

## The Effect of Phosphate on Lanthanide Sorption by an Oxide Mineral: X-ray Absorption and Magnetic Studies

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*The feasibility of using phosphate to enhance radionuclide immobilization on mineral surfaces was examined using trivalent lanthanide ions as chemical analogues of actinide radionuclides. Phosphate dramatically increased the amount of lanthanide sorbed on aluminum oxide surfaces at pH 5, the product apparently being ultra-fine particles of  $\text{LnPO}_4$ .*

High-level radioactive wastes containing actinide elements have been introduced to the environment with the advent of nuclear weapons and nuclear energy. Sorption of the actinides by soil materials decreases their mobility and bioavailability. Understanding their sorption mechanism is important for forecasting their behavior in soils and designing environmental remediation procedures.

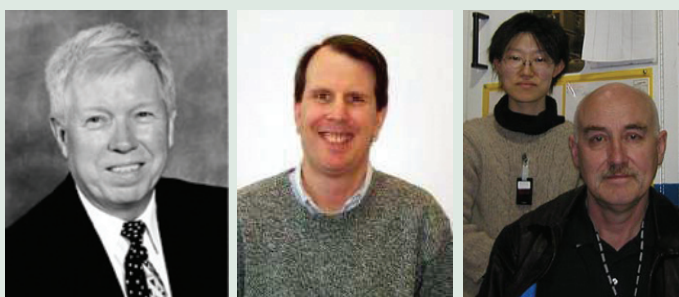
Sorption studies involving radionuclides, such as  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{241}\text{Am}$ , are relatively rare because the U.S. Nuclear Regulatory Commission grants few licenses for the possession and handling of these elements. Furthermore, it is difficult to control experi-

mental conditions because their oxidation states are unstable. Other actinide ions ( $^{232}\text{Th}^{4+}$ ,  $^{237}\text{Np}^{5+}$ , and  $^{238}\text{U}^{6+}$ ) and non-radioactive lanthanide ions ( $\text{Ln}^{3+}$ ) have served as chemical analogues for those unstable actinide ions in various environmental studies. The utility of these analogues, verified by numerous studies for solution chemistry, may also extend to mineral surface chemistry.

In this study, trivalent lanthanide ions ( $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Dy}^{3+}$ ) serve as chemical analogues of trivalent actinides to explore the sorption chemistry of actinide ions ( $\text{Ac}^{3+}$ ) on mineral surfaces as affected by phosphate, a ubiquitous oxyanion found on all oxide mineral surfaces in nature. The *in situ* immobilization of actinides by phosphate may be feasible considering both actinide and lanthanide phosphates are highly insoluble and stable in geological formations.

Orthophosphate has proven effective for immobilizing lead ( $\text{Pb}^{2+}$ ) as insoluble lead phosphate precipitates on phosphate minerals. Our study asked whether adsorbed phosphate anions at oxide mineral surfaces react with lanthanide ions, immobilizing lanthanide as phosphate surface precipitates analogous to the reaction observed with  $\text{Pb}^{2+}$ .

The amount of lanthanide ions sorbed on boehmite ( $\gamma\text{-AlOOH}$ ) surfaces, estimated by neutron activation analysis, dramatically increased in the presence of phosphate at pH 5 (**Figure 1**). The structure of the sorbed lanthanide was determined by x-ray absorption spectroscopy (beamlines X23B and X10C), as well as by magnetic susceptibility measurements (Institute for Rock Magnetism at University of Minnesota and Kansas State University) and electron paramagnetic resonance (EPR) spectroscopy (EMSL, Pacific Northwest National Laboratory).



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The extended x-ray absorption fine structure (EXAFS) shows that the sorbed lanthanide ions react with phosphate to form lanthanide phosphate precipitates of indeterminate size on the oxide surface (**Figure 2**). The superparamagnetic behavior of dysprosium and gadolinium in the surface precipitates indicates the lanthanide phosphate precipitates are uniform, ultra-fine particles (radii less than 10 Å assuming spherical particles) distributed on the oxide surface. Even in the absence of phosphate, sorbed  $\text{Gd}^{3+}$  ions apparently form precipitates on boehmite surfaces rather than being adsorbed as isolated ions as evidenced in EPR spectra (not shown).

To the extent that  $\text{Ln}^{3+}$  ions serve as suitable chemical analogues for  $\text{Ac}^{3+}$  ions, the results of this study predict the ubiquitous phosphate, adsorbed to all mineral surfaces in the environment, would enhance the sorption of  $\text{Ac}^{3+}$  ions leading to the mineral-surface precipitation of ultra-fine  $\text{AcPO}_4$  particles.

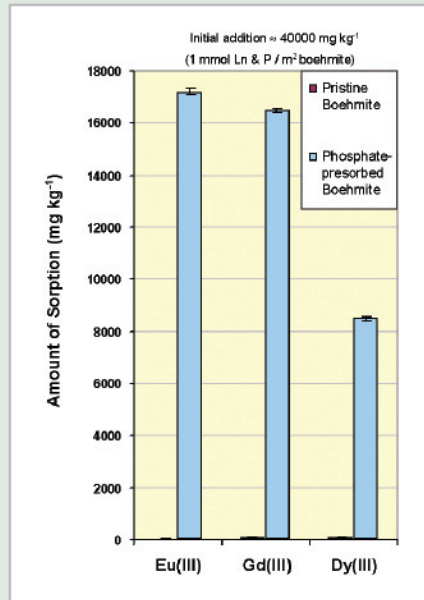


Figure 1. Amount of  $\text{Ln}^{3+}$  sorbed on boehmite ( $\gamma\text{-AlOOH}$ ) in the absence and presence of phosphate at pH 5.

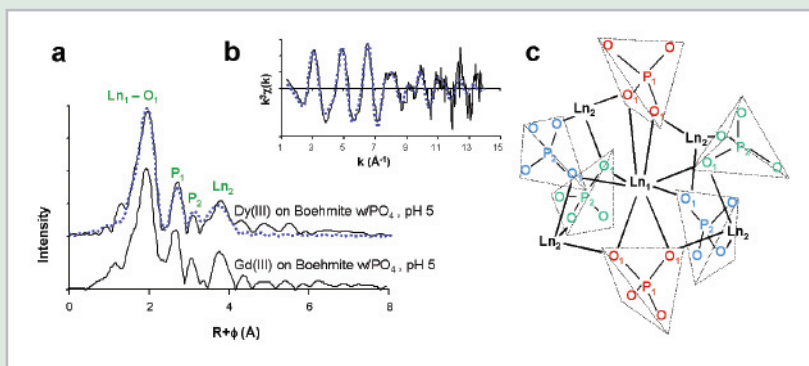


Figure 2. EXAFS data and proposed local chemical environment of  $\text{Ln}^{3+}$  ions sorbed on an aluminum oxide (boehmite) in the presence of phosphate: (a) experimental (solid lines) and simulated (dotted line) radial structure functions; (b) experimental (solid lines) and simulated (dotted line) scattering curve for Dy  $L_{\text{III}}$ -edge EXAFS; (c) local chemical environment showing proposed association of sorbed  $\text{Ln}^{3+}$  and phosphate.