*, edited by J. Wiegel and M.W.W. Adams, Taylor & Francis, London, pp. 77–126.

Schwarz, E. and Friedrich, B. (2003) The H$_2$-metabolizing prokaryotes. In *The Prokaryotes: An Evolving Electronic Resource for the Microbiological Community*, 3rd ed., release 3.14, edited by M. Dworkin, Springer-Verlag, New York. Available online at: http://link.springer-ny.com/link/service/books/10125/.

Shock, E.L. (1997) High-temperature life without photosynthesis as a model for Mars. *J. Geophys. Res*. 102, 23687–23694.

Singer, R.B. and McSween, H.Y., Jr. (1993) The igneous crust of Mars: compositional evidence from remote sensing and SNC meteorites. In *Resources of Near-Earth Space*, edited by J.S. Lewis, M.S. Matthews, and M.M.L. Guerrieri, University of Arizona Press, Tucson, pp. 709–736.

Sleep, N.H., Meibom, A., Fridriksson, Th., Colemen, R.G., and Bird, D.K. (2004) H$_2$-rich fluids from serpentinization: geochemical and biotic implications. *Proc. Natl. Acad. Sci. USA* 101, 12818–12823.

Stern, L.A., Kirby, S.H., and Durham, W.B. (1996) Peculiarities of methane clathrate hydrate formation and solid-state deformation, including possible superheating of water ice. *Science* 273, 1843–1848.

Stevens, T.O. and McKinley, J.P. (1995) Lithoautotrophic microbial ecosystems in deep basalt aquifers. *Science* 270, 450–454.

Tijhuis, L., van Loosdrecht, M.C.M., and Heijnen, J.J. (1993) A thermodynamically based correlation for maintenance Gibbs energy requirements in aerobic and anaerobic chemotrophic growth. *Biotechnol. Bioeng*. 42, 509–519.

Wegner, W.W. and Ernst, W.G. (1983) Experimentally determined hydration and dehydration reaction rates in the system MgO-SiO$_2$-H$_2$O. *Am. J. Sci*. 283-A, 151–180.

Wetzel, L.R. and Shock, E.L. (2000) Distinguishing ultramafic- from basalt-hosted submarine hydrothermal systems by comparing calculated vent fluid compositions. *J. Geophys. Res*. 105(B4), 8319–8340.

Whitehead, R.E.S., Davies, J.F., and Goodfellow, W.D. (1990) Isotopic evidence for hydrothermal discharge into anoxic seawater, Sudbury basin, Ontario, Canada. *Chem. Geol*. 86, 49–63.

Address reprint requests to:
Mitch Schulte
Department of Geological Sciences
University of Missouri
101 Geology Building
Columbia, MO 65203

E-mail: schultemd@missouri.edu