

## Phosphate Sorption on Boehmite with Eu(III): P K-edge EXAFS Fingerprinting

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### 보마이트 표면의 인산염 및 Eu(III) 수착: 인(P) X-선 흡수분석(EXAFS)에 의한 연구

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액티나이드(actinide)의 지질물질로의 수착은 핵에너지와 핵무기 개발로 인하여 인위적으로 자연환경에 노출된 핵종 원소의 이동성과 생물이용가능성을 낮추어 줄 수 있을 것으로 기대된다. 3가의 액티나이드 이온은 3가의 란타나이드(lanthanide) 이온과 유사한 화학적 성질을 띠므로, 3가 액티나이드의 산화광물 표면수착량은, 중성 또는 약한 산성의 pH 상태에서 3가의 란타나이드처럼, 인산염 이온( $\text{PO}_4^{3-}$ ) 이 수착된 상태에서 크게 증가될 것으로 사료된다. 본 연구에서는 3가액티나이드 이온의 화학적 동족체인 3가 유퀴륨 이온( $\text{Eu}^{3+}$ )이 인산염이 수착된 상태의 보마이트( $\gamma\text{-AlOOH}$ ; boehmite) 표면에 수착되는 삼성분 수착계를 X-선 흡수분석(EXAFS)을 통하여 관찰하였다. Eu X-선 흡수분석은 Eu- $\text{PO}_4$ -보마이트 삼성분 수착계에서 보마이트 표면에  $\text{EuPO}_4$  표면침전물이 형성되는 것을 지지하여 준다. 인산염이 보마이트 표면에  $\text{EuPO}_4$  표면침전물을 형성할 뿐 아니라 두자리 단핵 표면착물을 형성한 것을 P X-선 흡수분석을 통하여 확인하였다.

**주요어** : 액티나이드, 란타나이드, 삼성분, 두자리 단핵 착물

Actinide sorption to the geological materials can reduce the mobility and bioavailability of radionuclides released to the environment through the development of nuclear weapons and nuclear energy. Under circumneutral pH conditions, actinide sorption can be enhanced by phosphate anions sorbed on oxide mineral surfaces as indicated by the sorption of trivalent lanthanide ions ( $\text{Ln}^{3+}$ ), the chemical analog for trivalent actinide ions ( $\text{Ac}^{3+}$ ). In this paper, we examined a ternary sorption system of trivalent europium ions ( $\text{Eu}^{3+}$ ) sorbed onto boehmite ( $\gamma\text{-AlOOH}$ ) surfaces pre-sorbed with phosphate anions ( $\text{PO}_4^{3-}$ ), using extended X-ray absorption fine structure (EXAFS) spectroscopy. In the  $\text{Eu-PO}_4$ -boehmite ternary sorption system,  $\text{EuPO}_4$  surface precipitates were formed as implicated by  $\text{Eu L}_{\text{III}}$ -edge EXAFS spectroscopy. Phosphorus K-edge EXAFS fingerprinting indicated a bidentate mononuclear surface complex formation of phosphate sorbed on boehmite surfaces as well as  $\text{EuPO}_4$  surface precipitate formation.

**Key words** : actinide, lanthanide, ternary, bidentate mononuclear complex

### 1. Introduction

Actinide elements have been introduced to the environment since the advent of nuclear weapon and nuclear energy. Actinide sorption onto geo-

logical materials can be an important retarding mechanism of actinide mobility in soil and sedimentary environments. Actinide sorption study, however, is relatively rare since special permission is required to handle the radionuclides in the laboratory. With the solution chemistry demonstrating similar chemical behavior between lanthanides

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and actinides (Choppin, 1995), the behavior of lanthanides in the geological environments has been considered to represent that of actinides (Krauskopf, 1986). In many sorption studies, lanthanides have been used as chemical analogs for actinides (Yoon *et al.*, 2002; Rabung *et al.*, 2005; Xu *et al.*, 2005; Bradbury & Baeyens, 2002; Takahashi *et al.*, 2006; Naveau *et al.*, 2006; Stumpf *et al.*, 2007; Tan *et al.*, 2008; Tan *et al.*, 2009a; Tan *et al.*, 2009b; Guo *et al.*, 2009; Ishida *et al.*, 2009), and some studies have demonstrated similar sorption behavior between Eu(III) and Am(III) (Rabung *et al.*, 2000; Lee *et al.*, 2006; Sakuragi *et al.*, 2004).

Sorption quantity and mechanisms of trivalent lanthanide ions ( $\text{Ln}^{3+}$ ) can vary depending on the mineral sorbents (Ishida *et al.*, 2009). Spectroscopic studies of lanthanide and actinide sorption on pristine oxide minerals indicate lanthanide/actinide incorporation into oxide minerals (Takahashi *et al.*, 1998; Kim *et al.*, 2003), formation of inner-sphere complexes (Tan *et al.*, 2009; Rabung *et al.*, 2000; Takahashi *et al.*, 2006), and mineral surface precipitation (Yoon *et al.*, 2002). Under neutral to slightly acidic conditions, however, cation sorption on many oxide minerals may not be as significant as under alkaline conditions. In nature, anion sorption on oxide minerals under circumneutral conditions can affect the cation sorption onto the geological materials. Organic ligands, such as humic and fulvic acids, enhance the sorption of lanthanides and actinides, potentially by bridging the cation and the mineral surface (Tan *et al.*, 2009; Xu *et al.*, 2005). Inorganic ligands, such as phosphate, also enhance the lanthanide sorption by forming  $\text{LnPO}_4$  surface precipitates (Yoon *et al.*, 2002).

Sorption products in a ternary system can be observed either from the cationic element or from the anionic element in an extended X-ray absorption fine structure (EXAFS) study. EXAFS is a powerful atomic-scale method for sorption studies to determine the sorption species. In the previous study, we used Ln L<sub>III</sub>-edge EXAFS in the  $\text{Ln}^{3+}$ - $\text{PO}_4$ -boehmite ( $\gamma$ - $\text{AlOOH}$ ) ternary sorption system to find the lanthanide sorption product mainly as  $\text{LnPO}_4$  surface precipitates (~2 nm nanoparticles). In this paper, we present phosphorus K-edge EXAFS of  $\text{PO}_4^{3-}$ - and  $\text{Eu}^{3+}$ -sorbed boehmite for comprehensive understanding of the Eu- $\text{PO}_4$ -boehmite ter-

nary sorption system. The backscattering properties of P K-edge EXAFS, however, are not strong enough to supply reliable structural parameters around the phosphorus in the ternary sorption system. We investigated phosphate sorption products in the Eu- $\text{PO}_4$ -boehmite sorption system through a P K-edge EXAFS fingerprinting.

## 2. Experimental

### 2.1. Preparation of Mineral Sorbent and Phosphate Sorption Experiments

Boehmite ( $\gamma$ - $\text{AlOOH}$ ) was prepared by hydrolysis of aluminum tri-sec-butoxide (Gieselmann and Anderson, 1989) followed by acidification. The surface area of the synthesized boehmite, measured by the BET adsorption of  $\text{N}_2$  gas, was  $247 \text{ m}^2 \text{ g}^{-1}$ . Orthophosphate was adsorbed on boehmite surfaces prior to the addition of the  $\text{Eu}^{3+}$ . We performed phosphate adsorption at pH 4 and 5 where the highest phosphate affinity is observed (Bleam *et al.*, 1991). Phosphate (as  $\text{KH}_2\text{PO}_4$ ) was introduced to the boehmite suspension ( $1 \text{ g L}^{-1}$ ) to yield a phosphate surface coverage of  $1 \mu\text{mole m}^{-2}$ . After a 12-hour equilibration, we measured the phosphate concentration remaining in solution by analyzing the supernatant colorimetrically (Van Veldhoven and Mannaerts, 1987). Over 95 % and 90 % of phosphate added to the solution adsorbed to boehmite surfaces in all batches at pH 4 and 5, respectively.

### 2.2. $\text{Eu}^{3+}$ Sorption Experiments

Trivalent europium ions (as 99.99% pure  $\text{Eu}_2\text{O}_3$  dissolved in nitric acid) were added to suspensions of phosphate-modified boehmite so that the surface coverage, upon full adsorption of these ions from the solution, would be  $1 \mu\text{mole m}^{-2}$ . The suspensions were equilibrated at either pH 4 or 5, and the ionic strength was adjusted to 0.01 using  $\text{KNO}_3$ . After a 24-hour equilibration, we filtered the suspension using a polycarbonate membrane filter with  $0.22 \mu\text{m}$ -pore diameter to separate boehmite solids from the solution and dried the solids at room temperature. Concentrations of europium in the solids were  $8,110 \pm 57 \text{ mg kg}^{-1}$  and  $17,216 \pm 122 \text{ mg kg}^{-1}$  at pH 4 and 5, respectively (Yoon *et al.*, 2002).

### 2.3. Synchrotron X-ray Absorption Experiments

We mounted all powder boehmite samples in 1.5 mm-thick polycarbonate holders with kapton-tape (CHR-Furon) windows for Eu EXAFS and with mylar-film (Spex) windows for P EXAFS. Europium L<sub>III</sub>-edge EXAFS spectra and phosphorus K-edge EXAFS spectra were recorded at beamline X23B and X19A, respectively, at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Fluorescence spectra were collected using a Stern-Heald type ion chamber (Lytle *et al.*, 1984) purged with nitrogen for Eu L<sub>III</sub>-edge EXAFS, and a solid state passivated implanted planar silicon (PIPS) detector for P K-edge EXAFS. At the beamline X19A, the Si(111) double-crystal monochromator was detuned by 50% to eliminate higher-order harmonics of the X-ray beam, and fluorescence spectra were detected in a helium-purged sample chamber. We calibrated the monochromator energy with the iron K-edge

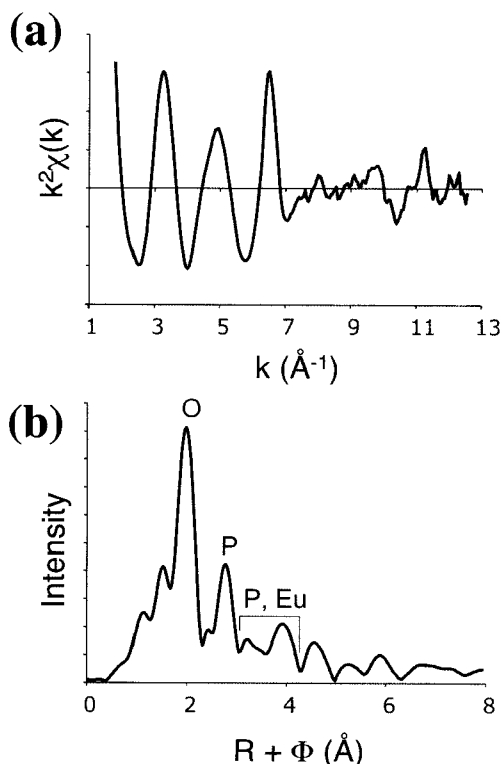
(7,112 eV), which lies close to the europium L<sub>III</sub> edge (6,977 eV), and with the phosphorus K-edge (2,149 eV). The EXAFS spectra were collected in the range of -150 eV to 625 eV relative to the europium L<sub>III</sub>-edge and phosphorus K-edge energies.

We analyzed the EXAFS data using MacXAFS version 4.1 (Bouldin *et al.*, 1995), averaging several scans of each sample, and removing glitches from monochromator-crystal defects. Each scattering curve was isolated by fitting a cubic polynomial to the post-edge region then subtracting the absorption edge from a normalized spectrum. We Fourier-transformed  $k^2$ -weighted fine structure scattering curves over the range of 2 to 12–13 Å<sup>-1</sup> for Eu EXAFS and 2–3 to 11 Å<sup>-1</sup> for P EXAFS, to generate radial structure functions (RSFs).

We used FEFF version 8.20 (Ankudinov *et al.*, 2002) to compute reference P K-edge EXAFS scattering curves of model structures. Model structures were FEFF-simulated based on the reported structure parameters by the crystal structure refinements and on the atomic models of phosphate sorption on boehmite generated based on the reported boehmite structure (Farkas *et al.*, 1977) and a *bond-valence theory* (Brown, 1981).

### 3. Results and Discussion

An experimental Eu L<sub>III</sub>-edge EXAFS scattering curve and the radial structure function (RSF) of Eu<sup>3+</sup> sorbed on phosphate-sorbed boehmite surfaces are shown in Fig. 1. Eu L<sub>III</sub>-edge EXAFS was slightly interfered by the absorption of trace amounts of iron in the sample at the Fe K-edge energy, and reliable structural parameters could not be obtained from the EXAFS spectrum. The experimental Eu EXAFS scattering curve and the RSF, however, show close similarities to those of dysprosium and gadolinium reported in Yoon *et al.* (2002). The Dy EXAFS results in the Dy-PO<sub>4</sub>-boehmite ternary sorption system indicate ~9 oxygen atoms in the first atomic shell, which is directly bonding to the central Dy atom with Dy–O bond distance  $R_{\text{Dy-O}}=2.37$  Å, and ~2 P atoms in the second atomic shell with  $R_{\text{Dy...P}}=3.09$  Å. Higher-shell atoms include 4 P atoms at  $R_{\text{Dy...P}}=3.68$  Å and 4 Dy atoms at  $R_{\text{Dy...Dy}}=4.16$  Å, indicating DyPO<sub>4</sub> surface precipitation on boehmite surfaces (Yoon *et al.*, 2002). The similarities between Dy and Gd



**Fig. 1.** An experimental Eu L<sub>III</sub>-edge EXAFS scattering curve (a) and a radial structure function (b) of Eu<sup>3+</sup> sorbed on boehmite surfaces in the presence of phosphate at pH 5.

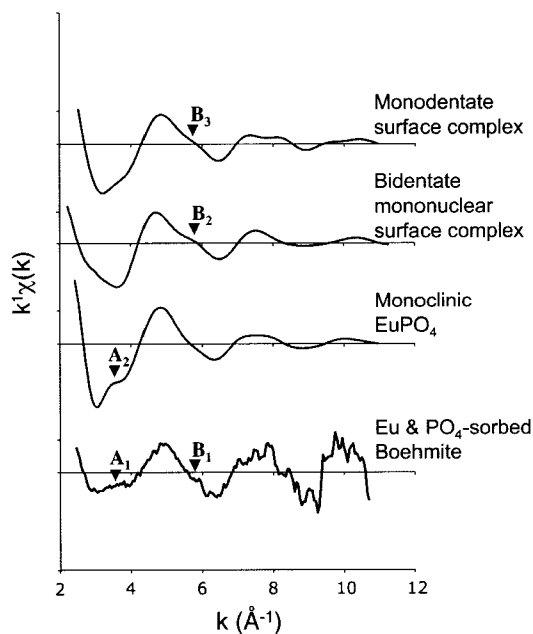
EXAFS and Eu EXAFS spectra indicate  $\text{Eu}^{3+}$  sorption on boehmite with pre-sorbed phosphate have resulted in  $\text{EuPO}_4$  surface precipitation.

Phosphorus sorption on boehmite surfaces maximizes at  $\sim\text{pH } 4$  reaching up to  $\sim 1.9 \mu\text{moles m}^{-2}$  and displays sorption of  $\sim 1 \mu\text{moles m}^{-2}$  at  $\text{pH } 5$  (Bleam *et al.*, 1991). In our experiments at  $\text{pH } 4$  and  $5$ , phosphate sorption is  $\sim 1 \mu\text{moles m}^{-2}$ , which indicates  $\sim 220 \mu\text{moles g}^{-1}$  on boehmite surfaces (Yoon *et al.*, 2002). Europium sorption on phosphate-sorbed boehmite surfaces is quantified to be  $53.6 \mu\text{moles g}^{-1}$  and  $113.8 \mu\text{moles g}^{-1}$  at  $\text{pH } 4$  and  $5$ , respectively (Yoon *et al.*, 2002). At both  $\text{pH}$  conditions, moles of sorbed phosphate severely exceeds those of sorbed  $\text{Eu}^{3+}$ , and more than half of the sorbed phosphate should not participate in  $\text{EuPO}_4$  surface precipitation, while some should, as evidenced in the Eu EXAFS. Here we investigated the state of phosphate on boehmite surfaces with  $\text{EuPO}_4$  surface precipitates using P K-edge EXAFS.

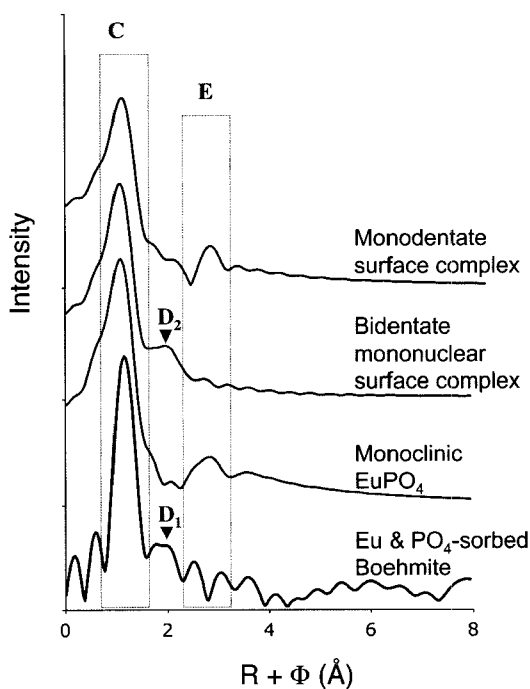
In Figs. 2 and 3, we showed experimental P K-edge EXAFS spectrum of the phosphate-sorbed boehmite with  $\text{Eu}^{3+}$  at  $\text{pH } 4$ , and FEFF-simulated ones of several model structures. The model struc-

tures include (1) a monoclinic monazite ( $\text{EuPO}_4$ ) structure (Ni *et al.*, 1995) and phosphate binding to the boehmite surface with (2) a bidentate mononuclear inner-sphere surface complex and with (3) a monodentate inner-sphere surface complex. In the fine structure scattering curves shown in Fig. 2, the feature  $A_1$  of the  $\text{Eu}^{3+}/\text{PO}_4$ -sorbed boehmite also appeared in the  $\text{EuPO}_4$  model structure ( $A_2$  in Fig. 2). The oscillatory feature  $A_1$ , therefore, can be attributed as a feature from  $\text{EuPO}_4$  surface precipitates, which were verified to form at boehmite surfaces from the Eu EXAFS. feature from In Fig. 2, the feature  $B_1$  in the experimental scattering curve of the  $\text{Eu}^{3+}/\text{PO}_4$ -sorbed boehmite appeared in the simulated scattering curve of the phosphate surface complexes ( $B_2$  and  $B_3$  in Fig. 2). Thus, the experimental P EXAFS curves showed indication of sorbed  $\text{PO}_4$  both as  $\text{EuPO}_4$  surface precipitates and as surface complexes.

In the RSF of the  $\text{Eu}^{3+}/\text{PO}_4$ -sorbed boehmite sample, peak C (Fig. 3) should appear by the scattering from the four oxygen atoms at  $R_{\text{P-O}} \approx 1.52 \text{ \AA}$ ,



**Fig. 2.** Phosphorus K-edge EXAFS scattering curves of FEFF-simulated model compounds compared with an experimental one (phosphate sorbed on boehmite with sorbed  $\text{Eu}^{3+}$  at  $\text{pH } 4$ ).



**Fig. 3.** Phosphorus K-edge EXAFS radial structure functions of FEFF-simulated model compounds compared with an experimental one (phosphate sorbed on boehmite with sorbed  $\text{Eu}^{3+}$  at  $\text{pH } 4$ ).

directly bonding to the central P atom in the phosphate structure. The RSF of the  $\text{Eu}^{3+}/\text{PO}_4$ -sorbed boehmite sample displayed a scattering peak  $D_1$  (Fig. 3) appearing at  $\sim 2 \text{ \AA}$  from the central P atom. Among the three model structure RSFs, the RSF of the bidentate mononuclear surface-complex structure displayed a scattering peak at  $\sim 2 \text{ \AA}$  (peak  $D_2$  in Fig. 3). The bidentate mononuclear surface-complex structure is the only model structure, which yielded a distance between Al in the boehmite at the surface and P in the sorbed phosphate of  $\sim 2 \text{ \AA}$ . In our model structure of a bidentate mononuclear surface complex, the distance  $R_{\text{P}\cdots\text{Al}} = 2.26 \text{ \AA}$ , which is closer than the second-neighbor distances in other model structures. In both structures of monodentate surface complex with the bond angle of  $109.5^\circ$  at the bridging oxygen and of bidentate binuclear surface complex, the distance  $R_{\text{P}\cdots\text{Al}} \approx 2.8 \text{ \AA}$ . In the  $\text{EuPO}_4$  structure, Eu second-neighbor atoms were located at the distance  $R_{\text{P}\cdots\text{Eu}} \approx 3.1 \text{ \AA}$ . Both second-neighbor Al and Eu atoms yielded scattering peaks in marked peak region E in Fig. 3. The peak  $D_1$ , therefore, should be a fingerprint for the existence of bidentate mononuclear surface complexes of phosphate at boehmite surfaces as the main phosphate surface complex species. Readers should note, however, it does not completely exclude the possibility of an existence of monodentate or bidentate binuclear surface complexes. Detail analyses of experimental scattering peaks in the peak region E (Fig. 3) are required for the distinction of Al and Eu second-neighbor atoms. The relatively weak backscattering intensity of the P K-edge EXAFS, however, makes it difficult to obtain reliable fitting results for the distinction of the scattering contribution by the second-neighbor atoms.

Other spectroscopic studies of phosphate sorption on Fe(III) (hydr)oxides report bidentate binuclear surface complexes (Nanzyo, 1986; Luengo *et al.*, 2006; Khare *et al.*, 2007). The size of an Al(III) octahedron is smaller than that of an Fe(III) octahedron as represented by the octahedral Al–O distance  $R_{\text{Al}-\text{O}} = 1.907 \text{ \AA}$  and octahedral Fe–O distance  $R_{\text{Fe}-\text{O}} = 2.02 \text{ \AA}$ , which are predicted by the bond valence theory (Brese and O’Keefe, 1991). Hence, the O $\cdots$ O distance in an Al(III) octahedron ( $2.58 \text{ \AA} \leq R_{\text{O}\cdots\text{O}} \leq 2.87 \text{ \AA}$  in the boehmite structure reported in Farkas *et al.* (1977)) is closer to the

O $\cdots$ O distance in the phosphate tetrahedron ( $R_{\text{O}\cdots\text{O}} = 2.48 \text{ \AA}$  with  $R_{\text{P}-\text{O}} = 1.52 \text{ \AA}$  and a bond angle of  $109.5^\circ$  at P) than that in an Fe(III) octahedron ( $2.68 \text{ \AA} \leq R_{\text{O}\cdots\text{O}} \leq 3.02 \text{ \AA}$  in the goethite structure reported in Yang *et al.* (2006)). Based on the described polyhedral geometries, phosphate sorption on Al(III) (hydr)oxides might have a higher chance for the sorbed phosphate to form bidentate mononuclear complexes than the sorption on Fe(III) (hydr)oxides.

Fingerprints from the P K-edge EXAFS for the  $\text{Eu}^{3+}/\text{PO}_4$ -sorbed boehmite indicated an existence of phosphate sorbed on boehmite surfaces forming bidentate mononuclear inner-sphere surface complexes. In the  $\text{Eu-PO}_4$ -boehmite ternary sorption system,  $\text{EuPO}_4$  surface precipitation was also verified by Eu L<sub>III</sub>-edge EXAFS. Analogous to  $\text{Eu}^{3+}$  sorption on  $\text{PO}_4$ -sorbed boehmite, trivalent actinide ions ( $\text{Ac}^{3+}$ ) can be immobilized on boehmite surfaces as  $\text{AcPO}_4$  surface precipitates in the existence of sorbed phosphate. With the same analogy, phosphate sorbed on boehmite surfaces in the  $\text{Ac(III)-PO}_4$ -boehmite ternary sorption system should form bidentate mononuclear inner-sphere surface complexes.

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