American Mineralogist, Volume 97, pages 1641–1652, 2012

Long-term solid-phase fate of co-precipitated U(VI)-Fe(III) following biological iron reduction by *Thermoanaerobacter*

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Abstract

The texture and mineralogy of solid phases resulting from biogeochemical metal reduction of U(VI)-FeOOH slurries was investigated over a period of four years. Solid-phase reaction products were analyzed with EXAFS, TEM, and XRD following fermentative reduction of uranium-loaded ferric hydroxide precursors with 0.01 and 0.05 cation mole fraction (CMF) U by cultures of *Thermoanaerobacter* sp. strain TOR-39. Only minor changes could be distinguished between 3 and 51 months for most slurries. Magnetite, goethite, uraninite, and minor akaganéite were present after 3 months at both U-CMFs. Akaganéite was not detected by XRD after 3 months, but was still observed by TEM after 50 months. Increasing uranium in the starting slurries led to a greater proportion of oxidized iron in the solid-phase products. Euhedral goethite and subhedral to euhedral magnetite were observed at all times. Uraninite was observed in clusters of <10 nm particles without any particular relationship to the iron minerals. HRTEM imaging indicated that even the smallest uraninite particles were well crystallized, with textures that remained consistent throughout the duration of experiments. X-ray absorption spectra after 3 months indicated 100% and 96.4% U(IV) in 0.01 and 0.05 CMF U slurries, respectively. EXAFS spectra were consistent with uraninite at both uranium levels, plus additional non-uraninite U(IV) for 0.05 CMF U. One 0.05 CMF U culture slurry was found to have a lower pH and a more oxidized final iron mineral assemblage; in this case uraninite was not observed by XRD, but large (101 nm average diameter) rounded uraninite grains were observed by TEM. These grains were observed in chains or aggregates often connected by necks, in textures suggestive of biological influence. HRTEM demonstrated each grain was composed of poorly oriented, primary, 2–5 nm uraninite crystallites. Uraninite crystal growth occurred by nanoparticle aggregation, but ripening was not observed even though incubation temperatures were held at 65 °C for 20 days. Thus, previous studies of biogenic nanoparticulate uraninite short-term reactivity are likely to be representative of systems aged over a period of years.

Keywords: Magnetite, uranium, nanoparticles, uraninite, geomicrobiology