

Serpentinite in the Earth System.

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Olivine ((MgFe)<sub>2</sub>SiO<sub>4</sub>) is the most abundant mineral in the upper mantle, which together with the crust comprises the upper 660 km of Earth. It is also a major component of stony meteorites and planetary bodies including Icy Worlds. When olivine comes into contact with water at temperatures less than 500°C, it alters to serpentine (Mg,Fe)<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>. This hydration reaction is often accompanied by a redox reaction producing Fe<sup>3+</sup> from Fe<sup>2+</sup>, and H<sub>2</sub> from water. H<sub>2</sub> is the first building block of life, and hence there is much attention on environments where H<sub>2</sub> and organic compounds can be produced abiotically.

Serpentine is also important in the Earth system in several other ways: It is a much weaker mineral than olivine and can facilitate slip on faults. Dehydration of serpentine increases pore water pressure and reduces normal stress on faults, leading to earthquakes in subducting slabs. Dehydration water from serpentine is released into the asthenospheric mantle wedge above the subducting slab, reducing the melting point and causing island arc volcanism. Finally, serpentine can be preserved to considerable depths in subducting slabs and may transfer water to other hydrous minerals where it can be recycled into the deep mantle.

Active serpentinization is thought to be occurring in a number of modern environments:

1. In the flow system of submarine vent fields such as the Lost City Hydrothermal Field (LCHF) in the Atlantis Massif on the mid-Atlantic Ridge. This is venting alkaline fluids rich in H<sub>2</sub>, CH<sub>4</sub>, alkanes and carboxylic acids at temperatures of 40–90°C, and is thought to have been active for at least 100 000 years. Large carbonate-brucite chimneys host microbial communities. Several papers in this volume use data from the Atlantis Massif and the LCHF.
2. A second submarine environment is the forearc region of subduction zones where fluid released from down dragged sediments and hydrated ocean crust is released into the overlying mantle. A famous example is the Marianas arc, where huge serpentine ‘volcanos’ formed of serpentine mud derived from depths up to 20 km are a major bathymetric feature. These volcanos vent low temperature, high pH fluids rich in H<sub>2</sub>. Fryer et al. [1] review the results of IODP (International Ocean Discovery Program) Expeditions and dredging and highlight the effect of

seamount subduction in dragging shallow material to depth and perhaps introducing microbes into deep low-temperature environments.

3. The other main environment is subaerial exposure of mantle rocks in ophiolite complexes, in particular, the Oman ophiolite which is famous for highly alkali blue pools. This has recently been the focus of the International Continental Scientific Drilling Program (ICDP) Oman Drilling Project that included drilling boreholes into an active subsurface hydrological system where active serpentinization appears to be occurring at low temperatures due to the presence of H<sub>2</sub>, high pH and strongly reducing fluids. De Obeso & Kelemen [2] detail alteration in Oman peridotite exposed to low-temperature (60°C) serpentinization, with steep gradients in  $f_{O_2}$  and  $f_{S_2}$  recorded in mineral assemblages. Such gradients can provide energy for microbial life.

Several contributors focus on experimental and mineralogical studies of the generation of H<sub>2</sub> and CH<sub>4</sub>, and on the extent of redox reactions during serpentinization. McCollom et al. [3] detail experiments showing that reaction rates of serpentinization and hydrogen generation are increased under high pH conditions typical of low and moderate temperature serpentinization systems. Grozveya et al. [4] highlight the role of fluid inclusions in olivine as microreactors in natural samples. Fluid inclusions are inferred to have been originally aqueous with dissolved CO<sub>2</sub> but now contain serpentine and oxide solid precipitates, with the water consumed and replaced by H<sub>2</sub> and CH<sub>4</sub>-rich fluids. These authors suggest that scavenging of H<sub>2</sub> and CH<sub>4</sub> from fluid inclusions is an alternative source for these components in hydrothermal fluids, compared to the normal assumption of ongoing redox reactions along the flow path. Mayhew [5] reviews the oxidation state of bulk rock serpentine and the mineral serpentine in samples from a range of environments, as listed above. Serpentinization is invariably accompanied by an increase in Fe<sup>3+</sup> concentrations and Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios. In recent years with the replacement of wet chemical analysis by XRF and ICP-OES/MS, determination of the oxidation state of iron in geochemical analyses has not been routine. This type of measurement has the potential to allow quantification of the bulk flux of H<sub>2</sub> associated with serpentinization and associated mineralization. Templeton & Ellison [6] emphasize the role of ferroan brucite (Fe,Mg)(OH)<sub>2</sub> in hydrogen generation. Brucite is commonly a primary product of serpentinization reactions and this suppresses the potential for formation of magnetite and Fe oxidation. However, ferroan brucite has the potential to reduce water, carbon dioxide and other species in secondary reactions producing hydrogen and Fe(II/III) oxides and hydroxides. Thus, there are a variety of routes to iron oxidation and hydrogen generation that do not directly involve serpentine.

Moving onto more specific effects on microbial activity, Lang & Brazelton [7] review the conditions for subsurface life in the subsurface of the LCHF, concluding that the combination of high pH, high T and lack of bioavailable CO<sub>2</sub> is very challenging, with implications for the habitability of the subsurface on ocean worlds such as Europa and Enceladus. Boyd et al. [8] resolve a paradox that early anaerobic autotrophic bacteria apparently used ferredoxins (iron-sulfur proteins) as electron donors despite the fact that the reduction potential of H<sub>2</sub> is not generally low enough to efficiently reduce ferredoxins. They show that a combination of high H<sub>2</sub> concentration and alkaline pH reduce the reduction potential of H<sub>2</sub>, an indication that serpentinizing systems are favourable for the emergence of autotrophic life.

Looking at astrobiology, Vance [9] reviews evidence for the occurrence of serpentine on Mars, Enceladus, Titan and Europa, and details a model for the rate of advance of a cracking front that predicts the extent of serpentinization and associated hydrogen generation over time as these bodies cooled.

Finally, Hansen et al. [10] document experiments on nanoindentation of the serpentine polymorph antigorite indicating that deformation at high pressures is dominated by sliding on shear cracks rather than dislocation movement.

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