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Dissolution of Plutonium(IV) Hydroxide by Desferrioxamine Siderophores and Simple Organic Chelators

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Plutonium is thought to exist mostly as low soluble plutonium(IV) species in the environment and, therefore, has low potential of becoming mobile. Due to their prevalence and high solution stability constants for Pu(IV), microbial siderophores could significantly affect plutonium solubility and mobility. In this study, the ability of trihydroxamate desferrioxamine siderophores to solubilize Pu(IV) solids was investigated. Both desferrioxamine B and E (DFB and DFE) are far less effective at solubilizing amorphous Pu(IV) hydroxide in neutral solution than are simple chelators, such as EDTA, citrate, and tiron, despite the fact that these chelators have smaller solution stability constants for Pu(IV) than do DFE and DFB. Positively charged, linear DFB is less effective than the neutral cyclic DFE. Hydroxamate siderophores may, in fact, passivate Pu(IV) hydroxide surfaces, thereby inhibiting solubilization by other chelators. PuO_2 solubilization under these conditions is far slower than that of Pu(IV) hydroxide.

Siderophores, iron chelators produced by microorganisms, are common in soils and may be responsible for mobilization and redeposition of Fe in some soils.[1] Siderophores are also good chelating agents for plutonium.[2] However, the ability of siderophores to solubilize, mobilize, or oxidize plutonium in the environment has not been well studied. We are examining the interactions of the trihydroxamate siderophores desferrioxamine E and B (DFB and DFE) with actinides in order to understand how they could affect actinide biogeochemistry. Here, we have evaluated the effect of DFB, DFE, and other chelators on the dissolution of plutonium hydroxide and plutonium oxide in neutral buffered solutions.

We used freshly prepared amorphous Pu(IV) hydroxide and high-fired PuO_2. The dry solids were placed in sealed plastic tubes with buffered (50 mM MOPS) solutions with or without added chelators or Fe (Supporting Information) to give a final concentration of 10 mM Pu(IV) if all the plutonium was dissolved. At regular intervals, a sample was centrifuged to remove suspended solids. Three aliquots were removed from the centrifugate for Pu analysis by liquid scintillation counting. We monitored these samples for up to 127 days (Table 1, Figure 1a). The solution concentration of Pu from dissolution of Pu(IV) hydroxide by buffer only, 0.23 μM, is within the previously reported range of solubilities for $Pu(OH)_4$ ($10^{-5}-10^{-11}$ mol kg^{-1}).[3] This concentration did not increase after the initial data point, indicating that equilibrium was already established, consistent with other studies.[4] The ligand-promoted dissolution was very slow: the

Table 1. Total Pu Solubilized (Total, μmol/g) and Solubilization Rates (μmol g^{-1} day^{-1}) for $Pu(OH)_4$ and PuO_2 with Selected Chelators[a]

	first experiment			second experiment		
chelator	day	total	rate[b]	day	total	rate[b]
		239-Pu(IV) Hydroxide				
none	50	0.20	0.004			
EDTA	127	62	0.49	253	107	0.42
citrate	127	22	0.17	253	18	0.072
tiron	127	13	0.10	253	11	0.043
DFB	127	0.95	0.007	253	0.38	0.0015
DFB−Fe	127	0.46	0.004	253	0.47	0.0018
EDTA−Fe	69	0.94	0.014			
DFE				330	6.4	0.021
DFB−EDTA				294	10	0.034
			239-PuO_2			
none	50	3.72	0.073			
EDTA	86	17	0.19	268	2.0	0.0074
citrate	86	6.2	0.072	268	1.1	0.004
tiron	86	6.0	0.069	268	2.2	0.0083
DFB	86	7.0	0.082	268	3.1	0.011
DFB−Fe	86	5.2	0.060	268	0.24	0.0009
EDTA−Fe	69	1.4	0.020			
DFE				330	5.2	0.017
DFB−EDTA				294	1.0	0.034
			242-PuO_2			
none	127	3.7	0.029	253	0.34	0.0014
EDTA	127	9.2	0.072	253	3.6	0.014
DFB	127	2.2	0.017	253	0.38	0.0015

[a] Reference 8. [b] Reference 9.

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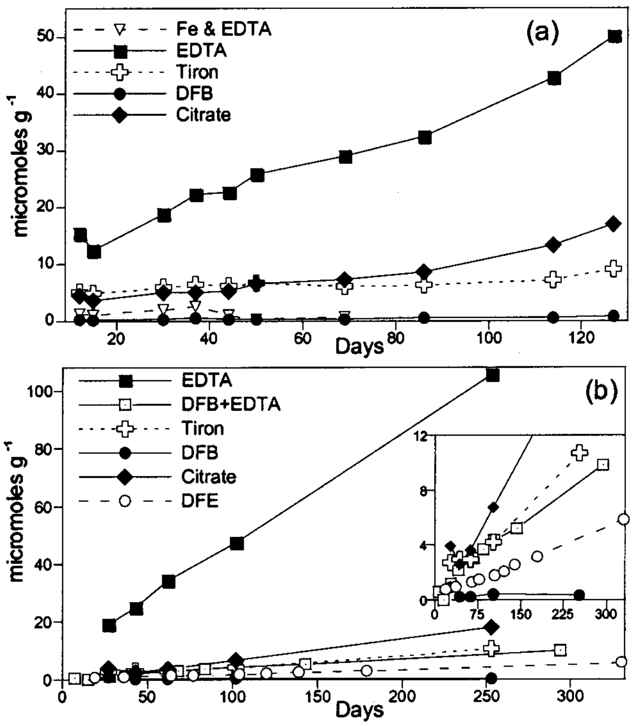

Figure 1. Dissolution of Pu(IV) hydroxide plotted in micromoles of Pu solubilized per gram of Pu solid: (a) first experiment; (b) second experiment; rates by linear fit (μmol g^{-1} day^{-1}), EDTA 0.38; citrate, 0.069; tiron, 0.037; DFB + EDTA, 0.033; DFE, 0.017; DFB, 0.

amount of Pu in solution was still increasing after 127 days. Of the chelators we studied, EDTA is the most efficient at solubilizing Pu(IV) hydroxide. The presence of Pu(IV)−EDTA in the solution was confirmed by UV−vis spectroscopy (data not shown). Citrate and tiron solubilize Pu(IV) hydroxide much more slowly, and DFB even more slowly. Only slightly more Pu was solubilized in DFB solution than in controls. Previous studies have suggested that dissolution rates for mineral oxides can be correlated with the solution stability constants for metal complexation.[5] However, the solution stability constant for the Pu(IV)−DFB complex is greater than those of the other Pu−chelator complexes (log β: EDTA, 27.2; citrate, 15.2; or ~45 (ML$_3$), DFB, 30.8, DFE, ~32.5). Even estimated log β values for single-moiety chelation by these multidentate ligands (log β, EDTA, based on NTA, 15; citrate, based on acetate, 4, Tiron, ~20; DFB and DFE, based on single hydroxamate, 12), do not correlate with dissolution efficiency. Solution stability constants, thermodynamic quantities, may not correlate directly with solubilization rates, kinetic values. The correlation may hold true for ligands with similar chelating moieties, but as is apparent here, *the stability constants for a group of ligands with different chelating moieties do not necessarily correlate to dissolution ability*. Adding Fe(III), which has log β's similar to Pu(IV), decreased the dissolution rate, presumably due to chelator competition.

The rate of PuO$_2$ dissolution was much slower for most chelators; none of the chelators solubilized more than 17 μmol g^{-1} PuO$_2$ in 86 days. No difference between ^{242}Pu and ^{239}Pu solubility was observed. Comparison of solubility rates was impossible due to large scatter in the data, and no trends were observable (figures in Supporting Information). The scatter could be due to colloidal Pu(IV) formation or fine suspended solids, not removed during the initial solid preparation or during sample centrifugation.[6,7] The amount of Pu in solution in control experiments, ~1−3 μM, is far above the solubility limit of PuO$_2$ (~10^{-17} M), supporting the presence of Pu species not removed by centrifugation.

Therefore, to gain a better understanding of the contribution from colloids or other particles, we performed a second experiment. All liquid was removed from each of the tubes, the Pu solids were washed 5 times with MOPS buffer, and then the same chelator solutions (10 mM) were again added to the solid, with the following exceptions: the control Pu hydroxide and ^{239}PuO$_2$ tubes (no chelator) were refilled with 2 mM DFE, and the tubes with Fe−EDTA were washed extensively with DFB to remove all Fe, and then refilled with a 10 mM EDTA and DFB solution. We monitored these samples for up to 330 days (Table 1, Figure 1b.) There was less scatter in the data, and all solubilization rates were lower. We attribute this to the removal of colloid species after the initial experiment and by the repeated washings with the buffer solution. Lower rates could have also resulted from solubilization of high-surface-area Pu (resorbed Pu on the oxide surface, Pu at defect sites) during the first experiment, leaving lower surface area Pu for solubilization during the second experiment. Overall, the chelator efficiency for Pu(OH)$_4$ was the same: EDTA was very effective, and citrate and tiron were about 5 and 10 times slower than EDTA, respectively. DFE and DFB were 20 and 280 times slower than EDTA, respectively. The slow rate for DFB was not due to DFB degradation (checked by NMR). The difference in rate between DFE and DFB may be due to their charge difference (positively charged DFB vs neutral DFE). An order of magnitude faster Fe solubilization has been observed with DFD$_1$ (the neutral, linear acetyl derivative of DFB) than with DFB.[10] EDTA solubilization of Pu(IV) hydroxide was over 10 times slower after the Pu was washed and mixed with DFB, suggesting that DFB passivates the surface. Hydroxamic acids have been shown to form surface species on metal oxides.[11] Again, far less PuO$_2$ was solubilized over the course of the experiment than Pu(IV) hydroxide, making

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(8) In 50 mM MOPS, pH = 6.8, DFE, 2 mM; other ligands, 10 mM.

(9) Rates are total micromoles of Pu solubilized per gram of solid, divided by total days, giving an average rate over the experiment, and are included for comparison. For all but the second experiment with Pu(IV) hydroxide, rates were not constant over the entire experiment, and/or Pu amounts were already at equilibrium, or were too varied between samples, so that true rates could not be calculated.

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comparison of chelators difficult (figure in Supporting Information).

A previous Pu dissolution study reported a different order of chelator efficiency, reported more Pu solubilized after 6 days than we observed after >100 days, and reported rate increases by adding Fe.[12] This may be due to the unknown Pu starting material[12] and differences in sample treatment causing more colloidal Pu to be present in the previous study.

Dissolution of Fe oxides by siderophores and hydroxamic acids is dependent on pH, siderophore concentration, and mineral form. Dissolution is more rapid at the beginning (<5 days), and hydroxamic acids are at least as efficient as other simple organic acids.[12] Rates calculated from these studies using data later in the dissolution process were from 0.01 μmol g^{-1} day^{-1} (pH 7.4, hornblende, 24 μM DFB) to more than 4 μmol g^{-1} day^{-1} (pH 6.5, goethite, 240 μM DFD$_1$). The solubilization of Pu(IV) hydroxide by 2 mM DFE gave a rate in this range, but the simple organic acids, citrate, tiron, and EDTA, were more effective than DFB or DFE. None of these ligands were able to solubilize much aged PuO_2. This is consistent with the ΔG and K_{sp} values for the two phases; Pu oxide is more stable than Pu hydroxide.

The hydroxamic acid dissolution of Fe involves initial surface complex formation followed by a polarization and weakening of the Fe−O bond, and then thermodynamically driven complex detachment.[13d] Ligand-promoted polarization of the metal−oxide oxygen bonds by hydroxamic acids may not weaken Pu−O bonds as much as Fe−O bonds, and therefore may not lead to detachment of the complex. The DFE−Pu(IV) solution complex differs from the DFE−Fe(III) complex;[14] surface species may also differ. We are currently investigating these surface species and how other microbial chelators affect Pu dissolution in order to better predict the long-term fate of Pu in the environment.

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Supporting Information Available: Complete experimental details and graphs of dissolution data for PuO_2.

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