Abiotic Fe(II) Oxidation Behavior in Trioctahedral Smectites: Rates, Extents, and Products

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Fe(II)-bearing trioctahedral smectites form during anoxic weathering of basaltic rock. They are predicted to have been widespread on the early Earth, where they represented a large pool of Fe(II). They are observed in the oceanic subsurface on the modern Earth, but degrade in the oxygenated environment at the surface. Due to difficultly in sampling and studying these minerals, their potential as electron donors for microorganisms remains poorly constrained. In this study we synthesized trioctahedral Fe(II)-bearing smectites in order to study the rate, extent and products of their oxidation by dissolved O_2 and nitrite, a reactive intermediary produced during denitrification. These studies provide controls for biological studies to be performed under similar conditions, and to characterize the signatures of abiotic oxidation.

Smectites were synthesized using a sol-gel method with hydrothermal aging performed under anoxic conditions. Structural forumlae were derived from bulk elemental abundances measured by ICP-OES following lithium metaborate fusion. Oxidation kinetics were measured on sispensions in a freshwater media and exposed to 5 mM sodium nitrite, a continuous flow of filtered air (21% O_2) or a microaerophilic gas mixture (78% N_2, 20% CO_2, 2% O_2). Oxidation extent was monitored throughout the 30 day experiments with a 1,10-phenanthroline assay on a subsample of smectite by dissolved by ammonium hydrogen fluoride.

Oxidation by nitrite was minimal over the timeframe of the experiments; literature on dioctahedral smectites has previously been contradictory on whether nitrite produces measurable oxidation. Dissolved O_2 caused partial oxidation of Fe(II) in the smectites with an unreactive portion remaining. Oxidation was more rapid in media equilibrated with the air relative to those under microaerophilic conditions, and proceded to a greater extent. This behavior is constsient with the incomplete oxidation seen in natural samples and reduced dioctahedral smectites and may be caused by non-nernstian redox behavior of iron resulting from the local environment of the iron within the structure. Mössbauer, TEM, and XRD analysis of synthesized smectites and oxidized products will also be presented. These analyses provide comparative data for interpreting future biotic studies and may elucidate path dependant effects and identify potential biosignatures of microbial iron oxidation.