

## ***In situ* microbial iron oxidation in acidic geothermal environments**

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The oxidation of ferrous iron is an important microbial metabolism in natural environments and is implicated in numerous paleobiological events in the evolutionary history of Earth. Although microbial Fe oxidation occurs across a wide temperature (~20-80 °C) and pH (~0-8) range, rates of microbial Fe oxidation have been determined traditionally in the laboratory under controlled conditions, and thus, there are relatively few studies that have examined rates of *in situ* microbial Fe (II)-oxidation. High-temperature geothermal systems provide a unique opportunity for dissecting properties of individual populations as well as interactions occurring among community members. This study investigated the rate of Fe (III)-oxide deposition in acidic geothermal springs coupled with analysis of key microbial populations implicated in Fe (II)-oxidation.

Glass slides (25 x 75 mm) were placed along transects within the main flow channel of Fe (II)-oxidizing geothermal springs corresponding to gradients in temperature, sulfide and dissolved oxygen. The slides were removed at various times and analyzed for total Fe deposition and population size using quantitative PCR with primers designed around specific microbial groups.

Results suggest that the deposition of Fe (III)-oxides corresponds with increases in putative Fe (II)-oxidizing populations. Deposition rates of Fe (III)-oxide ranged from approximately 44-155 ng Fe hr<sup>-1</sup> mm<sup>-2</sup> across a temperature range from 60-80 °C. Microorganisms thought to be dominant Fe (II)-oxidizing populations (e.g. *Metallosphaera yellowstonii* and potentially other novel members of the domain *Archaea*) were most abundant in the initial stages of Fe (III)-oxide formation, and deposition rates were as much as four times faster at 80 versus 60 °C. Founder populations of autotrophic, Fe (II)-oxidizing microorganisms potentially provide a pool of organic carbon for heterotrophic thermophiles, a subset of which may have capabilities for reducing Fe (III)-oxides formed during initial deposition. Iron cycling in acidic geothermal environments may be controlled by dynamic feedback interactions among flow, Fe (III)-oxide deposition, and microbiological responses to changes in dissolved oxygen and organic carbon.

## **Transitory brucite and the chemistry and mineralogy of serpentinite**

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The serpentinitization reaction '2olivine+3H<sub>2</sub>O=serpentine+brucite' yields a product that is ~20% brucite by mode. However, brucite is present in minor amounts or absent in many serpentinites. It appears that the presence of brucite in many serpentinites is transitory. During open-system serpentinitization, brucite is continuously formed in contact with olivine and continuously consumed when isolated from olivine and in contact with the serpentinitizing fluid. In partially serpentinitized rocks, brucite is preserved in relict intra-olivine veins that form during the onset of serpentinitization and at the edges of mesh-defining veins where the olivine-out reaction is actually occurring. The interiors of the mesh-defining veins lack brucite, but contain abundant magnetite. These observations indicate that relatively Fe-rich brucite and Fe-poor serpentine form directly by serpentinitization of olivine. However, the Fe-rich brucite quickly reacts with an ambient fluid to produce serpentine and magnetite. Thus brucite is continually and simultaneously formed and consumed during serpentinitization. Most magnetite in serpentinites forms directly from Fe-rich brucite. The brucite-out reaction 'brucite+SiO<sub>2</sub>=serpentine+magnetite + H<sub>2</sub>O + H<sub>2</sub>' requires an external source of silica. In many serpentinitizing peridotites this is provided by orthopyroxene via 'opx+H<sub>2</sub>O=serpentine+SiO<sub>2</sub>'. If silica sources are not available (e.g. in a dunite), the consequent serpentinite may contain significant modal brucite. The brucite-out reaction buffers oxygen near I-M and aSiO<sub>2</sub> to 2-3 log units below quartz. These extreme chemical conditions lead to the cascade of characteristic chemical events associated with serpentinitization.