

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

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Abiotic oxidation of Fe(II) in acidic natural water is slow, but acidophilic Fe(II) oxidizing microorganisms, such as *Acidithiobacillus ferrooxidans*, can rapidly oxidize Fe(II). These organisms play an important role in the oxidative dissolution of pyrite and the mobility of many trace elements, including As, released from sulfide mineral deposits. The mobility of As depends on the rates of microbial Fe(II) oxidation, abiotic Fe(III) hydrolysis, mineral precipitation, sorption, and photochemical Fe(III) reduction causing As(III) oxidation. Biogeochemical predictions for acidic, Fe(II)-rich natural waters require a coupled biotic-abiotic model that can capture these processes.

A series of batch experiments were conducted at four initial Fe(II) concentrations (10-159 mM) and four initial pH values (1.5-3.0) in the absence of As. A strain of *A. ferrooxidans* isolated from acid rock drainage was used. At least three main reactions can be delineated: microbial Fe(II) oxidation with pH increase, Fe(III) hydrolysis with a pH decrease, and mineral precipitation with pH decrease. Mineral precipitation and Fe(III) hydrolysis were constrained in separate batch experiments. Dissolved Fe(II) data were fit with a Monod expression, using parameters optimized by coupling the geochemical modeling code PHREEQC to UCODE, a least squares fitting code. PHREEQC was then used to incorporate microbial Fe(II) oxidation kinetics, Fe(III) hydrolysis kinetics, and mineral precipitation into a simulation of the batch experiments. The Monod expression captures the kinetics of Fe(II) oxidation over the range of pH and initial Fe concentrations. Even in a relatively simple system, the model requires a complex interplay of kinetic and equilibrium geochemistry.

Rates of abiotic As(III) oxidation were measured as a function of Fe(III) to As molar ratio (0.1-10,000) under a simulated natural light source in the absence of microorganisms. This reaction is driven by the photoreduction of Fe(III) causing oxidation of As(III) [1 and references therein]. The effect of pH and concentration on reaction rate was also measured. As(III) oxidation proceeds faster at higher Fe(III) concentrations, in an approximately log-linear manner with respect to Fe:As ratio, and is faster at higher pH values.

Microbial Fe(II) oxidation experiments were conducted in the presence of As(III) and light, and the experimental results were modeled using the PHREEQC code. The model was used to evaluate our understanding of coupled biotic/abiotic processes, especially the ability to incorporate kinetic expressions into biogeochemical models.

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Does Tl/Pb in basalts record low pressure degassing behaviour?

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Abstract

Thallium and lead are both incompatible in crystals involved in melting and crystallization of basalts but are fluid-compatible during low pressure degassing of magmas, and occur in considerable concentrations in volcanic aerosols. A compilation of crystalline and glassy basalts (n=628) from mid-ocean ridges (MORs), ocean islands (OIBs), arcs (ARCs) and continental (CONs) settings show sub-parallel but offset arrays of Tl-Pb covariation as a function of eruptive style, irrespective of geologic setting. Specifically, at a given Tl content, all subaqueously erupted basalts, whether from the OIB or ARC settings, glassy or crystalline, contain 5 to 10 times less Pb compared to subaerially equivalents.

Both Tl and Pb have a Kd fluid/melt of between 5 and 10, and Kd Tl/Pb decreases with Cl in the fluid, with Pb preferring Cl-rich fluids. Preferential Pb loss observed in subaqueous rocks could be due to degassing of Cl-rich fluids compared to subaerially erupted magmas, but the variability in Cl in natural basalts is not large enough to affect the change in Tl/Pb observed. Another possibility is that the lower pressure of degassing of subaerial magmas relative to subaqueous examples, leads to lower H₂S/SO₂ in the fluid and causes much higher compatibility of Tl relative to Pb in the fluid, and decreased Tl/Pb in a degassed magma. If fluid-melt partitioning for Tl and Pb can be experimentally calibrated at pressures below 2000 bars, the Tl/Pb ratio of basalts could potentially serve as a record of their degassing pressure.

Conclusion

Both Tl and Pb are geochemically similar but the ratio of these metals in erupted basalts differs with eruption mode, and is potentially a record of degassing pressure and fluid composition.