

Abstract

Cobalt plays a dual role in the environment as both an essential trace nutrient and a significant component of legacy radioactive waste (as the isotope ⁶⁰Co). Recent studies suggest that trihydroxamate siderophore desferrioxamine B (DFOB), a biogenic chelator with high affinity for Fe(III) that increases the bioavailability of iron, also forms exceptionally stable aqueous complex with Co(III). The fate, transport, and bioavailability of cobalt in terrestrial environments thus may be strongly coupled to siderophores. Siderophore-promoted dissolution of Co(III)-bearing minerals is one mechanism that may mobilize cobalt, but the biogeochemical process is largely unexplored. To investigate this mechanism, we measured the dissolution rates of heterogenite (CoOOH) as a function of pH in the presence of DFOB by batch experiments. Reductive Co dissolution was observed at acidic pH but not at circumneutral to basic pH, indicating pH-dependent dissolution pathways. In addition, we conducted flow-through experiments to examine the dissolution rates of synthetic Co-substituted goethites in the presence of DFOB. Total dissolution rates of both Fe and Co increased as the Co substitution concentration increased. These results pose a potential risk of mobilization of radioactive ⁶⁰Co to surface waters, aquifers, and soil systems in the area with large concentration of siderophore.

Objectives

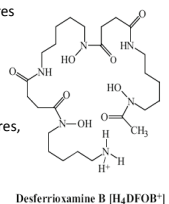
- To determine the dissolution rates and mechanisms of Co-bearing minerals in the presence of the siderophore Desferrioxamine B (DFOB) as a function of pH
- To study the effects of Co substitution for Fe in goethite on siderophore mediated Fe solubilization

Introduction

Iron deficiency often occurs in natural environments with oxic condition and neutral to alkaline pH, such as calcareous soils and marine systems, due to the low solubility and slow dissolution rate of iron oxide minerals. To overcome the low iron bioavailability, organisms produce and exude siderophores to facilitate iron solubilization.

Siderophores

- Low-molecular weight biogenic chelating agents with high affinity for Fe(III).
- Reported concentration of hydroxamate siderophores in soil solutions and natural waters ranges from 10⁻⁷-10⁻⁸ M.
- Desferrioxamine B (DFOB) is a common microbial siderophore in soils and natural waters.
- DFOB is representative of a large class of siderophores, the trihydroxamates.
- Binding constant for Co(III) exceeds that for Fe(III)!
logK_{Fe(III)HDFOB⁺} = 10³² logK_{Co(III)HDFOB⁺} = 10³⁷



Siderophore-promoted dissolution

Dissolution of metal oxides by siderophores favors a **ligand-promoted** dissolution mechanism, although a **reductive** mechanism may also be true as a result of electron transfer between surface metal and adsorbed ligands.



* where Me represents metal oxides or cations, sid represents siderophore ligands

Sample Preparation

Heterogenite (CoOOH) and four Co-substituted goethites (Co-Goethite) with different Co concentrations were synthesized and characterized for morphology, phase, surface area, and Co oxidation number.

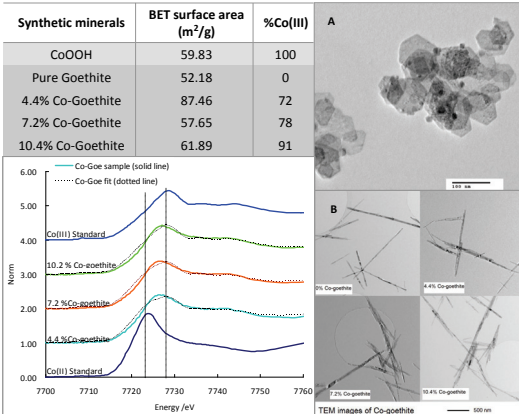


Figure 1. Stacked, normalized Co K-edge XANES spectra of synthetic Co-goethites for oxidation state feature. The fitting results are the sum of two standards. Co(III) is the dominant state in all synthetic Co-goethites.

Figure 2. TEM images of (A) platy-like heterogenite and (B) Co-goethite. All Co-goethites are needle-like particles without distinct morphology.

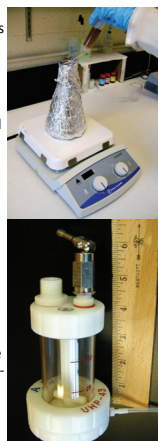
Experimental Methods

Batch experiments:

- For the dissolution of heterogenite (CoOOH) particles in 100 μM DFOB solution.
- Experiments were conducted at 25 °C and pH = 5, 6, 7, 8, and 9
- Samples were taken every 10 - 15 min and measured by UV-visible spectroscopy for Co(III)HDFOB⁺.
- Fast initial dissolution rates were determined by plotting [Co(III)HDFOB⁺] against dissolution time.

Flow-through experiments:

- For the dissolution of Co-substituted goethite (Co-FeOOH) particles loaded in continuous-flow stirred tank reactors (right picture).
- Flow rate was controlled at 4 - 7 ml/hr; temperature at 25 °C; pH = 5, 7, and 9.
- Samples of effluent solutions from the bottom of the reactors were taken once a day and measured by UV-visible spectroscopy and AAS / ICP-EMS.
- Steady-state dissolution rate were reached after 400 hours of reaction.



Results

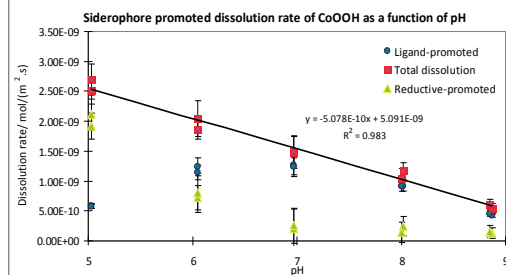


Figure 3. DFOB-promoted dissolution rates of CoOOH as a function of pH. Dissolution undergoes pH-dependent mechanisms, with dominant ligand-promoted pathway at neutral to alkaline pH, and dominant reductive pathway at acidic pH.

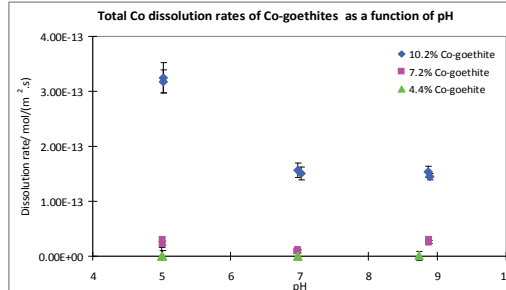


Figure 4. DFOB-promoted total Co dissolution rates of Co-substituted goethites as a function of pH.

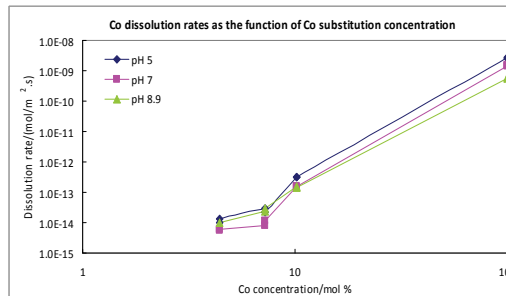


Figure 5. Total Co dissolution rates of heterogenite or Co-substituted goethites as a function of Co concentration in synthetic minerals. Data was plotted on log-log scale in this figure. Results show correlation between logarithm of total dissolution rates and logarithm of Co concentration.

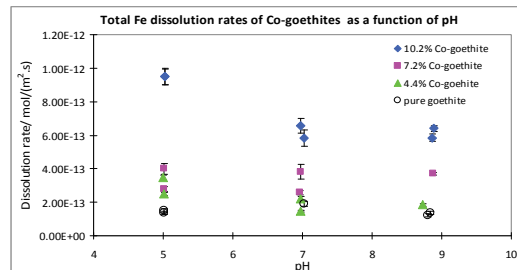


Figure 6. DFOB-promoted total Fe dissolution rates of Co-substituted goethites as a function of pH.

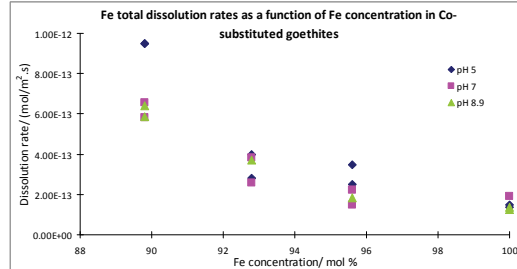


Figure 7. Total Fe dissolution rates of Co-substituted goethites as a function of Fe concentration in synthetic minerals. Plot shows the trend that increasing Co impurity in goethite also raises the Fe dissolution rates at all pHs.

Conclusions

DFOB-promoted dissolution mechanism of Co-bearing minerals depends on pH of solution, with dominant ligand-promoted pathway at neutral to alkaline pH, and significant reductive pathway at acidic pH.

Both Co and Fe dissolution rates increase with increasing Co substitution concentration, suggesting more labile crystal structure in the presence of DFOB.

Results imply an active role of siderophores in the biogeochemical cycling of Co in terrestrial environments, which may increase the risks of ⁶⁰Co mobilization.

References

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