

## Olivine and pyroxene surface reactivity during H<sub>2</sub>-generation

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The hydrothermal alteration of ultramafic rocks is commonly invoked as a key source of H<sub>2</sub> available for subsurface lithoautotrophic microbial communities. At a mechanistic level, H<sub>2</sub> generation is intimately related to changes in the oxidation state of Fe and the temperature-dependent partitioning of Fe into secondary phases such as serpentine, Fe-rich brucite and magnetite. However, few experimental studies have directly examined the dynamic links between solid-phase Fe speciation and the extent of H<sub>2</sub>-generation during multi-stage serpentinization reactions.

We will present a series of hydrothermal experiments designed to measure microscale changes in distribution and speciation of Fe during electron transfer reactions between olivine and pyroxene surfaces and saline fluids. Polished slabs and powders of olivine and pyroxene have been suspended in flexible Au/Ti reaction cells at 230°C-300°C, and the serpentinization reactions have been arrested after a few days, a few weeks and a few months to measure progressive changes in mineral surface chemistry as H<sub>2</sub> is evolved. Surface-sensitive X-ray scattering and spectroscopic measurements have been combined to measure the growth of new mineral phases (e.g. lizardite detected by surface X-ray diffraction), to determine the redistribution of Fe and Si within the reaction interface (using reflectivity and total external reflection X-ray fluorescence measurements), and to measure changes in the speciation and oxidation state of Fe (using surface-sensitive Fe XANES analyses). In particular, we are monitoring the formation of Fe(II)-brucite and Fe(II)/(III)-bearing serpentine during incipient reactions, and the subsequent formation of magnetite, as [H<sub>2</sub>] variably increases.

To date, little information exists regarding the rates and mechanisms of olivine serpentinization below 200°C. However, we will also speculate about how our interfacial measurements could be used to probe changes in surface-controlled electron transfer processes when H<sub>2</sub>-consuming microorganisms colonize olivine and pyroxene surface under highly reducing conditions.

## Extracellular electron transfer in microbial environments

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Dissimilatory metal-reducing bacteria (DMRB), such as *Geobacter* and *Shewanella* spp., occupy a distinct metabolic niche in which they acquire energy by coupling oxidation of organic fuels with reduction of insoluble extracellular electron acceptors (i.e., minerals). Their unique extracellular electron transfer (EET) capabilities extend to reduction of anodes (electrodes maintained at sufficiently positive potentials) on which they form persistent, electric current generating biofilms. This capability makes DMRB useful as anode catalysts in microbial fuel cells (MFCs) for alternative energy generation and degradation of organic wastes. One hypothesis describing the mechanism of EET by *Geobacter* and *Shewanella* spp. involves superexchange in which electrons are conducted by a succession of electron transfer reactions among redox proteins associated with the outer cell membranes, aligned along pilus-like filaments (e.g. pili), and/or throughout the extracellular matrix. Here theory is presented, previously developed to describe superexchange within abiotic redox polymers, to describe superexchange within DMRB biofilms grown on anodes. This theory appears to apply to recent *ex situ* measurements of electrical conductivity by individual pilus-like filaments of *S. oneidensis* MR-1 and *G. sulfurreducens* DL1, referred to as microbial nanowires. Microbial nanowires have received much recent attention because they are thought by some to impart electrical conductivity to DMRB biofilms and because of the prospect of microbe-produced conductive nanomaterials. This theory appears to apply to preliminary *in situ* demonstration of electrical conductivity of an anode-grown *G. sulfurreducens* DL1 biofilm. Characterization by cyclic voltammetry is also presented of glassy carbon BMAs (biofilm modified anodes) of DL1 (a wild type strain), KN400 (a variant that generates higher current density), and mutant strains in which outer membrane c-type cytochromes S or Z (OmcS, OmcZ) were deleted. These BMAs were characterized at 1) state of transition from planktonic cells grown utilizing fumarate as their electron acceptor to anode bound cells utilizing the anode as their electron acceptor; 2) during biofilm growth; 3) when fully grown; and 4) when fully grown under non-turnover condition after subsequently starved of acetate. The results indicate interesting aspects of EET by *G. sulfurreducens* DL1.