

# Europium retention onto clay minerals from 25 to 150 °C: Experimental measurements, spectroscopic features and sorption modelling

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## Abstract

The sorption of Eu(III) onto kaolinite and montmorillonite was investigated up to 150 °C. The clays were purified samples, saturated with Na in the case of montmorillonite. Batch experiments were conducted at 25, 40, 80 and 150 °C in 0.5 M NaClO<sub>4</sub> solutions to measure the distribution coefficients (K<sub>d</sub>) of Eu as a trace element (<10<sup>-6</sup> mol/L) between the solution and kaolinite. For the Na-montmorillonite, we used K<sub>d</sub> results from a previous study [Tertre, E., Berger, G., Castet, S., Loubet, M., Giffaut, E., 2005. Experimental study of adsorption of Ni<sup>2+</sup>, Cs<sup>+</sup> and Ln<sup>3+</sup> onto Na-montmorillonite up to 150 °C. *Geochim. Cosmochim. Acta* **69**, 4937–4948] obtained under exactly the same conditions. The number and nature of the Eu species sorbed onto both clay minerals were investigated by time resolved laser fluorescence spectroscopy (TRLFS) in specific experiments in the same temperature range. We identified a unique inner-sphere complex linked to the aluminol sites in both clays, assumed to be =AlOEU<sup>2+</sup> at the edge of the particles, and a second exchangeable outer-sphere complex for montmorillonite, probably in an interlayer position. The K<sub>d</sub> values were used to adjust the parameters of a surface complexation model (DLM: diffuse layer model) from 25 to 150 °C. The number of Eu complexes and the stoichiometry of reactions were constrained by TRLFS. The acidity constants of the amphoteric aluminol sites were taken from another study [Tertre, E., Castet, S., Berger, G., Loubet, M., Giffaut, E. Acid/base surface chemistry of kaolinite and Na-montmorillonite at 25 and 60 °C: experimental study and modelling. *Geochim. Cosmochim. Acta*, in press], which integrates the influence of the negative structural charge of clays on the acid/base properties of edge sites as a function of temperature and ionic strength. The results of the modelling show that the observed shift of the sorption edge towards low pH with increasing temperature results solely from the contribution of the =AlOEU<sup>2+</sup> edge complexes. Finally, we successfully tested the performance of our model by confronting the predictions with experimental K<sub>d</sub> data. We used our own data obtained at lower ionic strength (previous study) or higher suspension density and higher starting concentration (TRLFS runs, this study), as well as published data from other experimental studies [Bradbury, M.H., Baeyens, B., 2002. Sorption of Eu on Na and Ca-montmorillonite: experimental investigations and modeling with cation exchange and surface complexation. *Geochim. Cosmochim. Acta* **66**, 2325–2334; Kowal-Fouchard, A., 2002. Etude des mécanismes de rétention des ions U(IV) et Eu(III) sur les argiles: influence des silicates. Ph.D. Thesis, Université Paris Sud, France, 330p].

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## 1. Introduction

The radiative effects of nuclear waste are well known to drive an increase of temperature in the vicinity of the

storage site. According to the scenarios developed for the French underground repository design, the temperature of the bentonite barrier would reach 100 °C in the short term, thereafter decreasing with time (ANDRA, 2005). However, a greater rise in temperature, typically up to 150 °C, remains to be considered as an option in evaluating performance. Such a thermal history raises a question

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about the retention of radionuclides on clay minerals at elevated temperatures. Indeed, sorption measurements of radionuclide analogues (lanthanides, Cs, divalent cations, etc.) have so far been mainly carried out at room temperature (Baeyens and Bradbury, 1997; Aja, 1998; Wang et al., 2001; Coppin et al., 2002; Kowal-Fouchard, 2002; Stumpf et al., 2002a,b; Stumpf et al., 2004a; Rabung et al., 2005). These studies point to the existence of two main types of sites, with exchange on interlayer sites and surface complexation on the edges of the particles. These conclusions are based on macroscopic properties (distribution coefficients (Kd) and acidity–basicity) as well as spectroscopic studies. Moreover, numerous studies have focused on evaluating the effect of an aqueous ligand (organic or not) on the sorption of trivalent cations, such as Eu(III) and Am(III), onto clay minerals. All of these studies were performed at room temperature. We can mention, for example, the studies of Pshinko et al. (2004) and Wang et al. (2001), which deal with the effect of fulvic acid on the sorption of Eu(III) onto clays. In addition, Sakuragi et al. (2002) studied the effect of both calcium ions and humic acid on the sorption of Am(III)/Eu(III) onto kaolinite. The main conclusions of these room-temperature studies is that humic/fulvic acid, as well as an aqueous ligand, can either increase or decrease the distribution coefficients of Eu(III)/Am(III), depending on pH and ionic strength, the nature of sorbent and the nature of the humic/fulvic substances or aqueous ligand. Therefore, to study the temperature dependence of lanthanide sorption onto clays, we performed our experiments in a simple electrolyte, such as NaClO<sub>4</sub>, containing any competitor substances.

Some rare studies performed at higher temperatures with clay minerals (Angove et al., 1998; Tertre et al., 2005) show a weak but measurable thermal effect on the Kd of di- and trivalent cations. The authors found that the surface complexation increases slightly with increasing temperature, as generally observed for simple oxides, while there is only a negligible influence on the exchange processes at interlayer positions. On the other hand, Bauer et al. (2005) failed to detect any influence of temperature (up to 80 °C) on the pH dependence of europium sorption onto montmorillonite. Even in the spectroscopic field, there are very few studies characterizing sorbed lanthanides at elevated temperature. To our knowledge, only three research groups have developed specific experimentation for TRLFS measurements (time resolved laser fluorescence spectroscopy) at high temperature (see Kimura et al., 2002; Bauer et al., 2005; Lindqvist-Reis et al., 2005). For experiments in aqueous solution, the first and second group show clearly that the change in hydration of trivalent cations with increasing temperature can be observed via the fluorescence properties of these elements. We develop these results in the section “TRLFS reference spectrum of aqueous Eu between 25 and 150 °C”. On the other hand, using Eu sorption experiments onto smectite, Bauer et al. (2005) show that—at 60 and

80 °C—europium forms complexes with aqueous organic matter. According to these authors, this organic material was released by the HDPE containers used in the experiments. Therefore, because of this artefact, they could not accurately attribute the temperature dependence of fluorescence properties of Eu(III).

Our previous experimental studies (Tertre et al., 2005; Tertre et al., this issue) provided Kd values up to 150 °C for mono-, di- and trivalent metals, and proposed an original acidity–basicity model applicable up to 60 °C. For the room-temperature results, the data were again interpreted in terms of complexation and exchange processes. We considered silanol and aluminol sites in the acidity–basicity model, rather than weak and strong sites.

The objective of this study was to develop a model for the sorption of lanthanides (acting as chemical analogues of trivalent actinides) onto two contrasted clay minerals, kaolinite and Na-montmorillonite. This model is based on the previously cited studies, while presenting some additional Kd measurements and specific spectroscopic analyses. We focus here on the retention of Eu(III), since this element is one of the lanthanides available for spectroscopic analysis.

In this study, we present (a) new Kd measurements for sorption onto kaolinite up to 150 °C, (b) time-resolved-laser-fluorescence-spectroscopy (TRLFS) results for kaolinite, montmorillonite and single oxides at room temperature, as well as at 80 and 150 °C, (c) the sorption model inferred from these data and previously published measurements (Baeyens and Bradbury, 1997; Bradbury and Baeyens, 2002; Kraepiel et al., 1999; for trivalent and divalent cations; Liu et al., 2003; for caesium). The advantage of our model is that it makes use of an original acidity–basicity model and considers spectroscopic constraints. Thus, it can even be applied at high temperature, since previous spectroscopic data are only available at room temperature: e.g. Stumpf et al., 2001; for Cm(III) onto kaolinite and montmorillonite; Chisholm-Brause et al., 2004 and Kowal-Fouchard et al., 2004; for Eu(III) and uranyl onto montmorillonite.

## 2. Methods

### 2.1. Materials used for distribution coefficient measurements

Suspensions of kaolinite and Na-montmorillonite were prepared for sorption experiments following the same procedure as presented in Tertre et al. (2005). The kaolinite sample originates from St. Austell (UK), while the montmorillonite was isolated from the bentonite MX-80 and converted into the sodic form. The average grain size of particles is between 0.2–2 μm for both clay minerals, whereas the N<sub>2</sub> BET specific areas of the dried samples are 10 and 24 m<sup>2</sup>/g for kaolinite and Na-montmorillonite, respectively. As in the case of BET surface area, the cationic exchange capacity (CEC) is highly contrasted between the two clays. The exchange site density values range from

3.7  $\mu\text{mol/m}$  for kaolinite to 36  $\mu\text{mol/m}$  for Na-montmorillonite, according to the results reported by Coppin et al. (2002) and Baeyens and Bradbury (1997), respectively.

## 2.2. Distribution coefficient determination

The distribution coefficients ( $K_d$ ) of Eu(III) between kaolinite and 0.5 M  $\text{NaClO}_4$  solution were measured at 25, 40, 80 and 150 °C following the same protocol as presented in Tertre et al. (2005). Briefly, the protocol consists of:

- (1) Initial equilibration of the clay suspension (2.5 g/L) at selected pH, ionic strength and temperature over a period of one week. After one week of reaction at a given temperature, the clay suspension remains stable in term of pH, silica and aluminium aqueous concentrations (see Tertre et al., 2005).
- (2) Addition (without cooling) of 14 lanthanides, each at a concentration of  $10^{-6}$  mol/L. This concentration is similar to that used in the previous studies of Coppin et al. (2002) and Tertre et al. (2005), and is assumed not to exceed the solubility of possible secondary solids, a hypothesis that is discussed in more detail below.
- (3) Three days of reaction at the selected temperature to achieve sorption equilibrium.
- (4) Separation (without cooling) of the aqueous phase from the clay fraction by centrifugation at 2000g for 30 min for the runs at 25 and 40 °C, or by filtration at 0.2  $\mu\text{m}$  for the runs at 80 and 150 °C.
- (5) Analysis of the filtrates by ICP-MS, followed by  $K_d$  determination using mass balance equations for each lanthanide (in particular Eu). Measurements of aluminium and silica contents were also performed to check that clay dissolution was negligible during the runs, assuming no concomitant aluminosilicate precipitation.

We did not perform specific new  $K_d$  measurements for montmorillonite, since the published data in Tertre et al. (2005) were considered sufficiently exhaustive. However, the runs carried out for the spectroscopic measurements in the present study (see next section) provide additional  $K_d$  data for montmorillonite as well as for kaolinite.

## 2.3. Evaluation of possible artefacts

As mentioned in Tertre et al. (2005), all batch experiments were performed in PTFE containers. Sorption onto the walls of the containers was investigated in the presence of clay mineral. The maximum europium retention was found under alkaline conditions (6% at pH 8 and 25 °C). These experiments were performed for a lanthanide initial concentration of  $10^{-7}$  mol/L, which was 10 times lower than the concentration used in the sorption experiments ( $10^{-6}$  mol/L). Therefore, we assumed that the sorption

onto the containers was negligible under acidic and neutral conditions, and that the protocol was valid under alkaline conditions with a 6% confidential interval. Moreover, to ensure that fluoride ions, a strong ligand for aqueous lanthanides, were not released by the PTFE containers during experiments, some specific “blank” measurements were carried out at 25 and 150 °C using a pure 0.025 M  $\text{NaClO}_4$  background electrolyte solution. After 10 days (duration of the total batch experiments), the aqueous fluoride concentrations did not exceed  $10^{-7}$  mol/L, corresponding to the detection limit of the ionic chromatographic method used.

## 2.4. Evaluation of dissolution effects

Sorption measurements assume that the reactive sites are stable with respect to the solution during the duration of the process. This question becomes important at temperature as high as 150 °C, as well as the possible modification of the clay surface by sorption or coating of secondary phases. Even if the clay material is not transformed into another more stable phase within 10 days at 100 °C (Beaufort et al., 2001), the dissolution of a fraction of the particles is almost certain during the experimental runs, at least at elevated temperature. In a previous study using the same experimental protocol, Tertre et al. (2005) reported that dissolution reactions consume 6% of the smectite mass at 150 °C under alkaline conditions. On the other hand, Zysset and Schindler (1996) and Huertas et al. (1999) found, respectively, that smectite and kaolinite dissolution at 25 °C is negligible (around 0.3% in mass for both minerals). Nevertheless, Carroll and Walther (1990) mentioned that this value increases significantly with temperature (9% for kaolinite at 80 °C). Although dissolution is likely to occur at the same reactive site as sorption, its consequence is probably negligible during the development of fresh surfaces, because the dissolution rate is slower than the sorption process. We can assume that the sole effect of dissolution is a limited modification of the V/M ratio, which is nevertheless included in the calculation of  $K_d$  uncertainties. However, the worst scenario is incongruent dissolution associated with the precipitation of secondary phases, which can then form a coating onto clay surfaces. In this case, the secondary phases can compete with the clay material for lanthanide retention. To avoid incongruent dissolution, and to minimize its extent, we shortcut the first stage of reaction far from equilibrium by using starting solutions previously equilibrated with respect to quartz. This method was successfully used in Berger et al. (2002) for approaching chemical equilibrium with the aluminosilicate K-feldspar up to 300 °C, but without precipitation of secondary clay or hydroxides (which are common products when reactions are started very far from equilibrium). Then, we waited one week before adding the lanthanide-bearing solution and beginning the sorption process. According to methodological data reported in Tertre et al. (2005), most of the dissolution occurs during the first few days of equilibration

before the sorption stage. Consequently, we assume that sorption sites are not significantly perturbed by dissolution during the sorption stage, even at 150 °C.

### 2.5. Sample preparation for TRLFS measurements

The TRLFS spectrum and fluorescence times were acquired on clay suspensions at 25, 80 and 150 °C. The suspensions were prepared at various pH in 0.5 M NaClO<sub>4</sub> solutions (see Table 1 for characteristics of each sample). The protocol used for the sample preparation was similar to that developed for the sorption experiments, but with some specific adaptations to enhance the intensity of the TRLFS signal. As in the “sorption experiments”, the suspensions were left to react over several days before the addition of europium to the system. The equilibration lasted three days in standard PTFE containers kept at constant temperature in ovens. Compared with the “sorption experiments”, the main differences in the sample preparation protocol were as follows; a solid/liquid ratio taken as equal to 25 g/L (instead of 2.5 g/L), a starting europium concentration of 10<sup>-5</sup> mol/L (instead of 10<sup>-6</sup> mol/L), and the use of standard PTFE containers at all temperatures. After completion of the sorption, to concentrate the solid fraction and consequently enhance the TRLFS signal, the containers were centrifuged for 5 min in preheated supports with thermal insulating properties (PTFE). The concentrated solutions were sampled and immediately introduced into preheated quartz tubes, which were sealed by a blowing technique and placed in a specific furnace within the optical device. The furnace maintained the sample at the desired temperature, while allowing the laser beam to traverse the quartz tube.

Because the PTFE containers were not equipped with either injectors or internal filters, we briefly reduced the temperature during the 150 °C runs (for 5 min at 90 °C), to allow the addition of Eu and sampling of the suspension. The centrifugation step also involved a short drop in temperature. Despite our efforts to minimize cooling during the 5 min of centrifugation, we measured a temperature drop

to 80–90 °C for the 150 °C runs and down to 74 °C for the 80 °C-runs.

The TRLFS measurements were carried out with a tunable OPO Panther Continuous laser operating at 465 or 393 nm. The detection was performed by a Spectra-Pro-300 monochromator (Acton Research Corporation) coupled with a CCD camera (Princeton Instruments). The emission spectrum of Eu(III) was recorded in the range 550–650 nm using the software Winspec (Princeton Instruments). For measuring the emission decay, the delay time between laser pulse and camera gating was scanned with time intervals between 10 and 300 μs. To determine the fluorescence times of the sorbed species, the decay profiles were then fitted to (multi)-exponential laws.

Table 1 summarizes the experimental parameters for clay samples analysed by the TRLFS technique. As previously mentioned, the initial concentration of Eu(III) in these samples, before sorption, was close to 10<sup>-5</sup> mol/L. This is nearly 10 times higher than the value of 10<sup>-6</sup> mol/L used for experiments performed without spectroscopic study. Consequently, these samples were duplicated in order to measure the distribution coefficients. The K<sub>d</sub> values measured under such conditions (25 g/L and C<sub>Eu</sub> = 10<sup>-5</sup> mol/L), as reported in Table 1, are similar to those obtained with lower initial concentration and solid/solution ratio (2.5 g/L and C<sub>Eu</sub> = 10<sup>-6</sup> mol/L). The fact that the K<sub>d</sub> values are independent of the aqueous concentration suggests that the sorption sites are not saturated (linear region on a Langmuir isotherm).

To achieve a better characterization of the surface sites involved in the sorption of europium onto clays, we compared the previous results with TRLFS measurements performed for europium experimentally sorbed onto single oxides: γ-alumina (γ-Al<sub>2</sub>O<sub>3</sub>), gibbsite (Al(OH)<sub>3</sub>), quartz (SiO<sub>2</sub>) and amorphous silica. The γ-alumina sample provided by Merck® (ref: 90) has grain size ranging from 63 to 200 μm and a BET surface area of 135 m<sup>2</sup> g<sup>-1</sup> (Marmier, 1994). The gibbsite sample was previously used by Castet et al. (1993), and is a pure synthetic compound (α-Al(OH)<sub>3</sub> obtained from Riedel®-De Haën® AG SEELZE, Hannover-2504301). The quartz sample is the 50–125 μm size

Table 1  
Experimental conditions for samples of clay minerals analysed by TRLFS

No.	Sorbent	T (°C)	pH equi.	% sorbed	Measured logK <sub>d</sub>	Predicted logK <sub>d</sub>
25Kaol1	Kaolinite	25	4.5	44	1.5	1.4
25Kaol2	Kaolinite	25	7.7	96	2.6	2.5
80Kaol1	Kaolinite	80	3.9	39	1.4	1.4
80Kaol2	Kaolinite	80	6.1	95	2.8	2.5
150Kaol1	Kaolinite	150	4	56	1.7	1.8
150Kaol2	Kaolinite	150	5.1	100	3.5	3.0
25Mont1	Na-montmor.	25	3	50	1.6	1.7
25Mont2	Na-montmor.	25	7.1	100	3.6	3.5
80Mont1	Na-montmor.	80	2.7	71	2	1.9
80Mont2	Na-montmor.	80	4.2	100	4.7	4.6
150Mont1	Na-montmor.	150	2.6	94	2.8	2.6
150Mont2	Na-montmor.	150	3.6	100	4.6	4.4

fraction of the sample previously used by Gautier et al. (2001), with a BET surface of 0.061 m<sup>2</sup>/g. The amorphous silica is a silica powder distributed by Baker<sup>®</sup>. The runs performed with single oxides were conducted at 25 and 80 °C, but only at neutral pH and using suspensions prepared in 0.5 mol/L NaClO<sub>4</sub> solutions having a solid/solution ratio equal to 25 g/L. The rest of the protocol was identical to the clay experiments.

### 3. Experimental results and discussion

#### 3.1. Sorption data

Fig. 1A and B show the K<sub>d</sub> values for europium sorption onto kaolinite and Na-montmorillonite obtained in 0.5 M NaClO<sub>4</sub> suspensions as a function of pH (2.5–9.5)

and temperature (25, 40, 80 and 150 °C). Data are similar for the other lanthanides (not shown). Previous studies using Eu alone (Coppin, 2002; Tertre, 2005) yield the same K<sub>d</sub> values, suggesting that the results were unaffected by possible competition between the lanthanides at this concentration level (<10<sup>-6</sup> mol/L). For both minerals, we also report Eu data obtained at 25 °C by Coppin et al. (2002), who used similar procedures and clay samples. All these data show that the Eu(III) sorption is clearly pH dependent, with a net increase of K<sub>d</sub> with increasing pH. This behaviour is observed for both minerals and at all investigated temperatures. The strong influence of pH on K<sub>d</sub> is well known and can be explained by the contribution of sorption on sites exhibiting amphoteric properties at the edges of particles, which occurs in addition to sorption on the exchange sites. Therefore, two different sorption

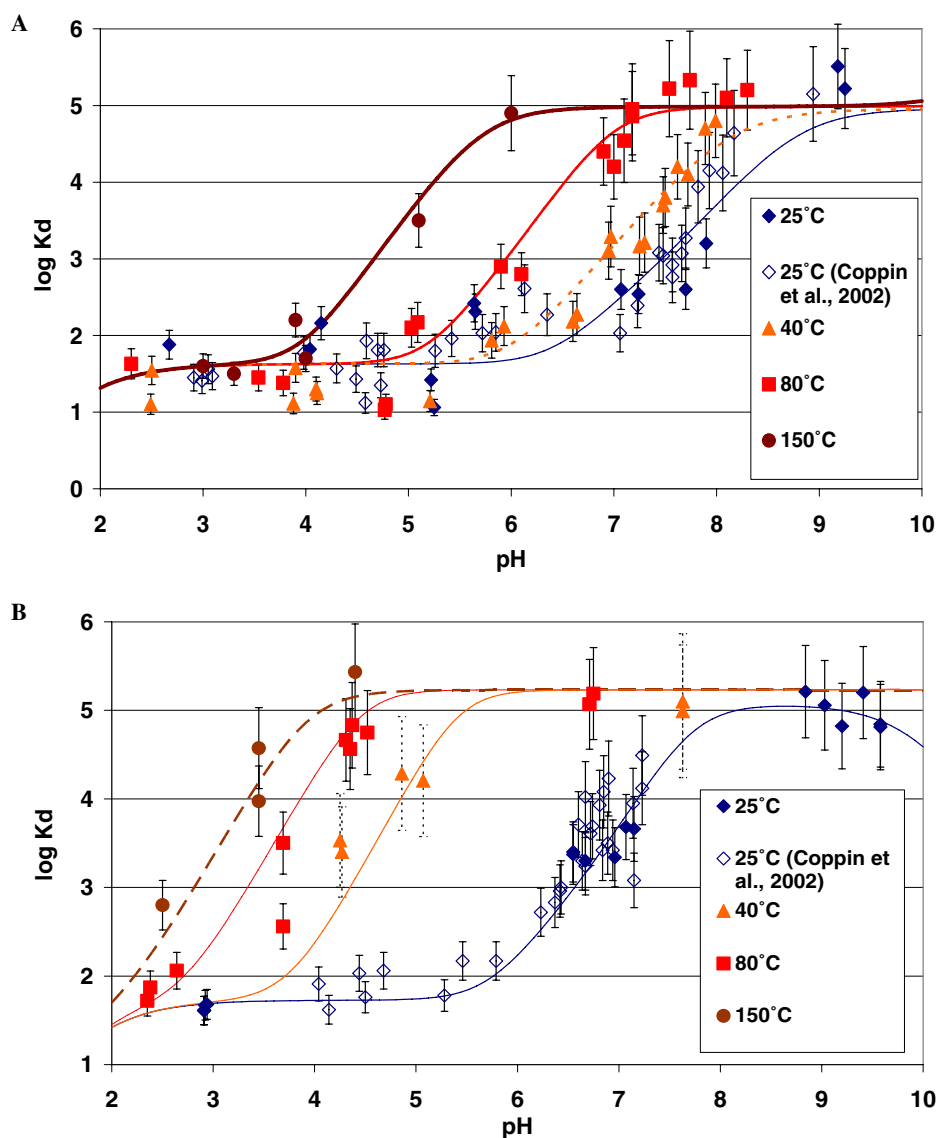


Fig. 1. Logarithm of the distribution coefficients of Eu between kaolinite (A) and 0.5 M NaClO<sub>4</sub> solutions at various temperatures and pH, compared with previous data on Na-montmorillonite (B) under the same conditions. Symbols refer to experimental measurements whereas curves indicate model results.

mechanisms are proposed in the literature: (1) exchange reactions with little or no dependence on pH, which dominate sorption at low pH, and (2) strongly pH-dependent surface complexation reactions, which dominate sorption under neutral and alkaline conditions (e.g. Baeyens and Bradbury, 1997; Bradbury and Baeyens, 2002; Kraepiel et al., 1999). The temperature increase leads to a shift of the sorption curves towards lower pH, which is more pronounced for the Na-montmorillonite than for kaolinite. As previously mentioned for the Na-montmorillonite in Tertre et al. (2005), we observe that exchange reactions are practically temperature-independent, whereas surface complexation reactions are endothermic. Nevertheless, for both minerals, the Kds obtained at 150 °C are very high even at acidic pH (pH > 4.5 for kaolinite and pH > 4 for Na-montmorillonite). This strong Kd increase at 150 °C, which contrasts with the behaviour observed at lower temperatures, raises questions about the nature of the retention at elevated temperature. It is debateable whether there is any diffusion of Eu inside the clay structure or precipitation of Eu-rich phases during the runs. The TRLFS spectroscopic analyses presented below, which allow a better characterization of the nature of Eu retention, are well suited to address this question.

### 3.2. TRLFS reference spectrum of aqueous Eu between 25 and 150 °C

For aqueous europium, the TRLFS method is usually performed at room temperature (Moulin et al., 1999; Choppin and Peterman, 1998; Plancque et al., 2003). To our knowledge, only two published studies have addressed

the acquisition and interpretation of fluorescence spectra of aqueous trivalent cations (Eu<sup>3+</sup> or Cm<sup>3+</sup>) at high temperature: Kimura et al. (2002) up to 227 °C (500 K) and Lindqvist-Reis et al. (2005) up to 200 °C. We therefore began by recording fluorescence spectra and lifetimes of aqueous europium between 25 and 150 °C in 0.5 M NaClO<sub>4</sub> solutions. The experiments were conducted using the same procedure as for the sorption experiments. In addition, thermodynamic calculations were carried out to identify the speciation of aqueous europium under the conditions of TRLFS acquisition. These calculations were performed with the computer code CHESS<sup>®</sup> (Van der Lee and Windt, 2002) and using the reaction constants reported in Table 2. At this stage, we do not allow precipitation in the calculations. For the purposes of calculation, we assumed NaCl as background electrolyte because of the lack of thermodynamic data for NaClO<sub>4</sub> at high temperature. The dissociation constants related to H<sub>2</sub>O, NaCl, NaOH and HCl are the same as those reported in Tertre et al. (2005), whereas the constants for hydrolysed and carbonated europium are reported from the studies of Turner et al. (1981); Wood (1990); Johnson et al. (1992) and Spahiu and Bruno (1995). Calculations were performed for 0.5 M NaCl solutions containing 10<sup>-5</sup> mol/L of total aqueous Eu(III) and with pH varying from 3 to 10. Although our experiments were run in hermetically sealed systems to prevent contamination by atmospheric CO<sub>2</sub>, the containers were opened for a few minutes to inject the europium and transfer the concentrated suspensions into the quartz tubes. Thus, due to possible minor contamination by CO<sub>2</sub>, we carried out speciation calculations assuming two boundary cases: absence of CO<sub>2</sub> contamination and full equilibrium with the

Table 2  
Thermodynamic constants used for calculating the aqueous speciation of europium

T (°C)	log K <sub>H<sub>2</sub>O</sub> (Tanger and Helgeson, 1997)	log K <sub>NaCl</sub> (Helgeson et al., 1981)	log K <sub>NaOH</sub> (reported values of Castet et al., 1993)	log K <sub>HCl</sub> (Ruaya and Seward, 1987)
<i>(A) Dissociation constants for H<sub>2</sub>O, NaCl, NaOH and HCl</i>				
25	-13.995	0.925	0.455	0.67
50	-13.271	1.023	0.336	0.73
90	-12.437	0.986	0.145	0.64
100	-12.259	0.977	0.098	0.62
150	-11.637	0.733	-0.141	0.41
Reference	Reaction	log K 25 °C	log K 150 °C	
<i>(B) Constants for aqueous and solid europium species</i>				
Spahiu and Bruno (1995)	Eu <sup>3+</sup> + H <sub>2</sub> O = Eu(OH) <sup>2+</sup> + H <sup>+</sup>	-7.8	-3.7	
..	Eu <sup>3+</sup> + 2H <sub>2</sub> O = Eu(OH) <sub>2</sub> <sup>+</sup> + H <sup>+</sup>	-16.4	-8.7	
..	Eu <sup>3+</sup> + 3H <sub>2</sub> O = Eu(OH) <sub>3(aq)</sub> + 3H <sup>+</sup>	-25.2	-13.7	
Turner et al. (1981)	Eu <sup>3+</sup> + 4H <sub>2</sub> O = Eu(OH) <sub>4</sub> <sup>+</sup> + 4H <sup>+</sup>	-35.3	-21.5	
Wood (1990)	Eu <sup>3+</sup> + CO <sub>3</sub> <sup>2-</sup> = Eu(CO <sub>3</sub> ) <sup>+</sup>	-8.0	—	
..	Eu <sup>3+</sup> + 2CO <sub>3</sub> <sup>2-</sup> = Eu(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup>	-12.9	—	
Johnson et al. (1992)	Eu <sup>3+</sup> + HCO <sub>3</sub> <sup>-</sup> + H <sub>2</sub> O = EuOHCO <sub>3(aq)</sub> + 2H <sup>+</sup>	-8.5	—	
..	Eu <sup>3+</sup> + 2HCO <sub>3</sub> <sup>-</sup> + H <sub>2</sub> O = EuOH(CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup> + 3H <sup>+</sup>	-15.2	—	
..	Eu <sup>3+</sup> + HCO <sub>3</sub> <sup>-</sup> + 2H <sub>2</sub> O = Eu(OH) <sub>2</sub> CO <sub>3</sub> <sup>-</sup> + 3H <sup>+</sup>	-17.8	—	
Johnson et al. (1992)	Eu <sup>3+</sup> + 3H <sub>2</sub> O = Eu(OH) <sub>3(s)</sub> + 3H <sup>+</sup>	-15.3	-9	
..	2Eu <sup>3+</sup> + 3HCO <sub>3</sub> <sup>-</sup> = Eu <sub>2</sub> (CO <sub>3</sub> ) <sub>3(s)</sub> + 3H <sup>+</sup>	-5.8	—	
Spahiu and Bruno (1995)	Eu <sup>3+</sup> + CO <sub>3</sub> <sup>2-</sup> + H <sub>2</sub> O = Eu(OH)(CO <sub>3</sub> ) <sub>(s)</sub> + H <sup>+</sup>	-7.8	—	

atmosphere. In both cases, at 25 °C and pH 3–7, the sole significant species of Eu(III) in solution is  $\text{Eu}^{3+}$ . At pH 7–8, the main species is  $\text{EuCO}_3^+$  if the solution is equilibrated with the atmospheric  $\text{CO}_2$  ( $p\text{CO}_2 = 10^{-3.5}$  atm), whereas the two species  $\text{Eu}^{3+}$  and  $\text{EuOH}^{2+}$  coexist in the absence of  $\text{CO}_2$  contamination. In any case, whatever its absolute concentration, the proportion of hydrolysed species increases with temperature at constant pH. As an example, the proportion of  $\text{Eu}(\text{OH})_{3\text{aq}}$  is nearly equal to 0% at 150 °C and pH 3, but rises sharply with increasing pH: 16% at pH 5 and 80% at pH 7, while  $\text{Eu}^{3+}$  dominates at 25 °C below pH 7. Moreover, we also note an increase in the proportion of carbonate species such as  $\text{EuCO}_3^+$  with increasing temperature, since  $\text{CO}_2$  is less soluble at high than at low temperatures. Consequently, even if  $\text{Eu}^{3+}$  is the main Eu(III) species at 25 °C over the entire pH range investigated (pH 3–7), this is not necessarily the case at higher temperature since hydrolysed and carbonate species can become preponderant. Fig. 2 reports the results of the speciation calculations performed at 25 and 150 °C as a function of pH and in the case of  $p\text{CO}_2 = 0$  atm. In comparison with Fig. 2A and B clearly show a shift of the percentages of hydrolysed species towards lower pH at 150 °C.

Then, in a second stage of the speciation calculations, we include the precipitation of mineral phases. As expected, the thermodynamic calculations indicate an oversaturation of Eu hydroxides and carbonates (in the  $\text{CO}_2$  system) under alkaline conditions (pH > 7.5 at 25 °C). For this reason, the subsequent TLRFS measurements were performed

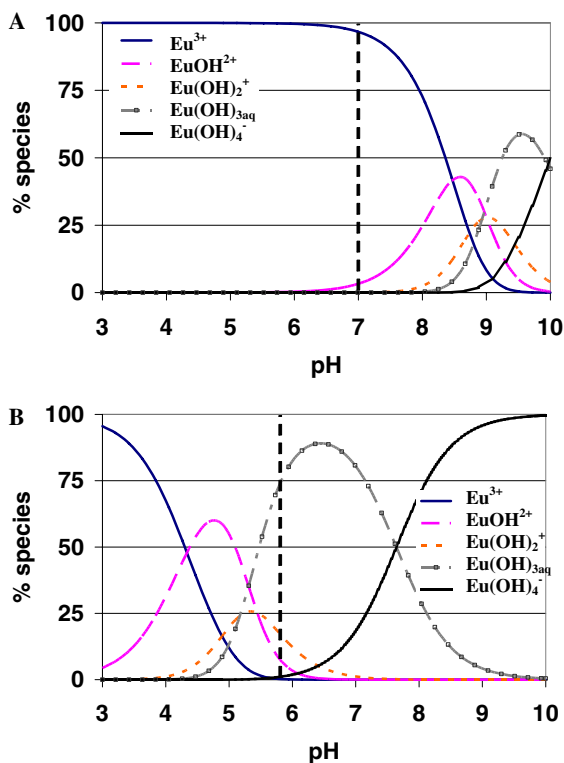


Fig. 2. Speciation of  $10^{-5}$  mol/L Eu(III) in 0.5 M  $\text{NaClO}_4$ ,  $\text{CO}_2$ -free solutions at 25 °C (A) and 150 °C (B). The vertical dotted line shows the value of neutral pH (5.8 at 150 °C, cf. 7.0 at 25 °C).

at lower pH, outside the stability range of these secondary phases.

Fig. 3 presents fluorescence spectra of Eu(III) in 0.5 M  $\text{NaClO}_4$  solutions at pH 3, for temperatures of 25, 80 and 150 °C. Spectra are characterized by two peaks, at 593 and 617 nm, corresponding to transitions from the excited state at  $17,374 \text{ cm}^{-1}$  ( $^5\text{D}_0$ ) to ground states at 374 and  $1036 \text{ cm}^{-1}$  ( $^7\text{F}_1$  and  $^7\text{F}_2$ ), respectively. The transition at 617 nm is hypersensitive and, as mentioned by Moulin et al. (1999) and Plancque et al. (2003), its intensity depends on the atomic environment of Eu(III). In our experiments at 25 °C, the  $I_{593}/I_{617}$  peak ratio is nearly equal to 1.5. This value is much lower than the range (4–8) reported in Plancque et al. (2003) at the same temperature and for similar conditions. Nevertheless, the same authors also mentioned that the  $I_{593}/I_{617}$  peak ratio could vary widely (even if the main species is always free europium) due to changes in the second co-ordination sphere of europium. Such changes can be caused by interaction with the electrolyte used. For example, the recent study of Rabung et al. (2005) shows that the  $I_{593}/I_{617}$  ratio is equal to 1.66 for free europium in  $\text{CaClO}_4$ , whereas this ratio falls to 1.2 when aqueous europium is complexed with nitrates at pH 3.5. Therefore, the low value of 1.5 obtained here for the  $I_{593}/I_{617}$  ratio can be explained by the presence of small quantities of aqueous nitrates, since the lanthanide stock solutions were conditioned in  $\text{HNO}_3$  4%.

In our experiments, the  $I_{593}/I_{617}$  peak ratio clearly decreases with increasing temperature (see Fig. 3). The same behaviour is observed at higher pH (not shown on the figure). Under acidic conditions (pH 3), the corresponding recorded lifetimes also decrease with temperature, from  $110 \pm 5 \mu\text{s}$  at 25 °C to  $95 \pm 5 \mu\text{s}$  at 150 °C. As mentioned by Kimura et al. (2002) for free aqueous europium, Lindqvist-Reis et al. (2005) for aqueous curium and Kirishima et al. (2004) for aqueous uranyl, both the fluorescence intensity and lifetime show a decrease with increasing temperature. Indeed, Kimura et al. (2002) found that the fluorescence time of free europium in 0.1 M  $\text{HClO}_4$

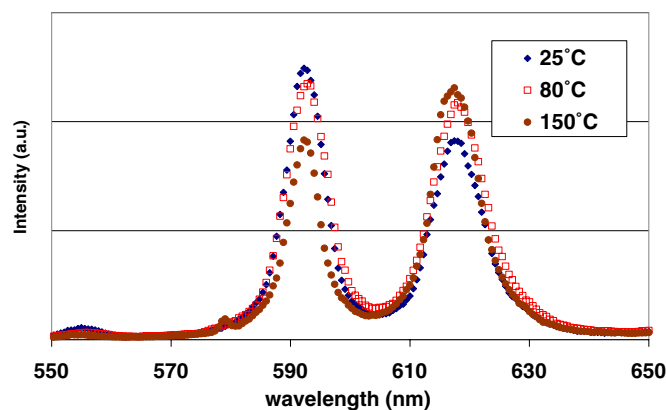


Fig. 3. Fluorescence spectra of aqueous Eu(III) in  $\text{NaClO}_4$  solutions at pH 3 at 25, 80 and 150 °C (similar spectra were recorded at neutral pH 7.0 at 25 °C, 6.5 at 80 °C and 5.8 at 150 °C).

solutions decreases from 111  $\mu\text{s}$  at 20 °C to 100  $\mu\text{s}$  at 130 °C. On the other hand, Lindqvist-Reis et al. (2005), working on the hydration of  $\text{Cm}^{3+}$  in 0.1 M  $\text{HClO}_4$  solutions from 20 to 200 °C, reported that the lifetime of free aqueous curium fell from  $64 \pm 3 \mu\text{s}$  at 25 °C to  $42 \pm 4 \mu\text{s}$  at 200 °C, which they interpreted by a temperature dependant equilibrium between  $[\text{Cm}(\text{H}_2\text{O})_9]^{3+}$  and  $[\text{Cm}(\text{H}_2\text{O})_8]^{3+}$ . Anyway, these authors (*op. cit.*) concluded that the decrease of the lifetime between 20 and 200 °C, under acidic conditions, was not due to changes in the environment around free curium. Their interpretation is consistent with speciation calculations clearly demonstrating that  $\text{Cm}^{3+}$  is the main aqueous form of curium (III) at 20 and 200 °C, when  $\text{pH} < 3$ . Consequently, following the conclusions of Lindqvist-Reis et al. (2005), the slight temperature effect observed here on the aqueous Eu(III) lifetime would not be due to a significant change of the aqueous speciation, and we assume that  $\text{Eu}^{3+}$  is the main species of Eu(III) in solution at pH 3 whatever the temperature.

At pH 7.0 and 25 °C, the lifetimes and fluorescence spectra (not shown here) are both similar to those obtained under acidic conditions. We can conclude that  $\text{Eu}^{3+}$  is the main form of aqueous europium under these conditions, as concluded also for acidic medium. This is in agreement with results of thermodynamic calculations presented in the last section. On the other hand, at neutral pH and 150 °C (pH 5.8) the  $I_{593}/I_{617}$  ratio decreases compared to that measured for the spectrum recorded under acidic conditions ( $I_{593}/I_{617} = 0.8$  at pH 3;  $I_{593}/I_{617} = 0.6$  at pH 5.8). At 150 °C and pH 5.8, the corresponding fluorescence lifetime was equal to  $50 \pm 10 \mu\text{s}$ . In their study performed at room temperature, Plancque et al. (2003) showed that the fluorescence times of  $\text{Eu}^{3+}$  and hydrolyzed complexes are clearly different ( $110 \pm 10 \mu\text{s}$  for  $\text{Eu}^{3+}$ ;  $50 \pm 5 \mu\text{s}$  for  $\text{EuOH}^{2+}$ ;  $40 \pm 5 \mu\text{s}$  for  $\text{Eu}(\text{OH})_2^+$  and  $\text{Eu}(\text{OH})_{3\text{aq}}$ ;  $180 \pm 20 \mu\text{s}$  for  $\text{EuCO}_3^+$ ). Therefore, our measured lifetime of  $50 \pm 10 \mu\text{s}$  can be attributed to the presence of hydrolysed species:  $\text{EuOH}^{2+}$ ,  $\text{Eu}(\text{OH})_2^+$  and  $\text{Eu}(\text{OH})_{3\text{aq}}$ . Given the uncertainty of the measurements ( $\pm 10 \mu\text{s}$ ), we cannot distinguish these three species. Nevertheless, this conclusion is in agreement with the speciation calculations showing that hydrolysed species are the main form of aqueous europium at neutral pH and 150 °C.

Consequently, the results obtained by fluorescence measurements and thermodynamic calculations imply that  $\text{Eu}^{3+}$  is the dominant form of aqueous Eu(III) between pH 3 and 7 at 25 °C, whereas the proportion of hydrolysed species increases not only with pH but also with temperature, becoming the dominant aqueous species above pH 4.3 at  $T = 150$  °C. The relative abundance of  $\text{EuCO}_3^+$  only becomes significant at low temperature and  $\text{pH} > 7$  in solutions equilibrated with the atmosphere. However, these conditions are not representative of our experimental runs, suggesting that carbonate species can be ignored for our purposes.

### 3.3. TRLFS spectrum of sorbed Eu(III)

Previous studies on lanthanide/clay systems using similar experimental protocols (Stumpf et al., 2001, 2002a,b; Coppin et al., 2002; Kowal-Fouchard et al., 2004; Rabung et al., 2005) have shown that Ln(III)-bearing phases do not precipitate during sorption experiments conducted at 25 °C. This was suggested by the consistency of the sorption data and further supported by TRLFS data (Stumpf et al., 2002a,b; Kowal-Fouchard et al., 2004). However, the  $K_d$  values obtained in the present study are much higher at 150 °C and near neutral pH than otherwise at lower temperatures. The possible precipitation of a europium-bearing phase is backed up by the thermodynamic calculations in this study, which also provide information on the saturation state of the solutions. Even at 25 °C, for pH higher than 7, the starting solutions (before Eu sorption is completed) are oversaturated with  $\text{Eu}_2(\text{CO}_3)_3$  and  $\text{Na}_3[\text{Eu}(\text{CO}_3)_3]6\text{H}_2\text{O}$  when equilibrated with the atmosphere, and with  $\text{Eu}(\text{OH})_3$  in absence of  $\text{CO}_2$ . To avoid any ambiguity in interpreting the  $K_d$  values, as well as improve characterization of the complexes sorbed onto the particles, we recorded fluorescence spectra and corresponding lifetimes for concentrated suspensions at 25 and 150 °C, after sorption of  $10^{-5}$  mol/L Eu. For both minerals, we analysed two samples for each temperature. One sample was prepared under acidic conditions, where sorption is independent of pH and mainly explained by an exchange process with the interlayer cations. A second sample was prepared at higher pH, where sorption is close to 100% and generally interpreted by surface complexation (Bradbury and Baeyens, 2002; Kowal-Fouchard, 2002). As mentioned in the methods section, the characteristics of these samples are reported on Table 1. Because most of the europium added to the system is sorbed onto the clays, or at least 50% at low pH, and given the increase of the clay fraction in the concentrated suspension, the monitored spectra are representative of the sorbed Eu, whatever the pH.

Fig. 4A and B present examples of the emission spectra of europium sorbed onto Na-montmorillonite at 25 and 150 °C, respectively, under two different pH conditions. Irrespective of temperature or mineral, the spectra are similar and show the presence of the most intense broad band at 617 nm. These spectra are clearly different from the aqueous Eu(III) spectrum, suggesting significant changes in the atomic environment of europium. Such a behaviour have been already reported in the literature for the clay/europium system at 25 °C under neutral and basic pH conditions, but is still discussed for the acidic conditions. Stumpf et al. (2002a,b) found that the  $I_{593}/I_{617}$  peak ratio is higher than 1 (equal to 2 at pH 3.5), whereas Kowal-Fouchard et al. (2004) found a lower value (equal to 0.6 at pH 3.1). We note that the two last authors recorded their fluorescence spectra with a similar montmorillonite and in 0.025 M  $\text{NaClO}_4$  solutions. While the main species of



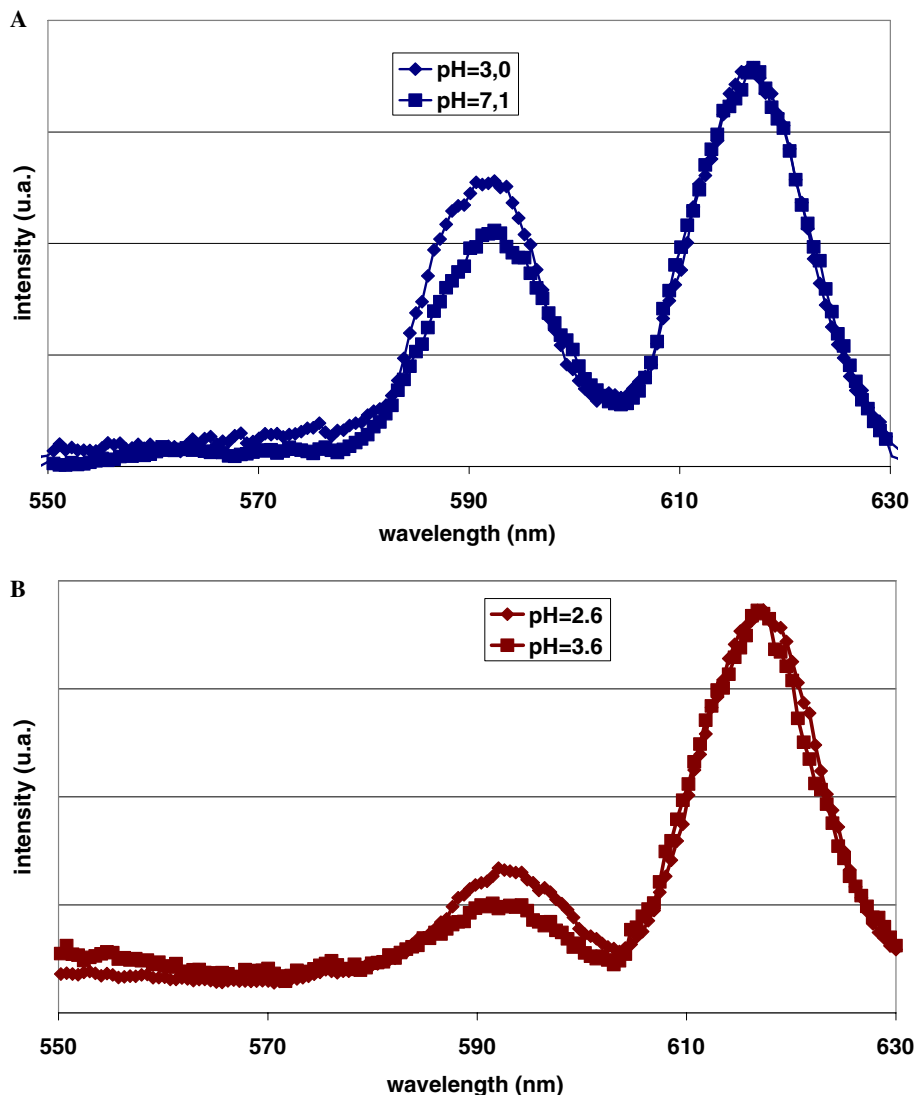


Fig. 4. Fluorescence spectra of Eu(III) sorbed onto Na-montmorillonite at 25 °C (A) and 150 °C (B).

Eu(III) in solution is  $\text{Eu}^{3+}$  in both cited studies, there is a difference in the results obtained by Stumpf et al. (2002a,b) and Kowal-Fouchard et al. (2004), who measured lifetimes of  $110 \pm 5$  and  $75 \pm 10$   $\mu\text{s}$ , respectively. No rational interpretation has yet been advanced for this discrepancy. One possible explanation could be a change in the second coordination sphere around free europium, as mentioned by Plancque et al. (2003). In any case, for our own experiments at 25 °C, the fluorescence spectra and lifetimes recorded under acid conditions for the clay/europium system are close to those observed by Kowal-Fouchard et al. (2004). Indeed, we measured a fluorescence time of  $85 \pm 10$   $\mu\text{s}$  for the montmorillonite/europium system (see Fig. 5) and  $88 \pm 10$   $\mu\text{s}$  for the kaolinite/europium system, whereas Kowal-Fouchard et al. (2004) measured a fluorescence time of 75  $\mu\text{s}$  for a montmorillonite/europium system at similar pH and ionic strength.

Moreover, as shown on Fig. 4A and B, the  $I_{593}/I_{617}$  peak ratio clearly depends on the pH of the suspension

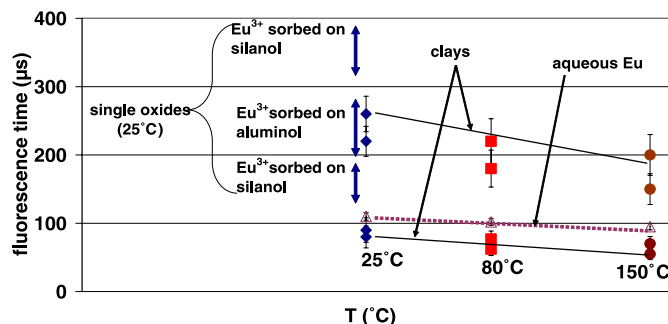


Fig. 5. Fluorescence times of Eu(III) sorbed onto kaolinite (similar results for Na-montmorillonite) as a function of temperature. Lifetimes of aqueous europium obtained in  $\text{NaClO}_4$  solutions at pH 3 are indicated on the figure. Blue arrows indicate lifetimes of europium sorbed onto silanol sites of amorphous silica and aluminol sites of gibbsite or alumina at 25 °C.

and decreases with increasing pH. This behaviour is in good agreement with the results of many studies (Stumpf et al., 2001; Stumpf et al., 2002a,b; Kowal-Fouchard et al., 2004; Rabung et al., 2005). We attribute this effect to a pH-related change in the atomic environment of the sorbed Eu(III), as suggested by the fluorescence time measurements. The decay curves obtained for all samples can be adequately fitted assuming two exponential decays corresponding to two different species. For the montmorillonite/europium system, one of the species has a fluorescence time of  $85 \pm 10 \mu\text{s}$  at  $25^\circ\text{C}$ , which decreases slightly with increasing temperature ( $74 \pm 10 \mu\text{s}$  at  $80^\circ\text{C}$  and  $66 \pm 10 \mu\text{s}$  at  $150^\circ\text{C}$ ). The other species has a fluorescence time equal to  $240 \pm 40 \mu\text{s}$ , which also slightly decreases with increasing temperature ( $200 \pm 40 \mu\text{s}$  at  $80^\circ\text{C}$  and  $170 \pm 45 \mu\text{s}$  at  $150^\circ\text{C}$ ). We should mention that the trends are similar in the kaolinite/europium system. At least at  $25^\circ\text{C}$ , these values are quite different from the lifetime obtained for solid  $\text{Na}_3[\text{Eu}(\text{CO}_3)_3]6\text{H}_2\text{O}$ , but are close to lifetimes for  $\text{Eu}_2(\text{CO}_3)_3(\text{solid})$  and  $\text{Eu}(\text{OH})_3(\text{solid})$  ( $310 \mu\text{s}$ ,  $80 \mu\text{s}$  and  $220 \mu\text{s}$ , respectively, according to Kowal-Fouchard, 2002). Even though europium carbonates and hydroxides can precipitate under neutral and basic conditions, lifetimes of 85 and 240  $\mu\text{s}$  were also recorded at low pH. This suggests that Eu-bearing carbonates or hydroxides did not precipitate during our experiments. The species with a lifetime of 85  $\mu\text{s}$  is assumed to be an outer-sphere complex since its lifetime is close to the value of  $110 \pm 10 \mu\text{s}$  (at  $25^\circ\text{C}$ ) for aqueous  $\text{Eu}^{3+}$  (Choppin and Peterman, 1998). The species with a lifetime of 240  $\mu\text{s}$  is assumed to be an inner-sphere complex bound to the edges of the particles. Regarding the behaviour of  $\text{Eu}^{3+}$  in solution, we assume that the effect of temperature on the lifetimes of the two sorbed complexes does not result from a significant change in the Eu(III) environment. On the contrary, it is more likely related rather to an intrinsic dependence of fluorescence time on temperature. To evaluate the relative abundance of each sorbed species as a function of pH, we calculated the proportion of outer-sphere complexes. Using the fit of the decay profiles, we estimated the proportion of outer-sphere complexes at each studied pH using the ratio between the number of sorbed complexes with a lifetime close to 85  $\mu\text{s}$  (generally specified as an europium outer-sphere complex) and the number of the total surface complexes. For experiments performed at  $25^\circ\text{C}$ , the proportion of outer-sphere complex is always higher than 90% for samples sorbed under acidic conditions (pH 3.0 for montmorillonite; pH 4.5 for kaolinite) and progressively decreases to less than 10% for samples sorbed at higher pH (pH 7.1 for montmorillonite; pH 7.7 for kaolinite). Our calculations show that the proportion of outer-sphere complexes at  $150^\circ\text{C}$  is always less than 20%, even under acidic conditions (pH 2.6 for montmorillonite; pH 4 for kaolinite), and then decreases below 5% at higher pH.

At this stage, we can draw three conclusions:

- For both mineral surfaces, adsorption is the sole process of Eu retention at the studied temperatures.
- Two sorbed species are detected for all samples, whatever the temperature. An outer-sphere complex is dominant under acidic conditions, and is assumed to be exchanged with the interlayer cations of the clay mineral. The second species, an inner-sphere complex, is predominant at higher pH, and is probably bound onto the edges of the particles.
- The nature of the complexes does not change with temperature, although all of the recorded lifetimes decrease slightly with increasing temperature.

As mentioned above, the lifetime of 240  $\mu\text{s}$  measured at  $25^\circ\text{C}$  (i.e. 170  $\mu\text{s}$  at  $150^\circ\text{C}$ ) corresponds to an inner-sphere complex and reflects the exclusion of water molecules in the first coordination sphere of Eu(III). According to the formula of Kimura et al. (1996), a lifetime of 240  $\mu\text{s}$  at  $25^\circ\text{C}$  would correspond to approximately four water molecules in the first coordination sphere of Eu(III). To ascertain the nature of the surface sites involved (silanol or aluminol), we carried out comparisons with spectra acquired on simple oxides. Although we do not attribute an additive property to former oxides, we assume that the single oxides and former oxides of an aluminosilicate have lifetimes of the same order of magnitude. As described in the experimental section, we performed some experiments at 25 and  $80^\circ\text{C}$  to study the sorption of Eu(III) onto simple oxides: alumina ( $\gamma\text{-Al}_2\text{O}_3$ ), gibbsite ( $\alpha\text{-Al}(\text{OH})_3$ ), quartz ( $\text{SiO}_2$ ) and solid amorphous silica. The runs were conducted at 25 and  $80^\circ\text{C}$  at neutral pH (7.0 at  $25^\circ\text{C}$ ; 6.3 at  $80^\circ\text{C}$ ), where there is known to be almost complete sorption of trivalent metals (Kosmulski, 1997; Rabung et al., 2000; Wang et al., 2000; Stumpf et al., 2001; Kowal-Fouchard et al., 2004). Under such pH conditions, sorption is mainly attributed to surface complexation on aluminol sites (for alumina and gibbsite) or silanol sites (for quartz and amorphous silica). In addition, we tested two different oxides for each type of site (aluminol or silanol) to evaluate the influence of the sorbent crystallographic structure on the lifetime of the sorbed species. Table 3 reports the characteristics of these samples and the corresponding measured lifetimes. In the case of europium sorption onto gibbsite and alumina, we detected only one sorbed species for both minerals with a lifetime close to 220  $\mu\text{s}$  at  $25^\circ\text{C}$ . This lifetime is in good agreement with the values reported in Rabung et al. (2000) and Kowal-Fouchard (2002) for trivalent metals sorbed onto  $\gamma$ -alumina (235  $\mu\text{s}$  and  $250 \pm 30 \mu\text{s}$ , respectively). Fluorescence time measurements are similar for  $\gamma$ -alumina and  $\alpha$ -gibbsite. This behaviour is not surprising because  $\gamma$ -alumina is unstable in aqueous solutions at high temperature (Laiti et al., 1998), and therefore its surface consists of sites similar to those involved in the case of  $\alpha$ -gibbsite. On the other hand, two lifetimes were measured at  $25^\circ\text{C}$  with quartz and amor-

Table 3  
Experimental conditions for samples of simple oxides

No.	Sorbent	$T$ (°C)	$\text{pH}_{\text{eq}}$	Number of sorbed species	Corresponding fitted lifetimes ( $\mu\text{s}$ )
25gibbs	Gibbsite	25	6.9	1	$220 \pm 30$
80gibbs	Gibbsite	80	5.9	1	$195 \pm 20$
25alum	$\gamma$ -Alumina	25	6.9	1	$232 \pm 30$
80alum	$\gamma$ -Alumina	80	6.1	1	$194 \pm 40$
25quar	Quartz	25	8.0	2	$41 \pm 20$ $352 \pm 30$
80quar	Quartz	80	6.5	2	$30 \pm 20$ $302 \pm 40$
25amorp-sil	Amorphous silica	25	7.2	2	$137 \pm 20$ $335 \pm 40$
80amorp-sil	Amorphous silica	80	6.1	2	$113 \pm 20$ $290 \pm 40$

For TRLFS analysis, the best fit of the decay profiles is obtained with one lifetime for the gibbsite and alumina system, whereas two lifetimes are needed for the quartz and amorphous silica systems.

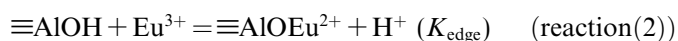
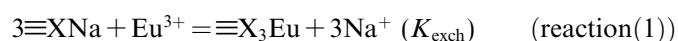
phous silica (see Table 3). We observe a short fluorescence time close to  $41 \pm 20 \mu\text{s}$  at 25 °C in the quartz/europium system. Such a short lifetime is very difficult to explain in terms of sorption and may be due to an inappropriate fitting of the lifetime data. Indeed, for this same system, Kowal-Fouchard (2004) measured two fluorescence times close to 130 and 350  $\mu\text{s}$ . Therefore, although we report the lifetime data obtained here for quartz/europium, the results are not used in the following discussion. On the other hand, the lifetimes measured in the amorphous silica/europium system suggest the existence of two distinct sorbed species. This behaviour is in good agreement with the results of Kowal-Fouchard et al. (2004). Indeed, these authors interpret the sorption of Eu onto amorphous silica (silica 60H Merck) at 25 °C by the presence of two sorbed complexes. A first species appears at pH 6–7 with a lifetime of  $130 \pm 20 \mu\text{s}$ , whereas a second species appears at higher pH with a lifetime of  $350 \pm 50 \mu\text{s}$ . For all the oxide samples, the lifetimes decrease slightly with increasing temperature as observed previously with clay suspensions.

The similar lifetimes for europium sorbed onto  $\text{Al}_2\text{O}_3$ ,  $\text{Al}(\text{OH})_3$  and both clay minerals (see Fig. 5) suggests that the inner-sphere complexes on clay surfaces are mainly bound to an aluminol site. Such a process has already proposed by Stumpf et al. (2001) for the sorption of Cm(III) onto the same clay minerals studied here. On the other hand, Kowal-Fouchard (2002) provided experimental evidence that surface complexes were bound to both aluminol and silanol sites. As mentioned by these authors, the silanol sites are only involved at alkaline pH when the aluminol sites are saturated. In contrast to Kowal-Fouchard's experiments, saturation of the edge sites is prevented by the concentration of europium and the water/clay ratio used in our systems. This also rules out any significant contribution of silanol sites to europium retention, since aluminol sites are the major sorption sites for Eu. Thus, not all the possible silanol sites are taken into account in the subsequent modelling of surface complexation. The complex formed could be a monodentate species, such as  $=\text{AlOHEu}^{2+}$  or  $=\text{AlOHEu}^{3+}$ , or a bidentate species such

as  $(=\text{AlOH})_2\text{Eu}^{3+}$  or  $(=\text{AlO})_2\text{Eu}^+$ . We currently have no objective arguments to support either of these hypotheses, so we consider the monodentate species for reasons of simplicity. This choice of stoichiometry is analogous to the approach adopted by Stumpf et al. (2001) for the sorption of Cm(III). In any case, the choice of complex species has no effect on the ability of the numerical modelling to reproduce the observed sorption results (the same fit can be obtained with different sets of values for the adjustable parameters).

#### 4. Surface complexation modelling and concluding remarks

We used the DLM (diffuse layer model) formalism to interpret our sorption data. The calculations were performed with the CHESS<sup>®</sup> computer code. We selected the Davis equations option to calculate the aqueous species activity coefficients. Following our experimental results and spectroscopic analyses, we take into account two kinds of reactive sites implying two distinct mechanisms: an exchange reaction with the compensating  $\text{Na}^+$  cations, described by reaction (1), and surface complexation on the amphoteric aluminol sites described by reaction (2). Note that, in order to satisfy the charge balance, the exchange reaction implies three exchange sites for each aqueous europium cation



To propose a model for the sorption of europium onto clays, we require the following input: (1) values of the site densities (aluminol sites and structural negative sites), (2) values of the exchange constants involving negative structural sites over the entire range of ionic strength, (3) values of the acid/base constants for the aluminol sites and the exchange reactions at the studied temperatures. This step is not trivial, so we applied the model proposed in Tertre et al. (in press) to the same clay minerals. Briefly, we quantify the influence of the permanent negative charge on the

acid/base surface chemistry of kaolinite and Na-montmorillonite using potentiometric titrations at 25 and 60 °C in 0.025–0.5 M NaClO<sub>4</sub> solutions. The experimental results are then fitted to the model, with the parameters used in the acid/base model as reported in Table 4. The main conclusion of this study is that the zero net proton consumption value is temperature independent between 25 and 60 °C, whereas the net proton consumption increases slightly with increasing temperature. The originality of our acid/base model is that it takes into account the effect of the negative potential, created by the negative structural charges of clay minerals, on the protonation/deprotonation reactions of the edge sites (i.e. aluminol and silanol sites). In this way, our acid/base model is useful for interpreting clay mineral potentiometric data obtained at different ionic strengths in the temperature range from 25 to 60 °C.

Because exchange and acid/base constants are not available at 80 °C and 150 °C, and due to the weak effect of temperature on the surface charge properties of the clays—at least between 25 and 60 °C—we initially ignore the temperature dependence of the exchange and acid base constants and use the values obtained at 25 °C for the whole range of temperatures. Then, we perform a test to evaluate the sensibility of the sorption model to the temperature depen-

dence of the acid/base constants. The test consists of increasing by one unit the pK<sub>a</sub> corresponding to the protonation of the aluminol site, while, at the same time, decreasing by one unit the pK<sub>a</sub> corresponding to the deprotonation of the aluminol site. These test conditions were chosen because the pK<sub>a</sub> of silanol and aluminol sites varies by less than one unit, at least between 25 and 60 °C (see Tertre et al., in press). The results of this test show that there was no significant change to the modelled sorption edge. Consequently, the modelled sorption curves are presented here at different temperatures (25, 40, 80 and 150 °C) and calculated from the acid/base model proposed at 25 °C. For the europium sorption reactions, we assume the exchange mechanism to be temperature-independent. In fact, the observed shift of the Eu sorption curves towards lower pH at higher temperature can be attributed solely to the presence of the ≡AlOEu<sup>2+</sup> complex.

Based on these assumptions, we can adjust the values of the intrinsic sorption constants by fitting the modelled sorption edge to the experimental data of the sorption runs (the TLRFS runs were not used for this fitting). We obtain satisfactory results for all the experimental conditions. Fig. 1A and B compare the experimental data with the calculated curves obtained for sorption of Eu(III) onto

Table 4  
Na-montmorillonite and kaolinite site densities and their acid/base constants, from Tertre et al. (in press)

Site	$\frac{\text{SiOH}}{\text{AlOH}}$	Density (μmol/m <sup>2</sup> )	Surface reactions	log K (25 °C) ± 0.3
<i>Na-montmor</i>				
=AlOH (complexation)	2	1.70	AlOH + H <sup>+</sup> = AlOH <sub>2</sub> <sup>+</sup> AlOH = AlO <sup>-</sup> + H <sup>+</sup>	5.1 -8.5
≡SiOH (complexation)	—	3.40	SiOH = SiO <sup>-</sup> + H <sup>+</sup>	-7.9
X <sup>-</sup> (exchange)	—	36.3	X <sup>-</sup> + H <sup>+</sup> = XH X <sup>-</sup> + Na <sup>+</sup> = XNa	-2.2 1.4
<i>Kaolinite</i>				
AlOH (complexation)	1	0.83	AlOH + H <sup>+</sup> = AlOH <sub>2</sub> <sup>+</sup> AlOH = AlO <sup>-</sup> + H <sup>+</sup>	4.8 -6.1
SiOH (complexation)	—	0.83	SiOH = SiO <sup>-</sup> + H <sup>+</sup>	-7.7
X <sup>-</sup> (exchange)	—	3.7	X <sup>-</sup> + H <sup>+</sup> = XH X <sup>-</sup> + Na <sup>+</sup> = XNa	-2.2 5.1

Table 5  
Sorption reactions and corresponding values of constants used for the modelling of europium sorption onto Na-montmorillonite

Na-montmorillonite	log K <sub>exch</sub>	log K <sub>edge</sub>			
	25–150 °C	25 °C	40 °C	80 °C	150 °C
<i>Sorption reactions</i>					
3XNa + Eu <sup>3+</sup> = X <sub>3</sub> Na + 3Na <sup>+</sup>	5.4 ± 0.4	—	—	—	—
AlOH + Eu <sup>3+</sup> = AlOEu <sup>2+</sup> + H <sup>+</sup>	—	-1.0 ± 0.2	2.5 ± 0.2	6.5 ± 0.3	7.5 ± 0.4
<i>Reactions of the acid/base model</i>					
X <sup>-</sup> + H <sup>+</sup> = XH	-2.2	—	—	—	—
X <sup>-</sup> + Na <sup>+</sup> = XNa	1.4	—	—	—	—
AlOH + H <sup>+</sup> = AlOH <sub>2</sub> <sup>+</sup>	—	5.1	—	—	—
AlOH = AlO <sup>-</sup> + H <sup>+</sup>	—	-8.5	—	—	—
SiOH = SiO <sup>-</sup> + H <sup>+</sup>	—	-7.9	—	—	—

Total site densities (in μmol/m<sup>2</sup>): AlOH = 1.70; SiOH = 3.40; X<sup>-</sup> = 36.3.

Table 6  
Sorption reactions and corresponding values of constants used for the modelling of europium sorption onto kaolinite

Kaolinite	$\log K_{\text{exch}}$	$\log K_{\text{edge}}$			
	25–150 °C	25 °C	40 °C	80 °C	150 °C
<i>Sorption reactions</i>					
$3\text{XNa} + \text{Eu}^{3+} = \text{X}_3\text{Na} + 3\text{Na}^+$	$11.0 \pm 0.4$	—	—	—	—
$\text{AlOH} + \text{Eu}^{3+} = \text{AlOEu}^{2+} + \text{H}^+$	—	$-2.3 \pm 0.3$	$-1.4 \pm 0.2$	$0.2 \pm 0.2$	$2.7 \pm 0.4$
<i>Reactions of the acid/base model</i>					
$\text{X}^- + \text{H}^+ = \text{XH}$	$-2.2$	—	—	—	—
$\text{X}^- + \text{Na}^+ = \text{XNa}$	$5.1$	—	—	—	—
$\text{AlOH} + \text{H}^+ = \text{AlOH}_2^+$	—	—	$4.8$	—	—
$\text{AlOH} = \text{AlO}^- + \text{H}^+$	—	—	$-6.1$	—	—
$\text{SiOH} = \text{SiO}^- + \text{H}^+$	—	—	$-7.7$	—	—

Total site densities (in  $\mu\text{mol}/\text{m}^2$ ): AlOH = 0.83; SiOH = 0.83;  $\text{X}^- = 3.7$ .

kaolinite and Na-montmorillonite, respectively. The numerical values of the intrinsic sorption constants are reported in Tables 5 and 6 for Na-montmorillonite and kaolinite, respectively. These tables also give the acid/base parameters. For Na-montmorillonite, the  $\log K_{\text{exch}}$  value for the Na/Eu exchange reaction is equal to  $6.5 \pm 0.8$ , which is not far outside the range of  $5.3 \pm 0.3$  to  $6.1 \pm 0.3$  proposed by Kowal-Fouchard (2002). By contrast, the formation constant of  $\equiv\text{AlOEu}^{2+}$  ( $K_{\text{edge}}$ ), the only temperature-dependent intrinsic value in our model, increases with temperature by 8 log units from 25 to 150 °C. However, these values cannot be compared with those used in the Kowal-Fouchard's model because of fundamental differences in surface complexation reactions between the two models for. In the present sorption model, the unique constant that varies with temperature is the constant related to the formation of the  $\equiv\text{AlOEu}^{2+}$  complex. This apparently contradicts the temperature dependence of the dissociation constants of surface sites present at the surface of single oxides (for example,  $\text{pK}_a$  for  $\equiv\text{SiOH}$  for quartz;  $\text{pK}_a$  for  $\equiv\text{AlOH}$  for  $\alpha$ -gibbsite). For single oxides, acid/base and electrokinetic measurements clearly show that the surface charges vary with temperature and these variations can be modelled by the temperature dependence of the surface site constants (Blesa et al., 1984; Brady, 1994; Mustapha et al., 1998; Wesolowski et al., 2000). Nevertheless, surface charge is always negative for clay minerals whatever the temperature, thus masking the variations of surface charge with temperature, at least between 25 and 150 °C (Brady et al., 1996; Thomas et al., 1999). Therefore, the corresponding acid/base constants used in our sorption model were assumed temperature independent.

The temperature dependence of the complexation reaction of europium onto aluminol sites can be quantified by an enthalpic term that is related to the intrinsic constant  $K_{\text{edge}}$  through the Van't Hoff formalism. By integrating  $\log K_{\text{edge}}$  with  $1/T$ , we obtain positive values of enthalpy: 150 kJ/mol for Na-montmorillonite and 95 kJ/mol for kaolinite. This latter value is close to the Eu enthalpy of sorption onto montmorillonite proposed by Tertre et al. (2005), as calculated from the measured  $K_d$ . However,

the  $K_d$  values cannot be taken as a strictly thermodynamic constants, and the significance of this positive enthalpy remains speculative. Among the elementary reactions involved in edge surface complexation, dehydration of the aqueous cation is probably the second step after diffusion toward the mineral surface. Thus, such a reaction is likely to be promoted with increasing temperature, as

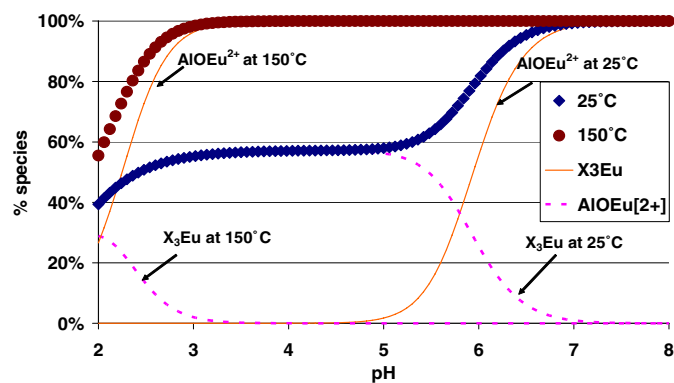


Fig. 6. Distribution of europium sorbed onto Na-montmorillonite as a function of pH in 0.5 M  $\text{NaClO}_4$  solutions at 25 and 150 °C. All data plotted on the graph refer to the results of the sorption model. Symbols represent total sorbed europium whereas curves represent the proportion of europium species sorbed onto the exchange sites and the aluminol sites.

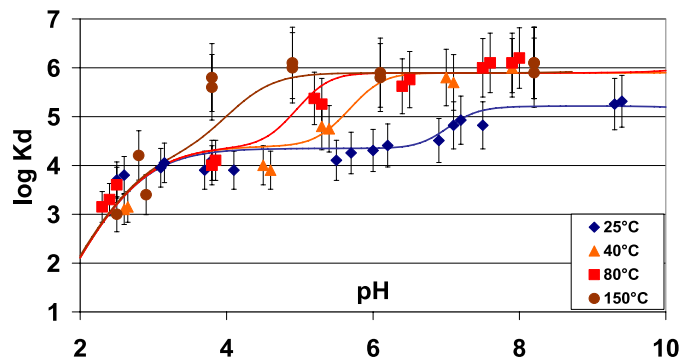


Fig. 7. Distribution coefficients of Eu(III) sorbed onto Na-montmorillonite in 0.025 M  $\text{NaClO}_4$  (Tertre et al., 2005; data points with symbols) compared with predicted values according to our model (curves).

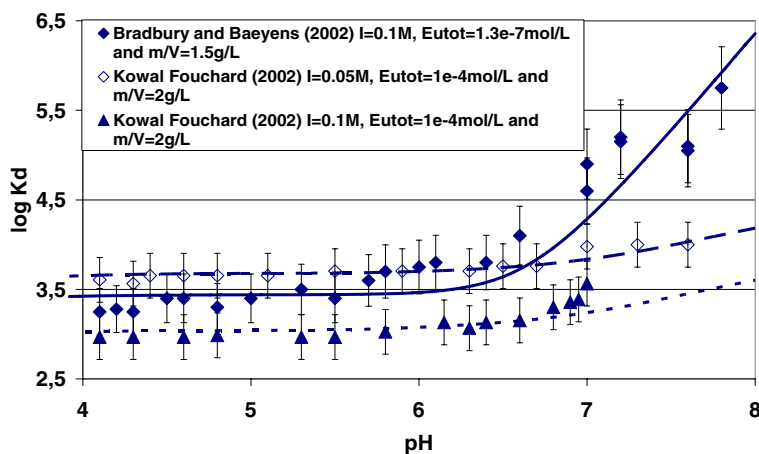


Fig. 8. Other published distribution coefficients of Eu(III) sorbed onto Na-montmorillonite (dots) compared with predicted values according to our model (curves).

demonstrated by Berger et al. (1994) for  $\text{Na}^+$  on silica surfaces. Hence, the higher the temperature, the stronger the chemical bonding between the metal and the aluminol site.

Fig. 6 presents the distribution of the sorbed Eu species onto Na-montmorillonite as a function of pH, at two temperatures (25 and 150 °C) and for  $I = 0.5$  M. This is consistent with the results of the spectroscopic study, showing a predominance of  $\text{X}_3\text{Eu}$  under acidic conditions and a predominance of  $\text{AlOEu}^{2+}$  under neutral conditions (pH 7.0 at 25 °C; pH 5.8 at 150 °C). Finally, we test our model, and the set of previously fitted intrinsic data, over a wide range of conditions. We first calculate the apparent  $K_d$  for the samples used in the TLRFS study, assuming a solid/liquid ratio of 25 g/L and an initial europium concentration of  $10^{-5}$  mol/L. Table 1 compares the predicted and measured  $K_d$  values. We find a relatively good agreement at all the temperatures. Without changing the adjusted parameters, we also apply the model to sorption experiments reported in Tertre et al. (2005) that were carried out with montmorillonite in 0.025 M  $\text{NaClO}_4$  solutions. As shown on Fig. 7, our model also reproduces the observed Eu retention at low ionic strength. Finally, we compare our model with the published data of other experimental studies. The test is limited to studies carried out at 25 °C (Bradbury and Baeyens, 2002; Kowal-Fouchard, 2002) because of the lack of data at higher temperatures. As in Table 1, Fig. 8 compares the predicted values of  $K_d$  with experimental measurements reported in the literature. Even though we only consider two sorption sites, our model fits data obtained over a wide range of conditions: from 0.05 M (Kowal-Fouchard, 2002) to 0.5 M (this study), and from an initial europium concentration of  $10^{-7}$  mol/L (Bradbury and Baeyens, 2002) to  $10^{-4}$  mol/L (Kowal-Fouchard, 2002). Nevertheless, our model underestimates sorption when the initial europium concentration is higher than  $10^{-3}$  mol/L (some data of Kowal-Fouchard, 2002; not reported here). Indeed, as mentioned above, sorption on silanol sites becomes significant under such

conditions because all the aluminol sites are saturated. Future investigations will be carried out to improve the model over a wider range of chemical conditions.

Finally, the conclusions presented here for  $\text{Eu}^{3+}$  can likely be extrapolated to other  $\text{Ln}^{3+}$ . However, the accurate modelling of other  $\text{Ln}^{3+}$  would involve extracting the sorption constants from experimental measurements. The required data are available in Tertre (2005).

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