Fe Isotope Fractionation During Reduction of Fe(III) to Fe(II)

A.D. ROSENBERG*, C.E. HODIERNE AND S.G. JOHN

Dept. of Earth and Ocean Sciences, University of South Carolina, USA (*correspondence: arosenberg@geol.sc.edu)

Phytoplankton growth, and thereby primary productivity, is limited in many regions of the ocean by insufficient iron (Fe) availability. In seawater iron exists in two different oxidation states – Fe(III) and Fe(II). While Fe(III) is thermodynamically stable in oxic environments, it can be reduced to Fe(II) by photochemical or biological reduction. In the ocean release of Fe(III) from ligands by reduction to Fe(II) is often necessary for Fe to become bioavailable to phytoplankton. Recently, techniques have been developed to measure dissolved Fe stable isotope ratios (δ^{56}Fe) in seawater and marine plankton, opening the door to using δ^{56}Fe as a tracer for biologically important Fe redox cycling in the oceans.

In order to clarify the impact that various reduction pathways have on Fe isotopic fractionation, the natural reduction of Fe(III)-L to Fe(II) was simulated in the lab by the reduction of Fe(III)-EDTA to Fe(II) in three ways: photochemically, chemically, and electrochemically. During photochemical reduction, Fe(III)-EDTA was reduced upon exposure to direct sunlight which promotes ligand-to-metal charge transfer. Chemical reduction was achieved by the addition of a reducing agent such as hydroxylamine hydrochloride. Electrochemical reductions were carried out using a rotating-disc electrode at a variety of overpotentials. Following reduction, Fe(II) was collected and purified for Fe isotope analysis by MC-ICPMS.

The reduction pathway has a large impact on the observed isotope effect. Photochemical reduction produces positive δ^{56}Fe values (+0.95 to +1.03 ‰) while chemical reduction produces negative δ^{56}Fe values (-1.73 to -2.20 ‰) with electrochemical reduction iron isotope ratios (-0.28 to -0.94 ‰) falling in between the two. Further investigation into isotopic fractionation during reduction of Fe(III) to Fe(II) may provide insight into the pathways by which Fe(III) is reduced and made bioavailable to phytoplankton in the oceans, leading to an overall greater understanding of marine iron cycling.

Linking nutrient and contaminant dynamics in rhizopheres of hyperaccumulators

C.E. ROSENFELD[1]*, R.L. CHANEY[2], A. LANZIROTTI[3] AND C.E. MARTÍNEZ[1]

[1]Pennsylvania State University, Department Ecosystem Science and Management, University Park, PA, USA, cer196@psu.edu (* presenting author), cem17@psu.edu
[2] USDA ARS Environmental Chemistry Laboratory, Beltsville, MD, USA Rufus.Chaney@ars.usda.gov
[3]Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL, USA lanzirotti@uchicago.edu

Trace metal contamination in soils is a global problem, causing plant and microbial toxicity, diminished crop production or decreased land cover. Some plants can grow, and even thrive, in heavily polluted soils though it is generally unclear how. Our goal was to elucidate linkages between contaminant and nutrient uptake in plants grown in metal contaminated soil.

We examined two ecotypes (Ganges and Prayon) of the metal hyperaccumulator, *N. caerulescens* (formerly *Thlaspi caerulescens*) grown on field-contaminated soil. Both ecotypes are known zinc (Zn) hyperaccumulators, while only the Ganges ecotype hyperaccumulates cadmium (Cd). At harvest, rhizosphere and plant thin sections were obtained for synchrotron-based μ-X-ray fluorescence (μ-XRF) and Zn-μ-X-ray Absorption Near Edge Structure (Zn-μ-XANES) spectroscopy.

Substantial Zn was accumulated by the plants (1390 mg Zn/kg), though there was no significant difference between ecotypes. Cadmium uptake, was significantly greater in the Ganges ecotype (750 mg Cd/kg) than the Prayon ecotype (90 mg Cd/kg). There was also greater Cd root-to-shoot translocation (root:shoot ratio = 0.13) than Zn (root:shoot ratio = 0.81). The Ganges ecotype took up significantly less Ca, which was also evident by the reduced rhizosphere Ca/Zn correlation in that ecotype. All rhizosphere soil regions investigated contained spectral features consistent with a combination of ZnS and ZnO, while bulk soil regions only occasionally contained such features. Inside the Ganges root, Zn speciation was most consistent with complexation by soft ligands (e.g. cysteine or histidine) while the Prayon roots contained Zn in a combination of mineral ZnO/Zn$(OH)_2$-like forms and hard-ligand (e.g. organic acids) complexes.

Nutrient biogeochemical cycles are often linked to differential metal accumulation in plants, as nutrient acquisition may be enhanced or inhibited because of contaminant uptake. In our plants, increased Cd uptake was correlated with decreased Ca uptake, decreased Zn-Ca co-location, and altered Zn speciation. On a larger scale, shifting Zn complexation in roots and the rhizosphere may impact Zn bioavailability to other organisms and mobility within contaminated ecosystems.

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