

## ADSORPTION OF $\text{Eu}^{3+}$ TO SMECTITES AND FLUORO-TETRASILICIC MICA

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**Abstract**—The adsorption of  $\text{Eu}^{3+}$  from aqueous solution to natural  $\text{Na}^+$ -montmorillonite (Kunipia F), synthetic saponite (Sumecton SA) and synthetic fluoro-tetrasilicic mica ( $\text{Na}^+$ -TSM) clay samples was investigated. Adsorption capacities derived from the isotherms were 1.02, 0.71 and 1.00 meq/g of clay, respectively, for Kunipia F, Sumecton SA and  $\text{Na}^+$ -TSM. The adsorption capacities were comparable to the cation exchange capacities of the clays, which were 1.19, 0.71 and 0.94 meq/g of clay, respectively. The greater slope of the TSM adsorption isotherm relative to the montmorillonite and saponite isotherms indicates a high affinity of  $\text{Eu}^{3+}$  for  $\text{Na}^+$ -TSM. The high affinity of TSM for  $\text{Eu}^{3+}$  was thought to be related to the large electronegativity of the octahedral fluorine groups in TSM. Photoluminescence of adsorbed  $\text{Eu}^{3+}$  was observed for saponite and TSM, but not for montmorillonite. Quenching of  $\text{Eu}^{3+}$  luminescence by Fe in the montmorillonite structure is the probable reason for this phenomenon. The luminescence intensity varied with the amount of adsorbed  $\text{Eu}^{3+}$  for saponite and TSM as a result of self-quenching.

**Key Words**—Adsorption, Europium (III) Ion, Fluoro-tetrasilicic Mica, Kunipia F, Montmorillonite, Photoluminescence, Sumecton SA, Synthetic Saponite.

### INTRODUCTION

Adsorption of  $\text{Eu}^{3+}$  onto layered silicates such as natural hectorite (Bergaya and van Damme, 1983), natural montmorillonite (Bergaya and van Damme, 1983; Takahashi *et al.*, 1998; Bradbury and Baeyens, 2002; Coppin *et al.*, 2002; Stumpf *et al.*, 2002; Rabung *et al.*, 2005; Okada *et al.*, 2006) and synthetic magadiite (Mizukami *et al.*, 2002) has been examined through cation-exchange reactions. The luminescence properties of the resulting  $\text{Eu}^{3+}$ -exchanged layered silicates have been investigated for the basic understanding of the host-guest interactions. It has been pointed out that the Fe in a natural montmorillonite quenched the luminescence of  $\text{Eu}^{3+}$  (Bergaya and van Damme, 1983). On the other hand, relatively intense luminescence has been observed for the magadiite system partly due to the absence of Fe in the silicate layer (Mizukami *et al.*, 2002). Based on the variation of luminescence intensity as a function of the quantity of adsorbed  $\text{Eu}^{3+}$ , it was proposed that the interlayer spatial distribution of  $\text{Eu}^{3+}$  affects luminescence intensity (Mizukami *et al.*, 2002). Recently,  $\text{Eu}^{3+}$ -montmorillonite was successfully used as an adsorbent with luminescence detection ability for 4-nonylphenol (Okada *et al.*, 2006). The adsorptive and sensing properties of various layered materials with adsorbed rare earth ions is worth further investigation to optimize the materials' performance. In the present study, the

adsorption and the photoluminescence of  $\text{Eu}^{3+}$  on smectites (a natural montmorillonite [Kunipia F], a synthetic saponite [Sumecton SA] and synthetic fluoro-tetrasilicic mica [ $\text{Na}^+$ -TSM]) were investigated.

Kunipia F and Sumecton SA have been investigated extensively for the construction of clay-based advanced materials (Ogawa and Kuroda, 1995; Ogawa and Kuroda, 1997; Shichi and Takagi, 2000; Ogawa, 2004). It has been noted that the Kunipia F and Sumecton SA smectites behaved differently. This has been shown by differences in the catalytic activity (Urabe *et al.*, 1988), the adsorption of phenols (Okada and Ogawa, 2003, 2004; Okada *et al.*, 2005a, 2005b), separation efficiency for optical resolution of a racemic mixture (Nakamura *et al.*, 1988) and the aggregation of the cationic cyanine dye after adsorption (Ogawa *et al.*, 1996; Miyamoto *et al.*, 2000). The differences have been ascribed to such factors as surface layer-charge density (Nakamura *et al.*, 1988; Ogawa *et al.*, 1996; Okada and Ogawa, 2003; 2004; Okada *et al.*, 2005a, 2005b) and the location of isomorphous substitution (Urabe *et al.*, 1988; Ogawa *et al.*, 1996). In contrast, there is no report on the effect of structural differences on metal ion adsorption behavior.

$\text{Na}^+$ -TSM ( $\text{Na}_2\text{Mg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2$  (Kitajima and Daimon, 1975; Kitajima *et al.*, 1976; Soma *et al.*, 1990)) exhibits swelling, ion exchange and adsorptive properties similar to those of smectites. As  $\text{Na}^+$ -TSM does not contain  $\text{Fe}^{2+/3+}$ , some applications as photofunctional materials (*i.e.* photoinduced electron-transfer reactions) have been investigated (Ogawa *et al.*, 1993, 2000; Kakegawa and Ogawa, 2005). The negative charge of  $\text{Na}^+$ -TSM is derived from octahedral lattice-site defects and is not due to isomorphous substitution. The hydroxyl groups in the octahedral sheet in smectites are replaced by F in  $\text{Na}^+$ -TSM. The difference in the structure of  $\text{Na}^+$ -TSM

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DOI: 10.1346/CCMN.2007.0550402

relative to the smectites was expected to result in different  $\text{Eu}^{3+}$  adsorption characteristics.

## EXPERIMENTAL

### Materials

$\text{Na}^+$ -montmorillonite (Kunipia F, supplied by Kunimine Ind. Co., obtained from Aterazawa mine, Yamagata, Japan) and synthetic  $\text{Na}^+$ -saponite (Sumecton SA, supplied by Kunimine Ind. Co., synthesized by a hydrothermal reaction) are reference clay samples of the Clay Science Society of Japan and were used as received.  $\text{Na}^+$ -TSM (supplied by Topy Ind. Co.) was used after removing non-expandable impurities by a dispersion-sedimentation method. The chemical compositions of these host materials are summarized in Table 1. Cation exchange capacities (CECs) of  $\text{Na}^+$ -montmorillonite,  $\text{Na}^+$ -saponite and  $\text{Na}^+$ -TSM are 1.19, 0.71 and 0.94 meq/g of clay, respectively (Ogawa *et al.*, 1992). Europium (III) trichloride hexahydrate (>99.99%) was purchased from Aldrich Co. and was used as received.

### Cation exchange with $\text{Eu}^{3+}$

Samples of  $\text{Na}^+$ -clays (0.1 g) were allowed to react with 50 mL aliquots of  $\text{EuCl}_3$  solution (pH 5) in 50 mL polypropylene vessels for 1 day at room temperature. The initial concentrations of aqueous  $\text{EuCl}_3$  solution were in the range 0.01–2.0 times as large as the CECs ( $7.9 \times 10^{-3}$ ,  $\sim 1.6 \text{ mmol L}^{-1}$  for Kunipia F,  $4.7 \times 10^{-3}$ ,  $\sim 9.5 \times 10^{-1} \text{ mmol L}^{-1}$  for Sumecton and  $6.5 \times 10^{-3}$ ,  $\sim 1.3 \text{ mmol L}^{-1}$  for  $\text{Na}^+$ -TSM). Blank samples containing 50 mL of  $\text{EuCl}_3$  solution, without adsorbents, were also prepared to estimate vaporization losses of solvents and the adsorption of  $\text{Eu}^{3+}$  on the polypropylene vessel. The resulting solids were separated by centrifugation (25 krpm for 10 min at 293 K). The amounts of  $\text{Eu}^{3+}$  adsorbed on clays were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis ( $\lambda = 381.967 \text{ nm}$ ) from the difference between the concentration of the remaining  $\text{Eu}^{3+}$  in the supernatant liquid and that of the blank sample.

### Specific surface area

Specific surface areas were determined using the BET equation (Brunauer *et al.*, 1938) from the nitrogen

adsorption isotherms obtained at 77 K. Prior to the adsorption experiments, the adsorbents were dried at 333 K under vacuum ( $10^{-1}$  torr) for 3 h.  $\text{Na}^+$ -clays were heat treated at 773 K for 1 h under air to determine the external surface area. The dehydration was confirmed by the basal spacings of the heat-treated  $\text{Na}^+$ -clays (1.0 nm).

### Equipment

X-ray diffraction (XRD) patterns were obtained using a Rigaku RAD IB using monochromatic  $\text{Cu-K}\alpha$  radiation, operated at 20 mA and 40 kV. Steady-state luminescence spectra were recorded on a HITACHI F-4500 fluorospectrophotometer. The ICP-AES was performed using a Rigaku Spectro Ciros CCD. Nitrogen adsorption isotherms were obtained at 77 K using a BELSORP 28 instrument (Bell Japan Inc.).

## RESULTS AND DISCUSSION

Figure 1 shows the adsorption isotherms of  $\text{Eu}^{3+}$  for Kunipia F, Sumecton SA and  $\text{Na}^+$ -TSM from aqueous solution. According to the Giles *et al.* (1960) classification, the  $\text{Na}^+$ -TSM isotherm is type-H and the Sumecton SA and Kunipia F isotherms are type-L. These isotherm types suggest a significant affinity of these clays for  $\text{Eu}^{3+}$ . Langmuir plots were fitted by linear regression of a graph of  $C_e/Q$  vs.  $C_e$  resulting in a linear equation of the form

$$C_e/Q = mC_e + b \quad (1)$$

where  $m$  is the slope and  $b$  is the intercept (Langmuir, 1918). The amount of  $\text{Eu}^{3+}$  adsorbed ( $Q$ ) in meq of  $\text{Eu}^{3+}/\text{g}$  of clay is plotted vs. the equilibrium concentrations ( $C_e$ ) in mmol  $\text{Eu}^{3+}/\text{L}$  in Figure 1. The plotted values are the measured data points. The plotted lines are graphs of the Langmuir equation using the fitted parameters for each data set (Figure 1). All Langmuir fits to the extrapolated data had  $r^2$  values of 0.96 or greater.

The maximum amounts of  $\text{Eu}^{3+}$  adsorbed on  $\text{Na}^+$ -TSM, Sumecton SA and Kunipia F were 1.00, 0.71 and 1.02 meq/g of clay, respectively, close to the CECs (0.94, 0.71 and 1.19 meq/g of clay for  $\text{Na}^+$ -TSM, Sumecton SA and Kunipia F, respectively). The XRD patterns were recorded under relative humidity of  $\sim 20\%$  (Figure 2). The basal spacings of  $\text{Na}^+$ -TSM, Kunipia F

Table 1. Chemical compositions of clays used in this paper (Okada *et al.*, 2005a).

Adsorbent	Chemical composition	Unit-cell weight (amu)	Ideal surface area ( $\text{m}^2/\text{g}$ )	BET surface area ( $\text{m}^2/\text{g}$ )
$\text{Na}^+$ -montmorillonite (Kunipia F)	$(\text{Na}_{0.53}\text{Ca}_{0.09})^{0.71+}$ $[(\text{Al}_{3.28}\text{Fe}_{0.31}\text{Mg}_{0.43})^{\text{oct}}(\text{Si}_{7.65}\text{Al}_{0.35})^{\text{tet}}\text{O}_{20}(\text{OH})_4]^{0.71-}$	784	704	6
$\text{Na}^+$ -saponite (Sumecton SA)	$(\text{Na}_{0.49}\text{Mg}_{0.14})^{0.77+}$ $[(\text{Mg}_{5.97}\text{Al}_{0.03})^{\text{oct}}(\text{Si}_{7.20}\text{Al}_{0.80})^{\text{tet}}\text{O}_{20}(\text{OH})_4]^{0.77-}$	810	681	135
$\text{Na}^+$ -TSM	$\text{Na}_2\text{Mg}_5\text{Si}_8\text{O}_{20}\text{F}_4$	786	702	7

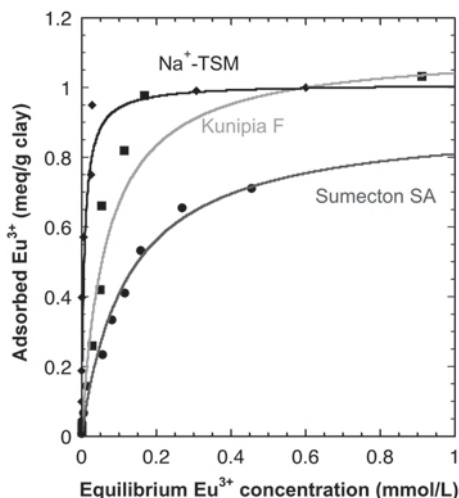


Figure 1. Adsorption isotherms of  $\text{Eu}^{3+}$  on Kunipia F (square), Sumecton SA (circle) and  $\text{Na}^+$ -TSM (diamond). Solid lines are graphs of the Langmuir equation calculated using the fitted parameters (Table 1) for each data set.

and Sumecton SA were 1.23, 1.23 and 1.29 nm, respectively and increased to 1.52, 1.53 and 1.50 nm after  $\text{Eu}^{3+}$  adsorption (Figure 2). Judging from the thickness of the silicate layer (0.96 nm), the gallery heights of the  $\text{Na}^+$ - and the  $\text{Eu}^{3+}$ -forms were 0.3 and 0.6 nm, respectively, indicating a change in hydration from a monolayer to a bilayer of water molecules in the interlayer space. The polarizing power is directly related to cation electric field (ionic charge/ion radii) which is

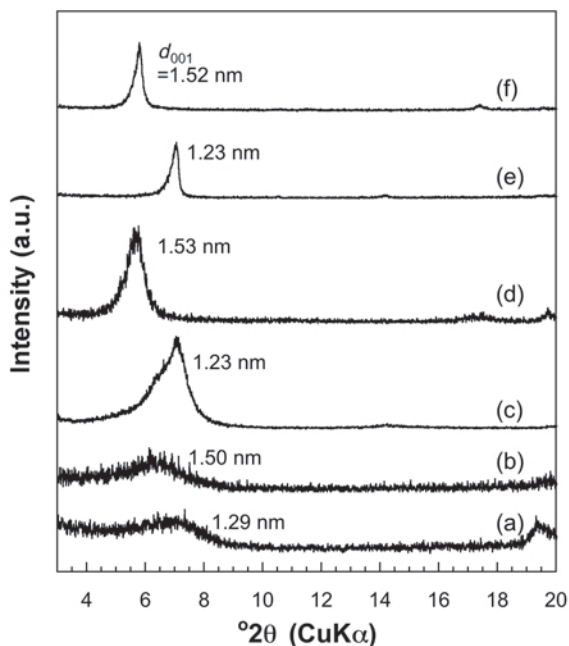


Figure 2. XRD patterns of (a) Sumecton SA, (b)  $\text{Eu}^{3+}$ -Sumecton SA, (c) Kunipia F, (d)  $\text{Eu}^{3+}$ -Kunipia F, (e)  $\text{Na}^+$ -TSM and (f)  $\text{Eu}^{3+}$ -TSM.

larger for  $\text{Eu}^{3+}$  (3.2) than for  $\text{Na}^+$  (0.98). As the polarizing power increased, the strength of the interactions between the cations and water molecules surrounding the cations increased. Therefore, it is thought that a larger amount of water was involved in the  $\text{Eu}^{3+}$ -form.

The type-H adsorption isotherm of TSM indicated a greater affinity for  $\text{Eu}^{3+}$  than the type-L isotherms of Kunipia F and Sumecton SA. Differences in  $\text{Eu}^{3+}$  affinity to clays were also revealed by the Freundlich affinity index ( $n$ ) values. The calculated values ( $n$ ) for the present system are listed in Table 2. The Freundlich equation (Freundlich, 1926) is expressed as

$$Q = K_f C_e^{1/n} \quad (2)$$

where  $K_f$  ( $\text{mmol g}^{-1}$ ) and  $n$  are constants pertaining to the maximum amount adsorbed and a conditional index which describes the shape of the isotherm (empirical adsorption characteristics), respectively. The  $n$  value for the TSM system (7.5) was quite larger than those for the Kunipia F (1.9) and for Sumecton SA systems (1.5) (Table 2). The significant affinity of  $\text{Sr}^{2+}$  in aqueous solution for a synthetic fluoro-mica was shown previously (Paulus *et al.*, 1992). The affinity of  $\text{Eu}^{3+}$  for TSM may be accounted for by the structural difference in the octahedral sheet (hydroxide or fluoride). The TSM clay contains highly electronegative F groups instead of the hydroxyls in smectites and this difference might explain the greater  $\text{Eu}^{3+}$  adsorption by TSM.

The  $n$  value for Kunipia F (1.9) was slightly larger than that for the Sumecton SA system (1.5). The interlayer expandability of smectites is related to electrostatic interactions between adjacent sheets that depend on the layer charge, cation type and cation position (van Olphen, 1977). Because the layer-charge density of Sumecton SA is smaller than Kunipia F, the attractive force between adjacent silicate layers that is mediated by exchangeable cations might be weaker in Sumecton SA. The difference in layer charge might give the greater  $\text{Eu}^{3+}$  affinity for Kunipia F than for Sumecton SA.

The Freundlich equations for the  $\text{Eu}^{3+}$ -TSM and  $\text{Eu}^{3+}$ -Kunipia provided poorer fits to the data than the Langmuir equations, as shown by the  $r^2$  values given in Table 2. In contrast, the Freundlich fit to the extrapolated data for the  $\text{Eu}^{3+}$ -TSM had a larger  $r^2$  value (0.99). We assume that  $\text{Eu}^{3+}$  adsorbed stoichiometrically to specific adsorption sites of  $\text{Na}^+$ -TSM and Kunipia F, while the  $\text{Eu}^{3+}$  adsorption occurred on relatively inhomogeneous adsorption sites of Sumecton SA.

The variation of luminescence spectra of the  $\text{Eu}^{3+}$ -exchanged Sumecton SA and  $\text{Na}^+$ -TSM are shown in Figures 3a and 3b, respectively. The luminescence bands ascribable to the  $^5\text{D}_0-^7\text{F}_1$  and  $^5\text{D}_0-^7\text{F}_2$  transitions of  $\text{Eu}^{3+}$  were observed at 592 and 614 nm, respectively (Carnall, 1976). On the other hand, luminescence was not observed for the  $\text{Eu}^{3+}$ -Kunipia F system (data are not shown). The quenching of  $\text{Eu}^{3+}$  luminescence in  $\text{Eu}^{3+}$ -exchanged Kunipia F was attributed to the 2 wt.%

Table 2. Parameters of the adsorption data fitted to the Freundlich equation.

Host	Maximum amount of adsorbed $\text{Eu}^{3+}$ (meq/g)	Type	Freundlich isotherm <sup>a</sup>		
			$K_f$ (meq g <sup>-1</sup> mM <sup>1/n</sup> )	$n$	$r^2$
Kunipia F	1.02	L	2.5	1.5	0.933
Sumecton SA	0.71	L	1.2	1.9	0.990
TSM	1.00	H	1.2	7.2	0.864

$$a : Q = K_f C_e^{1/n}$$

structural  $\text{Fe}^{2+/3+}$  as reported for  $\text{Eu}^{3+}$ -exchanged Wyoming montmorillonite ( $\text{Fe}^{2+/3+}$ :3 wt.%) (Bergaya and van Damme, 1983). The relative luminescence intensity depends on the strength and symmetry of the electric field around  $\text{Eu}^{3+}$ . The relative intensity of each of the transitions ( $I_{592}/I_{614}$ ) observed for the Sumecton SA and TSM systems barely changed with greater amounts of adsorbed  $\text{Eu}^{3+}$ , suggesting that  $\text{Eu}^{3+}$  was adsorbed in a similar manner. In contrast, the ratio differed depending on the clays; the ratio of the intensity ( $I_{592}/I_{614}$ ) for the Sumecton SA system was 0.7, while that for the TSM system was 1.8.

Several groups (Takahashi *et al.*, 1998; Stumpf *et al.*, 2002; Rabung *et al.*, 2005) have discussed the state of the  $\text{Eu}^{3+}$  adsorbed on smectites by using the  $I_{592}/I_{614}$  value. When the  $I_{592}/I_{614}$  value is comparable to the value (1.7) for the  $\text{Eu}^{3+}$  aquo ion (Zaitoun *et al.*, 2000),  $\text{Eu}^{3+}$  has a similar site symmetry (*i.e.* a highly symmetrical environment). A large amount of  $\text{Eu}^{3+}$  has been adsorbed as an outer-sphere complex between the  $\text{Eu}^{3+}$  aquo ion on a clay. In contrast, relatively low  $I_{592}/I_{614}$  has been a result of asymmetrical site symmetry of  $\text{Eu}^{3+}$ , suggesting the formation of an inner-sphere

complex of  $\text{Eu}^{3+}$  with the edge hydroxyl groups. Considering relatively large BET surface area (Table 1) of Sumecton SA (135 m<sup>2</sup>/g) compared to that for Na<sup>+</sup>-TSM (6 m<sup>2</sup>/g), the formation of an inner-sphere complex with the edge hydroxyls of Sumecton SA is a probable reason for the smaller  $I_{592}/I_{614}$  value. The lower intensity ratio was also observed for  $\text{Eu}^{3+}$ -doped silica gel, which was prepared under basic conditions (Selvan *et al.*, 1999; Zaitoun *et al.*, 2000), and magadiite systems (Mizukami *et al.*, 2002). The complexation of surface silanol groups with  $\text{Eu}^{3+}$  is a possible explanation for the relatively low  $I_{592}/I_{614}$ .

Figure 4 shows the relationship between the intensity of the <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>2</sub> luminescence band (at 614 nm) and the amount of the adsorbed  $\text{Eu}^{3+}$  on Sumecton SA and TSM. Amounts of adsorbed  $\text{Eu}^{3+}$  were expressed as the amount per ideal surface area (nm<sup>2</sup>) in order to examine the effect of  $\text{Eu}^{3+}$  spatial distribution on the luminescence. Ideal surface areas of clays ( $S_a$ ) were calculated from the unit-cell dimensions and unit-cell weights of the clays using the equation

$$S_a = (1/M) \times 6.02 \times 10^{23} \times 2 \times A \times 10^{19} \text{ m}^2 / \text{nm}^2 \quad (3)$$

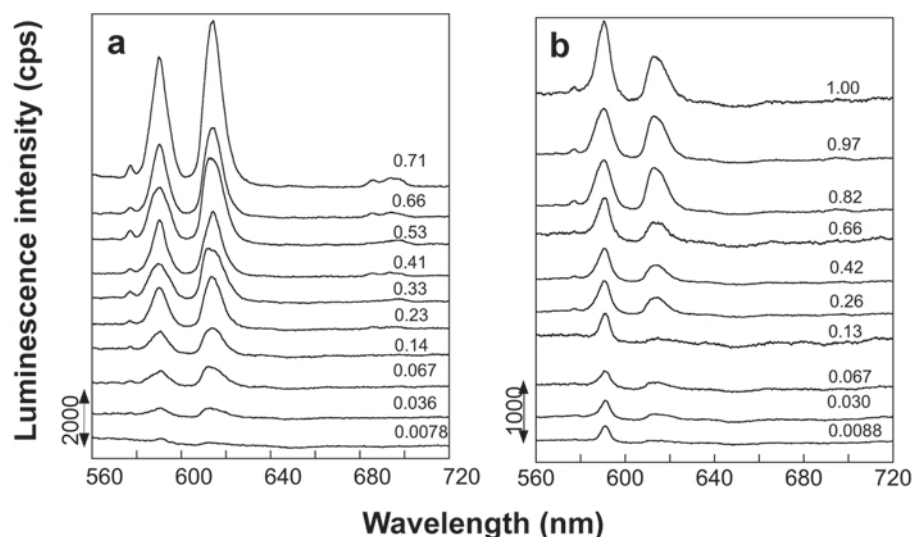


Figure 3. Luminescence spectra of reaction products of  $\text{EuCl}_3$  with (a) Sumecton SA and (b) Na<sup>+</sup>-TSM. The numbers along the right side of each figure designate the amount of  $\text{Eu}^{3+}$  (meq/g of clay).

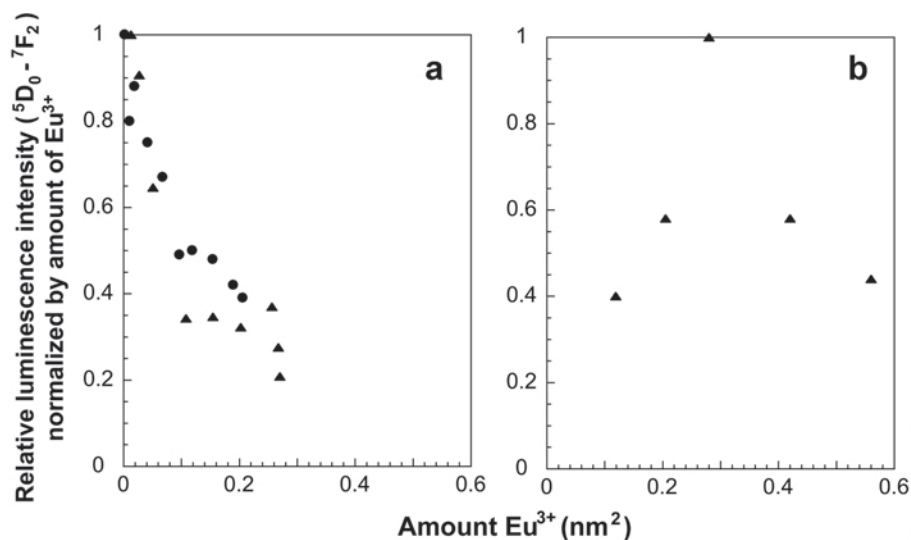


Figure 4. The dependence of luminescence intensity (<sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>2</sub> transition) on Eu<sup>3+</sup> concentration for (a) Sumecton SA (circle), Na<sup>+</sup>-TSM (triangle) and (b) magadiite (triangle, Mizukami *et al.*, 2002).

where  $M$  equals the unit-cell weight (Table 1) and  $A$  is the product of the  $a$  and  $b$  unit-cell dimensions and  $6.02 \times 10^{23}$  is Avogadro's number (van Olphen, 1977). For example, the ideal surface of Sumecton SA is given as  $S_a = (1/810) \times 6.02 \times 10^{23} \times 2 \times 0.514 \times 0.893 \times 10^{19} = 681$  (Table 1). The luminescence intensity was normalized using the amount of adsorbed Eu<sup>3+</sup> as indicated by the equation  $I_n = I_m/m$ ; where  $I_n$  denotes the normalized luminescence intensity,  $I_m$  denotes the observed luminescence intensity, and  $m$  denotes the amount of adsorbed Eu<sup>3+</sup>. These symbols were proposed in a previous study on the adsorption of Eu<sup>3+</sup> to magadiite (Mizukami *et al.*, 2002). In the Eu<sup>3+</sup>-magadiite system, the luminescence was intensified with increased amounts of adsorbed Eu<sup>3+</sup> up to 1.0 meq/g and 0.28 molecules/nm<sup>2</sup>. This is based on a surface area of  $0.73 \times 0.73$  nm<sup>2</sup> for each cell and a unit-cell weight of 902 atomic mass units (Brindley, 1969). A further increase in the amount of Eu<sup>3+</sup> adsorbed to magadiite weakened the luminescence due to concentration quenching at the greater Eu<sup>3+</sup> loading (Figure 4b). In contrast, a decreased normalized luminescence intensity with increased amounts of adsorbed Eu<sup>3+</sup> was observed for both the Sumecton SA and TSM systems (Figure 4a). This observation suggests that the concentration quenching occurred even when the amount of Eu<sup>3+</sup> loaded was quite small compared to that for the magadiite system. Normalized luminescence intensity differences between magadiite and the Sumecton SA and TSM clays might be due to the different nature of the negative sites in these clay minerals. Negative charge sites in smectites are mainly due to isomorphous substitution, whereas the negative charge sites in TSM are largely due to lattice defects. In contrast, the negative charge sites in magadiite are mostly pH-dependent silanol sites.

## CONCLUSIONS

The adsorption of Eu<sup>3+</sup> from aqueous solution to natural montmorillonite (Kunipia F), and synthetic saponite (Sumecton SA) and synthetic fluoro-tetrasilicic mica (Na<sup>+</sup>-TSM) was examined. The Eu<sup>3+</sup> adsorption capacities (1.02, 0.71 and 1.00 meq/g of clay for Kunipia F, Sumecton SA and Na<sup>+</sup>-TSM, respectively) were similar to the CECs (1.19, 0.71 and 0.94 meq/g of clay for Kunipia F, Sumecton SA and Na<sup>+</sup>-TSM, respectively), suggesting Eu<sup>3+</sup> adsorption by cation exchange. Adsorption isotherms indicated a high affinity of Eu<sup>3+</sup> for TSM relative to the smectites (Kunipia F and Sumecton SA). Luminescence quenching by structural Fe limited luminescence examination of the Kunipia F montmorillonite. The luminescence efficiency decreased with increases in the adsorbed Eu<sup>3+</sup>, indicating concentration quenching for both Sumecton SA saponite and TSM fluoro-tetrasilicic mica.

## ACKNOWLEDGMENT

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government and CREST (JST).

## REFERENCES

- Bergaya, F. and van Damme, H. (1983) Luminescence of Eu<sup>3+</sup> and Tb<sup>3+</sup> ions adsorbed on hydrated layer-lattice silicate surfaces. *Journal of the Chemical Society, Faraday Transactions 2*, **79**, 505–518.
- Bradbury, M.H. and Baeyens, B. (2002) Sorption of Eu on Na- and Ca-montmorillonites: Experimental investigations and modeling with cation exchange and surface complexation. *Geochimica et Cosmochimica Acta*, **66**, 2325–2334.
- Brindley, G.W. (1969) Unit cell of magadiite in air, in vacuo, and under other conditions. *American Mineralogist*, **54**, 1583.

- Brunauer, S., Emmett, P.H. and Teller, E. (1938) Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, **60**, 309–319.
- Carnall, W.T. (1976) The absorption and fluorescence spectra of rare earth ions in solution. In *Handbook on the Physics and Chemistry of Rare Earths*. Elsevier, North-Holland, The Netherlands.
- Coppin, F., Berger, G., Bauer, A., Castet, S. and Loubet, M. (2002) Sorption of lanthanides on smectites and kaolinite. *Chemical Geology*, **182**, 57–68.
- Freundlich, H. (1926) *Colloid and Capillary Chemistry*, Methuen, London, pp. 114–122.
- Giles, C.H., MacEwan, T.H., Nakhwa, S.N. and Smith, D. (1960) Studies in adsorption: Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *Journal of Chemical Society*, **111**, 3973–3993.
- Kakegawa, N. and Ogawa, M. (2005) Effective luminescence quenching of tris(2,2'-bipyridine)ruthenium(II) by methylviologen on clay by the aid of poly(vinylpyrrolidone). *Langmuir*, **20**, 7004–7009.
- Kitajima, K. and Daimon, N. (1975) Na-fluor-tetrasilicic mica  $[\text{Na}_2\text{Mg}_{2.5}\text{Si}_2\text{O}_{10}\text{F}_2]$  and its swelling characteristics. *Nippon Kagaku Kaishi*, 991–995.
- Kitajima, K., Daimon, N. and Kondo, R. (1976) Changes of swelling and dehydration characteristics of synthetic expandable layered minerals with cation exchange. *Nippon Kagaku Kaishi*, 597–602.
- Langmuir, I. (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, **40**, 1361–1402.
- Miyamoto, N., Kawai, R., Kuroda, K. and Ogawa, M. (2000) Adsorption and aggregation of a cationic cyanine dye on layered clay minerals. *Applied Clay Science*, **16**, 161–170.
- Mizukami, N., Tsujimura, M., Kuroda, K. and Ogawa, M. (2002) Preparation and characterization of Eu-magadiite intercalation compounds. *Clays and Clay Minerals*, **50**, 799–806.
- Nakamura, Y., Yamagishi, A., Iwamoto, T. and Koga, M. (1988) Adsorption properties of montmorillonite and synthetic saponite as packing materials in liquid column chromatography. *Clays and Clay Minerals*, **36**, 530–536.
- Ogawa, M. (2004) Photoprocesses in Clay-Organic Complexes. Pp. 191–259 in: *Handbook of Layered Materials* (S.M. Auerbach, K.A. Carrado and P.K. Dutta, editors). Marcel Dekker, New York.
- Ogawa, M. and Kuroda, K. (1995) Photofunctions of intercalation compounds. *Chemical Reviews*, **95**, 399–438.
- Ogawa, M. and Kuroda, K. (1997) Preparation of inorganic-organic nanocomposite through intercalation of organoammonium ions into layered silicate. *Bulletin of the Chemical Society of Japan*, **70**, 2593–2618.
- Ogawa, M., Nagafusa, Y., Kuroda, K. and Kato, C. (1992) Solid-state intercalation of acrylamide into smectites and Na-taeniolite. *Applied Clay Science*, **11**, 291–302.
- Ogawa, M., Inagaki, M., Kodama, N., Kuroda, K. and Kato C. (1993) Novel controlled luminescence of tris(2,2'-bipyridine)ruthenium(II) intercalated in a fluortetrasilicic mica with poly(vinylpyrrolidone). *Journal of Physical Chemistry*, **97**, 3819–3823.
- Ogawa, M., Kawai, R. and Kuroda, K. (1996) Adsorption and aggregation of a cationic cyanine dye on smectites. *Journal of Physical Chemistry B*, **100**, 16218–16221.
- Ogawa, M., Tsujimura, M. and Kuroda, K. (2000) Incorporation of tris(2,2'-bipyridine)ruthenium(II) in a synthetic swelling mica with poly(vinylpyrrolidone). *Langmuir*, **16**, 4202–4206.
- Okada, T. and Ogawa, M. (2003) 1,1'-Dimethyl-4,4'-bipyridinium-smectites as a novel adsorbent of phenols from water through charge-transfer interactions. *Chemical Communications*, 1378–1379.
- Okada, T. and Ogawa, M. (2004) *p*-Phenylenediammonium-smectites as adsorbents with colorimetric detection ability for phenols in water. *Bulletin of the Chemical Society of Japan*, **77**, 1165–1171.
- Okada, T., Morita, T. and Ogawa, M. (2005a) Tris(2,2'-bipyridine)ruthenium(II)-clays as adsorbents of phenol and chlorinated phenols from aqueous solution. *Applied Clay Science*, **29**, 45–54.
- Okada, T., Watanabe, Y. and Ogawa, M. (2005b) Photoregulation of adsorption behavior of phenol for azobenzene-clay intercalation compounds. *Journal of Materials Chemistry*, **15**, 987–992.
- Okada, T., Ehara, Y. and Ogawa, M. (2006) Adsorption and possible luminescence detection of 4-nonylphenol by  $\text{Eu}^{3+}$ -smectites. *Chemistry Letters*, **35**, 638–639.
- Paulus, W.J., Komarneni, S. and Roy, R. (1992) Bulk synthesis and selective exchange of strontium ions in  $\text{Na}_4\text{Mg}_6\text{Al}_4\text{Si}_4\text{O}_{20}\text{F}_4$  mica. *Nature*, **357**, 571–573.
- Rabung, Th., Pierret, M.C., Bauer, A., Geckeis, H., Bradbury, M.H. and Baeyens, B. (2005) Sorption of Eu(III)/Cm(III) on Ca-montmorillonite and Na-illite. Part I: Batch sorption and time-resolved laser fluorescence spectroscopy experiments. *Geochimica et Cosmochimica Acta*, **69**, 5393–5402.
- Selvan, S.T., Hayakawa, T. and Nogami, M. (1999) Remarkable influence of silver islands on the enhancement of fluorescence from  $\text{Eu}^{3+}$  ion-doped silica gels. *Journal of Physical Chemistry B*, **103**, 7064–7067.
- Shichi, T. and Takagi, K. (2000) Photophysics and photochemistry in clay minerals. Pp. 31–110 in: *Solid State and Surface Photochemistry*, vol. 5. (V. Ramamurthy and K.S. Schanze, editors). Marcel Dekker, New York.
- Soma, M., Tanaka, A., Seyama, H., Hayashi, S. and Hayamizu, K. (1990) Bonding states of sodium in tetrasilicic mica. *Clay Science*, **8**, 1–8.
- Stumpf, T., Bauer, A., Coppin, F., Fanghänel, T. and Kim, J.I. (2002) Inner-sphere, outer-sphere and ternary surface complexes: a TRLFS study of the sorption process of Eu(III) onto smectite and kaolinite. *Radiochimica Acta*, **90**, 345–349.
- Takahashi, Y., Kimura, T., Kato, Y., Minai, Y. and Tominaga, T. (1998) Characterization of Eu(III) species sorbed on silica and montmorillonite by laser-induced fluorescence spectroscopy. *Radiochimica Acta*, **82**, 227–232.
- Urabe, K., Sakurai, H. and Izumi, Y. (1988) Cation-exchange synthetic saponite as a 'heat-stable' acidic clay catalyst. *Journal of the Chemical Society, Chemical Communications*, **29**, 1250–1251.
- van Olphen, H. (1977) *An Introduction to Clay Colloid Chemistry* 2<sup>nd</sup> edition. Wiley-Interscience, New York.
- Zaitoun, M.A., Goken, D.M., Bailey, L.S., Kim, T. and Lin, C.T. (2000) Thermoanalysis and emission properties of  $\text{Eu}^{3+}/\text{Eu}^{2+}$  in  $\text{Eu}^{3+}$ -doped xerogels. *Journal of Physical Chemistry B*, **104**, 189–196.

(Received 1 August 2006; revised 16 March 2007; Ms. 1200; A.E. William F. Jaynes)