

## Lead(II) desorption from goethite mediated by hydroxamate ligands

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### Introduction

Siderophores are low molecular weight organic molecules secreted by plants and micro-organisms in response to Fe stress. More than 400 siderophores have been isolated, the majority of which possess either catechol or hydroxamate functional groups. With stability constants commonly exceeding  $10^{30}$ , siderophores are considered to have higher affinities for Fe(III) than for any other major or trace element dissolved in soil solution. Despite the abundance, ubiquity and structural diversity of siderophores in both terrestrial and aquatic ecosystems, their possible role in Pb mobilisation has received only brief attention. Here we show that three hydroxamate siderophores solubilise lead(II) chemisorbed to an iron(III) oxide adsorbent, significantly increasing the bioavailability of this toxin.

### Methods

Goethite [ $\alpha$ -FeOOH], prepared by standard methods and identified by X-ray diffraction, gave a specific surface of  $36 \text{ m}^2 \text{ g}^{-1}$  as determined by  $\text{N}_2$  multipoint BET analysis. Adsorption experiments were performed aseptically using a batch method with a goethite concentration of  $1.0 \text{ g l}^{-1}$  and an ionic strength of  $0.01 \text{ M NaClO}_4$ . Soluble Pb and Fe were measured between pH 3 and 8 by first adding Pb ( $10 \text{ }\mu\text{M}$ ) and then siderophore (10, 20, or  $40 \text{ }\mu\text{M}$ ) to the goethite suspension. Following 20 h reaction, Pb and Fe in solution were measured by ICP-MS (Pb detection limit  $\approx 0.1 \text{ ng g}^{-1}$ ) and ICP-AES, respectively.

### Results

The efficacy of Pb desorption varied with siderophore type and generally increased with pH and siderophore/Pb molar ratio. A trihydroxamate siderophore, at pH 6.5 and a siderophore/Pb molar ratio of 4, solubilised nearly 25% of the total sorbed Pb. In the presence of  $10 \text{ }\mu\text{M}$  ferrichrome, Pb adsorption largely mimicked that for the siderophore-free system, whereas significant amounts of Pb were desorbed with  $20 \text{ }\mu\text{M}$  ferrichrome at  $\text{pH} > 5.5$ . Rhodotorulic acid was the least effective Pb chelator, requiring  $20 \text{ }\mu\text{M}$  to desorb detectable amounts of Pb.

## Isotopic tracing of water filtration in oxidizing, fractured porous media

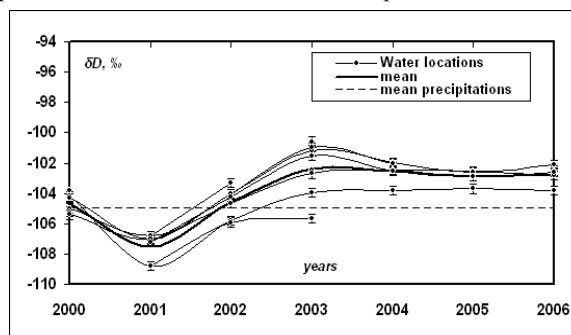
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The Krasnokamensk area, SE Siberia, Russia is known for its rich ore deposits. The Tulukuevskoe U deposit is hosted in Mesozoic (135 Ma) welded tuffs that are characterized by tectonic faulting, hydrothermal-metasomatic alteration, and oxidizing transformation. Further to environmental impacts caused by open pit mining, the migration of U from the ore body into the wall rocks and to the underlying aquifers is of particular interest for nuclear waste management purposes. Using the Tulukuevskoe open pit as a natural analogue, the conditions under which U can be mobilized, transported and precipitated are being investigated.

In this context the dynamics of isotope ( $^{18}\text{O}$ , D) composition of meteoric water filtering through the fractured-porous media was studied. We monitored 9 water locations for 7 years.

**Figure 1:**  $\delta\text{D}$  for meteoric water filtering through fractured-porous media of the Tulukuevskoe U deposit



We also studied the  $^{87}\text{Sr}/^{86}\text{Sr}$  and chemical composition of waters. The same type of analysis was performed for rain and snow precipitation. To explain the results obtained, the integration of water isotope parameters inside the fractured-porous media was modeled for many-years type of monitoring. The model calculations show that the mean extent of water filtration is from 2 to 3.5 years for the various water-sampling locations.

The model calculations based on  $\delta\text{D}$  behavior gave more realistic results, than those based on  $\delta^{18}\text{O}$  behavior. The oxygen isotope composition of infiltrating water obviously could be altered by oxidation and carbonatization of the media.  $^{87}\text{Sr}/^{86}\text{Sr}$  data supported this interpretation.