Serpentinization, Carbon, and Deep Life

Matthew O. Schrenk, William J. Brazelton

Department of Biology
East Carolina University
Greenville, North Carolina 27858-2502, U.S.A.
schrenkm@ecu.edu     brazeltonw@ecu.edu

Susan Q. Lang

Department of Earth Sciences
ETH Zürich
8092 Zürich, Switzerland
susan.lang@erdw.ethz.ch

INTRODUCTION

The aqueous alteration of ultramafic rocks through serpentinization liberates mantle carbon and reducing power. Serpentinization occurs in numerous settings on present day Earth, including subduction zones, mid-ocean ridges, and ophiolites and has extended far into Earth’s history, potentially contributing to the origins and early evolution of life. Serpentinization can provide the energy and raw materials to support chemosynthetic microbial communities that may penetrate deep into Earth’s subsurface. Microorganisms may also influence the composition and quantity of carbon-bearing compounds in the deep subsurface. However, conditions created by serpentinization challenge the known limits of microbial physiology in terms of extreme pH, access to electron acceptors, and availability of nutrients. Furthermore, the downward transport of surface carbon and subsequent mixing with calcium-rich fluids at high pH contributes to the precipitation and immobilization of carbonate minerals. The following chapter will explore the physiological challenges presented by the serpentinite environment, data from studies of serpentinite-hosted microbial ecosystems, and areas in need of further investigation.

THE PROCESS OF SERPENTINIZATION

Physical and chemical consequences of serpentinization

Serpentinization is an alteration process of low-silica ultramafic rocks, characteristic of the lower oceanic crust and upper mantle. These rocks are rich in the minerals olivine and pyroxene. Water-rock reactions result in the oxidation of ferrous iron from olivine and pyroxene, resulting in the precipitation of ferric iron in magnetite (Fe₃O₄) and other minerals, and in the release of diatomic hydrogen (H₂). At low temperatures (< ~150 °C) the reaction results in extremely high pH, commonly above 10. The combination of H₂ and CO₂ or CO under highly reducing conditions leads to formation of methane and other hydrocarbons through Fischer-Tropsch Type (FTT) synthesis (McCollom and Seewald 2001; Charlou et al. 2002; Proskurowski et al. 2008; McCollom 2013). Serpentinization also results in volume changes in the altered materials, making serpentinites less dense than their parent materials and facilitating uplift due to volume expansion. These reactions are highly exothermic, and may contribute to hydrothermal fluid circulation through the fractured materials (Lowell and Rona 2002; Allen and Seyfried 2004).
Furthermore, the Ca$^{2+}$ ions liberated from the water-rock reactions react with carbonate ions at high pH to induce calcium carbonate precipitation (Barnes et al. 1978; Neal and Stanger 1983; Fritz et al. 1992; Palandri and Reed 2004; Kelley et al. 2005). Carbonates can exist as fracture infillings in the host rock or can manifest as travertines or chimneys upon exiting the subsurface (Fig. 1).

Figure 1. Examples of serpentinization and calcium carbonate mineralization. Fractured serpentinite rock (A) from the Tablelands Ophiolite, Newfoundland, Canada, showing the complex mosaic of fractures and infilling associated with pervasive serpentinization. Carbonate chimneys formed in the marine serpentinite environments at the (B) Lost City Field and (C) Mariana Forearc. (B) reprinted with permission of AAAS from Kelley et al. (2005). (C) reprinted with permission of Annual Reviews from Fryer (2012).
Types of serpentinizing habitats

Serpentinization occurs in a diverse range of locations on Earth, particularly where tectonic processes lead to the uplift and exposure of mantle materials. Additionally, serpentinization may occur in the deepest habitable portions of Earth’s subsurface, ultimately constrained by the depths of fluid circulation.

The characterization of several of the systems described in more detail below is in the early stages (Tables 1 and 2). In some cases it is not yet possible to differentiate between locations where serpentinization is an active process from those locations where fluids pass through reacted serpentinites, leading to the dissolution of the rock.

Identifying serpentinization habitats. The large carbonate deposits that commonly form when alkaline waters exit from peridotites are often the most readily recognized feature of active serpentinization. The first descriptions of springs affected by serpentinization are from continental locations, some of which are associated with large travertine deposits (Barnes et al. 1978). Detection of active serpentinization in oceanic settings is more challenging. In some instances, such as the Rainbow vent field, a hydrothermal system with primarily basalt-hosted characteristics (high-temperature metal-rich fluids) may also have characteristics indicative of reaction with ultramafic rocks, i.e., unexpectedly high hydrogen and methane concentrations (Table 1; Charlou et al. 2002). But the discovery of the low-temperature, alkaline Lost City system came about much in the same way as many of those found in land-based systems: through the serendipitous observation of large carbonate deposits (Kelley et al. 2001). Detecting the presence of a Lost City-type system is challenging, as fluids do not reach the temperatures of basalt-hosted systems and low metal content in the fluids result in only minor particle precipitation. Therefore, the typical methods to detect active venting of marine basalt-hosted hydrothermal systems, such as water column temperature and optical backscatter anomalies are of limited usefulness.

Serpentinizing ophiolites. Remnants of seafloor serpentinization are present along continental margins in ophiolite sequences. Continental springs seep alkaline, volatile-rich fluids from ultramafic rocks. The ophiolites themselves originate from a number of different tectonic events including subduction, extension, and plume-related events (Dilek and Furnes 2011). The distinctive plant flora associated with serpentinites has been the subject of study for several decades, although the microbiology of these systems is less well understood. The serpentinization of ophiolites can continue for hundreds of millions of years after emplacement. Seep fluid compositions are generally lacking in dissolved ions as the original source water is meteoric, although in some cases dissolved ions such as sulfate may be present from the contributions of paleo-seawater, or the dissolution of mineral salts (Table 2). In some cases accretion of marine sediments and organic matter can contribute to the carbon and nutrient budgets of these environments (Hosgormez et al. 2008).

The Coast Range and Josephine ophiolites in the western United States were amongst the first serpentinizing ophiolites to be intensively studied (Barnes et al. 1967; Barnes and O’Neil 1971). Multiple Ca-OH type springs and seeps emanate from rocks that are Jurassic-Cretaceous in age at temperatures less than ~50 °C.

The Samail ophiolite in the Sultanate of Oman is one of the most extensive known continental ophiolites, comprised of oceanic crust and upper mantle (ultramafic) lithologies that are >350 km long, ~40 km wide and have an average thickness of ~5 km (Neal and Stanger 1983; Nicolas et al. 2000). Stable isotope and $^{14}$C dating of the carbonate veins indicate the majority of veins were formed at low (<60 °C) temperatures in the recent (<50,000 years) past, during interaction with meteoric groundwater (Barnes et al. 1978; Nicolas et al. 2000; Kelemen and Matter 2008; Kelemen et al. 2011). Alkaline water and gases emanating from the peridotites have high concentrations of methane, hydrogen, and short-chain hydrocarbons, and
mean residence times on the order of years to decades (Fritz et al. 1992). In recent years, this ophiolite has been studied as a potential site for the sequestration of atmospheric carbon dioxide through geo-engineering strategies aimed at mineral carbonation (Kelemen and Matter 2008).

The Zambales Ophiolite in the Philippines is one of the first locations where stable isotope geochemistry was applied to determine the source of volatile gases (Abrajano et al. 1988, 1990). The authors of these studies determined that the hydration of peridotites through serpentinization contributes to the gas compositional signatures at the site (Abrajano et al. 1990).

The Tekirova Ophiolites of Turkey have emitted significant quantities of H2 and CH4 gas emissions for millennia, contributing an estimated 150 to 190 tons of CH4 per year (Etiope et al. 2011). Gases at the Chimaera seep at this site have been aflame for centuries and can be attributable to the “eternal flame” mentioned in ancient Greek literature. The methane in the fluids is generated largely through serpentinization and to a lesser extent the thermogenic degradation of complex organic matter (Hosgormez et al. 2008).

The Bay of Islands Ophiolite in Newfoundland, Canada was emplaced nearly 500 Ma ago. The site contains pH >12 springs enriched in H2 (~1 mg L⁻¹) and CH4 (~0.3 mg L⁻¹) that

<table>
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<th>Sediment Depth</th>
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<th>pH</th>
<th>H2(aq) mM</th>
<th>δD, H2 (%) VSMOW</th>
<th>H2S(aq) mM</th>
<th>CH4(aq) mM</th>
<th>δ13C, CH4 (%) VPDB</th>
<th>δD, CH4 (%) VSMOW</th>
<th>ΣCO2 mM</th>
<th>formate µM</th>
<th>acetate µM</th>
<th>NO3⁻ mM</th>
<th>SO4²⁻ mM</th>
<th>O2(aq) mM</th>
<th>Cl mM</th>
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</tbody>
</table>

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*aCharlou et al. 2002
bKeir 2010
cHaggerty and Fisher 1992; Mottl et al. 2003
dMottl et al. 2003
eKelley et al. 2001, 2005; Proskurowski et al. 2006; Lang et al. 2010
fCharlou et al. 1998, 2002; Douville et al. 2002
gCharlou et al. 1998, 2002, 2010; Douville et al. 2002; Proskurowski et al. 2006
hCharlou et al. 2010
iMelchert et al. 2008; Schmidt et al. 2011
emanate from largely barren, heavily serpentinized terrain (Szponar et al. 2012). The extremely long time period of serpentinization is speculated to be punctuated and linked to geophysical changes in the environment, such as glaciation/deglaciation events.

Ultramafic rocks of the Gruppo di Voltri (Liguria, Italy) host highly reducing, pH 10.5-12 springs forming carbonate deposits (Cipolli et al. 2004). At Cabeço de Vide (Portugal), deep wells access aquifers in the serpentinite subsurface (Marques et al. 2008).

Oceanic core complexes and mid-ocean ridges. Ocean core complexes are sections of deep oceanic lithosphere exhumed to the seafloor by detachment faults formed along the flanks of slow to intermediate spreading ridges. The extensive faulting and fracturing associated with this uplift as well as the latent heat of the rock promotes fluid circulation that can result in serpentinization. Ultramafic rocks may constitute up to 20% of slow spreading mid-ocean ridges; therefore the process of serpentinization represents a significant, yet understudied phenomenon (Früh-Green et al. 2004).

Since its discovery in 2000, the Lost City Hydrothermal Field (LCHF), near the Mid-Atlantic Ridge, has been one of the most intensively studied sites of active serpentinization. At
Lost City, the Atlantis Massif has been uplifted ~5,000 m relative to the surrounding terrain. Tall calcium carbonate chimneys at the LCHF rise up to 60 m from the seafloor and serve as conduits for hot, highly reducing, high-pH hydrothermal fluids (Table 1; Fig. 1b). Venting fluids at the LCHF range from 40 to 91 °C, and are rich in hydrogen and methane (Kelley et al. 2001, 2005). Hydrothermal activity has been sustained at the LCHF for at least 30,000 years and potentially >100,000 years, as evidenced by 14C and U/Th dating of the extensive calcium carbonate deposits that abound in the vent field (Früh-Green et al. 2003; Ludwig et al. 2011).

Attempts to access the serpentinite subsurface of the Atlantis Massif through the Integrated Ocean Drilling Program at Hole 1309D during Expeditions 304 and 305 sampled igneous rocks for microbiological analysis from up to 1,391 m below the seafloor (Mason et al. 2010). The

<table>
<thead>
<tr>
<th>Ophiolite</th>
<th>Units</th>
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<td>mV</td>
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**Fluid Chemistry**

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**Gas Chemistry**

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<td>0.03 to 0.6 mM</td>
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<td>CH4</td>
<td>vol%</td>
<td>0 to 4.3</td>
<td>−28.5 to −15.9</td>
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<td>iso-Butane</td>
<td>vol%</td>
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<td>0 to 0.3 μM</td>
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<td>vol%</td>
<td>0.0001 to 0.0012</td>
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<tr>
<td>Total</td>
<td>vol%</td>
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<tr>
<td>Hydrocarbons</td>
<td>%</td>
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Table 2. Geochemical characteristics of continental serpentinite springs

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<tr>
<td>Ophiolite</td>
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<td></td>
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<tr>
<td>Coast Range</td>
<td>Cazadero, CA</td>
<td>Del Puerto</td>
<td>Tablelands</td>
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aBarnes et al. 1978; Neal and Stanger 1983; Bath et al. 1987; Fritz et al. 1992
bBarnes et al. 1978
cBlank et al. 2009
dSzponar et al. 2012
eBarnes et al. 1978
fMarques et al. 2008
gCipolli et al. 2004
hAbrajando et al. 1988, 1990
iEtiope et al. 2011; Hosgormez et al. 2008
study found a highly heterogeneous petrology, consisting largely of gabbros, but with regions of serpentinized peridotites.

In addition to the LCHF, slow- and ultraslow-spreading mid-ocean ridges support a number of well-studied high-temperature (>300 °C) hydrothermal systems influenced by serpentinization. In these systems, the flow pathway for magmatically driven hydrothermal circulation passes through ultramafic rocks, facilitating water-rock reaction, imparting a strong volatile signature upon the hydrothermal fluids. Compared to the LCHF, fluids from these systems have higher temperatures, higher metal concentrations, and are more acidic, but, in contrast to purely basalt-hosted systems, have highly elevated hydrogen and methane concentrations (Table 1). The Rainbow (36° 14′ N) and Logatchev (14° 45′ N) vent fields along
the Mid-Atlantic Ridge are the best studied of these systems. Fluids from both fields exit large sulfide deposits at temperatures >300 °C and contain elevated concentrations of hydrogen, methane, and C2-C5 hydrocarbons (Charlou et al. 2002). Over the past decade, several more high-temperature vent fields hosted in peridotites have been discovered along the Mid-Atlantic Ridge, including a second field close to Logatchev, named Logatchev-2 (14° 43′ N) and, further south, the Ashadze I and II (12° 58′ N) and Nibelungen vent fields (8° 18′ S) (Melchert et al. 2008; Charlou et al. 2010; Schmidt et al. 2011).

Similar settings occur on the Central Indian Ridge and the Southwest Indian Ridge in the Indian Ocean. Kairei Field at the Central Indian Ridge contains features of both ultramafic- and basalt-hosted hydrothermal fields, including high H2 and Si concentrations and a low CH4/H2 ratio (Takai et al. 2004). These characteristics can be explained by the serpentinization of troctolites (olivine-rich gabbros) and subsequent reaction with basalt.

Recent discoveries may expand the known breadth of hydrothermal systems that are influenced by serpentinization. Studies of the ultraslow spreading Gakkel Ridge in the Arctic Ocean indicate extensive hydrothermal activity hosted in ultramafic rocks at high latitudes (Edmonds et al. 2003). Additionally, the deepest hydrothermal vents known to date, up to 5,000 m below the sea surface, have been discovered near the Mid-Cayman Rise in the Caribbean Sea (German et al. 2010). Vent plumes along the Mid-Cayman Rise are consistent with the presence of both high-temperature “black smoker type” venting as well as moderate-temperature, serpentinization-influenced vent fields. Ongoing investigations are serving to better define the characteristics of these systems and their associated biological communities.

A potential shallow sea analog to the LCHF may exist in the Bay of Prony, New Caledonia, where brucite-rich, carbonate towers vent 22-43 °C, freshwater, pH 11 fluids (Cox et al. 1982; Launay and Fontes 1985). This site, which was visited by a French research cruise in 2011, may represent an interesting transition between marine and terrestrial serpentinite hydrothermal settings.

Subduction zones and mud volcanoes. A second important location of serpentinization in the marine environment is associated with the hydration of oceanic crust at subduction zones. At these sites, fluids from the subducting plate can hydrate the mantle of the overriding plate and cause serpentinization. Density changes associated with serpentinization of the mantle lead to diapirs of the hydrated materials that in some cases reach the seafloor, forming “mud volcanoes”. Fluid compositions change with distance from the trench, indicating variability in the conditions of serpentinization (Mottl et al. 2003). The best studied of these systems is the Mariana Forearc, where the Pacific Plate is subducted beneath the Philippine Plate (Fryer 2012). Mud volcanoes vent high pH fluids (up to 12.5) rich in hydrogen, methane, formate, and acetate (Haggerty and Fisher 1992; Mottl et al. 2003). High 13C contents of methane and relatively low C1/C2 ratios in pore fluids point to a mantle source for these carbon species. A second serpentinization-influenced seep site has been identified in the Southern Mariana Forearc (Ohara et al. 2011), and similar mud volcanoes exist in regions associated with subduction such as in the Caribbean Sea.

Precambrian shields. Ultramafic rocks found in Precambrian continental shield environments in the Fennoscandian Shield, South Africa, and Canada are important additional sites of serpentinization, potentially contributing to global hydrogen and hydrocarbon budgets (Sherwood Lollar et al. 1993). As fluids circulate through these systems, serpentinization of ultramafic rocks leads to hydrogen generation and potentially to abiogenic synthesis of organic matter (McCollom 2013; Sephton and Hazen 2013).

Serpentinization on other planets. Evidence of past serpentinization has been detected on the surface of Mars and has been important for helping to model planetary habitability and define the source of atmospheric gases (Ehlmann et al. 2010). Serpentinization may even drive
hydrothermal circulation in small planetary bodies of the outer solar system and contribute to the energy budget of Europa’s subsurface ocean (Vance et al. 2007).

**BIOLOGICAL CONSEQUENCES OF SERPENTINIZATION**

Although the picture of the global serpentinite biosphere is still emerging, themes can be gleaned from both geochemical and microbiological studies of serpentinite-hosted microbial ecosystems. The impact of serpentinization upon fluid chemistry imposes a unique set of conditions upon the organisms and biological activities operative in such ecosystems (Tables 1 and 2, Fig. 2). Serpentinizing environments are typically rich in electron donors such as \( \text{H}_2 \) and \( \text{CH}_4 \), and in some cases, short-chain hydrocarbons and formate. The availability of terminal electron acceptors is frequently limited, however, particularly in continental systems. Moreover, the microbial communities in serpentinizing ecosystems face physiological challenges in terms of high pH and low concentrations of dissolved inorganic carbon.

Common biological observations in the most extreme alkaline fluids at many of the sites include low cell abundances (typically less than \( 10^5 \) cells/mL, and as low as \( 10^2 \) cells/mL) and low taxonomic diversity (Schrenk et al. 2004; Tiago et al. 2004; Brazelton et al. 2010). Greater biomass (but not necessarily greater diversity) can be seen in surface-attached habitats, where serpentinization fluids mix with ambient water; the densely-populated biofilms of Lost City carbonate chimneys are a dramatic example. In many of these systems the cycling of hydrogen, methane, sulfur, and fermentative processes appear to be important metabolic activities.

**Metabolic strategies in serpentinite-hosted ecosystems**

An important consideration for the ability of life to persist in extreme environments is the balance between the energy necessary for biosynthesis and activity, and that required for repair and maintenance (Hoehler 2007). Developing a framework for the productivity of serpentinite-hosted subsurface environments requires a greater understanding of microbial physiology in such ecosystems and the energetic costs associated with coping strategies. Therefore, an important step toward developing quantitative models of habitability in these ecosystems is to inventory the taxonomies and metabolic capabilities of the native microorganisms. A review of our as yet limited knowledge on this topic follows.

**Hydrogen cycling.** The most obvious electron donor in serpentinizing habitats is the copious quantity of hydrogen produced through serpentinitization reactions (Tables 1 and 2). The oxidation of this hydrogen under aerobic or anaerobic conditions can provide abundant metabolic energy to local communities (McCollom 2007, 2013). The ubiquity of this energy source in serpentinitizing environments is reflected in the microbiology of these systems through genomic and cultivation-based studies (Tables 3 and 4; Takai et al. 2004; Perner et al. 2010; Brazelton et al. 2012).

Hydrogen stimulates the metabolic activity of Lost City chimney biofilms, as evidenced by microcosm experiments (Brazelton et al. 2011). Work by Perner et al. (2010) at the Logatchev vent field (14° 4’ N) showed molecular and geochemical evidence for carbon fixation linked to hydrogen oxidation. The diversity of hydrogenase genes (associated with hydrogen oxidation) increased with increasing hydrogen concentrations (Perner et al. 2007, 2010).

Spring fluids from the Tablelands Complex within the Bay of Islands Ophiolite (Newfoundland, Canada) have been sampled and used in comparative community (meta-)genomic analyses. Metagenomic data contained a high proportion of sequences related to Betaproteobacteria within the order Burkholderiales who appear to oxidize hydrogen as a source of energy and assimilate carbon using the Calvin-Benson-Bassham (CBB) pathway (Brazelton et al. 2012). The metagenomic data also identified Clostridiales-like organisms that
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possess genes for hydrogen production typically associated with fermentation and are presumed to inhabit anoxic regions of the subsurface underlying the springs. Therefore, these serpentinite springs harbor the genetic potential for both microbial oxidation and production of hydrogen.

Recent studies of a subsurface Outokumpu borehole in Finland have also reported phylotypes within the Betaproteobacteria and Clostridiales in waters up to 1,400 m below the land surface (Itävaara et al. 2011). Elevated cell abundances are associated with a layer containing serpentinized peridotites, although the pH of the bulk borehole water is ~9.

Figure 2. Schematic of putative biogeochemical processes in continental (A) and marine (B) serpentinization settings. Question marks indicate sources of uncertainty due to lack of data and should be considered speculative. Each schematic represents an idealized setting and reflects reality to varying degrees for each actual natural environment. This diagram is most representative of low-temperature, actively serpentinizing systems such as the Lost City hydrothermal field. Many serpentine-hosted marine systems (e.g. Rainbow and Logatchev) feature sulfide chimneys rather than carbonate chimney deposits and have lower pH fluids compared to this diagram.
The detection of both Betaproteobacteria (typically order Burkholderiales) and Clostridia (typically order Clostridiales) appears to be a common theme in serpentinite-hosted ecosystems. As mentioned above, both taxa have been identified in high-pH serpentinite springs in Canada and Finland, and they are also present (but not dominant) in Lost City carbonate chimneys (Brazelton et al. 2010). These taxa also dominate the microbial community structure of a 3-km borehole in South Africa (Moser et al. 2005). Fluids from this borehole are moderately basic (pH ~9) and enriched in H₂ (up to 3.7 mM), but serpentinization does not appear to be active at this site. Therefore, further work should investigate whether the presence of particular phylotypes of Betaproteobacteria and Clostridia are diagnostic of serpentinization-driven ecosystems and whether these phylotypes are ubiquitous in other high pH, H₂-rich environments irrespective of serpentinizing activity.

As explained above, metagenomic evidence indicates that the Betaproteobacteria harbor genes for hydrogen oxidation (Brazelton et al. 2012), a partial explanation for their ubiquity in these environments. It is unknown whether they also harbor adaptations for survival at high pH. While the Betaproteobacteria seem most likely to inhabit transition zones where hydrogen and oxygen are both available, the Clostridia seem to be more abundant in the deepest, most

<table>
<thead>
<tr>
<th>Habitat Type of Analysis</th>
<th>Reference</th>
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<tr>
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<td>Rainbow</td>
<td>mcrA gene</td>
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<td>16S rDNA, mcrA</td>
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Table 4. Bacteria characteristic of serpentinite habitats

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<td>Rainbow</td>
<td>dsrAB</td>
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(Table 4 is continued on facing page)
Serpentinization, Carbon, and Deep Life

anoxic portions of serpentinizing ecosystems (Fig. 2; Brazelton et al. 2010, 2012; Itävaara et al. 2011). The Clostridia in these environments are expected to be capable of fermentation that can involve the use of a single organic compound as both oxidant and reductant. This mode-of-growth may allow them to overcome the lack of exogenous oxidants in the most extreme zones of these environments. However, other strains of alkaliphilic Clostridia isolated from soda lakes are capable of autotrophic or mixotrophic growth (Sorokin et al. 2008). Deciphering the carbon assimilation strategies of subsurface Clostridiales will be of critical importance in studying the biogeochemistry of the serpentinizing subsurface.

**Sulfur cycling.** The presence of sulfate in continental and marine settings, when combined with the hydrogen that is a by-product of serpentinization reactions, presents the ideal conditions for microbial sulfate reduction. In freshwater systems dissolved ions are frequently scarce, and sulfate may not be present in appreciable concentrations (Table 2). In marine settings, deep seawater contains high concentrations of sulfate that would be available to microbial communities in the mixing zones with hydrothermal fluids. In some instances such as the Lost City field, where fluids do not reach high enough temperatures to induce the precipitation of anhydrite (CaSO₄), sulfate can also be present in the end-member hydrothermal fluid (Kelley et al. 2005).

One of the earliest published studies on the microbiology of serpentines examined the alkaline springs of Oman using culture-dependent approaches and documented the presence of sulfate-reducing bacteria (Bath et al. 1987). Recent cultivation-independent studies, however, are notable for their lack of evidence for typical sulfate-reducing bacteria such as Deltaproteobacteria (Brazelton et al. 2006, 2010). Some of the ubiquitous Clostridia discussed above (in particular the *Desulfotomaculum* group) are suspected to be capable of sulfate reduction (Moser
et al. 2005; Lin et al. 2006; Chivian et al. 2008). Taxonomy, however, is not a reliable predictor of sulfate-reduction capability, so additional genetic and physiological experiments are required to assess the role of Clostridia in the sulfur cycle of serpentinite springs.

Nevertheless, several lines of evidence point to sulfate reduction as an active process at the Lost City hydrothermal field. The continued study of the LCHF towers and the Atlantis Massif has led to improved resolution of the distribution of microbial communities and their relationship to the geochemistry at the site (Fig. 2). The concentrations of hydrogen, sulfate, and sulfide vary widely across the field and indicate that sulfate reduction actively influences fluid compositions (Proskurowski et al. 2008; Lang et al. 2012). Bacterial sulfate reduction was also detected at 5 to 8 °C in mat samples from the carbonate towers of Lost City (higher temperatures were not tested), and taxonomic and functional genes (dsrAB) related to Desulfotomaculum were present (Dulov et al. 2005; Gerasimchuk et al. 2010). Work by Delacour et al. (2008a) also showed geochemical evidence for sulfate reduction in the Atlantis Massif below the LCHF.

The reduced, dissolved sulfide that results from sulfate reduction can also contribute to the electron donor budget and can support microbial carbon fixation. Metagenomic analyses of hydrothermal chimneys from Lost City found high abundances of genes related to the autotrophic sulfur-oxidizing Gammaproteobacterium Thiomicrospira crunogena (Brazelton and Baross 2010). These organisms are presumed to be abundant at oxic-anoxic interfaces within the chimney walls. Fluids venting from the chimneys appear to have a different microbial community composition than the chimneys themselves, suggesting that the carbonate-hosted biofilms may not accurately represent conditions in the subsurface (Brazelton et al. 2006).

**Methane-cycling.** The presence of hydrogen and reducing conditions make hydrogenotrophic methanogenesis a thermodynamically favorable process in many serpentinization systems. The occurrence of biological methane production may be limited, however, by the availability of dissolved inorganic carbon at high pH, as discussed in more detail below. Abiogenic methane is also an abundant source of electrons in many of these systems, and the potential for both aerobic and anaerobic methanotrophy is reflected in the occurrence of pmoA genes (Mason et al. 2010) and ANME (Anaerobic Methanotrophic archaea) phylotypes and associated mcrA genes (Mottl et al. 2003; Kelley et al. 2005), respectively.

Methane is frequently present in fluids passing through serpentinizing ophiolites, even when hydrogen concentrations are below detection limits (Table 2). Genes related to known methanogens were detected in the Del Puerto Ophiolite in the California Coast Range (Blank et al. 2009), although the abundance of the putative methanogens is unknown. Sequences related to methanogens were present but extremely rare in the metagenomic dataset from the Bay of Islands Ophiolite, Newfoundland, but no genes diagnostic of methanogenesis were identified (Brazelton et al. 2012). It is unclear whether the low abundance of these sequences reflects a small contribution from surface soil methanogens or instead suggests the presence of a more inaccessible, methanogen-rich deep subsurface habitat. Surprisingly, this metagenomic dataset also lacks any pmoA genes or other sequences expected to represent methanotrophic bacteria (Brazelton et al. 2012). This initial data from the Bay of Islands Ophiolite thus implies that methane cycling in continental serpentinites may be limited by as yet unknown factors.

Studies of the actively venting carbonate towers at Lost City have revealed low-diversity microbial communities dominated by a single archaeal phylotype (based upon 16S ribosomal RNA gene sequences), termed Lost City Methanosarcinaceae (LCMS; Schrenk et al. 2004). LCMS have been found in numerous samples of different chimneys associated with active venting at the Lost City (Brazelton et al. 2006) and are marginally related to the ANME taxa commonly found at gas hydrates and associated with anaerobic methane oxidation. However, further studies have shown extensive functional and physiological diversification within the LCMS biofilms that is not reflected by the rRNA data (Fig. 3). Imaging of the biofilms revealed
Figure 3. Physiological and phylogenetic diversification of “single species” archaeal biofilms from the LCHF hydrothermal chimneys. Panel A is a TEM thin section through a biofilm of LCMS showing the morphological diversity of cells within the carbonate chimney. Scale bar is 1 μm. Panel B shows the phylogenetic diversity of nitrogenase (nifH) genes from the same biofilms. The single species biofilms harbored at least 18 different clusters of methanogen-related nifH genes likely involved in nitrogen fixation. [Figures are reproduced with permission of the American Society for Microbiology from Brazelton et al. (2011).]
multiple cell morphologies within a single cluster of carbonate-attached LCMS cells, and the biofilms are capable of both production and oxidation of methane (Brazelton et al. 2011). The biofilms also contain diverse nitrogenase genes (\textit{nifH}; involved in nitrogen fixation) and the highest percentage of transposase genes (involved in gene duplication and transfer) of any environmental sample analyzed to date (Brazelton and Baross 2009; Brazelton et al. 2011).

As the Lost City carbonate chimneys age and are no longer exposed to actively venting fluids, the microbial community composition shifts from LCMS-dominated populations, to a distinct group of ANME-1 archaea (Brazelton et al. 2010). Interestingly, little evidence exists for the presence of archaea in the subsurface rocks obtained from drilling the Atlantis Massif (Mason et al. 2010). Renewed efforts to study the root zone beneath the LCHF in a highly systematic manner are planned over the next several years.

Methanogenic and methanotrophic archaea have been observed at other marine serpentinizing settings as well (Table 3). Methanogenic archaea within the order Methanococcales have been noted at some sites at Logatchev (Perner et al. 2007, 2010), and high abundances of methanogenic archaea related to the Methanococcales have been reported from the Central Indian Ridge and the Southwest Indian Ridge (Takai et al. 2004). This latter report detected the presence of \textit{Methanopyrus kandleri} strain 116, a hyperthermophilic microorganism isolated from another environment, and grown in culture at temperatures as high as 122 °C (the current upper temperature limit for life) under elevated hydrostatic pressure (Takai et al. 2008). Finally, microbiological studies of IODP Site 1200 core samples at South Chamorro Seamount have shown a high abundance of archaea that, based on the increasing concentrations of carbonate and bisulfide in ascending fluids, appear to be anaerobically oxidizing ascending CH4 while reducing sulfate (Mottl et al. 2003).

Putative aerobic methanotrophic bacteria (e.g. \textit{Methylococcales}) are widespread in Lost City chimneys and fluids, and they have also been detected at the Rainbow hydrothermal field (Table 4; Nercessian et al. 2005; Roussel et al. 2011). Presumably, these bacteria occupy zones near the surface where both methane and oxygen are available. Methane and oxygen-rich zones are also found in continental serpentine settings (such as the Bay of Islands Ophiolite, discussed above) that seem to lack methanotrophic bacteria, though, so additional factors may favor the growth of these methanotrophic bacteria in marine settings.

\textbf{Heterotrophy/fermentation.} Serpentinite settings include many sources of organic carbon; indeed, these environments are unusual in that organic carbon is typically much more biologically available than inorganic carbon (discussed in detail below). Processes associated with serpentinization can lead to the abiogenic generation of numerous short-chain hydrocarbons in addition to methane (Proskurowski et al. 2008). Mantle-derived carbon exists in the ultramafic rocks within fluid inclusions and along grain boundaries (Kelley and Früh-Green 1999). Additionally, downwelling fluids can mix with the serpentinizing fluids and contribute photosynthetically-derived organic carbon (Abrajano et al. 1990). For example, seawater-derived organics were observed in drill cores from beneath the Atlantis Massif (Delacour et al. 2008b). A third source of organic carbon could include the biomass and metabolic byproducts produced by autotrophs in the deep sea, seafloor, and continental subsurface. Also worth consideration is a recent study of a granitic deep subsurface habitat suggests that viral lysis of autotrophic microorganisms supplies dissolved organic matter that can feed heterotrophic microbial communities and limit overall population sizes (Pedersen 2012)

These sources of organic compounds may support the growth of heterotrophic and fermentative archaea and bacteria. Alkaliphilic heterotrophs were observed using culture-dependent approaches in the alkaline springs of Oman (Bath et al. 1987). A number of heterotrophic alkaliphiles have also been isolated from high pH wells in Portugal (Tiago et al. 2004, 2005, 2006). At Cabeço de Vide in Portugal, alkaliphilic heterotrophic bacilli and
Actinobacteria are common in aerobic enrichment cultures (Table 4; Tiago et al. 2004). They are speculated to use organic materials near more oxidizing mixing zones within the ophiolite. In at least one case a novel alkaliphilic heterotroph within the Gammaproteobacteria that was capable of growth up to pH 12.4 was isolated from South Chamorro Seamount and other locations of the Mariana forearc (Takai et al. 2005).

Elevated concentrations of potentially fermentable substrates (hydrocarbons and organic acids) have been observed in many locations (Table 1 and 2; Haggerty and Fisher 1992; Proskurowski et al. 2008; Lang et al. 2010; Itävaara et al. 2011), but in situ fermentation activity has yet to be confirmed. Analysis of microbial populations from the igneous rocks obtained from drilling the Atlantis Massif revealed functional genes involved in hydrocarbon degradation (Mason et al. 2010). Potentially fermentative Clostridia have been detected in many serpentinite settings (discussed above), and it is possible that fermentation is an advantageous metabolic strategy in environments where oxidants are scarce.

**Challenges of high pH**

One of the primary challenges for life in high pH environments is the maintenance of a proton motive force across the cytoplasmic membrane. Proton gradients sustain ATP synthesis through oxidative phosphorylation or photophosphorylation in a large fraction of characterized species (Fig. 4). Typically, the proteins involved in the main pH homeostasis mechanisms of these extremophiles are constitutively expressed, so that these microorganisms are prepared for sudden shifts to the extreme end of the pH range (Krulwich et al. 2011). Alternatively, organisms can rely upon metabolic processes such as fermentation to obtain ATP via substrate level phosphorylation. However, these processes generate less energy per mole of reactant than oxidative processes, and ionic gradients are still required for molecular transport across the cytoplasmic membrane. At high pH, the calculated proton-motive force (PMF) may drop to almost zero (Fig. 4; Krulwich 1995). Microorganisms found in alkaline soda lakes rely upon ionic gradients involving Na⁺ or K⁺ to substitute for protons and to generate ATP (Krulwich 1995). It is unknown whether organisms in low ionic strength solutions, such as serpentinizing ophiolites, use alternative ions in their membrane transport mechanisms.

High pH also provides problems in terms of the stability of ribonucleic acid (RNA), a critical molecule in the transcription, translation, and regulation of genes. It is well known that RNA is unstable in alkaline solutions, and high pH is commonly avoided in laboratory procedures aimed at RNA isolation. Hydroxyl groups attack phosphate groups, thereby disrupting the polymeric backbone of the RNA molecule through transesterification reactions (Li and Breaker 1999). The chemical impacts of ultrabasic conditions upon RNA structure may be an important reason why cytoplasmic pH, even within alkaliphiles, is typically orders of magnitude more neutral than external pH (Krulwich 1995). However, more information about molecular strategies enhancing RNA stability still remains to be explored, and in fact these may be attractive targets for biotechnological applications.

**Limitations to carbon fixation**

Serpentinization supplies copious energy to the subsurface environment in terms of reducing power. When mixed with oxidants from surface and subsurface sources, these systems provide a strong thermodynamic drive in terms of chemical disequilibria that can be harnessed by autotrophic microbial populations (McCollom 2007). One of the primary challenges in these systems, however, is the limited availability of inorganic carbon. Under high pH conditions, the predominant form of dissolved inorganic carbon (DIC) is carbonate rather than bicarbonate. During water-rock reactions, concentrations of calcium ions become elevated in the fluids; when combined with the high pH conditions that are also a result of serpentinization reactions, inorganic carbon is rapidly precipitated as calcite and aragonite (Barnes et al. 1978; Neal and Stanger 1983; Fritz et al. 1992; Palandri and Reed 2004; Kelley et al. 2005). As a result,
extremely low concentrations of DIC are typical in high pH fluids from marine and terrestrial systems (Table 1 and 2).

At the alkaline marine Lost City field, the lack of any radiocarbon in methane indicates that the precursor carbon source is mantle derived, implying that any modern seawater DIC is precipitated prior to the abiogenic formation of methane (Proskurowski et al. 2008). Consequently, biological communities may be inorganic carbon-limited (Bradley et al. 2009b). Microbial communities in these systems may rely on carbon sources other than DIC. The majority of serpentinite-hosted ecosystems have high concentrations of CH₄ that may provide a carbon source if microorganisms have the ability to oxidize it and assimilate it into biomass. Thermodynamic studies indicate that in addition to CH₄ and n-alkanes, the formation of CO and organic acids as metastable intermediaries can be thermodynamically favorable under the reducing, high H₂ conditions present in many serpentinizing environments (Shock 1992; Shock and Schulte 1998; McCollom and Seewald 2001, 2003; Seewald et al. 2006). Both CO
and formate have been formed abiogenically in controlled laboratory studies at temperatures >175 °C (McCollom and Seewald 2001, 2003; Seewald et al. 2006). At the high temperature, acidic Rainbow field, CO is present at detectable concentrations of ~5 μmol/kg (Charlou et al. 2002). Fluids from both Lost City and the Marianas Forearc have elevated concentrations of the organic acids formate and acetate (Haggerty and Fisher 1992; Lang et al. 2010). There are several indications that formate at Lost City is indeed formed abiogenically in the subsurface, although the presence of acetate is more likely to be due to the degradation of biomass (Lang et al. 2010).

When high-pH, calcium-rich fluids exit the subsurface and are again exposed to inorganic carbon either in the form of seawater DIC (marine systems) or atmospheric CO$_2$ (terrestrial systems), solid carbonate precipitates. Microorganisms could mobilize solid carbonate minerals by dissolution, perhaps by the localized secretion of organic acids. Some organisms living at the oxic/anoxic interface may also be able to access the inorganic carbon before it precipitates. A recent study used the $^{14}$C content of biomass in the chimneys at the Lost City field to distinguish between seawater-derived and mantle-derived carbon sources (Lang et al. 2012). In some locations, the carbon source assimilated by the chimney communities was >50% mantle-derived.

Functional and metagenomic studies have revealed a number of genes associated with carbon fixation in these systems. These include the genes encoding the RuBisCO enzyme of the Calvin Benson Bassham cycle and genes associated with the reverse tricarboxylic acid (rTCA) cycle. The metagenomic data from the Lost City field included putative homologs of Type I RuBisCO (Brazelton and Baross 2010), which is the form typically expressed when carbon dioxide is limiting (Dobrinski et al. 2005; Berg 2011). Genes for carbonic anhydrase and carboxysomes, which may aid in concentration of carbon dioxide within the cell, were also found (Brazelton and Baross 2010). As with the methane metabolisms, to date no studies have demonstrated the in situ expression of carbon fixation genes in serpentinite-hosted ecosystems.

Recently, metagenomic analyses of terrestrial serpentinites have also detected Type I RuBisCO in pH 12 waters from the Tablelands Ophiolite in Canada. The sequences appear to be associated with facultatively anaerobic Betaproteobacteria that were also found to harbor genes required for oxidation of H$_2$ and carbon monoxide (CO). Utilization of CO is an intriguing possible strategy in environments that experience low to moderate levels of serpentinization, where high pH conditions can limit CO$_2$, and H$_2$ may be limiting due to its rapid consumption by many organisms. Therefore, some organisms may occupy a niche where CO, even at low concentrations, could provide reducing power as well as a carbon source, thereby obviating any need for either H$_2$ or CO$_2$ (Brazelton et al. 2012).

In ultramafic-hosted high-temperature seafloor vents, Perner et al. (2010) recently demonstrated the connection between H$_2$ availability and carbon fixation rates. The study found carbon fixation genes important in both the CBB and reverse tricarboxylic acid (rTCA) cycles. These results were mirrored by a much higher diversity of NiFe hydrogenase genes involved in H$_2$ uptake in an ultramafic hydrothermal vent site, compared to a basaltic site. The authors also demonstrated that addition of H$_2$ stimulated carbon fixation rates under anoxic conditions.

Sources of nutrients

To date, the concentrations of macro-nutrients essential to microbial communities such as nitrate, ammonia, and phosphate are unknown in the majority of these environments. Available N-sources may be low, and the propensity for nitrogen fixation has been noted in serpentinite-hosted ecosystems. Multiple varieties of $nifH$ genes have been found in chimney materials from the LCHF (Fig. 3b; Brazelton et al. 2011). Their closest relatives are found in methanogenic archaea, such as the predominant LCMS phylotypes found in the chimneys. Studies of fluids ascending through South Chamorro Seamount sediments also showed a small increase in ammonia concentrations that could reflect microbial nitrogen fixation (Mottl et al. 2003).
Phosphorus (P) is critical to the synthesis of new biomass and the functioning of cells. The mineral brucite, often formed through the mixing of high pH serpentinite springs with carbonate-bearing waters, is effective at scavenging P from solution. Holm and colleagues pointed out the importance of Na+ in solubilizing P from brucite and its analogies to a primitive phosphate pump (Holm and Baltscheffsky 2011). Additionally, under phosphorus-limited conditions, microorganisms have been known to substitute sulfur for phosphorus in their membrane lipids (Van Mooy et al. 2006). A similar phosphorus conservation strategy has been proposed for microbial populations inhabiting carbonate chimneys at the LCHF, where glycosyl head groups replace phosphatadyl head groups in bacterial membrane lipids (Bradley et al. 2009a).

Microbe-mineral interactions

In addition to direct impacts upon carbon flux through their growth and metabolism, microbes can impact carbon flow in serpentinite habitats through their interaction with solid phases. The dense biofilm communities of the LCHF can create favorable niches for themselves within the carbonate chimneys that may serve to buffer the organisms against the effects of oxygen and high pH. The cells and their polymeric matrix can serve as nucleation sites for carbonate precipitation (Fig. 5; Blank et al. 2009). Microorganisms can provide the conditions required for precipitation of carbonates: elevated dissolved inorganic carbon (respiration), and nucleation sites from extracellular polymeric substances (EPS), or degradation of EPS resulting in the release of cations. However, microbial activities may also inhibit the precipitation of carbonates, by cation capture by EPS, consumption of DIC, and acidification (sulfide oxidation; Blank et al. 2009).

Microbial communities in direct contact with ultramafic rocks potentially utilize solid electron acceptors. Some of the byproducts of serpentinization are the production of magnetite and other Fe (III)-bearing minerals. Menez et al. (2012) reported the association of organic matter, potentially the by-product of biology, with ferric minerals in the ocean crust. In this setting, perhaps the minerals play a role in the sustenance of subsurface microbial communities. The ability of microbial activities to contribute to the release of solid carbon phases from mantle rocks also has not been explored. Whether microbes play an active or passive role in the process of serpentinization remains to be investigated.

Serpentinization and the origins of life

Prior to the differentiation of the lithosphere on early Earth, exposed ultramafic rocks were probably more prevalent than they are today (Sleep et al. 2004). Throughout the Archean Eon, the crust was likely to have been more mafic than the modern crust and hence more likely to support serpentinization (Arndt 1983; Nisbet and Fowler 1983; Nna-Mvondo and Martinez-Frias 2007). Evidence consistent with serpentinization and its metamorphic products occurs in exposures of the approximately 3.8 Ga Isua supercrustal belt of western Greenland (Friend et al. 2002; Sleep et al. 2011). Hydrogen and oxygen isotopic properties of serpentine minerals in these rocks suggest that they were formed by reaction of ultramafic rocks with seawater. Serpentinization is also evident in >2.5 Ga Archean komatites of the Kuhmo greenstone belt in Finland (Blais and Auvray 1990). In general, the meager geological evidence that is available for the Hadean and Archean Eons is consistent with serpentinization being more widespread during that time than it is today (Sleep et al. 2011).

Sites of active serpentinization are attractive venues for origin of life scenarios for several reasons outlined below, all of which are consequences of the highly reducing and high pH fluids generated by exothermic serpentinization-associated reactions. Uncertainty of the early atmosphere’s redox state has challenged the formation of a consensus by the origin of life community regarding the most thermodynamically favorable prebiotic chemical pathways. Serpentinization-driven systems, however, provide highly reducing local environments with high H2 concentrations where prebiotic organic synthesis is clearly favored regardless of
atmospheric conditions because abiotic organic synthesis can be observed in such environments even today (Proskurowski et al. 2008). Earlier work has suggested that H₂ may play a critical role in the sustenance and long-term survival of microbial communities (Morita 2000). If this is true, it may be especially important in the discontinuous and ancient niches presented in many serpentinite rocks.

In addition to promoting abiotic synthesis of organics, H₂-rich environments are ideal locations for early metabolic evolution because hydrogen transfer is at the heart of almost every biochemical reduction or oxidation reaction in modern metabolic pathways (Nealson et al. 2005). Thus it is parsimonious to suppose that the first metabolic pathways were fueled by geochemically derived H₂. Interestingly, enzymes that catalyze H₂ oxidation or production (i.e., hydrogenases) contain iron and/or nickel at their catalytic sites. Both iron and nickel are
generally enriched in serpentinites, but the exact mineral phases involved in organic synthesis reactions associated with serpentinization have yet to be identified (Foustoukos and Seyfried 2004; Sleep et al. 2004; McCollom and Seewald 2007).

Most enzymes involved in modern biological carbon fixation pathways also have minerals as essential components of their catalytic sites. The reductive acetyl-CoA (or Wood-Ljungdahl) pathway is utilized for both carbon fixation and ATP generation by methanogenic archaea and acetogenic bacteria (Berg et al. 2010). Remarkably, the iron/nickel minerals found at the active sites of Wood-Ljungdahl enzymes can catalyze at least some of the steps in this pathway on their own without any organic components (Huber and Wächterhäuser 1997; Cody et al. 2000; Cody 2004). The simplicity (Fuchs and Stupperich 1985; Berg et al. 2010) and phylogeny (Pereto et al. 1999) of proteins involved in the Wood-Ljungdahl pathway are also consistent with their ancient origin. Almost all organisms that utilize this pathway today are fueled by H2, and the exceptions almost certainly represent later evolutionary innovations (Bapteste et al. 2005). The rare congruence among these geological, chemical, and biological data supports the emerging view that the earliest biochemical pathways were driven by H2 and evolved as mimicry of pre-existing geochemical reactions (Cody and Scott 2007) that would have been favored in serpentinizing environments.

The greatest appeal of hydrothermal environments, in general, as key sites in the origin of life is the presence of diverse catalytic mineral surfaces in geological, physical, and chemical gradients that are formed as a result of the dynamic mixing associated with hydrothermal circulation (Baross and Hoffman 1985; Martin et al. 2008). In the presence of strong gradients, chemical reactants are more likely to be far from equilibrium with respect to each other, and therefore the thermodynamic favorability of them reacting to generate new products is greatly improved (Shock and Schulte 1998). Serpentinite-hosted hydrothermal systems, in particular, feature characteristic gradients in temperature, redox, geochemistry, porosity, and pH that have their own advantages for prebiotic and early evolution scenarios. In the detailed model proposed by Martin and Russell (2007), the pH gradient between serpentinization-derived fluids and ambient seawater causes protons to leak out of iron sulfide compartments that they predict would form on ancient chimney deposits. The iron sulfide “bubbles” are considered to be the precursors to the modern lipid membrane (Russell et al. 1994; Russell and Hall 1997), and their leakage of protons would have resulted in a chemiosmotic potential (Fig. 4a; Lane and Martin 2010) that could have been harnessed by the first enzymes to catalyze H2-fueled carbon fixation. Regardless of whether these particular details are exact descriptions of how the origin of life actually occurred, it is clear that chemical potential gradients involving hydrogen species were important aspects of early metabolic processes, just as they are critical in all organisms today (Sleep et al. 2011).

Although a discussion of possible prebiotic pathways for the synthesis of specific biomolecules is outside the scope of this review, it should be noted that most proposals for the evolution of genetic information systems (e.g. “RNA world” theories) are compatible with a H2-rich setting. The building blocks of any genetic information system require an energy source and favorable thermodynamic conditions for organic synthesis, and serpentinite-hosted systems clearly fit these criteria, as we have described above. The H2-rich chimneys of serpentinization-driven hydrothermal systems, for example, contain abundant micro-compartments for concentration of reactants and feature temperature ranges similar to those in the polymerase chain reaction (PCR), ideal for nucleic acid synthesis (Kelley et al. 2005; Baaske et al. 2007).

The mineralogy of serpentinites may have also provided advantages for prebiotic chemistry. Phosphate availability on early Earth could have been a severe limitation to the origin of nucleic acids, but Nisbet and Sleep (2001) have noted that the “RNA world” could have existed within pores in serpentinites that are rich in the phosphate-containing mineral...
hydroxyapatite. As mentioned earlier, the mineral brucite, commonly associated with active marine serpentinization, is an effective scavenger of both boron and phosphorous. Phosphates, including pyrophosphate, can accumulate in brucite over millions of years on the seafloor, and then become desorbed when exposed to high Na⁺ concentrations and the high pH conditions within serpentinites. It has been shown that pentoses, such as ribose, that make up the building blocks of RNA can be stabilized by boron (Ricardo et al. 2004), so high pH fluids circulating through serpentinites that contain boron-enriched brucite may have supported RNA synthesis (Holm et al. 2006). As the geochemical reaction of serpentinization consumes water, discontinuous fracture networks or surface-exposed serpentinites could have provided the additional benefit of hydration-dehydration reactions and concentration by evaporation that may have been necessary for polymer synthesis.

WHERE DOES THE ABIOTIC CARBON CYCLE END AND BIOGEOCHEMISTRY BEGIN?

Studies of serpentinizing environments to date have shown that these ecosystems host low-abundance, low-diversity microbial communities. However, these habitats coincide with environments where abiotic carbon transformations are taking place. In addition to basic ecological questions about the relative balance of autotrophy and heterotrophy in various niches within serpentinite habitats, it is also intriguing to consider the boundary between living and non-living. Where do biogenic processes end, and where does abiogenic organic geochemistry become the predominant process? What does this imply for the magnitude and extent of the global subsurface biosphere (Schrenk et al. 2010)? What role does abiogenic organic chemistry play in the flux of carbon from the deep Earth into the surface biosphere?

Abiogenesis in thermodynamic and experimental studies

The reducing conditions and high hydrogen concentrations arising from the serpentinization reactions can make the abiogenic synthesis of organic carbon molecules thermodynamically favorable. Biologically relevant compounds such as methane, hydrocarbons, carboxylic acids, alcohols, and amino acids are thermodynamically favored over inorganic constituents when buffered at the appropriate temperatures, redox conditions, and H₂ fugacities, or when reducing hydrothermal fluids mix with oxic seawater (Shock 1990; Amend and Shock 1998; Shock and Schulte 1998; McCollom 2013). Methane is typically the most thermodynamically stable organic compound, but its formation may be kinetically inhibited, leading to the formation of other organic compounds.

Numerous experimental studies have focused on the abiogenic formation of methane and n-alkanes, with synthesis pathways attributed to Fischer-Tropsch-type and/or Sabatier-type reactions (for in depth recent reviews, see McCollom and Seewald 2007; Proskurowski 2010; McCollom 2013). One of the earliest experiments demonstrated elevated concentrations of methane, ethane, and propane when an aqueous solution was reacted with olivine at high temperatures and pressures (Berndt et al. 1996), although a later study used ¹³C-labeled bicarbonate under similar conditions to demonstrate that most of these compounds were in fact generated from the thermal decomposition of organic matter present in the reaction vessel or the catalysts (McCollom and Seewald 2001). Nonetheless, these experiments spurred a large number of variations over the past decade, focusing on the importance of the starting carbon source (e.g. bicarbonate, formate, oxalic acid, CO₂), the type of mineral catalyst (e.g. NiFe-alloy, magnetite, chromite, olivine, hematite), as well as the roles of temperature and pressure (Horita and Berndt 1999; McCollom et al. 1999; Rushdi and Simonet 2001; McCollom and Seewald 2003; Foustoukos and Seyfried 2004; Rushdi and Simonet 2004). These experiments have repeatedly demonstrated the abiogenic synthesis of methane, branched and straight-chained alkanes up to C-27, alkenes, alkenones, formate, and long-chain alcohols.
A largely independent series of experiments has focused on the synthesis and stability of amino acids, peptides, and proteins. Multiple laboratory studies have demonstrated that amino acids can be synthesized from inorganic constituents under aqueous conditions designed to simulate hydrothermal (although not necessarily serpentinite) environments (Óro et al. 1959; Lowe et al. 1963; Wolman et al. 1971; Kamaluddin and Egami 1979; Hennet et al. 1992; Yanagawa and Kobayashi 1992; Marshall 1994; Islam et al. 2001; Aubrey et al. 2009). In these experiments, glycine is frequently the amino acid synthesized in the highest yield. While many organic compounds are thermodynamically stable, and able to be synthesized abiogenically in laboratory conditions, identifying their presence in the environment is often complicated by the presence of biologically produced compounds.

Distinguishing biotic from abiotic processes

A grand challenge in the study of microbial ecosystems near the limits of habitability is developing criteria to accurately discriminate between biological and abiological processes. In serpentinizing ecosystems some of the classical discriminants for life, e.g. organic carbon compounds, are also potentially produced by abiotic processes (Sephton and Hazen 2013). The microbial contribution to the net flux of methane from serpentinizing environments is one of the most intriguing questions in this field. Although serpentinization of ultramafic rock is associated with only a small fraction of total hydrothermal circulation (<10%), it can supply up to ~75% of the abiogenic methane from mid-ocean ridges (Cannat et al. 2010; Keir 2010). In many cases isotopic and geochemical evidence indicates that abiogenic FTT and/or Sabatier reactions lead to the production of CH4 and, occasionally, higher hydrocarbons. In other cases, the thermogenic alteration of organic matter contributes to methane production (Hosgormez et al. 2008). Due to the overlap of biogenic and abiogenic processes, and complex physiological adaptations of microbial populations (e.g. under carbon limitation), serpentinite-hosted ecosystems present a challenge to deciphering biogenic from abiogenic methane sources (Bradley and Summons 2010). For these reasons, serpentinites are being explored as astrobiological analogs to aid in understanding potential sources of methane on Mars (Mumma et al. 2009).

The most thorough studies of the provenance of organic compounds are associated with the study of methane and n-alkanes. Early studies relied upon the isotopic ratios of carbon (13C/12C) and hydrogen (2H/1H) in methane to distinguish the sources (Fig. 6; Abrajano et al. 1988). Stable isotope evidence alone can be misleading however. The fractionation factors associated with the abiogenic formation of CH4 through FTT-synthesis may be as large as those associated with biological processes (McCollom and Seewald 2006). Additionally, the δ13C value of methane from most serpentinization environments does not reflect this full fractionation factor, possibly due to carbon limitation (Proskurowski et al. 2008). In these cases, 14C data may be better suited to differentiate between distinct carbon sources and can potentially constrain abiotic versus biotic origins (Lang 2012). Further studies of hydrocarbon distribution patterns, coupled with isotopic systematics have provided additional means to separate the various sources of small organic molecules (Sherwood Lollar et al. 2006). These interpretations are complicated by the fact that many of these compounds have both biogenic and abiogenic origins, and can be influenced by contributions from the thermogenic degradation of sedimentary organic matter (Hosgormez et al. 2008; Bradley and Summons 2010; Szponar et al. 2012).

It is less clear when and where microbial communities contribute to methane production and consumption. Isotopic and genetic evidence from these systems provide strong clues that the process is occurring but would be strengthened by a better understanding of the organisms catalyzing the process and their physiologies. As discussed above, genes found in methanogenic taxa have been documented in a number of environments, including Del Puerto Ophiolite and at the LCHF (Table 3; Kelley et al. 2005; Blank et al. 2009). The expression of these genes has not yet been reported, however. To our knowledge, there have not been any reports of laboratory cultivation of pure methanogenic isolates from high-pH serpentinite habitats.
However, stable isotope microcosm experiments have demonstrated the capability of biomass from the LCHF towers to both produce and consume methane (Brazelton et al. 2011). Estimates of methanogenic production rates can be used to approximate the maximum contributions of biotic methane (Bradley and Summons 2010). Quantifying the impacts of methane cycling relative to abiogenic processes is important to quantifying carbon flux through these systems. The isotope signatures of biomass and biomarkers such as membrane lipids can provide clues to the sources of carbon for deep life in serpentinites, and the biochemical pathways used to sustain cell growth. Diether lipids at the LCHF display an extraordinary enrichment in $^{13}$C that has been attributed to extreme carbon limitation in the chimney ecosystem (Bradley et al. 2009b). Studies of organic compounds in the Atlantis Massif associated with IODP Hole 1309D demonstrate that the majority of the organic matter associated with serpentinites at that location are seawater-derived (Delacour et al. 2008b). In many cases, differentiating between mantle, thermogenic, and biological processes remains equivocal. Problematically, high contributions of biologically derived compounds may swamp small amounts of abiogenically derived organic compounds that are large enough to represent the next steps of pre-biotic synthesis. A thorough carbon budget of these systems, in addition to an improved understanding of the microbiological processes, is necessary to complete the picture.

**Linking abiotic and biological processes**

A missing link between the abiogenic synthesis of organics and the microbial isolates obtained to date are that none of the organisms in culture have been demonstrated to utilize the small organic compounds (e.g. ethane, propane, formate) that can result from serpentinization. Radiocarbon analysis of organic carbon and biomass in the LCHF chimneys, for example, is indicative of biological utilization of mantle-derived carbon (Lang et al. 2012). However, it has not yet been determined whether this organic carbon results from direct assimilation of abiogenic organic matter or if a microbial community first oxidizes these reduced compounds.

![Figure 6](image-url)
to a more accessible form. Many of the microorganisms that appear to inhabit the deepest, most anoxic portions of serpentinite ecosystems are closely related to the bacterial order Clostridiales, a group known to include fermentative organisms (Brazelton et al. 2006, 2012; Itävaara et al. 2011), but further work is required to establish the metabolic strategies of the Clostridiales-like organisms in serpentinites. If these organisms utilize organic carbon derived from serpentinization associated abiotic reactions, then fermentation in these systems could be considered, somewhat non-intuitively, to be a kind of primary production as it would be the generation of new biomass from non-biological carbon and energy. In completing the picture of carbon flow in the serpentinite subsurface, it is important to consider the metabolic products of such processes and their influence upon fluid chemistry.

COMMON THEMES AND UNCHARTED TERRITORY

One of the most interesting features of serpentinites is that they allow access to observe a set of variables that may constrain the limits of life on Earth. While there is substantial energy in terms of electron donors to support microbes in these systems, electron acceptors are typically limiting. They have discontinuous fluid circulation pathways that may both benefit and trap subsurface life. Furthermore, because these rocks originate in Earth’s deep interior, they may extend beyond the thermal and pressure limits of habitability. Clearly, there is a balance between energy production and energy demand that needs to be incorporated into models and tested empirically. These studies should be coordinated with physiological studies of microorganisms from serpentinite habitats to determine whether they host unique adaptations to cope with the environmental stresses of the high pH environment. Additionally, it is important to study dormancy and survival in these populations. Many of the species recovered from deep subsurface habitats are related to those known to produce spores. Spore formation could be an important dispersal and survival strategy in serpentinites and other deep subsurface environments.

It is critical to document the extent of the deep biosphere to include in global compilations of microbial biomass and to constrain their activities and contributions to subsurface biogeochemistry. Quantification of the rock-hosted subsurface biosphere is in its nascent stages and is completely unaccounted for in compilations of global microbial abundances. Important facets of this problem include developing strategies to decipher abiogenic and biogenic sources of methane and other organic molecules. Additionally, the magnitude of microbial contributions to biogeochemical cycles needs further investigation in serpentinizing ecosystems, linking genomic and geochemical approaches. Finally, it is imperative to better understand the ability of microorganisms to interact with solid phases in terms of either mobilizing deep carbon or inducing carbonate precipitation. This becomes particularly important as researchers are looking to serpentinites as a site of carbon sequestration (Kelemen and Matter 2008).

Serpentinization reactions can lead to the abiotic synthesis of small organic molecules, as has been shown through experiment, observation, and theory. Ultramafic rocks were likely more prevalent early in Earth’s history during the origin and evolution of the biosphere. Some have speculated that water-rock reactions played a role in the origins of life associated with deep-sea hydrothermal vents. Furthermore, serpentinites have been documented on the surface of Mars and serpentinization may be operative elsewhere in our solar system. Microorganisms in serpentinite settings may host relicts of these ancient microbe-mineral processes. Although delineating biotic from abiotic processes is challenging at the edge of the biosphere, it is critical that we are not deterred as it may help us to define the limits of our biosphere, and ultimately the transition between prebiotic Earth and life.
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