

The kinetics of biologically-mediated mineral oxide reduction and biomineralization using time-resolved X-ray diffraction

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The ways in which microorganisms catalyze or inhibit the breakdown and formation of minerals have broad implications for stable isotope geochemistry, acid mine drainage, climate change investigations, the search for life on other planets, and the evolution of life on this planet. We are investigating the kinetics of microbial-mineral interactions using X-ray diffraction (XRD), an old technique applied in a new way.

With the advent of the high-resolution imaging plate, we can take XRD scans in rapid succession (one every 2-10 minutes) and analyze changes in mineral phases as time progresses. This "time-resolved" XRD technique, combined with Rietveld analysis of the diffraction data, has allowed us to decipher discrete changes in unit cell parameters, phase abundances, and atomic displacements.

Total membrane (TM) fractions of the facultative anaerobe *Shewanella oneidensis* MR-1 can catalyze reduction of solid-phase metal cations (Ruebush *et al.*, 2006). In our experiments, these TM fractions were placed in a silica glass capillary with the manganese oxide birnessite, HEPES buffer (pH=7.0) and Na-formate, which serves as an electron donor. Using a Rigaku II D/Max X-ray microdiffractometer with a Mo-source, we succeeded in monitoring changes in mineralogy within the reaction cell. Our experiments revealed that the reduction of Mn began within minutes and continued until the birnessite had reacted completely. A secondary phase, rhodochrosite (MnCO₃), appeared upon the bioreduction of the birnessite.

We conducted the experiment at TM concentrations of 1.4 mg/ml and 3.5 mg/ml, Na-formate concentrations of 1M and 2M and total birnessite weights of .3 and .6 mg. The rate of reduction and re-mineralization was fastest with low TM and high formate concentration, and slowest with high TM and low formate concentration.

References

Ruebush S.S., Icopini G.A., Brantley S.L., and Tien M. (2006), *Geochim. Cosmochim. Acta* **70** 56-70.

Rhodium, gold and other highly siderophile elements in chondrites

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Osmium isotopic data and concentrations of the highly siderophile elements (HSE) Re, Os, Ir, Ru, Pt and Pd, recently obtained on chondrites by isotope dilution and Carius tube digestion in reverse aqua regia indicate systematic differences in the HSE composition of chondrite groups, notably in Re/Os and Pd/Ir. Unfortunately, these studies did not provide data for two other HSE, Rh and Au, because both elements are monoisotopic. Yet, Rh and Au may be critical elements for (1) a comprehensive understanding of the different HSE patterns of the chondrite groups and their origin; (2) distinguishing likely lunar impactor populations during the late heavy bombardment; and (3) for a complete characterization of the HSE pattern of the Earth's primitive mantle and its origin.

Here, we report abundances of Re, Ir, Ru, Pt, Pd, Rh and Au for a set of carbonaceous, ordinary, enstatite and R-chondrites. The new Rh and Au data, along with previous high-precision HSE concentration data on whole rocks of chondrites, require the presence of several distinct components in order to explain their CI-normalized patterns. (1) Carbonaceous chondrites show nearly flat HSE patterns from Re to Pt with CI-like or lower Re/Ir. Ordinary and enstatite chondrites show systematic fractionations from Re to Ir (decreasing) and from Ir to Pt (increasing) indicative for a complex high temperature history of ordinary and enstatite chondrites and the presence of at least two refractory components. (2) Most chondrites show a sometimes substantial drop in normalized abundance between Pt and Rh, suggesting the removal of a refractory metal phase from solar gas in a narrow temperature range (near 1400 K), and likely before condensation of the major fraction of Ni and Fe occurred (< 1350 K). (3) Chondrites are characterized by variable enrichment or depletion of Pd and Au, suggesting the variable presence of a component depleted in refractory siderophiles and enriched in moderately volatiles.