Iron isotopes as a tracer in an acid-sulfate soil system

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Iron isotopes have been extensively studied in many systems and the fractionation factors are at least experimentally well understood for many common processes on earth's surface, including Fe-oxide mineral formation, precipitation reactions, and biological transformations such as microbially-mediated reductive dissolution of hematite. In complex environments, these well-undestood fractionations can be applied to assess the transport and speciation of Fe. However, only a few attempts have been made to understand the fractionations occuring in sulfur-rich systems, and these have been limited to acid mine drainage and hydrothermal vents. Salt marshes, tidal flats, and terrestrial floodplain environments, though well studied from the perspective of nutrients, trace metal cycling, and light stable isotopes (particularly C and S), have received little attention, yet are Fe-rich as a result of Fe monosulfide and pyrite formation.

Here we examine Fe isotope fractionation and Fe speciation in acid sulfate soil profiles and sediments from the Murray River system (South Australia), in order to gain an understanding of processes, pathways and biogeochemical cycling of Fe and associated metals through this environment. Inland acid sulfate soils are present in most fresh and saline wetland systems in the Murray-Darling Basin, largely due to the build-up of sulfide minerals during high pool levels. This situation has existed since the installation of locks in the 1930's. Prolonged recent drought led to oxidation of sulfide minerals and soil acidification with severe impacts on the local soil ecosystem. However, in the floodplain soils, desiccation of pyrite-laded, organic rich sediment allows Fe oxidation, then re-flooding events release acid to the river. Prelimary results from two oxidized soil samples of have a small range of light, near-zero δ^{57}Fe values. However, significant fractionation has been observed between primary sulfide minerals and their oxidation products in other acid sulfate soils in Australia. This is consistent with previously observed isotope fractionation between oxidized Fe minerals precipitated from Fe-rich sulfidic mine drainage [1, 2]. Additional data regarding the exact Fe mineral phases present in the soils, as well as sequential extractions of these phases and isotopic analysis of the extracts may provide additional constraints on Fe translocation in these environments.

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Coupled geochemical processes limiting phytosiderophore-promoted iron uptake from soils

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Graminaceous plant species (grasses) exude multidentate complexing agents called phytosiderophores (PS) for the purpose of iron aquisition, in particular under conditions of iron deficiency stress. Upon release from the root surface, the ligands diffuse into soil solution and solubilize iron from iron bearing phases in the soil, forming iron complexes which are taken up at the root surface.

Although the mechanism of action of PS has been intenisively studied, this was mostly done in hydroponics or in soil suspensions with a low soil to solution ration that did not allow to investigate coupled geochemical processes. The aim of the current project is to quantitatively understand the geochemical and geophysical processes limiting PS promoted iron uptake.

In the present work the rate of iron mobilization from various soils by the PS deoxymugineic acid (DMA) was examined in batch experiments, both with and without addition of a sterilant (sodium azide) to prevent biodegradation of the DMA ligand. Both clay and sandy soils, differing in iron availability were included.

Fe mobilization corresponded with 10 to 60% of the added DMA. The extent to which Fe was mobilized positively correlated with Fe availability parameters (e.g. DTPA-extractable Fe) and negatively correlated with the clay content of the soils. Especially in soils of low Fe availability, Fe mobilization was strongly compromised by the mobilization of competing cations like Cu, Zn, Ni and Co.

In absence of sterilant, all metal-DMA complexes were removed from solution within 4 days. Depending on the soil, Fe mobilization reached a maximum after 0.25 to 8 hours.. Except for one soil, maximum Fe mobilization was not dependent on sterilant addition. Also when sterilant was added, FeDMA concentrations eventually decreased, indicating that processes other than biodegradation significantly compromise the FeDMA concentration.

These results strongly indicate that for improving the understanding of plant iron acquisition, the kinetics and thermodynamics of coupled rhizosphere processes need to be studied coherently.