

Formation of Outer- and Inner-Sphere Complexes of Lanthanide Elements at Montmorillonite-Water Interface

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The distribution of 14 lanthanide elements (Ln) between water and montmorillonite's surface was simultaneously determined by ICP-MS. From the dependence of the distribution coefficients on the atomic number of Ln, the formation of outer- or inner- sphere complexes with the surface of montmorillonite was estimated. The formation of the outer-sphere complex was also confirmed by the quenching of the fluorescence from Eu(III) ion due to the hydrated water.

In order to understand the behavior of lanthanide elements (Ln) at the earth's surface, it is necessary to clarify the aqueous-solid distribution between clay minerals and water.^{1,2} At the lower pH region (pH < 6) where the contribution of ligands such as carbonate and hydroxide ions is little, outer- and inner-sphere complexes with clay minerals can be considered as the sorbed species.² In this letter, we will point out the differences of sorbed species of Ln sorbed on montmorillonite among various pH by their distribution coefficients (K_{sorb}) determined with ICP-MS. Even when the difference of K_{sorb} over Ln is subtle, the simultaneous determination of the distributions by ICP-MS enabled us to distinguish the differences. The formation of outer-sphere complex was confirmed by the Eu(III) fluorescence corresponding to 5D_0 to 7F manifold. The fluorescence is effectively quenched not by D_2O but by H_2O , with which we can deduce hydration state of Eu(III) by the lifetime measurement.^{3,4}

A montmorillonite was received from Nakalai Tesque Inc. Prior to the distribution study, removable Ln initially involved in the sample were excluded by being washed with acid and water. X-ray diffraction and transmission electron microscope analyses showed that the mineral phase was montmorillonite. The cation exchange capacity was 30 meq/100 g.⁵ For the distribution study, a 10 mL of water containing constant concentrations of Ln (100 ppb) was mixed with montmorillonite (10 mg), while I (ionic strength) was kept at 0.020 M by NaCl. The pH was adjusted by adding a small amount of NaOH or HCl solution. The suspension was shaken for 24 h and the aqueous phase was separated by filtration (0.45 μm). The Ln in the solution were once separated by a column containing ion-exchange resin (AG50W-X8), since it is needed to separate Cl^- ion to prevent the formation of Ln-chloride ion in ICP-MS. The concentrations of Ln eluted from the column were determined by ICP-MS (VG PQ-3) with employing In and Bi as internal standards.⁶ The precision and accuracy was better than 3% for all Ln. The lifetime of Eu(III) fluorescence was measured as reported previously.⁵

The apparent distribution coefficient (K_{app}) was obtained from the concentrations of Ln in the aqueous phase by Eq (1):

$$K_{\text{sorb}} \text{ (or } K_{\text{app}}) = R ([\text{Ln}]_{\text{init}} - [\text{Ln}]_{\text{aq}}) / [\text{Ln}]_{\text{aq}} \quad (1)$$

where $[\text{Ln}]_{\text{init}}$ and $[\text{Ln}]_{\text{aq}}$ denote the concentrations of dissolved Ln before and after the filtration; R, water-montmorillonite ratio (mL/g). Since we defined K_{sorb} as the ratio of sorbed species against free ions in the aqueous phase, formations of Ln-hydroxide and carbonate complexes in the aqueous phase above pH 5.5 were corrected to obtain K_{sorb} in Figure 1 using their stability constants.^{1,7-9} The concentration of carbonate ion was estimated by assuming the equilibrium with air.¹ The results show that the influence of complex formation does not affect the tendency shown below. In some patterns, we can find some lower data for La than expected from the overall trend, as similarly found in the distribution between water and Fe hydroxides.¹⁰ However, we do not refer to the point further in this study, and mainly deal with the overall trend of $\log K_{\text{sorb}}$ against the atomic number (Z) of Ln.

In the $\log K_{\text{sorb}}$ patterns (Figure 1), the slope of the pattern against Z increased with pH. The difference between lower and higher pH may be closely related with the two sorption sites in the montmorillonite.^{1,2} The one is the $-\text{OH}$ site at the edge of the montmorillonite, while the other is the non-specific site to which Ln are attracted by permanent charges in the lattice of montmorillonite induced by the isomorphic substitution.^{1,2} Since the sorption to the $-\text{OH}$ group may increase with pH

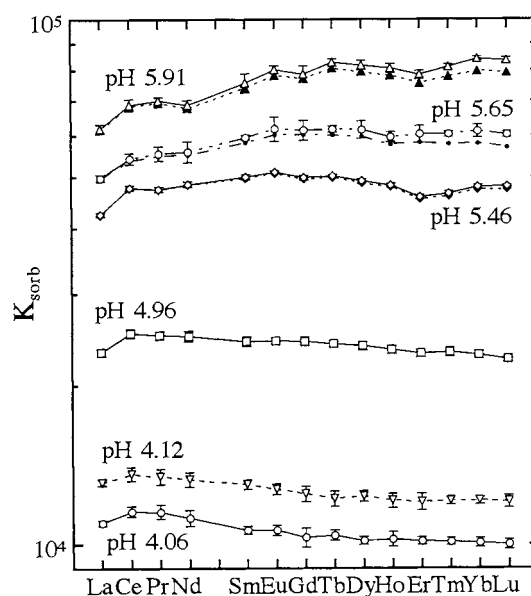


Figure 1. The distribution coefficients of lanthanide elements (Ln) between aqueous phase and montmorillonite's surface, K_{sorb} (mL/g), at various pH (I: 0.020 M). The closed and open symbols show the data before and after the correction of the formation of Ln-carbonates and hydroxides in the aqueous phase, respectively.

owing to the deprotonation of the group, it is suggested that sorption reaction with the $-OH$ sites are dominant in the higher pH region. On the other hand, it is suggested that Ln are sorbed to the non-specific sites at lower pH. These results are consistent with the sorbed species expected from the slope of $\log K_{\text{sorb}}$ in the following discussion.

At pH 5.91, the increasing dependence of $\log K_{\text{sorb}}$ on Z is clearly observed. Similar dependence is frequently found for the stabilities of Ln-hydroxide complexes that form more stable inner-sphere complexes with heavier Ln ions.^{8,9} This is due to the lanthanide contraction, since the electrostatic attractive force is larger between smaller ions (= heavier Ln) and ligands. From the similar dependences between the sorption and the hydrolysis, it is suggested that Ln mainly form inner-sphere complex with the $-OH$ sites on montmorillonite at higher pH region.^{1,2} The formation of inner-sphere complex between Pb(II) and montmorillonite at relatively higher pH condition was also reported by employing XAFS.¹¹

At the pH lower than 5, the dependence was opposite to the decreasing order of $\log K_{\text{sorb}}$ against Z. The difference of $\log K_{\text{sorb}}$ pattern between lower and higher pH is due to the change of sorbed species on montmorillonite, because only aqua ions of Ln are considered as dissolved species in discussing K_{sorb} . Since the total number of water molecules associated with Ln ions is larger for heavier Ln,¹² the decrease of $\log K_{\text{sorb}}$ against Z can be ascribed to the larger sizes of hydrated Ln ions for heavier Ln. Hence, the present results suggest that the hydrated ions of Ln form outer-sphere complexes with the surface of montmorillonite by being attracted by the permanent charges in the mineral. Although the similar discussion was found for alkali metal ions,^{1,2} the present results based on the simultaneous analyses of Ln by ICP-MS have revealed the tendency even for Ln whose mutual differences in the sizes of hydrated ions would be smaller than alkali metal ions.

The hydration states of Eu(III) sorbed on montmorillonite at pH 5 were estimated by the lifetime of Eu(III) fluorescence (τ / ms).⁵ In Figure 2, the dependence of k_f ($= 1/\tau$, decay constant of the fluorescence) on the mole fractions of H_2O in (H_2O+D_2O) solution (X_{H_2O}). As references, the similar depen-

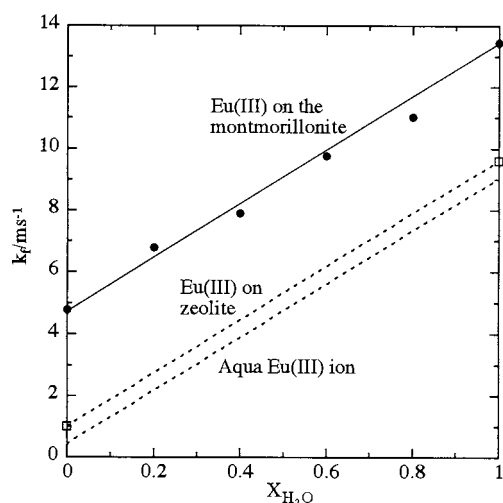


Figure 2. The fluorescence decay constant, k (ms⁻¹), of Eu(III) sorbed on the montmorillonite at pH 5 and $I = 0.020$ M at various X_{H_2O} ($= [H_2O]/([H_2O]+[D_2O])$). Similar dependences for aqua Eu(III) ion⁵ and Eu(III) sorbed on zeolite¹³ are also plotted.

dences of aqua Eu(III) ion and Eu(III) sorbed on the zeolite were shown.^{4,13} In the zeolite, it was estimated that the aqua Eu(III) ion was sorbed on zeolite as outer-sphere complex from the dependence.¹³ In montmorillonite system, the quenching by the montmorillonite itself was observed as seen in the large k_f values for the sample at $X_{H_2O} = 0$. However, the slope was also similar to that of aqua ion,⁴ showing that hydrated Eu(III) ion is sorbed on the montmorillonite as an outer-sphere complex. Similar results were also obtained for Lu by using XAFS.¹⁴

Especially in the pattern at pH above 5.46, we can recognize tetrad effects that produce concave curves in $\log K_{\text{sorb}}$ pattern consisting of four parts, La-Ce-Pr-Nd, (Pm)-Sm-Eu-Gd, Gd-Tb-Dy-Ho, and Er-Tm-Yb-Lu.^{10,15,16} Similar curves were found in the distribution of Ln between water and Fe hydroxides.¹⁰ These curves are produced by the variation over Ln of differences in the stabilities of Ln species in the aqueous phase and at the solid-water interface.^{10,16} Therefore, the appearance of the tetrad effect reflects the change of Ln species by the sorption reaction. The fact that the tetrad effect is not clearly observed at pH below 4.96 may show that the structural change of Ln species by the sorption is not intensive. This suggests that the hydrated ions are directly sorbed at lower pH, which agrees with the estimation by the slope of $\log K_{\text{sorb}}$ vs. Z.

By employing ICP-MS to the distribution study, the different behavior of each Ln was elucidated in their sorption reaction on a montmorillonite. As the results, it was revealed that the inner-sphere complexes with the surfaces of the montmorillonite are formed at higher pH where the $-OH$ sites are deprotonated, while the hydrated Ln are sorbed to the non-specific site on the montmorillonite at lower pH. Comparing with the spectroscopic results, it was shown that the systematics of K_{sorb} over Ln is related with the hydration state of the sorbed species.

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