

Selenium speciation in rhizosphere soils and *Aster eatonii* roots: Implications for plant uptake

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As a result of phosphate mining activities, soils and waters in the Western Phosphate Resource Area, USA contain elevated concentrations of selenium (Se). However, the bioavailability, water solubility, and toxicity of Se are dependent on speciation, which is not well understood in complex environments, such as plant rhizospheres. Research that addresses Se cycling in rhizosphere soils is required to more accurately predict Se bioavailability and environmental impact. This research investigates rhizosphere influence on Se speciation using both molecular and macroscopic experiments on natural environmental samples. X-ray spectroscopy, laboratory extractions, and greenhouse studies are used to determine variation in Se speciation in rhizosphere soil and bulk soil.

Multiple Se oxidation state maps of *Aster eatonii* roots with attached rhizosphere soil show reduced Se species in the rhizosphere soils with oxidized Se species inside roots. Results may indicate that rhizosphere processes are oxidizing and mobilizing Se from reduced insoluble species in soils to species such as Se(VI) that are actively accumulated in plant roots. In greenhouse studies, Se(VI) was the predominant species detected in rhizosphere soil, plant roots, and control soils spiked with Se(IV) sorbed onto goethite, suggesting that Se(IV) is readily oxidized and mobilized in both rhizosphere soil and in bulk soil. Currently, laboratory extractions are being conducted to provide information on whether rhizosphere processes facilitate Se mobilization.

By integrating rhizosphere Se speciation information with known ecological and biogeochemical processes, we are developing a better understanding of reaction processes allowing plant uptake of Se. This detailed information will facilitate a better understanding of Se biogeochemical cycling in the rhizosphere environment.

The role of Fe-oxides and quartz in the sequestration of carbonaceous matter in 2.72 Ga Banded Iron Formations, Dharwar Craton, India

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The Archean BIF, composed of dark grey Fe-oxide and white microquartz bands, (Dharwar Craton, Lower Bababudan Group) is a typical Archean hydrothermal seawater precipitate, as shown by its REE element characteristics. The massive Fe-oxide bands consist of euhedral crystals of former magnetite in part replaced by hematite (\pm goethite). A porous network of euhedral former crystal shapes walled by hematite and filled in with hematite spherules, is observed in the silica close to the Fe-oxide bands. The quartz bands, generally thicker than the Fe-oxide bands, contain a few discontinuous Fe-oxide alignments of micrometric magnetite-hematite spherules, which fill in negative crystal shapes of quartz. In the quartz bands, carbonaceous matter (CM) occurs as nanometric intergrowth in the magnetite-hematite spherules (CM1), and as nanometric nodules at the interface between the quartz and the spherules (CM2). Furthermore, CM embeds the hematite spherules in the porous network (CM3). Low N contents (0.09 ppm) and high C/N ratios are typical for CM1, while CM2 shows high N contents (0.9 ppm) and low C/N ratios. This corresponds to a higher maturity degree for CM1 than for CM2. Raman spectroscopy confirms the high maturity (as indicated by the vitrinite reflectance of 2-3%) performed of CM1 from the quartz matrix, while CM3 has a lower maturity degree, as CM2. $\delta^{13}\text{C}$ vary between -17 and -26 ‰, being significantly higher in Fe-oxide rich layers than in the silica ones. Biologically derived CM ($\sim\delta^{13}\text{C}=-24$ ‰) is protected in silica layers. Lower $\delta^{13}\text{C}$ -19 ‰ and low N-contents are the result of CM degradation through a catalytic effect of the Fe-oxides. The acidification during CM decay may be the mechanism for the transformation of magnetite to hematite under reducing conditions.