Rates and Products of Fe(II) Oxidation in Trioctahedral Smectites

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Trioctahedral Fe(II) smectites form during the anoxic hydrothermal alteration of basalt. They are common in the modern subsurface oceanic crust, have been detected on Mars, and have been predicted to occur on icy bodies within the solar system such as Ceres, Enceladus and Europa. Before Earth's oxygenation, these clays would have been exposed on the ocean floor, providing an Fe(II) pool ~100 times larger than inferred dissolved iron concentrations in the Archean ocean. In addition, Fe(II) smectites are predicted to have been major detrital minerals on the early Earth. On the surface of modern Earth, however, they rapidly and irreversibly oxidize upon exposure to air. Due to the difficulty in sampling and preserving these clays, their role in the biogeochemical iron cycle remains poorly understood, including their availability as an electron donor to iron oxidizing microorganisms.

To better understand the oxidation of these minerals and provide proper controls for future biotic studies, we have synthesized a variety of trioctahedral Fe(II)-bearing smectites representative of the range of compositions observed in altered basalts. Syntheses were performed using a hydrothermal sol-gel method under anoxic conditions, and the products were confirmed to be tioctahedral, turbostratic 2:1 phyllosilicates using powder XRD. Compositions determined by ICP-OES using lithium metaborate fusion and acid digestion provide structural formulas consistent with Fe(II) trioctahedral smectites.

The oxidation rate of these synthetic clays was measured colorimetrically during exposure to dissolved O_2 or nitrite, a reactive intermediate produced during denitrification believed to cause abiotic oxidation of dissolved Fe(II) by nitrate-reducing iron-oxidizing bacteria. Oxidation in air equilibrated water (P_{O2} ~0.2) was incomplete, but proceeded more rapidly and to a greater extent in smectites with a greater Fe content. When exposed to nitrite (as 5 mM $NaNO_2$), no oxidation was detectable compared to oxidant-free controls. Ongoing studies under microaerophilic conditions ($P_{O2} = 0.02$) indicate that oxidation proceeds but at a slower rate than in air-equilibrated water, again with only a portion of Fe(II) oxidizing. XRD and TEM analyses of the solid-phase oxidation products under all conditions will also be presented.