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Interaction of Eu(III) ion and non-porous silica: Irreversible sorption of Eu(III) on silica and hydrolysis of silica promoted by Eu(III)

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Abstract

The interaction of Eu(III) with non-porous silica was studied using sorption–desorption experiments and Eu(III) was characterized by laser-induced fluorescence spectroscopy. The independence of Eu(III) sorption on ionic strength, the increased affinity of silica for heavier rare earth ions, and the removal of water in the inner-sphere of Eu(III) due to sorption demonstrate that the formation of an inner-sphere complex of Eu(III) with silanol groups at the silica surface is an important process in the initial reaction. A further decrease in the number of hydrated water molecules with time and the irreversibility of the Eu(III) sorption suggest that a new phase incorporating Eu(III) and Si(IV) forms at the silica surface. The presence of Eu(III) greatly promoted the dissolution of silica, which indicated that Eu(III) was effectively hydrolyzing the Si─O─Si bonds. The formation process of the Eu(III)–silicate phase is discussed.

Keywords: Europium(III); Unporous silica; Solid–water interface; Sorption; Laser-induced fluorescence spectroscopy

1. Introduction

The interaction of silica with rare earth elements (REE) is important from several perspectives. In geochemistry, REE abundances in cherts (siliceous sedimentary rocks) have been studied to predict the paleoenvironment in which the cherts formed [1,2]. Chert is an authigenic rock, which is amorphous at the initial stage of the sedimentary processes, and turns into quartz during diagenetic processes in the deep sea floor. To understand the basic reaction between silica and the REE dissolved in seawater, the process of dissolved REE incorporation into SiO_2 needs to be studied on the molecular scale. On a related topic, there have been many studies on the dissolution of silica in the presence of alkaline and alkaline earth ions related to weathering and alteration during water–rock interactions [3–5]. The previous studies suggested that silica could be dissolved faster in the presence of these ions. However, there have been no studies of the effect of rare earth ions on the dissolution of silica. If rare earth ions can be effective catalysts for the dissolution of silica, then the reaction would be of great importance, particularly from the viewpoint of radioactive waste management, because the waste contains REE as fission products and trivalent actinides [6]. Considering the necessity of preserving the glass material in the long term, the interaction between silica and REE is of great importance, because REE can also be regarded as analogues of Am(III) and Cm(III), long-lived actinides in radioactive waste.

In the current study, the interaction between Eu(III) and non-porous silica was examined. Initially, the sorption of Eu(III) on silica was studied. Similar experiments were conducted with other REE to examine the dependence of the sorption reaction on the ionic radii, which is related to the REE species at the solid–water interface [7–9]. Characterization of Eu(III) species at the interface was also conducted by laser-induced fluorescence spectroscopy (LIF), and some results from this technique have already been reported by Takahashi et al. [10]. From the LIF results, it was suggested that Eu(III) was incorporated in the bulk silica or in a bulk-like

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silica phase. This has been verified by the Eu(III) desorption experiments, and the dissolution of silica in the presence of Eu(III). The possibility that Eu(III)–silicate was formed at the silica–water interface is discussed based on the present results.

2. Experimental

2.1. Materials

Non-porous amorphous silica (Aerosil 200; surface area, $2.0 \times 10^2\,m^2\,g^{-1}$; SiOH density, $2.5\,nm^{-2}$) was purchased from Japan Aerosil Co. Ltd. Montmorillonite (Nacalai Tesque, Kyoto, Japan) employed in this study had a surface area of $5.5 \times 10\,m^2\,g^{-1}$, as determined by BET analysis (N_2). The cation exchange capacity (CEC) of the montmorillonite was $3.0 \times 10\,meq\,100\,g^{-1}$, as determined by the modified Schofield method (pH 8, 2.0 mM NH_4Cl). Other reagents were analytical grade or better.

2.2. Sorption experiments

Non-porous silica was mixed with an $EuCl_3$ solution in which the total concentration of Eu(III) was constant at 0.20 mM, and the solid–liquid ratio of non-porous silica was $8.0\,g\,dm^{-3}$. The ionic strength was adjusted using $NaClO_4$, and the pH was adjusted using NaOH and $HClO_4$ solutions. The dissolved fraction of Eu(III) remaining in the solution was determined by batch experiments using Eu-152 tracer detected by a NaI scintillation counter, or by using stable isotopes measured by ICP-MS (VG, PQ-3). The ICP-MS method was similar to that used by Takahashi et al. [9,11]. Sorption of all REE (except for Pm) on the silica was conducted using ICP-MS to examine the dependence of sorption on the ionic radii of REE. All the experiments were conducted at room temperature.

2.3. LIF experiments

The prepared suspension of non-porous silica was continuously stirred in a quartz cell, and directly exposed to a pulsed laser beam (395 nm) from a dye laser pumped by an excimer laser. When the percentage of Eu(III) sorbed was less than 90%, the suspension was placed into a quartz tube and centrifuged. The separated aqueous phase was removed, and the slurry at the bottom of the quartz tube was exposed to the laser beam. The fluorescence lifetime (τ) of Eu(III) emission at 615 nm was measured with a photomultiplier connected to a digitizing oscilloscope. The experimental method was similar to our previous study [12].

2.4. Dissolution of silica

Dissolved Si was measured using a graphite-furnace atomic absorption spectrometer (GF-AAS; Shimadzu, AA-6650) equipped with an auto-sample exchanger. Glass materials were not used for this experiment. The time dependence of the Si dissolved fraction was monitored over 1–6 h. All of the sample solutions were filtered through a 0.45 μm membrane filter (PTFE; Advantec, Tokyo) and were acidified to 1% HNO_3 before the GF-AAS measurements. The detection limit of our system was around $10\,\mu g\,Si\,kg^{-1}$.

2.5. Desorption experiments

After sorption on non-porous silica (aging time: 1 day), the dissolved fraction of Eu(III) was examined 1 h after the acidification to examine the reversibility of Eu(III) sorption on silica. As a reference, similar experiments were also conducted with Ba(II), where the initial concentration of Ba(II) (0.20 mM) was identical to that of Eu(III). In addition, the reversibility of the sorption–desorption of Eu(III) was examined in the montmorillonite system, where the solid–liquid ratio was $4.0\,g\,dm^{-3}$. Similar experiments in the absence of sorbents were also conducted to confirm the reversibility of Eu(III) precipitation–dissolution processes in our experimental system.

3. Results and discussion

3.1. Sorption of Eu(III) on non-porous silica

Assuming equilibrium with atmosphere, the total Eu(III) concentration in this study (0.20 mM) exceeds the solubility above pH 6.3 (Fig. 1). This estimation is consistent with the pH dependence of the Eu(III) fraction remaining in the solution, without the addition of non-porous silica (Fig. 2). In the presence of non-porous silica, sorption experiments were conducted at $I = 0.020$ and 0.10 M (Fig. 2). The Eu(III) dis-

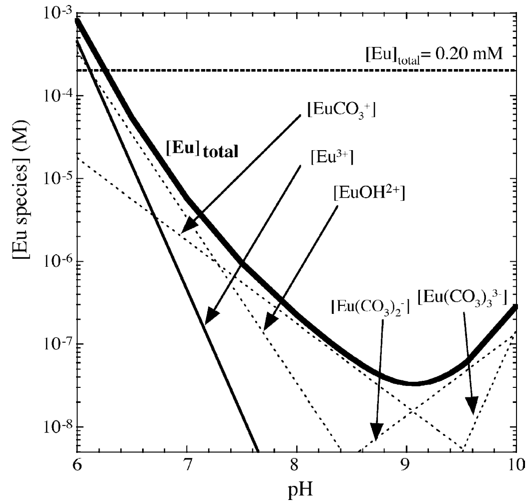

Fig. 1. Solubility of Eu(III) determined by equilibrium with the solid phase of $EuOHCO_3$, calculated according to Runde et al. [13]. The total concentration of Eu(III) ($[Eu]_{total}$) in our experiments is indicated ($[Eu]_{total} = 0.20$ mM).

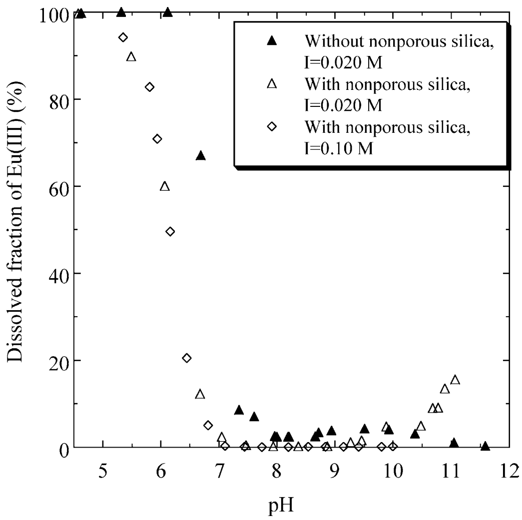

Fig. 2. The pH dependence of the dissolved fraction of Eu(III) at $I = 0.020$ and 0.10 M in the presence of non-porous silica (8.0 g dm^{-3}) when the initial concentration of Eu(III) is 0.20 mM. The dissolved fraction of Eu(III) without the addition of silica, and after the separation by filtration (0.45 μm), is also displayed.

solved fraction decreased due to the sorption on non-porous silica at above pH 5. In the case of clay minerals, the amount of sorption decreases with the increase in ionic strength, mainly due to the reduction in the electrostatic effect at the surface [14]. The present results show that the electrostatic effect is not important for the Eu(III) sorption on silica, and that the inner-sphere complex of Eu(III) with silanol groups forms at the silica surface. When the REE fraction remaining in the solution was plotted with the order of the atomic number, it was found that heavier REE are sorbed on the silica to a greater extent than lighter REE (Fig. 3). This suggests that the smaller ion (i.e., heavier REE) has an increased affinity for the silica surface due to the increased stability of the complex with silanol groups. The increased affinity of silica for smaller ions also supports the hypothesis that the inner-sphere complex forms between Eu(III) and silanol groups.

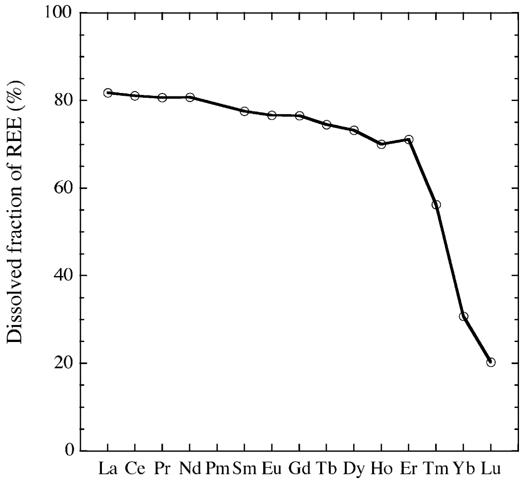

Fig. 3. Dissolved fraction of REE in the presence of non-porous silica. Initial REE concentration, 50 μg kg^{-1}; non-porous silica concentration, 8.0 g dm^{-3}; $I = 0.020$ M; pH 5.0.

3.2. *Characterization of Eu(III) species by LIF*

The formation of the inner-sphere complex has been confirmed by the LIF characterization of Eu(III) species [15–17]. The emission of Eu(III) around 592 and 615 nm (Fig. 4a) irradiated by dye laser at 395 nm is effectively quenched by OH oscillators of H_2O hydrated to Eu(III). However, the effect can be negligible for OD oscillators of D_2O bound to Eu(III). Based on this isotopic effect on the lifetime of Eu(III) emission, the number of water molecules in the inner-sphere of Eu(III) (N_{H_2O}) can be obtained:

$$N_{H_2O} = k\left(\frac{1}{\tau_{H_2O}} - \frac{1}{\tau_{D_2O}}\right), \tag{1}$$

where τ_{H_2O} and τ_{D_2O} are the lifetimes in H_2O and D_2O systems, respectively, while the k-value is 1.07 [17]. In the case of the Eu(III)–silica system, $1/\tau_{D_2O}$ (emission decay constant) is almost constant around 0.33 m s^{-1} when using D_2O as the solvent (Fig. 4b), which shows that the contribution

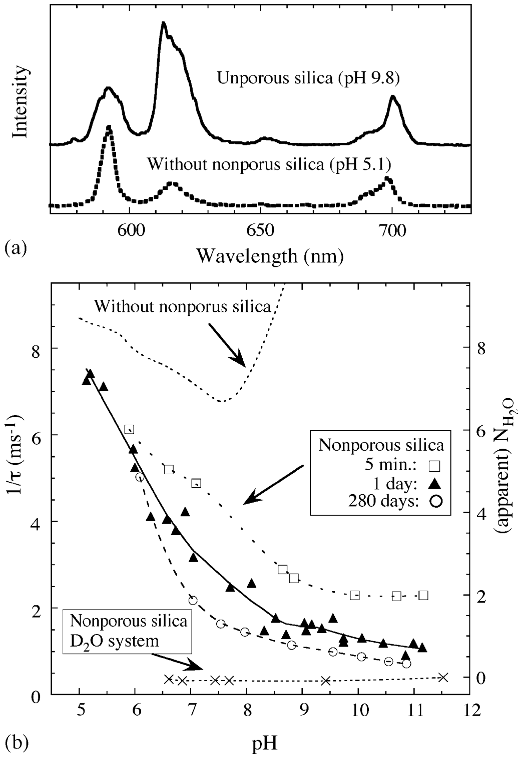

Fig. 4. (a) Fluorescence spectra of Eu(III) for aqua complex (pH 5.1 without non-porous silica) and Eu(III) incorporated in unporous silica. (b) The number of water molecules bound to Eu(III), N_{H_2O}, in the non-porous silica system at various ages, calculated from Eq. (1). Reciprocals of the fluorescence lifetimes (τ) in the non-porous silica system using D_2O as solvent, and in the absence of non-porous silica are also shown. Initial concentration of Eu(III), 0.20 mM; concentration of non-porous silica, 8.0 g dm^{-3}; $I = 0.020$ M. Most of the results were reported by Takahashi et al. [10].

of other species to the quenching can be negligible in the system. The N_{H_2O} values in the Eu(III)–silica system were calculated (Fig. 4b) based on the relationship in Eq. (1).

In the absence of non-porous silica, and below pH 7.5, the N_{H_2O} decreased due to the formation of dissolved complexes, such as Eu(III)–hydroxide and Eu(III)–carbonate (Fig. 1), while the N_{H_2O} increased at above pH 7.5 due to the energy transfer among Eu(III) ions in the Eu(III) precipitates [10,18,19]. The energy transfer which causes the apparent increase in the N_{H_2O} was not observed for Eu(III) in the non-porous silica system, demonstrating that Eu(III) does not exist as homogenous Eu(III) precipitates in the presence of non-porous silica. At above pH 5 in the non-porous silica system, the N_{H_2O} values were lower than the hydration number of Eu(III) (i.e., 9), demonstrating that the inner-sphere complex of Eu(III) and silanol groups was forming. Such a change in the local structure of Eu(III) can be suggested also in the change of relative intensity of each peak in the emission spectra (Fig. 4a). These results are consistent with the results in Section 3.1. Moreover, it was found that the N_{H_2O} value decreased with increased aging time. After 280 days above pH 8, the N_{H_2O} values decreased to less than one, demonstrating that almost no water molecules remained in the inner-sphere of Eu(III). This result suggests that the Eu(III) sorbed on silica is gradually incorporated in the bulk silica with time. We assume that the following two events are important in the overall process: (1) hydrolysis of the Si–O–Si bonds by Eu(III), which enhances the dissolution of silica and (2) binding of Eu(III) at the silica surface to hydrolyzed silanol at the surface. These assumptions were verified in the following experiments.

3.3. Dissolution of silica in the presence of Eu(III)

The dissolution of silica is generally enhanced with an increase in pH (Fig. 5). In addition, it is suggested that the addition of Eu(III) promotes the dissolution of silica at a pH of less than 8. Many geochemical studies have revealed that silica dissolution is enhanced in the presence of various alkaline and alkaline earth ions [3–5,20]. Dove et al. [4,5] demonstrated that the dissolution rate depends on the affinity of the metal ion for the silica surface and the exchange rate constant of hydrated water to the metal ion (k_{ex}). It is suggested that the k_{ex} is related to silica dissolution because the motion of water at the surface becomes more rapid due to the presence of the metal ion at the silica surface. This is supported by the k_{ex} values of water hydrated to different ions; k_{ex} (s^{-1}) = $10^{9.0}$ (Na^+), $10^{9.2}$ (K^+), $10^{8.5}$ (Ca^{2+}), $10^{9.3}$ (Ba^{2+}), and $10^{0.52}$ ($OSi(OH)_3^-$). Because of this, metal ions with a larger k_{ex} value promote the hydrolysis of Si–O–Si to a larger degree [4,5].

However, there have been no studies on silica dissolution in the presence of rare earth ions. Trivalent rare earth ions have an increased affinity for the silica surface in comparison with the affinity displayed by alkaline and alkaline earth ions. The k_{ex} value for the exchange of hydrated water is ca. $10^{8.8}$ (s^{-1}) for Eu(III) [21], which is comparable with that of Na^+, K^+, Ca^{2+}, and Ba^{2+}. Therefore, it is expected that silica dissolution is also promoted by Eu(III). To demonstrate the effect of Eu(III) more clearly, the time dependence of the silica dissolution was examined in the presence of Eu^{3+} or Ba^{2+} at pH 5.5 (Fig. 6). Previous studies have shown that Ba^{2+} is the most effective ion among alkaline and alkaline earth ions in promoting silica dissolution [5]. Our results clearly demonstrate that at pH 5.5 the presence of Eu^{3+} promotes silica dissolution to a greater degree than Ba^{2+}. Promotion of the dissolution of silica by Eu(III) shows that the hydrolysis

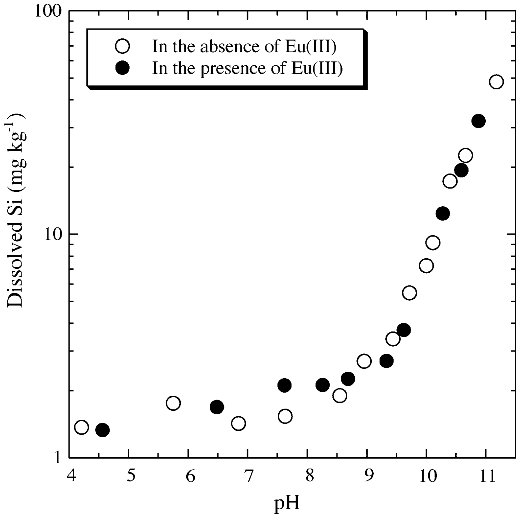

Fig. 5. The pH dependence of dissolved Si (mg kg^{-1}) in the non-porous silica system in the absence and presence of Eu(III) 1 h after the preparation. Initial concentration of Eu(III), 0.20 mM; concentration of non-porous silica, 8.0 g dm^{-3}; I = 0.020 M.

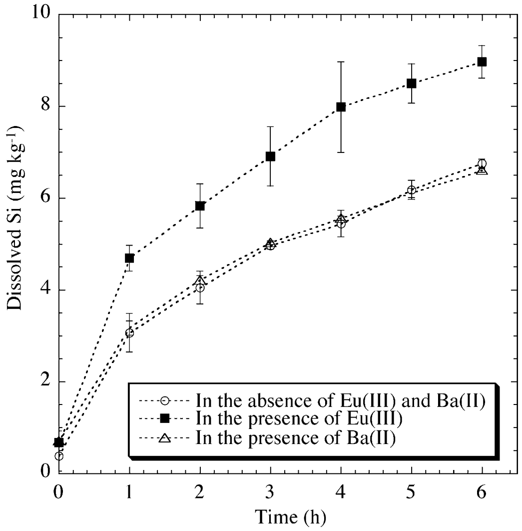

Fig. 6. Time dependence of dissolved Si (mg kg^{-1}) in the absence of Eu(III) and Ba(II), and in the presence of Eu(III) or Ba(II). Initial concentrations of Eu(III) and Ba(II), 0.40 mM; concentration of non-porous silica, 1.0 g dm^{-3}. The ionic strength was 0.10 M, while the pH was maintained at 5.5 by hydroxylammonium chloride (0.020 M).

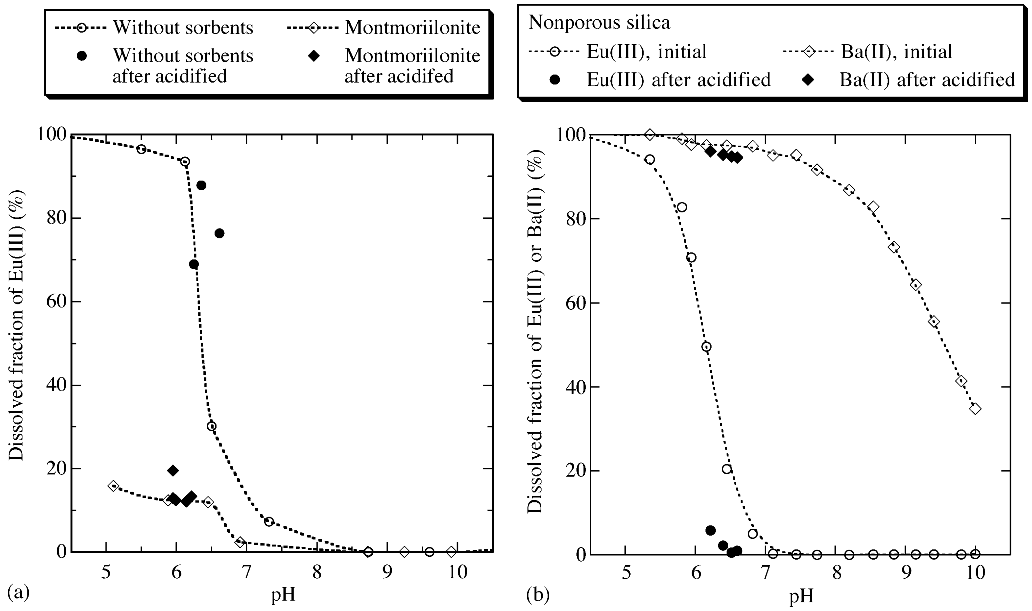

Fig. 7. (a) Dissolved fraction of Eu(III) in the absence of sorbents, and in the presence of montmorillonite (4.0 g dm^{-3}). The dissolved fractions of Eu(III) before and after the acidification of the samples which were initially at a pH above 8 were compared. (b) Dissolved fractions of Eu(III) and Ba(II) in the presence of non-porous silica (8.0 g dm^{-3}). The dissolved fractions before and after the acidification of the samples, which were initially at a pH above 8 were compared. Initial concentrations of Eu(III) and Ba(II), 0.20 mM; I = 0.020 M.

of the Si–O–Si bonds is facilitated by the presence of Eu^{3+} at the silica surface.

3.4. Desorption experiments

The desorption of Eu(III) and Ba(II) from the silica was examined by acidification (pH 6) of the suspension, which was initially at above pH 8. In the absence of silica, or in the montmorillonite system, the dissolved fraction of Eu(III) after acidification was plotted on the initial sorption curve (Fig. 7a). These results show that the precipitation–dissolution reaction in the absence of silica, and the sorption–desorption reaction in the montmorillonite system are reversible.

In contrast, the desorbed fraction in the silica system was decreased in comparison with the initial sorption curve, suggesting that the reaction is not reversible in the non-porous silica system (Fig. 7b). Similar results were also observed for the N_{H_2O} data [10]. After acidification to pH 6.5, the N_{H_2O} values for Eu(III) species initially at above pH 9 were routinely low. The N_{H_2O} values after the acidification were lower than 2, which is much lower then the initial N_{H_2O} value at pH 6.5 (Fig. 4). The irreversibility of the sorption, combined with the N_{H_2O} results, suggest that the Eu(III) sorbed at the surface forms a new phase, which is resistant to Eu(III) desorption by acidification. The formation of the phase is also compatible with the LIF results (Fig. 4), which showed that the N_{H_2O} decreased dramatically with time. The irreversibility is somewhat unclear for Ba(II) (Fig. 7b). It appears that the formation of the new phase is more important for Eu(III), although Ba(II) can also promote silica dissolution.

3.5. Possible formation process of the Eu(III)–silicate phase at the silica surface

The present results have revealed the following aspects of the interaction between Eu(III) and silica: (1) Eu(III) forms an inner-sphere complex with the silanol group at the silica surface, (2) the decrease in the N_{H_2O} value with time suggests that most water molecules hydrated to Eu(III) are finally excluded, (3) Eu(III) promotes the hydrolysis of the Si–O–Si bonds as suggested by the effective dissolution of silica in the presence of Eu(III), and (4) Eu(III) sorption on silica is irreversible. Based on these results, formation process of Eu(III)–silicate phase at the silica surface is discussed as follows. After the initial sorption, Eu(III) induces the hydrolysis of Si–O–Si bonds in the vicinity of the Eu(III) ion. The hydrolyzed silanol group at the silica surface can form a complex with Eu(III). It is speculated that the repeated recombination of hydrolyzed silanol with Eu(III) or the coverage of the Eu(III) at the surface by the silicic acid dissolved in water will result in the formation of a new phase consisting of Eu, Si, and O at the silica surface, where the water molecules hydrated to Eu(III) are eventually excluded.

The formation of a new phase has also been suggested in the corrosion of glass materials containing Y and La, where the new phase was thought to be composed of Y or La hydroxides [22]. If the new phase is homogeneous Eu(III) hydroxides, the energy transfer among Eu(III) ions induces reduction of lifetime of Eu(III) fluorescence [10]. In this study, however, the quenching effect was not observed in the LIF data, which suggests that the new phase is not made up of homogeneous Eu(III) hydroxides, but incorporates Si to form Eu(III)–silicates. To confirm the formation of the Eu(III)–silicate in our silica samples, scanning and transmission electron microscopy must be conducted in the future.

In summary, the present results show that REE sorption on silica can be an irreversible reaction, and that the dissolution of silica is promoted by rare earth ions. Based on the results, the hydrolysis of silica by REE and the formation of a new phase containing REE and Si at the surface are important processes in understanding the behavior of REE in nature, and also in radioactive waste glass.

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