

Fe and S redox cycling during a biostimulation episode at the Old Rifle, CO aquifer

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In-situ bioremediation studies have shown that adding electron donor to groundwater stimulates the activity of metal- and sulfate-reducing bacteria, profoundly impacting the cycling and speciation of redox-sensitive elements such as iron and sulfur, and changing the redox status of contaminants such as U(VI) to insoluble U(IV) products. While numerous studies have examined the impact of bioreduction in laboratory-based studies, very few have examined Fe and S speciation changes at the molecular to pore scales *in situ* in a biostimulated aquifer. In this study, we used in-well columns to obtain direct access to sediment speciation at different time points during a bioremediation experiment at the Old Rifle site, CO, transitioning dominantly from iron-reducing to sulfate-reducing regime.

We investigated Fe and S speciation at the molecular scale using X-ray absorption spectroscopy (XAS). Chemical extractions of reduced sediments revealed the rates of Fe(II) and sulfide formation. Bulk Fe EXAFS showed a significant change of Fe redox status with ongoing bioremediation. Results provide evidence for the reduction of the entire S pool to monosulfide and elemental sulfur. The speciation of FeS grain coatings that appear under sulfate-reducing conditions was probed using electron microscopy and micro-XAS. Results showed elemental sulfur accumulating in the coatings which appear to also concentrate uranium.

REE microdistribution in laterite from Madagascar

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Despite of relatively low REE concentrations, laterites are attractive as REE ion-adsorption deposit because REE are sorbed on mineral surfaces (readily leached) and HREE are enriched in comparison to LREE. However, in laterites, the REE distribution is difficult to assess due to the small size of the host phases and their low REE concentrations. We present here an innovative approach to determine the microscale REE distribution by combining geochemical data (whole-rock elementary and isotopic composition) with high-resolution *in-situ* techniques including FE-SEM, EMP and synchrotron μ -XRF and μ -XAS (LUCIA beamline at SOLEIL, France). The investigated laterite developed by weathering of tonalitic rock in Madagascar. The weathering profile includes from bottom to top: fresh tonalite, saprolite, oxidized-soil layer and top-soil. Bulk-rock composition reveals REE-mobility along the profile. REE are significantly leached from the top-soil and they accumulate in the oxidized layer, which is also enriched in Mn⁴⁺ and other redox sensitive elements. In this oxidized soil, all REE concentrations are 3-4 times the bed-rock concentrations, but Ce reaches 9 times the bed-rock concentration. In all studied samples, electron images and XRF mapping indicate that the main Ce portion is hosted by REE-phosphates, which belong to the rhabdophane group in the saprolite and to the alunite-jarosite group in the oxidized-soil and top-soil. The CeIII/CeIV ratio in these minerals (determined from the Ce_LIII edge XANES) reflects that of the bulk-rock values. The highest Ce concentrations are localized in porous zones enriched in Mn-oxide of the oxidized-layer. Although cerianite and alunite-jarosite minerals appear as the main REE-hosts, Mn-oxides also contain significant REE amount. In comparison, clay-rich domains show low Ce concentrations. Our *in-situ* results confirm that phosphates are crucial REE-carriers in common laterites.