Kinetic modeling of microbial Fe(II) oxidation, Fe(III) hydrolysis, and mineral precipitation in acid waters

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Acidophilic Fe(II)-oxidizing microorganisms are widespread in acidic mine-impacted waters and are the primary drivers for Fe(II) oxidation at low pH. The resulting changes in Fe chemistry have profound effects on trace element redox cycling and mobility in the environment. Sorption, precipitation, or redox activity of Fe(III)-containing mineral phases control the mobilization or sequestration of metal(loids) of concern in natural waters. Although Fe(II) oxidation is microbially-mediated, biogeochemical predictions for an acidic, Fe(II)-rich natural water require a coupled biotic-abiotic process model.

We present experimental and model results from a series of batch experiments conducted at four initial Fe(II) concentrations (10, 50, 100, and 159 mM), three initial pH values (2.0, 2.5, and 3.0), and inoculated with a pure strain of *Acidithiobacillus ferroxidans* isolated from acid rock drainage near a molybdenum mine. The pH, aqueous Fe(III), Fe(II), direct cell counts, and solid phase precipitates were monitored over the course of the experiments. For all inital Fe(II) concentrations except 10 mM, the pH increased initially, due to the acid-consuming stoichiometry of Fe(II) oxidation, but then decreased due to the combined effects of Fe(III) hydrolysis and precipitation of schwertmanite ($Fe_8O_8(OH)_6SO_4$) and/or jarosite ($KFe_3(SO_4)_2(OH)_6$). The Fe(III) concentration in the 10 mM Fe experiments was too low to precipitate jarosite, and only an increase in pH from Fe(II) oxidation was observed. The amount of pH increase due to Fe(II) oxidation was greatest at an initial pH of 2 for all initial Fe concentrations. The final pH in all bottles at 50 mM, 100 mM, and 159 mM Fe was very similar (pH 2), regardless of inital pH, because of equliibrium with mineral precipitates, primarily jarosite. Since the decrease in pH was due to both hydrolysis and precipitation, the kinetics of Fe(III) hydrolysis were measured in a separate experiment. PHREEQC, a geochemical model with the ability to incorporate multiple kinetic expressions, was used to simulate the experimental results by including kinetic expressions for microbial Fe(II) oxidation, Fe(III) hydrolysis, and jarosite precipitation. In addition, we compared various proposed kinetic formulations for microbial Fe(II) oxidation from the literature to our experimental results.

C, Sr isotopes in cap carbonate and and *Ce anomaly* in BIFs of Jucurutu Formation, Seridó Belt, NE, Brazil

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BIFs associated with Neoproterozoic glaciations are an important pillar of the Snowball Earth hypothesis and are regarded as accumulation of Fe^{+2} in ice-capped anoxic ocean. BIFs at Jucurutu (Mina do Bonito), Florânea (Cabeço da Mina) and São Mamede (Riacho Fundo) towns, Seridó Belt (itabirite and Fe ores, amphibole-itabirite, and tremolite schist) are overlain by Jucurutu marbles. Micro-drilled carbonate samples from the Jucurutu Formation exhibit $\delta^{13}C$ values as low as -12‰ in the first meter, followed by mantle values (-6 to -4‰) and then by positive values up section (+4 to +10‰). Surprisingly, $\delta^{13}C$ values for carbonates that overlie itabirites at Riacho Fundo and at Cabeço da Mina are all positive. Perhaps, the difference of C isotope behavior between basal carbonates at Mina do Bonito (negative), and Riacho Fundo and Cabeço da Mina (positive) reflect, perhaps, topographic control during deposition.

C-isotope stratigraphy for carbonates of the Jucurutu Formation support their deposition as cap carbonate. Negative $\delta^{13}C$ values are followed upsection by positive values. Sr isotope ratio for Jucurutu carbonates (~0.7074) approach Sr isotope ratios for Sturtian II cap carbonates (e.g. Maiberg, Pedro Leopoldo, Mirassol D´Oeste among others) between 740 and 635 Ma.

Negative Ce anomaly values (<0.10) result from Ce depletion or fractionation with metallic oxides, therefore, it indicates oxidizing conditions of the ocean water [1]. On the other hand, positive values (>0.10) reflect anoxic conditions of the ocean water. The values of Ce/Ce* in the BIFs vary from 0.54 to 2.46, indicating extremely anoxic environment, which seems to support the hypothesis of deposition of BIFs in an ocean capped by ice.

[1] Kato *et al.* (1996). *Journal Southeast Asian Earth Sci.* **14** 161–164.