Adsorption of Pb(II) and Eu(III) by Oxide Minerals in the Presence of Natural and Synthetic Hydroxamate Siderophores

STEPHAN M. KRAEMER,^{*,†,‡} JIDE XU,[§]
KENNETH N. RAYMOND,[§] AND
GARRISON SPOSITO[†]

Division of Ecosystem Sciences, University of California,
Berkeley, California 94720-3110, Institute of Terrestrial
Ecology, Swiss Federal Institute of Technology, Grabenstrasse
3, CH-8952, Schlieren, Switzerland, and Department of
Chemistry, University of California,
Berkeley, California 94720-1460

Trihydroxamate siderophores have been proposed for use as mediators of actinide and heavy metal mobility in contaminated subsurface zones. These microbially produced ligands, common in terrestrial and marine environments, recently have been derivatized synthetically to enhance their affinity for transuranic metal cations. However, the interactions between these synthetic derivative and adsorbed trace metals have not been characterized. In this paper we compare a natural siderophore, desferrioxamine-B (DFO-B), with its actinide-specific catecholate derivative, *N*-(2,3-dihydroxy-4-(methylamido)benzoyl)-desferrioxamine-B (DFOMTA), as to their effect on the adsorption of Pb(II) and Eu(III) by goethite and boehmite. In the presence of 240 μM 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 μM 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.

Introduction

A number of laboratory and field experiments have implicated soluble complexes involving biologically produced organic ligands as the cause of enhanced mobility of transuranic radionuclides in subsurface environments [for reviews, see McCarthy et al. (1, 2)]. These highly toxic radioactive elements are known to form strong complexes with biological ligands that affect both their sorption by soil minerals and their uptake by microorganisms (2, 3). Otherwise, in the absence of competing ligands, their sorption to metal oxides, clay minerals, and soil or sediment solids is strong (4–7).

One biological ligand of current interest, proposed as a mediator of actinide and heavy metal mobility, is the microbial siderophore (8–12). These organic ligands are metal chelators with low relative molecular mass that are synthesized by microorganisms as a response to diminished Fe(III) solubility. Most microbial siderophores are hexadentate ligands, typically with either catecholate or hydroxamate complexing functional groups (13). Figure 1 shows the molecular structure of the hydroxamate siderophore, desferrioxamine-B (DFO-B), that is produced by the soil actinomycete, *Streptomyces pilosus* (14). Concentrations of microbial siderophores ranging up to 240 μg per kg soil have been measured in bioassays (15). Watteau and Berthelin (16) cite 126 μM as a typical soil solution concentration of DFO-B. Only a few studies of the interactions of DFO-B and synthetic analogues with mineral phases, including adsorption and ligand-promoted dissolution processes, have been conducted previously (17–20).

Microbial siderophores are outstanding in their specificity for Fe(III). For example, the stability constant of the 1:1 Fe(III) complex of DFO-B ($10^{30.6}$) is about 16 orders of magnitude larger than that for its 1:1 Cu(II) copper complex (9). This specificity of microbial siderophores is an important prerequisite for effective iron binding in soil solutions, where the concentrations of competing cations, such as Ca^{2+} , can exceed Fe(III) concentrations by many orders of magnitude. However, some 1:1 metal-DFO-B complexes actually approach or even exceed the stability of the Fe(III) complex. For example, the Th(IV) and Pu(IV) complexes have stability constants equal to $10^{26.6}$ and $10^{30.8}$, respectively (21). The presence of siderophores, therefore, could have an important effect on the mobility of actinides in soil environments.

However, high stabilities of the complexes do not necessarily translate into increasing mobility of the metal ions involved. A recent study (12) found increased adsorption of Cu, Zn, and Cd on montmorillonite in the presence of DFO-B at pH < 8. This enhanced adsorption could be caused by ternary surface complexation, electrostatic attraction, or even surface precipitation of the trace-metal-siderophore complexes. Thus, as often noted in the literature, the presence of organic ligands can lead either to enhanced metal transport or enhanced adsorption (26–31). If the formation of soluble complexes competes effectively with metal sorption by a soil matrix, the mobility of metal ions increases, but secondary adsorption of the metal complex reduces metal ion mobility (27, 28). The same considerations apply to the adsorption of metal ions on mobile colloidal particles, in which case adsorption can lead to increased mobility by facilitated transport (6, 29). It is apparent that multiple factors influence metal mobility in the presence of sorbing mineral surfaces and chelating biological ligands.

In this paper, we compare the interactions of two hydroxamate siderophores with the lanthanide Eu(III) and with Pb(II) adsorbed by goethite ($\alpha\text{-FeOOH}$) and boehmite ($\gamma\text{-AlOOH}$). Europium is a well-known surrogate for transuranic metals (2, 30, 31), whereas lead is a hazardous trace metal. In the absence of competing organic ligands, lead and europium should adsorb strongly to oxide mineral surfaces (11, 32, 33). One of the two siderophores selected, DFO-B, is a common trihydroxamate siderophore (16) whose free amine group remains protonated at pH < 10 (11). The other, DFOMTA [*N*-(2,3-dihydroxy-4-(methylamido)benzoyl)desferrioxamine B], is a derivative of DFO-B prepared by attaching a catecholate group to the free amine group [Figure 1 (34)]. At low pH, this ligand forms trishydroxamate complexes with Fe(III), whereas at high pH it forms bishy-

* Corresponding author phone: +41-1-633-6077; fax: +41-1-633-1118; e-mail: stephan.kraemer@ito.umnw.ethz.ch.

[†] Division of Ecosystem Sciences, University of California.

[‡] Swiss Federal Institute of Technology.

[§] Department of Chemistry, University of California.

FIGURE 1. Molecular structures of desferrioxamine B and DFOMTA. The two trihydroxamate siderophore derivatives differ only in the substituent on the terminating amine group (R).

droxamate-monocatechol iron complexes with the catechol group replacing the terminal hydroxamate group (34). Pu(IV) and Th(IV) are coordinated by both hydroxamate and catecholate groups (21). Due to the strong coordination of lanthanides by salicylamide complexes (35), it is likely that Europium complexation by DFOMTA involves the loss of one proton from the catechol group and bidentate coordination through the amide oxygen and one adjacent phenolate. The addition of the catecholate group leads to a large increase in the rate of Fe^{3+} complexation as well as to a very high affinity for transuranic metal cations (21, 34). For example, the 1:1 complexes $\text{Th}(\text{DFOMTA})^-$ and $\text{Pu}(\text{DFOMTA})^-$ have stability constants equal to $10^{38.6}$ and $10^{41.7}$, respectively. Thus, in principle, DFOMTA could be an excellent agent for desorbing toxic metal cations from oxide minerals. Therefore, the objective of our research was to compare the effectiveness of these two biological ligands as desorbers of trace metals from two representative oxides.

Experimental Section

Materials. Goethite was synthesized by the method of Schwertmann and Cornell (36) and freeze-dried. Powder X-ray diffraction confirmed that the synthesized solid was goethite. Its specific surface area was $35 \pm 3 \text{ m}^2/\text{g}$, as determined by the static BET method. Synthetic boehmite ($\gamma\text{-AlOOH}$) was provided as a gift by Condea Vista. It has a specific surface area of $180 \text{ m}^2/\text{g}$, as determined by the static BET method and a p_{znc} value of 8.6 (37).

The sample of desferrioxamine B (DFO-B) used was produced by Ciba-Geigy (Desferal) and received as a gift from the Salutar Corporation. *N*-(2,3-dihydroxy-4-(methylamido)benzoyl)desferrioxamine B (DFOMTA) was synthesized according to the procedure described by Hou et al. (34).

Solutions containing desferrioxamine B mesylate or DFOMTA, Pb ICP standard solution (Ultra Scientific), Eu ICP standard solution (GFS), Fe ICP standard solution (Ultra Scientific), Na perchlorate (GFS, ACS grade), MOPS buffer (4-morpholine propane sulfonic acid; Boehringer, reagent grade), Eu(III) perchlorate hydrated solution (GFS, reagent grade), Fe(III) perchlorate hexahydrate (GFS, ACS grade), and perchloric acid (Fisher, Optima) were prepared with high-purity $18 \text{ M}\Omega \text{ cm}^{-1}$ water (Milli-Q Plus, Millipore).

Analytical Methods. Concentrations of DFO-B and DFOMTA were measured colorimetrically with a Shimadzu UV-160 spectrophotometer by absorbance at 463.2 and 451 nm, respectively, as the Fe(III) complex in the presence of excess Fe at pH 1.5 (11). Iron, Pb, and Eu were determined by ICP-AES (Thermo Jarrel-Ash) using emission lines at 238.2, 220.3, and 381.9 nm, respectively. Proton activity was measured with Ross combination electrode calibrated with buffers at pH 4.0, 7.0, and 10.

Adsorption Measurements. Lead(II) and Eu(III) adsorption edge measurements (relative amount adsorbed as a

function of pH) were performed in 0.01 M NaClO_4 and 5 mM MOPS buffer at a solids concentration of 0.5 g/L, open to the atmosphere, and at ambient temperature ($22 \pm 2^\circ \text{C}$). MOPS is a nonmetal-complexing pH buffer (38). It was ascertained by equilibrium speciation modeling that Eu(III) and Pb(III) solids were not expected under our experimental conditions. All samples were prepared in duplicate. Blanks (i.e., without adsorbent) were prepared over the pH range 3–9 to investigate Pb and Eu adsorption to container walls, which was found to be $< 3\%$ of the initial concentration (unless reported otherwise below). In the batch adsorption experiments, 10 mg of goethite and 10 mL of electrolyte were placed in 40 mL Teflon bottles. Lead or Eu and DFO-B or DFOMTA stock solutions were added to yield concentrations of 3.38 μM (Pb and Eu), 240 μM (DFO-B), and 100 μM (DFOMTA), respectively (Table 1). Predetermined amounts of acid or base then were added to reach the desired pH value for each sample. The sample bottle was filled with electrolyte and buffer to yield a final volume of 20 mL and then placed on a rotary shaker for 18 h. The equilibrated samples were centrifuged at 16000 rpm and 25°C (Du Pont, RC-5B refrigerated centrifuge). Finally, 9 mL of the supernatant solution was acidified using 60 μL of concentrated HClO_4 for Pb and Fe analysis, and another 9 mL was collected for pH measurements. Soluble iron concentrations after 18 h were $\leq 3 \mu\text{M}$ in all samples.

Adsorption isotherms and envelopes for DFO-B on goethite have been reported by Kraemer et al. (11). Adsorption isotherms for DFOMTA on goethite were measured at a solids concentration of 2.5 g/L with reaction times of 1 h. Short reaction times were chosen to minimize iron oxide dissolution. Soluble iron concentrations after 1 h were $\leq 6 \mu\text{M}$. The adsorption measurements were performed in 0.01 M NaClO_4 solution with 5 mM MOPS buffer, open to the atmosphere, and at ambient temperature. All samples were prepared in duplicate. Blanks (i.e. without goethite) were prepared over the pH range 3–9 to investigate adsorption to container walls, which was found to be $< 2.5\%$ of the initial DFOMTA concentration. In these batch studies, 5 mL of a 10 g/L goethite stock suspension (prepared the previous day) and 5 mL of electrolyte (including MOPS buffer) were placed in 40 mL Teflon centrifuge bottles. Then DFOMTA stock solution was added to give a concentration of 150 μM (Table 1). Predetermined amounts of acid or base were added to reach the desired value for each sample (i.e., pH 3–9). The sample bottle was filled with electrolyte solution to yield a final mass of 20 g and placed on a rotary shaker for 1 h. The samples were centrifuged at 16 000 rpm and 25°C (Du Pont, RC-5B refrigerated centrifuge). Finally, 10 mL of supernatant solution was collected for quantitation of dissolved Fe and ligand concentrations.

Results and Discussion

Effect of Siderophores on Lead and Europium Sorption. In the absence of an organic ligand, both Pb(II) and Eu(III) adsorb increasingly onto goethite with increasing pH [Figures 2 and 5 ((11) square symbols)]. Under our experimental conditions, $\text{pH}_{50} \approx 5.5$ for Pb (11) and 6.3 for Eu adsorption on goethite. Very similar behavior was observed for Eu(III) on boehmite (Figure 3, square symbols). These results are consistent with previous observations for lead (39–44) and lanthanide adsorption (32, 45) on goethite. For Pb(II), significant reduction in the amount adsorbed occurs only at $\text{pH} > \text{pH}_{50}$ (11). However, the presence of 240 μM DFO-B had a pronounced effect on Eu adsorption by goethite and boehmite: less than 20% adsorption was observed over the entire pH range investigated (Figures 2 and 3).

In the presence of 100 or 10 μM of DFOMTA, almost total loss of Eu(III) from solution was observed between pH 4 (100 μM) or 5.5 (10 μM) and 7, respectively, with decreasing loss

TABLE 1. Experimental Conditions for Adsorption Studies

experiment	Me _{total} [μ M]	ligand _{total} [μ M]	pH	solid/liquid [g/L]	reaction time [h]
lead adsorption edge ^a	3.38	none	3.5–7.5	0.5 (goethite)	18
lead adsorption edge	3.38	100 (DFOMTA)	3.5–8	0.5 (goethite)	18
lead adsorption edge	3.38	150 (DFOMTA)	3.5–9	2.5 (goethite)	1
Europium adsorption edge	3.38	none	3–9	0.5 (goethite)	18
Europium adsorption edge	3.38	none	3–8	0.5 (boehmite)	18
Europium adsorption edge	3.38	240 (DFO-B)	3–9	0.5 (goethite)	18
Europium adsorption edge	3.38	240 (DFO-B)	3–8	0.5 (boehmite)	18
Europium adsorption edge	3.38	100 (DFOMTA)	3–8	0.5 (goethite)	18
Europium adsorption edge	3.38	10 (DFOMTA)	3–8	0.5 (goethite)	18
DFO-B adsorption envelope ^a	none	240 (DFO-B)	3–9	13.0 (goethite)	1
DFOMTA adsorption envelope	none	150 (DFOMTA)	3–8.5	2.5 (goethite)	1

^a From ref 11. FIGURE 2. Adsorption edge for Eu(III) (3.38 μ M) on goethite in the absence of siderophore (squares) and in the presence of 240 μ M DFO-B (circles). Error bars indicate twice the standard deviation of duplicate sample measurements. FIGURE 3. Adsorption edge for Eu(III) (3.38 μ M) on boehmite in the absence of siderophore (squares) and in the presence of 240 μ M DFO-B (circles). Error bars indicate twice the standard deviation of duplicate sample measurements.

below pH 4 or above pH 7 (Figure 4a,b; square symbols). Nearly the same behavior of Eu(III) was observed in blank samples (i.e., in the absence of goethite, but in the presence of 100 or 10 μ M DFOMTA) with a somewhat lower Eu loss between pH 6 and 8 and a somewhat greater loss below pH 5 (Figures 4a,b; circles).

The adsorption edge of Pb(II) on goethite was strongly influenced by the presence of 100 μ M DFOMTA, with maximum adsorption occurring between pH 5 and 6 (Figure 5). At low pH, the adsorption of Pb(II) was increased slightly in the presence of DFOMTA, relative to adsorption in the absence of ligand, whereas at pH > pH₅₀, adsorption was strongly decreased. The loss of Pb(II) from solution in the

FIGURE 4. Adsorption edge for Eu(III) (3.38 μ M) on goethite in the presence of (a) 100 μ M or (b) 10 μ M DFOMTA (squares). Loss from solution in the absence of goethite is shown by circles. Error bars indicate the standard deviation of duplicate sample measurements. (Measurements in the absence of goethite were not made in duplicate.)

absence of goethite, measured in blank experiments, was < 4% both in the absence and in the presence of DFOMTA.

Sorption of DFO-B and DFOMTA. The adsorption envelope of DFOMTA on goethite (Figure 6) showed a maximum near pH 5 (surface excess $\approx 13 \mu\text{mol/g}$), with decreasing adsorption toward higher and lower pH. This behavior can be understood as the resultant effect of interplay between adsorptive and adsorbent charge (46). At pH < 6, DFOMTA is a neutral species, whereas the surface of goethite is positively charged. As pH increases from 3.5 to 6.2, DFOMTA becomes increasingly anionic [$\log K_5^H = 6.22$ (34)], and, therefore, it adsorbs strongly onto the goethite surface. At pH > 6.2, the goethite surface charge continually decreases [$p\text{znc} = 8.1\text{--}8.5$ (37, 44)], thus increasingly repelling the

FIGURE 5. Adsorption edge for Pb(II) ($3.38 \mu\text{M}$) on goethite in the absence (squares) and in the presence of $100 \mu\text{M}$ DFOMTA (circles). Error bars indicate twice the standard deviation of duplicate sample measurements. Data in the absence of siderophore from Kraemer et al. (17).

FIGURE 6. Adsorption envelopes on goethite for $150 \mu\text{M}$ DFO-B [circles, data from Kraemer et al. (17)] and $150 \mu\text{M}$ DFOMTA (triangles). Error bars indicate twice the standard deviation of duplicate sample measurements.

DFOMTA anion. This interplay of surface and adsorptive charge typically produces a resonance in the adsorption envelope near $\text{pH} = \log K$ for protonation, as seen in Figure 6. The adsorption envelope of DFO-B is considerably different [Figure 6, data from ref 11], indeed more like that of a weakly adsorbing monovalent cation (47, 48), with a surface excess of only $1.5 \mu\text{mol/g}$ achieved at $\text{pH} < 7$. Above $\text{pH} 7.5$, DFO-B adsorption increases somewhat, to about $2.5 \mu\text{mol/g}$. This behavior also is predictable, given $\log K_a^H = 8.3$ for the conversion of DFO-B to a neutral species from the cationic form produced by protonation of its amine group (34).

Europium-Siderophore Interactions. The close correspondence between the Eu(III) adsorption edges on goethite (Figure 2) and boehmite (Figure 3) in the absence of ligands is consistent with previous observations (49). It is most likely a result of the similar $\text{p}K_{\text{a}}$ values for the two oxide minerals (37). Surface precipitation of lanthanides requires much higher solution concentrations than were used in the present study (45). Our model calculation of the solubility of amorphous $\text{Eu}(\text{OH})_{3(s)}$ as a function of pH [solubility product constant from (50)] indicated undersaturation at the Eu concentration ($3.38 \mu\text{M}$) used in our experiments.

Model calculations using PHREEQC (51) also indicated the dominance of the complex, EuHDFO^+ in the aqueous speciation of Eu(III) at $\text{pH} > 5$ for a DFO-B concentration of $240 \mu\text{M}$ and a Eu(III) concentration of $3.38 \mu\text{M}$ in 0.01 M background electrolyte solution. Therefore, the dramatic reduction in adsorbed Eu(III) at $\text{pH} > 5$ in the presence of DFO-B (Figures 2 and 3) can be attributed to the formation

FIGURE 7. Adsorption envelope for $150 \mu\text{M}$ DFOMTA (squares) and $3.38 \mu\text{M}$ lead in the presence of DFOMTA (triangles). Error bars indicate twice the standard deviation of duplicate sample measurements. $[\text{MOPS}] = 5 \text{ mM}$; $I = 0.01 \text{ M NaClO}_4$.

of a strong cationic complex that is then repelled from the positively charged surface of either goethite or boehmite. That this suppression of the adsorption edge continues above pH 8 suggests that the EuHDFO^+ complex does not adsorb strongly on the two oxide minerals. The same qualitative result was observed by Kraemer et al. (11) in the Pb(II) adsorption edge for goethite, but the reduction in adsorbed Pb was much less than for Eu. This difference is expected, however, given the much smaller stability constant for the 1:1 complexes of DFO-B with Pb^{2+} , nearly all of which are cationic species (9). Bearing in mind that goethite and boehmite dissolution are occurring during the desorption experiments, we may also conclude that DFO-B is an effective desorber of toxic metal cations from these minerals, despite its high specificity for Fe^{3+} and even Al^{3+} (10).

The effect of DFOMTA on Eu(III) desorption was dramatically different from the effect of DFO-B. In the neutral to slightly acidic pH range, almost total removal of Eu from solution was observed at DFOMTA concentrations of either 10 or $100 \mu\text{M}$ (Figure 5a,b). This result is influenced to a degree by the presence of goethite, an observation consistent with the formation of metal-DFOMTA precipitates. In an auxiliary experiment with the Eu concentration increased to $50 \mu\text{M}$ at a DFOMTA concentration of $100 \mu\text{M}$ in the absence of goethite, visible precipitate formation occurred (data not shown). The formation of a Eu-DFOMTA precipitate likely is favored by two stereochemical factors: the high coordination number of lanthanides [8–9 (30)] and the multidentate character of the DFOMTA ligand. The high coordination number of Eu allows simultaneous coordination of the metal ion by more than one multidentate ligand. This is also evidenced by the occurrences of ternary and quaternary lanthanide complexes (52). The multidentate character of DFOMTA even may foster the formation of polymer networks, in which Eu bridges between ligands.

Precipitation of Pb-DFOMTA complexes was not observed in blank experiments with $3.38 \mu\text{M}$ Pb(II). Indeed, the actinide-specific siderophore had a pronounced diminishing effect on Pb(II) adsorption by goethite at $\text{pH} > 5$ (Figure 5). The adsorption edge for Pb(II) measured in the presence of $150 \mu\text{M}$ DFOMTA, in fact, is nearly congruent with the adsorption envelope of DFOMTA at this concentration (Figure 7). Comparing lead adsorption in the absence (Figure 4) and in the presence of $150 \mu\text{M}$ DFOMTA (Figure 7), we infer that DFOMTA adsorption at $\text{pH} < 5$ induces Pb(II) adsorption in excess of what occurs in the absence of ligands, whereas at $\text{pH} > 5$, decreasing adsorption of DFOMTA and the strong affinity of the ligand for Pb(II) act to diminish Pb(II) adsorption. Similar observations of enhanced sorption of Eu(III) on goethite and boehmite at below pH_{50} and reduced

adsorption above pH₅₀ in the presence of humic acid have been reported in the literature (49). These findings accord with the conceptual scheme of Murphy and Zachara (28), who proposed that anionic organic ligands will enhance trace metal adsorption at pH values below the intersection of the ligand adsorption envelope with the free-metal adsorption edge (just above pH 5 in the present experiments), whereas they will diminish trace metal adsorption above this pH value. In this respect, Pb-DFOMTA interactions in the presence of goethite qualitatively resemble trace metal-humic acid interactions under the same conditions.

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