

Sorption of lanthanides on smectite and kaolinite

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Abstract

Experiments were carried out to investigate the sorption of the complete lanthanide series (Ln or rare earth elements, REE) on a kaolinite and an a Na-montmorillonite at 22°C over a wide range of pH (3–9). Experiments were conducted at two ionic strengths, 0.025 and 0.5 M, using two different background electrolytes (NaNO₃ or NaClO₄) under atmospheric conditions or N₂ flow (glove box). The REE sorption does not depend on the background electrolyte or the presence of dissolved CO₂, but is controlled by the nature of the clay minerals, the pH and the ionic strength. At 0.5 M, both clay minerals exhibit the same pH dependence for the Ln sorption edge, with a large increase in the sorption coefficient (K_D) above pH 5.5. At 0.025 M, the measured K_D is influenced by the Cation Exchange Capacity (CEC) of the minerals. Two different behaviours are observed for smectite: between pH 3 and 6, the K_D is weakly pH-dependent, while above pH 6, there is a slight decrease in log K_D . This can be explained by a particular arrangement of the particles. For kaolinite, the sorption coefficient exhibits a linear increase with increasing pH over the studied pH range. A fractionation is observed that due to the selective sorption between the HREEs and the LREEs at high ionic strength, the heavy REE is being more sorbed than the light REE. These results can be interpreted in terms of the surface chemistry of clay minerals, where two types of surface charge are able to coexist: the permanent structural charge and the variable pH-dependent charge. The fractionation due to sorption observed at high ionic strength can be interpreted either because of a competition with sodium or because of the formation of inner-sphere complexes. Both processes could favour the sorption of HREEs according to the lanthanide contraction. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Rare earth elements (REE) are commonly used as petrogenetic tracers in internal geodynamic studies of the Earth. Since the beginning of the 1980s, scientists have used the REEs as geochemical tracers of surface processes. The REE pattern has been used

as a chemical tracer of regional groundwater mixing (Johannesson et al., 1997) to investigate the dynamics of soils in humid tropical regions (Braun et al., 1998), or to evaluate the residence time of particles in the seawater column (Tachikawa et al., 1999). Another field of application of the REEs concerns the storage/disposal of nuclear waste. Prediction of the retention mechanisms of these elements is a fundamental concern in evaluating the suitability of proposed sites for the geologic disposal of nuclear

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waste. In studies of prospective disposal sites, lanthanides (Ln) are sometimes used as chemical homologues for trivalent actinides, such as Am^{3+} (Chapman and Smellie, 1986). Clay minerals are known to be highly efficient in radionuclide retention in natural systems, and they are often proposed as backfill in future nuclear waste repositories (e.g. Meunier and Velde, 1998).

Given the complexity of surface processes, it is important to understand the mechanisms, which can influence the REE patterns. The REE concentrations in solution can be influenced by complexation reactions, by anionic ligands, the dissolution and/or precipitation of minerals containing or incorporating REE in their structure, as well as by redox reactions and adsorption onto mineral or organic solid phases.

Because of their high specific surface area and their abundance in natural superficial environments, clay minerals are of crucial importance for adsorption (Awwiller and Mack, 1991). Over the past 20 years, experimental studies have been performed to investigate the interaction between clay minerals and REE. These studies have focused on the different aspects of the sorption mechanisms: irreversibility of the sorption mechanisms (Bonnot-Courtois and Jafrezic-Renault, 1982; Miller et al., 1983), migration into the clay structure (Miller et al., 1982), relation with the cation exchange capacity (Olivera et al., 1988), the nature of interlayer cations (Maza-Rodriguez et al., 1992), competition with the background electrolytes (Berger, 1992), the effect of pH (Bruque et al., 1980; Laufer et al., 1984; McBride, 1980), and complexation by humic acids (Takahashi et al., 1999). However, the published data are often disparate and it is difficult to compare the results obtained by different experimental protocols. Furthermore, the experiments are generally conducted with a single lanthanide (Aja, 1998), while the complete series is commonly used to interpret natural observations. The available data do not allow any definitive conclusions on elementary aspects of Ln^{3+} sorption, which is the dominant species along with carbonate complexes commonly encountered at the pH of natural waters (Deberdt et al., 1998; Deberdt, 2000). It is uncertain whether or not sorption leads to fractionation of the REE series and little is known about the nature of the chemical bonds between the metal cations and the clay structure.

The purpose of the present study is threefold: (1) to collect sorption data on the complete lanthanide series as a function of pH, ionic strength and the mineralogical structure of the clay, (2) to correlate the data with chemical properties of the clay surface, and (3) to ascertain whether or not the sorption mechanisms fractionate the lanthanide abundance pattern. In this study, we use the term fractionation in the sense of “fractionation due to sorption”. The experiments were conducted at room temperature, using kaolinite and montmorillonite samples.

2. Origin of charges on clay minerals

Clay minerals have charges on their surface, which determine their cation-exchange capacities and dispersion/flocculation behaviour. These charges govern the rate of chemical weathering.

There are two kinds of charges at the surfaces of clay-sized minerals. The layer or permanent charge arises from substitution of Si^{IV} or Al^{III} by cations of lower valency. Another type of charge, variable in nature, is generally located at the edges of the mineral particles, where structural patterns end as broken bonds, or at gibbsite basal planes (kaolinite). The origin of the variable surface charge is different in kaolinite and in smectite. In contrast to kaolinite, each aluminous octahedral layer in smectite is bound to two silica-rich tetrahedral layers. For kaolinite, the variable charge can be related to the reactions between ionisable surface groups located at the edges or at the gibbsite basal plane and the ions present in aqueous solution. In the case of smectites, with siloxane surfaces present on the basal planes, only the broken bonds at the edges contribute to the variable charge. The bridging $\text{Si}-\text{O}-\text{Si}$ bonds at the siloxane surfaces tend to be highly hydrophobic (Iler, 1979) and, therefore, proton adsorption at these sites is expected to be very weak (Blum and Lasaga, 1991; Huertas et al., 1998). The silanol groups ($\equiv\text{Si}-\text{OH}$) at the crystal edges of kaolinite and smectite contribute exclusively to the negative charge, through formation of $\equiv\text{SiO}^-$ surface complexes (Abendroth, 1970; Iler, 1979). Nevertheless, they can contribute to the positive charge at very low pH. Wanner et al. (1994) suggested that the adsorption of aqueous aluminium onto the silanol sites of

smectites reduces their contribution to the total charge. The silanol groups are less basic than the aluminol groups, which become charged at pH above 5.5 (Huertas et al., 1998). The aluminol groups at the edges are amphoteric. They undergo protonation at low pH and deprotonation at high pH, resulting in the formation of the surface complexes $\equiv\text{AlOH}_2^+$ and $\equiv\text{AlO}^-$ (Carroll-Webb and Walther, 1988; Huang, 1981; Huang and Stumm, 1973). The $\equiv\text{AlOH}$ groups at the basal planes are also amphoteric; however, they exhibit a more acidic character (Kawakami and Yoshida, 1985). Consequently, the formation of $\equiv\text{AlOH}_2^+$ complexes at the basal planes occurs at lower pH compared to the aluminol groups at the edges. The total charge of a clay particle is a function of the permanent and variable charges. The variable charge will be compensated by a chemisorption of cations on the amphoteric sites, even when the permanent one will be compensated by a physisorption of cations.

3. Materials and methods

3.1. Starting clays

The experiments were carried out with two types of clays: a kaolinite and a dioctahedral smectite. The kaolinite is a well-crystallized fine-grained kaolinite ($\leq 2 \mu\text{m}$) from St. Austell (UK), with a BET surface area of $11.7 \text{ m}^2/\text{g}$. It is distributed under the trade name SUPREME and was supplied by English China Clays. The smectite used was the $< 0.2 \mu\text{m}$ fraction of the Ceca bentonite separated by sedimentation techniques and saturated with Na (Day, 1965), with a BET surface area of $32 \text{ m}^2/\text{g}$. A detailed description of the kaolinite and smectite used in our

experiments can be found in Bauer and Berger (1998) and Bauer and Velde (1999). The cation exchange capacity of the initial clays was determined according to the method proposed by Meier and Kahr (1999) using the complexes of copper(II) ions with triethylene-tetramine and tetraethylene-pentamine. We obtained values of $3.7 \text{ meq}/100 \text{ g}$ for kaolinite and $75 \text{ meq}/100 \text{ g}$ for smectite. Table 1 shows the oxide composition of the starting materials determined by X-ray fluorescence (XRF), with the loss on ignition (LOI) determined gravimetrically, as well as the calculated structural formula for smectite.

The REE concentrations of the dried clay samples were determined by extracting these elements from the clay with hot Aqua Regia (Table 2). The analyses were carried out on an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS, Elan 6000, Perkin-Elmer). “Blank” experiments were conducted to observe the release of REE from the starting clays (see below).

3.2. Experimental setup

The REE sorption edges were measured at 22°C over a wide range of pH (2.6–8.7) and at two ionic strengths (0.5 and 0.025 M). The experiments were performed in polycarbonate containers with a solid/solution ratio of $2.5 \text{ g}/\text{l}$. Analytical grade NaNO_3 (Prolabo, RP Normapur) or NaClO_4 (Prolabo, RP Normapur) were used as background electrolytes to buffer the ionic strength of the solutions. The pH was adjusted to the desired values using NaOH (Prolabo, RP Normapur), HNO_3 (Merck, PA) or HClO_4 (Prolabo, RP Normapur). All the solutions were prepared with deionized water (Milli-Q Reagent Water System from Millipore) with a resistivity of $> 18 \text{ M}\Omega \cdot \text{cm}^{-1}$. REE stock solutions containing 1

Table 1

Oxide composition of the starting materials determined by XRF, the loss of ignition (LOI) determined gravimetrically and the calculated structural formula for smectite

Smectite Ceca (Wyoming-Na): $(\text{Si}_{7.98}\text{Al}_{0.02})^{\text{IV}}(\text{Al}_{3.105}\text{Fe}_{0.3128}^{3+}\text{Fe}_{0.0443}^{2+}\text{Mg}_{0.5109})^{\text{VI}}\text{O}_{22}(\text{Na}_{0.4475}^+\text{K}_{0.012}^+\text{Ca}_{0.0984}^{2+})^{\text{CE}}$.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	LOI	Total
Smectite Ceca	60.5	20.10	3.15	0.40	2.60	0.70	1.75	0.07	0.15	–	–	11.05	100

Table 2

Initial lanthanides contents in $\mu\text{g/g}$ of the starting clays, determined by ICP-MS

Ln (ppm)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Kaolinite St. Austell	19.5	48.60	4.78	17.90	3.88	1.05	4.23	0.67	3.95	0.76	2.24	0.33	2.43	0.43
Smectite Ceca	9.97	36.20	2.33	8.69	1.97	0.12	2.26	0.29	1.54	0.24	0.67	0.96	0.55	0.01

ppm of each of the 14 lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) were prepared from a multi-element standard solution (Spektrascan TEKNOLAB). This concentration is below the solubility of any of the solid phases.

In the first step, the solids were equilibrated with an REE-free solution until a stable pH was reached. An aliquot containing all the 14 REE was then added in order to reach an initial concentration of 130 ppb for each REE. After different reaction times, ranging from 2 h to 7 days (see below), the solid was separated from the solution by centrifugation (2500 rpm for 40 min). The supernatant was diluted, one part was acidified (2% HNO_3) for further Ln and Al chemical analysis, and the other part used for Si analysis. The experiments were replicated in a glove box under pure N_2 flow to avoid aqueous REE complexation with dissolved carbonate species. We evaluated the protocol blank by reacting clay minerals with background electrolytes for 3 days without any addition of REE.

3.3. Solution analysis

The aqueous REE and Al contents were analysed by ICP-MS (Perkin-Elmer Elan-6000). The detection limit is 5 ppt for the Ln and 0.1 ppb for aluminium. The precision is better than 5%. We used ^{115}In as an internal standard to correct for instrumental instability. The isobaric interference corrections are given in Aries et al. (2000). Aqueous Si concentrations were measured using the molybdate colorimetric method (Strickland and Parksons, 1972) with a Technicon Analyser II colorimeter.

3.4. Solid phase analysis

The evolution of the clay mineral structure and the formation of secondary phases were monitored by XRD. The solids were extracted by centrifuga-

tion, then saturated with SrCl_2 at 50°C overnight, washed and sedimented on glass slides before air-drying. XRD scans were recorded on a Philips PW 1130 diffractometer with a stepping motor-driven goniometer using Ni-filtered $\text{Cu-K}_{1,2}$ radiation (fine focus tube, Philips PW 2213/20). Divergence slit, receiving slit and scatter slit were 1° , 0.1 mm and 1° , respectively. The step size was 0.01° and the counting time 3 s. XRD measurements showed that the structure of the clay minerals did not change during the course of the experiments (Fig. 1). The formation of secondary phases was not observed.

3.5. Sorption coefficients

The amount of Ln sorbed by the clay fraction was calculated from the decrease of the aqueous Ln concentrations at the end of the experiment. The calculation requires that no other reaction consumes the aqueous Ln, such as adsorption onto the container walls. In order to check this assumption, we carefully removed the suspension at the end of the experiments and refilled the containers with 2% HNO_3 solution. After 3 days of reaction time, this washing solution was analysed for REE content. We found no significant Ln in the washing solutions (i.e. less than 5 ppb), indicating that the drop of the REE concentration during the experiments is due to their sorption onto the clay minerals rather than any other process.

A convenient method to represent the sorption data is the sorption coefficient, K_D , defined as the solid/solution concentration ratio. The K_D (in ml/g) values are normalized to solid mass/solution volume ratio according to Eq. (1):

$$K_D \text{ (ml/g)} = \frac{(C_{\text{initial}} - C_{\text{final}}) V}{C_{\text{final}} M} \quad (1)$$

where C_{initial} and C_{final} are the aqueous concentrations ($\mu\text{g/l}$) of the lanthanides at the beginning and

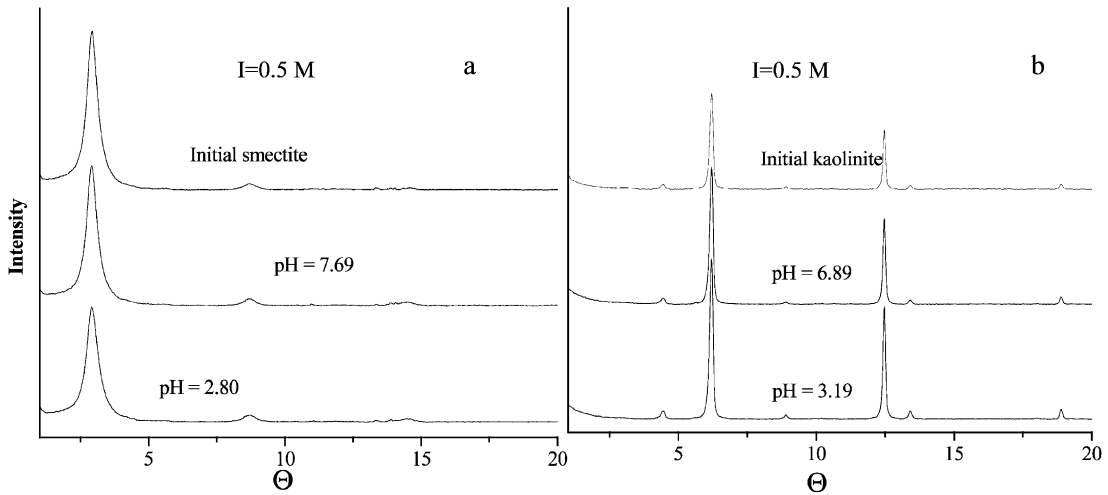


Fig. 1. X-ray diagrams indicate for smectite (a) and kaolinite (b) no change in mineralogy during the experiment.

at the end of the experiment, V is the solution volume (ml) and M is the mass of solid (g), so K_D has the dimensions of ml/g.

If all the available sorption surface sites are unsaturated, the numerical value of K_D does not depend on the V/M ratio. The range of significant K_D values is limited by the accuracy of the solution analysis. When the sorption is weak, K_D cannot be determined by Eq. (1) if the C_{final} is lower than 5% of the C_{initial} . This is because the variation concentration in solution is beneath the estimated experimental uncertainties. When the sorption is high, the measurement of K_D is limited by the blank of the experimental protocol or the detection limit of the analytical method. However, values of K_D within the range 10^1 – 10^6 ml/g are thought to be significant.

4. Results

4.1. Kinetics

The time necessary to establish a steady-state concentration during adsorption experiments is an important factor to consider in an experimental protocol. We monitored the Ln content of the solutions in contact with clays over a duration of 7 days. As an

example, Fig. 2 shows the results obtained for Eu near pH 4, with kaolinite ($I = 0.025$ and 0.5) and smectite ($I = 0.5$). The results indicate that at least 24 h are necessary to obtain a “steady state” between the Ln aqueous concentration and the clay fraction. Based on these results, we performed our experiments with a 72-h reaction time. This experimental run time is significantly longer than the 10-min period proposed by Bonnot-Courtois and Jaffrezic-Renault (1982), or the 20-min duration used by Bruque et al. (1980).

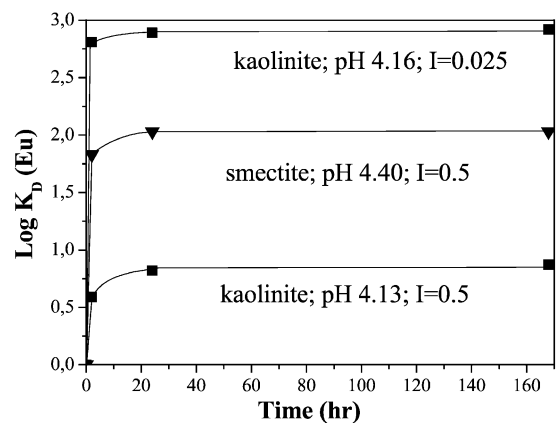


Fig. 2. Logarithm of calculated K_D for Eu as a function of time, for kaolinite ($I = 0.025$ and 0.5 M) and smectite ($I = 0.5$ M) at pH near 4.

4.2. Clay dissolution

Clay dissolution during the experimental runs is reflected by the release of Si and Al into solution. The concentrations of these elements obtained after 3 days of reaction are plotted as a function of pH in Fig. 3. The highest measured Al concentration in the runs does not exceed 5 mg/l for kaolinite, (89% of the values are lower than 2.7 mg/l), and 10 mg/l for smectite (80% of the values are lower than 5.4 mg/l). For $I = 0.025$ M, the minimum concentration of Al in solution is observed near pH 6. For 0.5 M, the minimum appears to be near pH 7, this being consistent with the result proposed by Baeyens and

Bradbury (1997). We have no explanation for the difference observed between the two ionic strengths for smectite in the pH range above pH 6. With smectite, the Si concentrations in solution are lower than 11.2 mg/l and 90% of the values are lower than 5.6 mg/l. With kaolinite, the Si concentrations in solution are below the detection limit (1 ppm in the raw solution).

The dissolution of starting clays can also release some lanthanides, which can interfere with our K_D calculations. The REE contents measured in solution after 3 days of the “blank” experiments are reported in Table 3. In most cases, the measured lanthanide concentrations are all of the same order of magni-

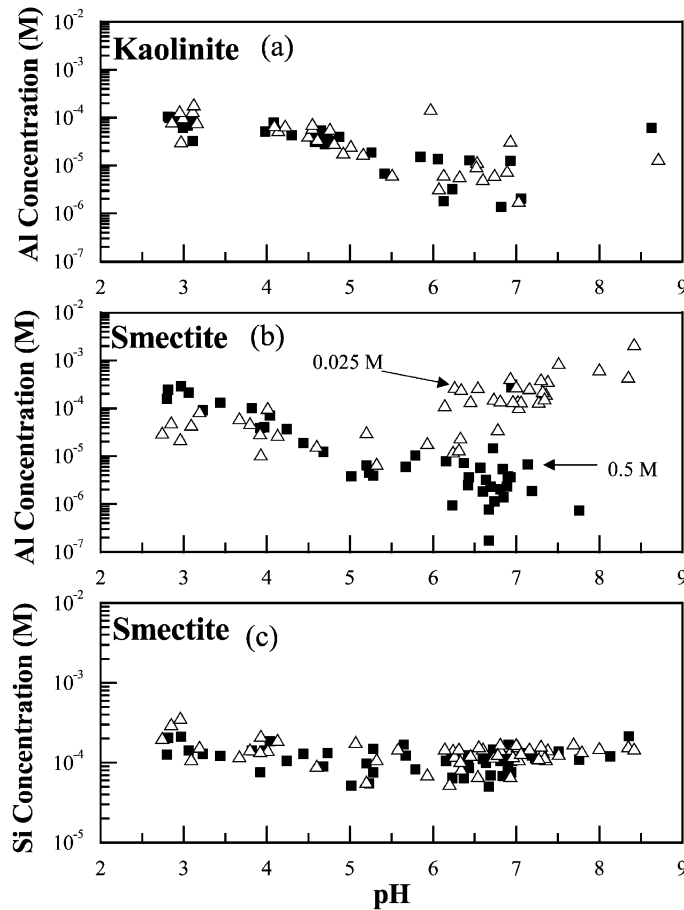


Fig. 3. Aqueous Si and Al concentrations after 3 days of reaction for $I = 0.5$ M (■) and for $I = 0.025$ M (△). Al concentration for kaolinite (a) and smectite (b), and Si concentration for smectite (c).

Table 3

Lanthanides concentrations (ppb) released in “blank” experiments conducted in 0.5 M NaNO₃ solutions at pH around 4

Ln (ppb)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
No clays	0.2	< 0.1	< 0.1	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
7 g/l Kaolinite	1.9	4.3	0.6	3.6	0.9	0.2	1.6	0.4	0.9	0.7	0.2	0.3	0.9	0.3
7 g/l Smectite	7.7	10.1	1.3	6.0	1.3	0.3	1.7	0.3	1.2	0.3	0.7	0.2	0.6	0.2

tude, or lower than the REE analytical uncertainties, except for the smectite in which La, Ce and Nd concentrations in solution are slightly higher (> 6 ppb).

4.3. Sorption edge

The 14 lanthanides all show the same qualitative behaviour in the sorption process. As an example,

the log K_D values obtained for Ho are presented in Fig. 4 as a function of pH, for the two clay minerals and the two ionic strengths. We did not observe significant differences in experiments conducted with different background electrolytes (NaClO₄ or NaNO₃) or in the absence or presence of dissolved CO₂ (glove box or air). At low ionic strength, the K_D values for kaolinite and smectite show a weak dependence on pH. However, the dependence of

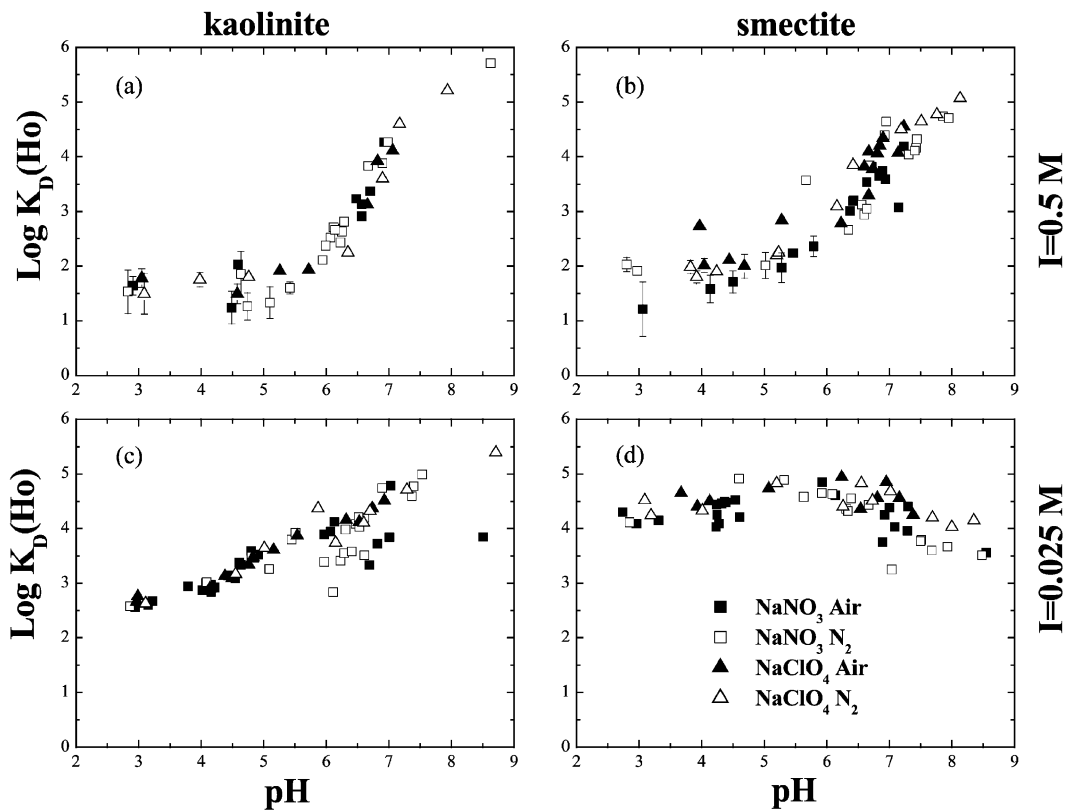


Fig. 4. Logarithm of calculated K_D for Ho as a function of pH, and ionic strength and nature of clays. The error bars correspond to the calculation uncertainties.

sorption on pH is more marked for kaolinite than for smectite. In the case of kaolinite, the sorption coefficient exhibits a linear increase with increasing pH over all the studied pH range (estimated slope: 0.49). $\log K_D$ is equal to 2.6 at pH 2.86, and reaches 5.40 at pH 8.71 (Fig. 4c). In the corresponding smectite diagram, two different behaviours can be identified: from pH 2.9 to 6, K_D is weakly pH-dependent (the $\log K_D$ values range between 4.1 and 4.9), while above pH 6, $\log K_D$ shows a slight decrease from 4.9 at pH 6 to 3.5 at pH 8.5 (Fig. 4d).

By contrast, at high ionic strength, the logarithm of sorption coefficients for smectite and kaolinite shows a marked pH dependence, with a significant increase between pH 6 and 8.5. In this pH range, the $\log K_D$ values increase from 1.9 to 5.7 for kaolinite (Fig. 4a) and from 2.2 to 5.1 for smectite (Fig. 4b). Below pH 6, the sorption coefficients remain constant around 1.7 for kaolinite (Fig. 4a), but evolve slightly as a function of pH for smectite, from 1.2 at

pH 2.5 to 2.7 at pH 5.5, with an average value around 2 (Fig. 4b). An increase of sorption below pH 6 with decreasing ionic strength was observed for Ni and Zn by Baeyens and Bradbury (1997) and for Nd and Eu by Sinitsyn et al. (2000).

4.4. Fractionation

In Fig. 5, the K_D values obtained for the whole series of lanthanides are plotted as a function of the atomic number. Similar variations of the K_D value are observed depending on the ionic strength. At low ionic strength, the sorption coefficients show a very high stability throughout the REE series. The Yb/Pr K_D ratio, for example, does not exceed 1.2 in any of the experiments. The lower values observed for La, Ce and Nd are attributed to the release of these elements from the starting clays. At high ionic strength, a significant increase of the K_D values from LREEs to HREEs is observed, with a Yb/Pr

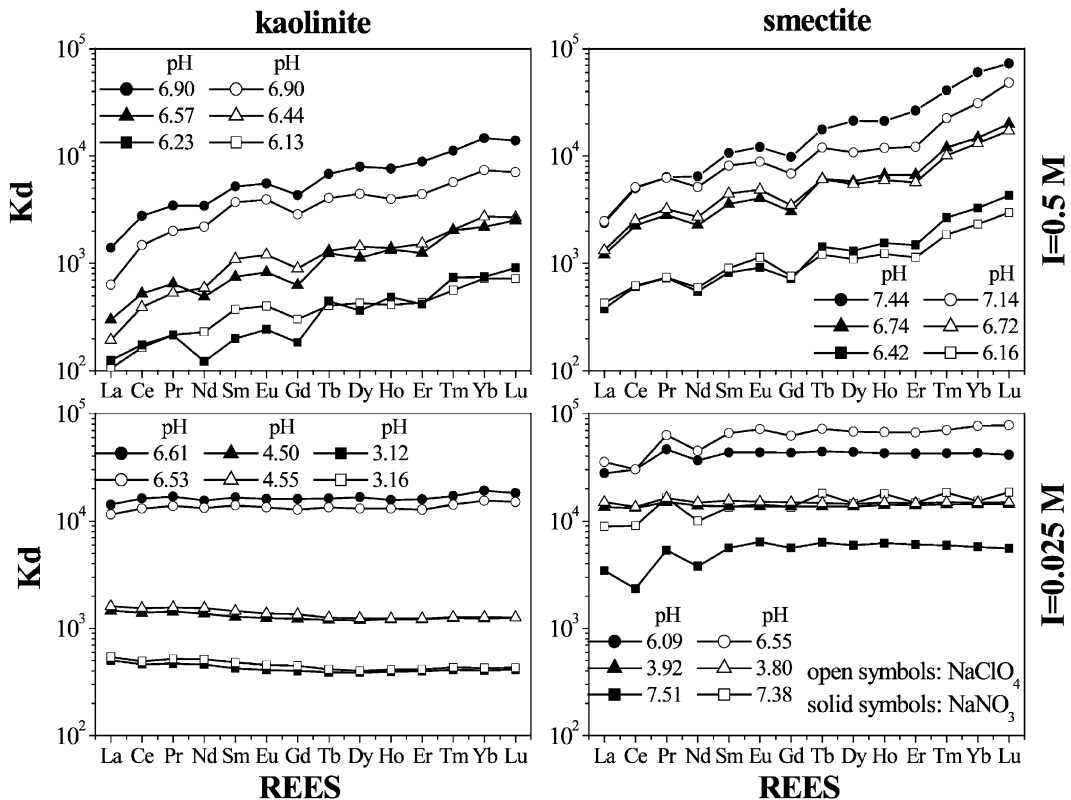


Fig. 5. Plot of K_D values as a function of REE atomic number at different pH and ionic strengths.

K_D ratio higher than 3.1. This shows that some fractionation of the REEs results from the adsorption process. A detailed analysis reveals the tetrad effect in the lanthanide series, as described by Kawabe (1992). Four parts can be distinguished within the series: La–Nd, Nd–Gd, Gd–Er and Er–Lu.

5. Discussion

5.1. Clay dissolution

Most of the aqueous silica concentrations for smectite are lower than 5.6 mg/l, which is near the quartz solubility, thus suggesting a dissolution of clay corresponding to less than 0.7% of the starting material. The data for Al vary over three orders of magnitude and suggest a dissolution of less than 1% for kaolinite and generally less than 3.5% for smectite (just three of the values are higher than 5%). These results suggest that the surface of the clays minerals are affected by complex reactions and that the sorption of the lanthanides occurs in a “dynamic” process. However, the kinetics of the adsorption mechanism are thought to be much faster than the dissolution reaction (Baeyens and Bradbury, 1997).

5.2. Sorption edges

The results presented in Fig. 4 can be easily understood by taking into account the surface chemistry of the clay particles. At high ionic strength, the Na/Ln ratio in solution is high and the exchangeable sites of smectites, with predominant non-specific adsorption, are saturated by Na. Thus, the experiments conducted at $I = 0.5$ monitored the Ln sorp-

tion on the other types of sites, involving specific adsorption onto the amphoteric sites at the edges of the particles. These sites being roughly the same for kaolinite and smectite ($\equiv\text{Al}-\text{OH}$ and $\equiv\text{Si}-\text{OH}$), the two minerals exhibit the same pH-dependent Ln sorption edge. Note that K_D increases strongly within the pH range 6–7, which is above the pH_{PZNPC} for kaolinite (Brady et al., 1996; Huertas et al., 1998; Motta and Miranda, 1989), but beneath the value for smectites in a 0.5-M solution (Avena and De Pauli, 1998; Baeyens and Bradbury, 1997; Wanner et al., 1994) (Table 4).

By contrast, at low ionic strength, the competition between Ln and Na for electrostatic adsorption is different. In the case of smectite, the permanent negative charge leads to an exchange reaction, which is independent of pH. This reaction is superimposed on the pH-dependent sorption process and becomes predominant. For kaolinite, which has a much lower measured CEC (3.7 meq/100 g as against 75 meq/100 g for smectite), the exchange reaction is of less importance and does not totally mask the pH-dependent sorption. Sorption by cation exchange is characterized by a strong dependence on background electrolyte concentration and a weak dependence on pH. Fig. 4 shows this phenomena at low pH. In this pH range, sorption is mainly on the interlayer sites of the montmorillonite, whereas with increasing pH the edges become increasingly important due to their increasing negative charge. As already observed for Ni and Zn by Baeyens and Bradbury (1997) or for Np by Turner et al. (1998), the sorption of Ln onto smectite decreases above pH 6 at low ionic strength. As suggested by Kraepiel et al. (1999), this can be explained by a particular arrangement of the particles under these conditions. It involves a basal plane/edge attraction, which decreases the number of reactive

Table 4

The values of pH corresponding to the pH_{PZNPC} for kaolinite and smectite at 25°C, reported in the recent literature

Mineral	Background electrolyte	pH	Sources
Na-montmorillonite	0.1 and 0.5 M NaClO ₄	7.8 and 6.5	Baeyens and Bradbury (1997)
Na-montmorillonite	0.006–0.088 M NaCl	8.5–8	Avena and De Pauli (1998)
Montmorillonite	0.005–0.5 M NaNO ₃	6.1–7	Wanner et al. (1994)
Kaolinite	0.001–0.1 M KClO ₄	~ 5.5	Huertas et al. (1998)
Kaolinite	0.1 M NaCl	3.9–4.3	Brady et al. (1996)
Kaolinite		4.5	Motta and Miranda (1989)

sites at the edges available for the cation adsorption. Turner et al. (1998) explained this observation by the carbonate complexation of the metal ions at high pH. Given the high (bi)carbonate concentrations at alkaline pH and the corresponding LnHCO_3^{2+} and LnCO_3^+ aqueous complexes (Haas et al., 1995), the weak CO_2 effect observed in our experiments suggests that such aqueous complexes have no effect on the chemisorption, which dominates at high pH. However, our results show the same decrease in both the free atmosphere and in the glove box experiments, thus supporting Kraepiel's assumption for REE.

5.3. Fractionation

Koepfenkastro et al. (1991) observed an opposite fractionation (LREEs are more sorbed than HREEs) for REE sorption onto metal oxides. In agreement with the results of Cantrell and Byrne (1987), they explain the observed fractionation by a stronger complexation of HREE with carbonate ions compared to the LREE. In the present study, the use of two electrolytes and an N_2 atmosphere dismisses the assumption that the observed fractionation is related to the formation of aqueous complexes with the nitrate or carbonate anions. Bonnot-Courtois and Jaffrezic-Renault (1982) reported a similar fractionation at $I = 0.1$ M of NaNO_3 between La, Ce, Nd, Sm, Eu, Tb, Yb and Lu. In their study, Yb and Lu are strongly sorbed relative to the other lanthanides, which they explained as being due to the decrease of the ionic radius with increasing atomic number. Aagard (1974) also observed the same results. In the present study, the data suggest that the concentration of cations in solution (i.e. the salt effect) interferes with this phenomena. To take account of the salt effect, we propose two possible explanations.

(1) At high ionic strength, the density of sorbed Na^+ at the particle surface is so high that it behaves as a barrier for REE sorption. This steric constraint inhibits the sorption of competitors with a larger ionic radius, as observed with the LREE when compared to the HREE (lanthanide contraction). At low ionic strength, the steric effect of Na^+ is negligible and all the REEs are sorbed to the same extent.

(2) Sorption at high ionic strength corresponds to chemisorption on the pH-dependent variably charged

edge of the particles, indicating desolvation of cations to form inner-sphere complexes. The fractionation reflects the variation in desolvation energy with the atomic number of the REE. By contrast, experiments conducted at low ionic strength show the effects of physical sorption onto exchangeable sites, which are assumed to have less influence on the REE pattern because of the formation of outer-sphere complexes dominated by electrostatic attraction. This assumption is supported by other experimental studies suggesting that the lanthanides are sorbed as inner-sphere complexes at the variably charged surfaces of metal oxides (e.g. Rabung et al. (1998), for Eu(III) on hematite and Yb on quartz).

6. Conclusion

REE sorption on kaolinite and Na-montmorillonite not only depends on the nature of the clay minerals and on pH, but also on the ionic strength. At 0.5 M, both minerals exhibit the same pH-dependent REE sorption edge. At this high ionic strength, REE chemisorption alone takes place on amphoteric sites at the edge of particles to compensate for the variable charge. At 0.025 M, the measured K_D is influenced by the CEC of the minerals. At this low ionic strength, the permanent charge is compensated at low pH by a physical sorption of REEs on the basal planes. For smectite, the K_D decrease observed in the basic pH range can be explained by a particular arrangement of the particles (basal plane/edge attraction). A fractionation is observed between the HREEs and the LREEs at high ionic strength, with the HREEs being more strongly sorbed than the LREEs. These results can be interpreted in terms of the surface chemistry of clay minerals, with two coexisting types of surface charge, permanent (at the basal planes for smectite or the gibbsite planes for kaolinite) and variable charge at the edges. The fractionation observed at high ionic strength could be interpreted as either a consequence of a competition effect with sodium or the formation of inner-sphere complexes. Both processes could enhance the sorption of HREE according to the lanthanide contraction. To improve our understanding of the elementary processes controlling the REE sorption processes, spectroscopy measurements are required

to characterize the nature of the surface complexes. A Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLFS) study is currently under way to evaluate the speciation of surface-sorbed REEs.

These results also show up the difficulty of using the REEs as natural tracers. The different behaviours observed at the two ionic strengths suggest a modification of REE distribution takes place between matter in suspension and in solution during the mixing of waters of different salinity in estuaries. Moreover, the effect of a colloidal phase on the distribution of REEs between the different phases (solid and solution) is not yet elucidated and remains a very important question. A large amount of microkaolinite seems to be present in the inorganic colloid phase, and may play an important role in the confinement of REE in solution (Deberdt, 2000). Therefore, the results obtained in this study could contribute to a better understanding of the colloid phase effect in oceans and rivers.

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