

4.2.23

Iron isotope fractionation during adsorption of Fe(II) on Fe(III) oxides

N. TEUTSCH^{1,2}, U. VON GUNTEN¹, T.B. HOFSTETTER¹
AND A.N. HALLIDAY²

¹Department of Water Resources and Drinking Water,
EAWAG, Switzerland (vongunten@eawag.ch;
hofstetter@eawag.ch)

²Isotope Geology and Mineral Resources, ETH Zurich,
Switzerland (deutsch@erdw.ethz.ch;
halliday@erdw.ethz.ch)

Field Study

Large Fe isotope fractionations have been observed during an in situ deferrisation process in a reduced ground water. The experiment included five repeated cycles of injection of oxygen-containing water into the aquifer, followed by extraction of water. We hypothesise that the large fractionation (up to 3.5 ‰) observed in the extracted groundwater is due to abiotic fractionation. The heavier Fe(II) is preferentially adsorbed to the newly formed FeOOH surfaces. $\delta^{57}\text{Fe}$ was linearly correlated with dissolved Fe concentrations ($R^2 = 0.95$) throughout all five cycles in the course of more than two months. This reproducible pattern indicates that the same process occurs during repeated injection/extraction cycles.

Laboratory Experiments

Further investigations of the Fe isotope fractionation during abiotic processes are being conducted. Laboratory column experiments enable us to directly investigate if the sorption of Fe(II) on Fe(III) oxide surfaces leads to fractionation of Fe isotopes. Furthermore, in these controlled systems we can explore the various parameters influencing fractionation of Fe (e.g., surface area, speciation of the surface, speciation of Fe(II), flow rate etc.). Breakthrough curves (BTC) of Fe(II) in chromatography columns filled with goethite coated quartz sand were measured. Preliminary analyses of $\delta^{57}\text{Fe}$ indicate that heavier Fe(II) is preferentially adsorbed to the goethite surfaces, leaving the solution isotopically lighter. This observation is in agreement with our results from the in situ deferrisation experiments.

4.2.31

Zinc speciation in an artificially contaminated soil: Formation of a new mineral phase within 3 years

R. KRETZSCHMAR¹, S. PFISTER¹, A. VOEGELIN¹ AND
A.C. SCHEINOST²

¹Institute of Terrestrial Ecology, ETH Zurich, Switzerland
(kretzschmar@env.ethz.ch; pfister@env.ethz.ch;
voegelin@env.ethz.ch)

²European Synchrotron Radiation Facility (ESRF), Grenoble,
France (scheinost@esrf.fr)

The bioavailability and toxicity of Zn in contaminated soils strongly depend on its speciation. Initially, Zn speciation is determined by the primary contaminants. Over time, primary phases dissolve and Zn may adsorb to various soil components and eventually become incorporated into newly forming mineral phases. The practical relevance of this process for the attenuation of Zn bioavailability depends on the time scale over which new mineral phases form and the thermodynamic stability of the newly formed phase.

In this study, a field soil (pH 6.4, 1.5% organic carbon, 15% clay) was contaminated with filter dust from a brass foundry containing 98% zincite (ZnO). We followed the dissolution and redistribution of Zn over 4 years using bulk and micro XAFS analysis.

Bulk XAFS shows that within 18 months, most zincite dissolved and Zn attached to various soil components, mainly as an outer sphere complex. Micro XAFS reveals both remnants of undissolved zincite as well as regions of Zn specifically adsorbed to Mn/Fe oxides and beginning formation of a Zn bearing solid phase (phyllosilicate or mixed layered hydroxide). After 36 months, we observe a second shell in the bulk XAFS spectrum (~2.1 Zn at 3.11 Å; 1st shell 5.8 O at 2.04 Å), further supporting the formation of a Zn bearing mineral. Micro XAFS data for the same time reveal tetrahedrally coordinated specifically adsorbed Zn in Mn rich zones, Zn attached to organic material as an outer sphere complex, and octahedrally coordinated Zn in large diffuse parts of the soil matrix with a spectrum similar to the bulk XAFS.

Our results show that in a near neutral soil, ZnO dissolved within one to two years. A short transient phase, during which Zn is predominantly bound as an outer sphere complex, was followed by specific Zn adsorption and the onset of the formation of a Zn mineral phase. These results demonstrate that within a few years, Zn may be redistributed and attenuated in a near neutral soil. In ongoing studies, we investigate the long term efficiency of this immobilization process, e.g., during soil acidification.