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### **Dissolution of Fe(III)(hydr)Oxides by Aerobic Microorganisms**

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The overall objective of this collaborative project has been to determine the rates and mechanisms whereby microbes dissolve Fe(III)(hydr)oxides in aerobic soil environments. Information about the rates and mechanisms of Fe(III)(hydr)oxide dissolution is fundamental for a wide range of hydrobiogeochemical processes, yet little is known about the mechanism of dissolution promoted by siderophore-producing microorganisms. Fe(III)(hydr)oxides sorb radionuclides and organic contaminants; thus their dissolution may cause remobilization of these sorbed pollutants. The specific research objectives pursued at Berkeley were: (1) dissolution of Al-substituted goethites, (2) dissolution mechanisms of goethite, and (3) effects on adsorbed trace metals. The results obtained were reported in five technical journal articles:

1. Kraemer, S.M., S.-F. Cheah, R. Zapf, J. Xu, K.N. Raymond, and G. Sposito. 1999. Effect of hydroxamate siderophores on Fe release and Pb(II) adsorption by goethite. *Geochim. Cosmochim. Acta* 63:3003-3008.
2. Coccozza, C., C.C.G. Tsao, S.-F. Cheah, S.M. Kraemer, K.N. Raymond, T.M. Miano, and G. Sposito. 2002. Temperature dependence of goethite dissolution promoted by trihydroxamate siderophores. *Geochim. Cosmochim. Acta* 66:431-438.
3. Cervini-Silva, J., and G. Sposito. 2002. Steady-state dissolution kinetics of aluminum-goethite in the presence of desferrioxamine B and oxalate ligands. *Environ. Sci. Technol.* 36:337-342.
4. Kraemer, S.M., J. Xu, K.N. Raymond, and G. Sposito. 2002. Adsorption of Pb(II) and Eu(III) by oxide minerals in the presence of natural and synthetic hydroxamate siderophores. *Environ. Sci. Technol.* 36:1287-1291.
5. Cheah, S.-F., S. M. Kraemer, J. Cervini-Silva, and G. Sposito. 2003. Steady-state dissolution kinetics of goethite in the presence of desferrioxamine B and oxalate ligands: Implications for microbial acquisition of iron. *Chem. Geol.* 198:63-75.

## **Siderophore-promoted dissolution of Al-goethites**

Steady-state dissolution rates of synthetic low-substitution Al-goethites (mol % Al < 10) at pH 5 in the presence of the trihydroxamate siderophore, desferrioxamine B (DFO-B), and the common biological ligand, oxalate, were investigated. The siderophore-promoted Fe release rate increased both with the level of Al substitution and with DFO-B concentration up to about 100  $\mu\text{M}$ , after which a plateau occurred, suggesting a saturation effect from DFO-B adsorption as a precursor to dissolution. At concentrations above 200  $\mu\text{M}$ , oxalate also enhanced the Fe release rate which, however, was not influenced by Al substitution. For Al-goethites with mol % Al < 4, the Fe release rate in the presence of 40  $\mu\text{M}$  DFO-B together with varying concentrations of oxalate was typically greater than the corresponding sum of dissolution rates in the presence of the two ligands alone.

This synergism was hypothesized to be the combined result of the ability of oxalate to adsorb strongly at the goethite surface, thus promoting Fe release, and of the high selectivity of DFO for Fe(III). Ferric oxalate complexes formed during dissolution will likely lose  $\text{Fe}^{3+}$  by ligand substitution with DFO-B, leading to the production of  $\text{Fe}(\text{HDFO-B})^+$  and uncomplexed oxalate, the latter of which, in turn, could adsorb to the goethite surface again. For Al-goethites with mol % Al > 4, synergism was not apparent, which may signal the effect of a decreased surface density of Fe-OH sites associated with Al for Fe substitution. The oxalate-promoted release rates of Al did not scale with those of Fe, indicating incongruent dissolution. However, Al release rates in the presence of DFO-B did scale approximately with those of Fe but were not affected by the concentration of the siderophore. These results are consistent with the presence of  $\text{Al}(\text{OH})_3$  inclusions in Al-goethite.

## **Dissolution mechanisms of goethite**

The temperature dependence of goethite dissolution kinetics in the presence of DFO-B and its acetyl derivative, desferrioxamine D1 (DFO-D1) were investigated. At 25 and 40  $^\circ\text{C}$ , DFO-D1 dissolved goethite at twice the rate of DFO-B, whereas at 55 $^\circ\text{C}$ , the behavior of the two ligands was almost the same. Increasing the temperature from 25 to 55  $^\circ\text{C}$  caused little or no significant change in DFO-B or DFO-D1 adsorption by goethite. A pseudo-first-order rate coefficient for dissolution, calculated as the ratio of the mass-normalized dissolution rate coefficient to the surface excess of siderophore, was approximately the same at 25 and 40  $^\circ\text{C}$  for both siderophores. At 55  $^\circ\text{C}$ , however, this rate coefficient for DFO-D1 was about half that for DFO-B.

Analysis of the temperature dependence of the mass-normalized dissolution rate coefficient via the Arrhenius equation led to an apparent activation energy that was larger for DFO-B than for DFO-D1, but much smaller than that reported for the proton-promoted dissolution of goethite. A compensation law was found to relate the pre-exponential factor to the apparent activation energy in the Arrhenius equation, in agreement with what has been noted for the proton-promoted dissolution of oxide minerals and for the complexation of  $\text{Fe}^{3+}$  by DFO-B and simple hydroxamate ligands in

aqueous solution. Analysis of these results suggested that the siderophores adsorb on goethite with a only single hydroxamate group in bidentate ligation with an Fe(III) center.

An investigation of the effects of DFO-B and a common biological ligand, oxalate, on the steady-state dissolution of goethite at pH 5 and 25 °C was also conducted. The main goal of our study was to quantify the adsorption of the ligands and the dissolution of goethite they promote in a two-ligand system. In systems with one ligand only, the adsorption of oxalate and DFO-B each followed an L-type isotherm. The surface excess of oxalate was approximately 40 mmol kg<sup>-1</sup> at solution concentrations above 80 μM, whereas the surface excess of DFO-B was only 1.2 mmol kg<sup>-1</sup> at 80 μM solution concentration. In the two-ligand systems, oxalate decreased DFO-B adsorption quite significantly, but not vice versa. For example, in solutions containing 40 μM DFO-B and 40 μM oxalate, 30% of the DFO-B adsorbed in the absence of oxalate was displaced.

The mass-normalized dissolution rate of goethite in the presence of DFO-B alone increased as the surface excess of the ligand increased, suggesting a ligand-promoted dissolution mechanism. In systems containing oxalate only, mass-normalized goethite dissolution rates were very low at concentrations below 200 μM, despite maximal adsorption of the ligand. At higher oxalate concentrations (up to 8 mM), the steady-state dissolution rate continued to increase, even though the surface excess of adsorbed ligand was essentially constant. Chemical affinity calculations and dissolution experiments with variation of the reactor flow rate showed that far-from-equilibrium conditions did not obtain in systems containing oxalate at concentrations below 5 mM.

The dissolution rate in the presence of DFO-B at solution concentrations between 1 and 80 μM was approximately doubled when oxalate was also present at 40 μM solution concentration. The dissolution rate in the presence of oxalate at solution concentrations between 0 and 200 μM was increased by more than an order of magnitude when DFO-B was also present at 40 μM solution concentration. Chemical affinity calculations showed that, in systems containing DFO-B, goethite dissolution was always under far-from-equilibrium conditions, irrespective of the presence of oxalate.

These results were described quantitatively by a model rate law containing a term proportional to the surface excess of DFO-B and a term proportional to that of oxalate, with both surface excesses being determined in the two-ligand system. The pseudo first-order rate coefficient in the DFO-B term has the same value as measured for goethite dissolution in the presence of DFO-B only, while the rate coefficient in the oxalate term must be measured in the two-ligand system, since it is only in this system that far-from-equilibrium conditions obtain. These latter conditions do not exist in the system containing oxalate only, but they do exist in the DFO-B/oxalate system because the siderophore is able to remove Fe(III) from all Fe-oxalate complexes rapidly, leaving the uncomplexed oxalate ligand in solution free to react again with the goethite surface. This synergy observed in the two-ligand system implies that the production of modest quantities of siderophore in the presence of very low concentrations of oxalate would be an extremely effective mechanism for the microbially-induced release of Fe from goethite.

## Effects on adsorbed trace metals

Trihydroxamate siderophores such as DFO-B have been proposed for use as mediators of actinide and heavy metal mobility in contaminated subsurface zones. These microbially produced ligands recently have been derivatized synthetically to enhance their affinity for transuranic metal cations. However, the interactions between the synthetic derivative and adsorbed trace metals have not been characterized. Therefore, DFO-B, was compared with its actinide-specific catechol derivative, N-(2,3-dihydroxy-4- (methyl-amido)benzoyl)- desferrioxamine-B (DFOMTA), as to the effect on the adsorption of Pb(II) and Eu(III) by goethite and boehmite. In the presence of 240  $\mu\text{M}$  DFO-B, a strongly depleting effect on Eu(III) adsorption by goethite and boehmite occurred above pH 6. By contrast, almost total removal of Eu(III) from solution in the neutral to slightly acidic pH range was observed in the presence of either 10 or 100  $\mu\text{M}$  DFOMTA, due primarily to the formation of metal-DFOMTA precipitates. Addition of DFOMTA caused an increase in Pb(II) adsorption by goethite below pH 5, but a decrease above pH 5, such that the Pb(II) adsorption edge in the presence of DFOMTA strongly resembled the DFOMTA adsorption envelope, which showed a maximum near pH 5 and decreasing adsorption toward lower and higher pH.

## Overall conclusions

It has long been known that DFO-B, by virtue of its large affinity for Fe, can affect the amount of bioavailable Fe. Our kinetics model described above illustrates two mechanisms through which this affinity can affect Fe release kinetics. DFO-B alone adsorbs moderately to the goethite surface and, therefore, can modestly increase the rate of goethite dissolution in the absence of other ligands (ligand-promoted dissolution). However, in reality, for soils and other biologically active environments, a variety of organic ligands is always present, with oxalate being the most common. Our data indicate that comparable rates of goethite dissolution are to be expected in the presence of either 500  $\mu\text{M}$  oxalate or just 40  $\mu\text{M}$  oxalate combined with only 10  $\mu\text{M}$  DFO-B, despite the fact that negligible dissolution occurs in the presence of 40  $\mu\text{M}$  oxalate alone, and rather little in the presence of 10  $\mu\text{M}$  DFO-B alone. Oxalate adsorption onto goethite at 40  $\mu\text{M}$  concentration is at about 70% of its maximal value, thereby providing a rich potential source of soluble Fe if the driving force for continual Fe–oxalate detachment from the goethite surface could somehow be increased. Adding a small concentration of predatory DFO-B ligands, which have little propensity to be lost from solution by adsorption, can serve this purpose by depleting the aqueous solution phase of Fe – oxalate complexes, thus increasing the thermodynamic pressure for Fe–oxalate desorption. The remarkable advantage that accrues to the microbial producer of the siderophore also can be inferred from our data, which imply that DFO-B concentrations well in excess of 100  $\mu\text{M}$  would be required in order to achieve the same dissolution rate as is observed in the presence of only 10  $\mu\text{M}$  DFO-B, and with just enough oxalate present to adsorb abundantly while serving as prey for the siderophore.

**Personnel supported by this project:**

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