



Gallium sorption on montmorillonite and illite colloids: Experimental study and modelling by ionic exchange and surface complexation



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ABSTRACT

The migration of metals as gallium (Ga) in the environment is highly influenced by their sorption on clay minerals, as montmorillonite and illite. Given the increased usage of gallium in the industry and the medicine, the Ga-associated waste may result in environmental problems. Ga sorption experiments were carried out on montmorillonite and illite colloids in a wide range of pH, ionic strength and Ga concentration. A Ga sorption model was developed combining ionic exchange and surface complexation on the edge sites (silanol and aluminol-like) of the clay sheets. The complexation constants were estimated as far as possible from the Ga hydrolysis constants applying the linear free energy relationship (LFER), which allowed to reduce the number of free parameters in the model.

The Ga sorption behaviour was very similar on illite and montmorillonite: decreasing tendency with pH and dependency on ionic strength at very acidic conditions.

The experimental data modelling suggests that the Ga sorption reactions avoid the Ga precipitation, which is predicted in absence of clay colloids between pH 3.5 and 5.5. Assuming this hypothesis, clay colloids would affect Ga aqueous speciation, preventing precipitation in favour of sorption. Ga sorption on montmorillonite and illite can be explained on the basis of three main reactions: Ga³⁺ exchange at very acidic conditions (pH < ~3.8); Ga(OH)₄⁻ complexation on protonated weak sites in acidic-neutral conditions (between pH ~5.2 and pH ~7.9); and Ga(OH)₃ complexation on strong sites at basic conditions (pH > ~7.9).

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1. Introduction

Clay minerals, as montmorillonite and illite, are ubiquitous in the environment. Due to their surface properties and sorption capacity, they highly influence the contaminants partitioning between aqueous and solid phases in the geosphere, strongly affecting their mobility in natural waters.

Clays can have contrary effects on the contaminant migration through the environment. On one hand, the contaminant movement can be retarded by the sorption onto clay surfaces. On the other hand, mobile clay colloids can act as vehicle of contaminants adsorbed onto their surfaces (Buddemeier and Hunt, 1988; Karathanasis, 1999; Karathanasis et al., 2005; Kersting et al., 1999; Novikov et al., 2006; Penrose et al., 1990; Smith and Degueldre, 1993).

Ga is a trivalent element that shows a strong tendency to form insoluble phases (Stumm and Morgan, 1996). Moreover, Ga presents strong tendency to hydrolyse, which is related with high sorption on oxides and clays (Balistrieri et al., 1981; Bradbury and Baeyens, 2005b; Hachiya et al., 1984; James and Healy,

1972; Righetto et al., 1991). Because of that, clay colloids can have significant influence on Ga speciation and migration (Gaillardet et al., 2003), by increasing its limited presence in waters.

Ga is widely used in the semiconductor and light emitting diode (LED) industries (Yu and Liao, 2011) and in the medical field (Collery et al., 2002; Gasparini et al., 1998; Lee et al., 1998). In addition, combustion of fossil fuels can contribute to the Ga emission to the environment (Yu and Liao, 2011). Because of the increased usage of Ga, the Ga-associated waste may result in environmental problems (Edelman, 1990; Kuroda et al., 1991; Lin and Hwang, 1998). Nevertheless, the studies concerning Ga behaviour in the environment are very scarce. Better understanding on the Ga interactions with geological materials is necessary.

Among the physical–chemical characteristics of Ga, its amphoteric character could determine its sorption behaviour. Ga hydrolysis starts at very acidic conditions (pH ~ 1) and the GaOH²⁺, Ga(OH)₂⁺, Ga(OH)₃⁰ are formed successively by increasing pH. At pH > 5–6, the anion Ga(OH)₄⁻ dominates aqueous speciation (Baes and Mesmer, 1986; Wood and Samson, 2006; Benézéth et al., 1997; Diakonov et al., 1997).

Ga sorption studies on different oxides (Al₂O₃, FeOOH, MnO₂, SiO₂) and carbonates (CaCO₃, MgCO₃) (Lin et al., 1997; Persson et al., 2006; Pokrovsky et al., 2004) showed a common tendency:

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maximum sorption at acidic-neutral pH which decreases abruptly around pH 8–10. This tendency was explained by surface complexation models.

Importantly, recent studies evidenced that the presence of oxides as goethite and silica (Persson et al., 2006; Pokrovski et al., 2002) prevents the precipitation of Ga oxy-hydroxides, due to their rapid interaction with the monomeric Ga aqueous species.

With regard to clays, elementary investigations were carried out on Ga sorption on bentonite under very acidic conditions, in which maximum sorption was observed at pH 3 (Chegrouche and Bensmaili, 2002). On kaolinite, the maximum Ga sorption was observed between pH 3 and 6 (Takahashi et al., 1999). However, the effects of the ionic strength or the Ga loading were not taken into consideration in these studies. The possible reactions implicated on the Ga sorption on clays have not been proposed in previous studies. As far as we know, there are no published papers that explain Ga sorption on clays on the basis of surface complexation or ionic exchange.

Illite and montmorillonite are 2:1 clays and consist of two SiO₄ tetrahedral (T) sheets bound to either side of an AlO₆ octahedral (O) sheet (expressed as T:O:T) (Dixon, 1989). Isomorphous substitutions of Al and Si give a permanent negative charge to the structure that is compensated by exchanging cations. In addition, montmorillonite and illite exhibit pH-dependent charge in the broken silanol and aluminol edges of the T:O:T sheets. Therefore, two sorption mechanisms exist on montmorillonite: cation exchange at permanently charged sites and surface complexation on the variably charged silanol and aluminol groups.

The aim of the present study is to determine experimentally the Ga sorption on montmorillonite and illite colloids under a wide range of pH, ionic strength and Ga loading. This experimental data was then modelled combining ionic exchange and surface complexation on the edge sites of clay sheets.

In order to reduce the number of free parameters in the model, the complexation constants were estimated applying the linear free energy relationship (LFER) equations on silanol and aluminol sites, which correlate the surface complexation constants and the Ga hydrolysis constant in solution (Balistrieri et al., 1981; Hachiya et al., 1984; James and Healy, 1972; Righetto et al., 1991).

2. Material and methods

2.1. Materials

The illite used in this study was the natural illite du Puy (Gabis, 1958) (France): its cationic exchange capacity (CEC) is 22.5 meq 100 g⁻¹ (Baeyens and Bradbury, 2004) and its BET area is 97 m² g⁻¹ (Poinsot et al., 1999b). The montmorillonite was obtained from the FEBEX bentonite mined at the Cortijo de Archidona deposit (Almeria, Spain). The CEC of the montmorillonite is 102 meq 100 g⁻¹ and its BET area is 33 m² g⁻¹ (Huertas et al., 2000). Further details on Illite du Puy and FEBEX bentonite can be found in the studies of Fernández et al. (2004) and Huertas et al. (2000). Previous to sorption experiments, both clays were purified and exchanged with the Na cation.

A Ga ICP standard solution (TraceCert[®], SigmaAldrich) 1001 ± 2 mg L⁻¹ in 5% (w/w) HNO₃ was used for sorption experiments.

The electrolytes and suspensions were prepared using water according to EN ISO 3696:1987, grade I, free of organic contaminants. The reagents were of analytical grade and used without further purification. All the experiments described below were run at room temperature.

2.2. Clay colloidal suspensions preparation

The “natural” clay (100 g L⁻¹) was washed three times with 1 M NaClO₄ to eliminate all the soluble salts and to obtain the homoionic Na-form. Colloidal particles (size <500 nm) were obtained by washing with deionised water and consecutive centrifugations at 600 g during 7 min. For the sorption experiments, colloidal suspensions of 1 g L⁻¹ were prepared diluting the suspensions with the NaClO₄ electrolyte at different ionic strengths.

2.3. Sorption experiments

Two types of Ga sorption experiments were carried out: sorption as a function of pH and sorption isotherms. Ga sorption as a function of pH (between pH 3 and 11) was studied at a fixed Ga concentration of 4 × 10⁻⁵ M. Ga sorption isotherms were performed at fixed pH (7.4, 8.7 or 9.0) varying the total Ga concentration from 6.6 × 10⁻⁶ M to 8.0 × 10⁻⁵ M. The sorption experiments were carried out at two ionic strengths (0.2 and 0.01 M) using NaClO₄ as electrolyte.

Sorption experiments were carried out according with the following procedure: an aliquot of 20 mL of the clay suspension at the selected ionic strength (pH 7.0 illite, pH 8.3 bentonite) was introduced in a polyethylene tube. Then, an aliquot of the Ga stock solution (1 mM or 4 mM in HCl 0.1 M) was added. After that, the pH was adjusted to the desired value, using HCl or NaOH 0.1 M.

Then, the tubes were sealed and maintained in continuous stirring for 7 days. After that, pH was measured and samples were ultra-centrifuged (645,000 g, 30 min.). After the solid separation, Ga concentration was determined in the supernatant solution by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Jobin-Yvon, JY38 Plus).

The distribution coefficient, K_d , was calculated by means of the following equation:

$$K_d = \frac{[Ga]_{tot} - [Ga]_{sol}}{[Ga]_{sol}} \frac{1}{[col]} \quad (1)$$

where $[Ga]_{tot}$ is the total Ga concentration (M), $[Ga]_{sol}$ is the Ga concentration in solution (M) and $[col]$ is the clay colloid concentration (g mL⁻¹).

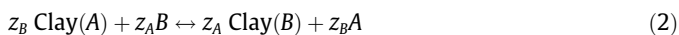
The K_d values could be affected by other elements released to the aqueous phase at low pH, where clays are unstable (May et al., 1986; Brady and Walther, 1989). The Al concentration in the supernatant of the clay suspensions at pH 3 ($I = 0.01$ M) was measured (ICP-OES, Varian 735-ES), in order to evaluate the competence between the cations Al³⁺ and Ga³⁺ for the sorption sites in the modelling procedure.

2.4. Modelling background

In this study, the modelling calculations were aided by CHES v 2.4 code (van der Lee, 1999). Two Ga sorption mechanisms were considered: ionic exchange on the permanent negative charge of the clays and the surface complexation on the hydroxyl groups on the edges of the clay sheets.

2.4.1. Ionic exchange

The ionic exchange reaction between a cation B, with charge z_B , which exists in the aqueous phase, and a cation A, with charge z_A , at the exchange sites of the clay can be defined by the following reaction:



The cation exchange reactions can be described in terms of selectivity coefficients. Following the Gaines and Thomas convention (Gaines and Thomas, 1953), the selectivity coefficient corresponding to the reaction (2) is expressed by the following equation:

$${}^B_A K_{\text{SEL}} = \frac{(N_B)^{z_A} (a_A)^{z_B}}{(N_A)^{z_B} (a_B)^{z_A}} \quad (3)$$

where a_A and a_B are the activities of the cations A and B, and N_A and N_B are the equivalent fractional occupancies. The equivalent fractional occupancy of a cation Y, N_Y , is defined as the equivalents of Y adsorbed per colloidal mass expressed in grams divided by the cationic exchange capacity CEC (expressed in eq g⁻¹). The activity coefficient of a cation Y (a_Y) at 20 °C is calculated in this work by means of the Davies' approximation:

$$\text{Log } a_Y = -0.51 \cdot z_Y^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 \cdot I \right) \quad (4)$$

where I represents the ionic strength of the solution.

2.4.2. Surface complexation

2.4.2.1. Acidity reactions. Complexation reactions are controlled by the amphoteric reactions of the hydroxyl groups ($\equiv\text{SOH}$) on the clay expressed by the following reactions



SOH_2^+ , SOH and SO^- represent the positively charged, neutral and negatively charged surface sites, respectively, and K_{a1} and K_{a2} are the intrinsic equilibrium acidity constants. The activity coefficients for all the surface species are assumed to be equal. The classical diffuse double layer (DDL) model (Dzombak and Morel, 1990; Huang and Stumm, 1973; Stumm et al., 1970) is generally applied to describe the surfaces of oxides. In clays, surface potential is ambiguous because sorption sites are located in different sorption planes (basal plane and edges). For this reason, a non-electrostatic (NE) model was used in this study, as proposed also by other authors for montmorillonite and illite (Bradbury and Baeyens, 1997, 2009a; Missana and García-Gutiérrez, 2007).

2.4.2.2. Sorption sites definition. For montmorillonite and illite, the existence of different types of sorption edge sites has been reported by different authors (Baeyens and Bradbury, 1997; Bradbury and Baeyens, 2009a; Missana et al., 2008; Missana and García-Gutiérrez, 2007): sites that exhibit very low density and high reactivity (strong sites $\equiv\text{S}^{\text{S}}$) and sites that exhibit high density and low reactivity (weak sites $\equiv\text{S}^{\text{W}}$). A model using one type of strong sites and two types of weak sites was developed by Baeyens and Bradbury (1997) and Bradbury and Baeyens (2009a) that successfully explains the cations sorption on montmorillonite and illite, respectively.

A simplified model using one type of strong sites and one type of weak sites was applied in this study (Missana et al., 2009, 2008, 2002; Missana and García-Gutiérrez, 2007).

The values of site density and the acid–base constants were taken from Missana et al. (2009) and they are summarized in Table 1. This work compiled the constants of protonation/deprotonation that were obtained for the FEBEX montmorillonite and the illite du Puy (Missana et al., 2008); and the weak sites density.

The weak sites density for the FEBEX montmorillonite was 1.82 $\mu\text{eq}/\text{m}^2$ (Missana et al., 2002). The weak sites density for the illite was 0.95 $\mu\text{eq}/\text{m}^2$ (Bradbury and Baeyens, 2005a, normalized to the BET area of 97 $\text{m}^2 \text{g}^{-1}$).

Table 1

Site density and acidity constants of illite and montmorillonite (compiled by Missana et al., 2009).

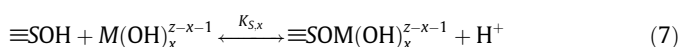
	Illite	Montmorillonite
Strong sites ($\equiv\text{S}^{\text{S}}$)		
Density, $\mu\text{eq g}^{-1}$ ($\mu\text{eq}/\text{m}^2$) ^a	2.04 (0.021)	2.01 (0.061)
Reactions	LogK	LogK
$\equiv\text{S}^{\text{S}}\text{OH}_2^+ \xleftarrow{K_{\text{S}^{\text{S}}\text{OH},a1}} \text{S}^{\text{S}}\text{OH} + \text{H}^+$	-4.5	-4.8
$\equiv\text{S}^{\text{S}}\text{OH} \xleftarrow{K_{\text{S}^{\text{S}}\text{OH},a2}} \text{S}^{\text{S}}\text{O}^- + \text{H}^+$	-9.5	-9.9
Weak sites ($\equiv\text{S}^{\text{W}}$)		
Density, $\mu\text{eq g}^{-1}$ ($\mu\text{eq}/\text{m}^2$) ^a	92.2 (0.95)	60.1 (1.82)
Reactions	LogK	LogK
$\equiv\text{S}^{\text{W}}\text{OH}_2^+ \xleftarrow{K_{\text{S}^{\text{W}}\text{OH},a1}} \text{S}^{\text{W}}\text{OH} + \text{H}^+$	-5.9	-5.3
$\equiv\text{S}^{\text{W}}\text{OH} \xleftarrow{K_{\text{S}^{\text{W}}\text{OH},a2}} \text{S}^{\text{W}}\text{O}^- + \text{H}^+$	-9.5	-8.4

^a Normalized to BET area, Section 2.1.

The strong sites density of FEBEX montmorillonite was experimentally determined previously to be 0.061 $\mu\text{eq}/\text{m}^2$ (Missana and García-Gutiérrez, 2007). For illite du Puy, the density was 0.021 $\mu\text{eq}/\text{m}^2$ (Missana et al., 2008). The acidity constants of protonation/deprotonation of these strong sites cannot be obtained from the titration curves, because of their low density, but it is generally obtained from the best fit of experimental sorption data (Missana et al., 2009).

2.4.2.3. Complexation reactions. Metals with amphoteric behaviour as Ga can form aqueous hydroxo-complexes with neutral, positive and negative charge. The three types of species could interact with sorption edge sites on clays.

Positive and neutral species can interact with the surface sites ($\equiv\text{SOH}$) according with the following reaction:

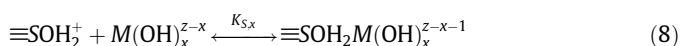


where z is the valence of the metal M (for Ga, $z = 3$) and x varies from 0 to a maximum value which is limited by the coordination chemistry of M (for Ga, maximum $x = 4$, up to 3 for cationic and neutral species).

This reaction implies one proton release and the monodentate complex formation (one atom of the metal M associated to one atom of oxygen on the surface).

The complexation constants corresponding to the reaction (7) ($K_{\text{S},x}$) can be anticipated from the hydrolysis constants of the metal M , applying the theory of the linear free energy relationship (LFER). LFER bases on the analogy between the surface complexation reactions and the reactions in the aqueous phase.

Complexation reactions of the anionic species of the metal M ($x > z$) with the protonated surface sites ($\equiv\text{SOH}_2^+$) can be described by the following reaction:



In this case, complexation reactions cannot be related with hydrolysis reactions, and the corresponding constants cannot be anticipated applying the LFER theory.

3. Results and discussion

3.1. Ga aqueous speciation

Ga speciation as a function of pH was calculated with the CHES code. The thermodynamic database used was the standard EQ3/6 database including hydrolysis reactions and constants summarized

Table 2

Ga hydrolysis and solubility reactions and constants from Benézéth et al. (1997) and Baes and Mesmer (1986).

Reactions	LogK
$\text{Ga}^{3+} + \text{H}_2\text{O} + \xleftarrow{K_{h,1}} \text{Ga}(\text{OH})^{2+} + \text{H}^+$	-2.85
$\text{Ga}(\text{OH})^{2+} + \text{H}_2\text{O} + \xleftarrow{K_{h,2}} \text{Ga}(\text{OH})_2^+ + \text{H}^+$	-4.43
$\text{Ga}(\text{OH})_2^+ + \text{H}_2\text{O} + \xleftarrow{K_{h,3}} \text{Ga}(\text{OH})_3^0 + \text{H}^+$	-4.66
$\text{Ga}(\text{OH})_3^0 + \text{H}_2\text{O} + \xleftarrow{K_{h,4}} \text{Ga}(\text{OH})_4^- + \text{H}^+$	-3.72
$\text{Ga}^{3+} + 3\text{H}_2\text{O} + \xrightarrow{\quad} \text{Ga}(\text{OH})_3(\text{am}) + 3\text{H}^+$	-5.64

All data refer to infinite dilution.

in Table 2 taken from Benézéth et al. (1997) and Baes and Mesmer (1986).

Ga(III) is an element of low solubility. However, clay colloids could stabilize Ga in suspension hampering its precipitation, as was evidenced in the presence of goethite and silica (Persson et al., 2006; Pokrovski et al., 2002). Without dismissing this hypothesis, speciation calculations were performed both including (Fig. 1a) and excluding (Fig. 1b) the reaction of $\text{Ga}(\text{OH})_3(\text{am})$ precipitation, at ionic strength of 0.01 M and total Ga concentration of 4×10^{-5} M (representative of experimental conditions).

In absence of stabilizing effect (Fig. 1a), the precipitation of $\text{Ga}(\text{OH})_3(\text{am})$ occurs at pH between 3.5 and 5.6, which will be considered below in the modelling efforts.

In both the cases (allowing or not Ga precipitation, Fig. 1a and b respectively), the speciation diagrams show that Ga^{3+} is the main species in solution at pH < 3. Then, Ga hydrolysis species form successively as the pH increases. From pH 6, the anion $\text{Ga}(\text{OH})_4^-$ becomes the only species in solution. The anion predominance

could influence the overall Ga sorption on clay colloids, which will be taken into account for the modelling procedure.

3.2. Ga sorption experimental data description

Fig. 2 shows the experimental $\text{Log}K_d$ values as a function of pH (Fig. 2a) and the Ga sorption isotherms (Fig. 2b) on montmorillonite and illite colloids (1 g L^{-1}), at two ionic strengths (0.01 and 0.2 M).

Red points in Fig. 2a indicate that Ga concentration in solution was below the detection limit. In these cases, a minimum $\text{Log}K_d$ of 5.0 is estimated according with the detection limit, i.e., the real $\text{Log}K_d$ values must be >5.0.

Fig. 2 shows that Ga sorption behaviour is very similar on illite and montmorillonite. In both clays, the curves of $\text{Log}K_d$ as a function of pH at $I = 0.2 \text{ M}$ (Fig. 2a) present high sorption around pH 4 ($\text{Log}K_d > 4.6 \text{ mL g}^{-1}$), followed by a decrease up to pH 8.5. Then, $\text{Log}K_d$ values are approximately constant between pH 8.5 and 11. In general, a decreasing tendency in the Ga sorption is observed as pH increases, suggesting that anion complexation could be playing an important role.

In addition to experimental values, Fig. 2a illustrates the simulation of the “apparent” $\text{Log}K_d$ values corresponding to the Ga precipitation in absence of clay colloids. In the pH range of Ga precipitation (4–5.8), the experimental $\text{Log}K_d$ values are always higher than the “apparent” $\text{Log}K_d$ values expected due to precipitation. This indicates that, although Ga precipitation cannot be dismissed up to now, the observed experimental K_d could not be explained only by a precipitation process.

Ga sorption did not show dependence on ionic strength at pH higher than 4.8. At lower pH, higher $\text{Log}K_d$ values were observed

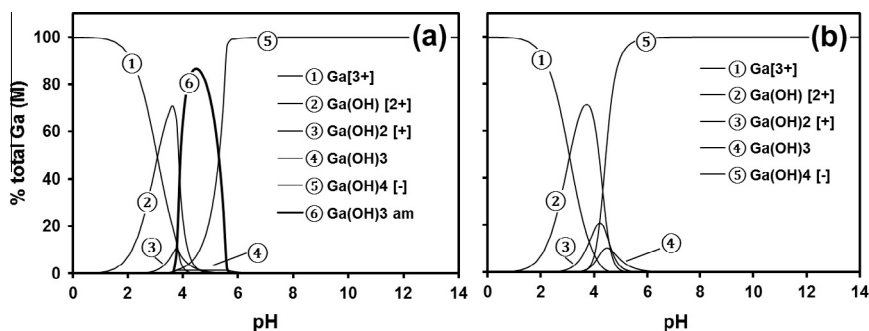


Fig. 1. Speciation of Ga(III) as a function of pH according to reactions and constants summarized in Table 2, (a) including and (b) excluding the precipitation reaction of amorphous $\text{Ga}(\text{OH})_3$.

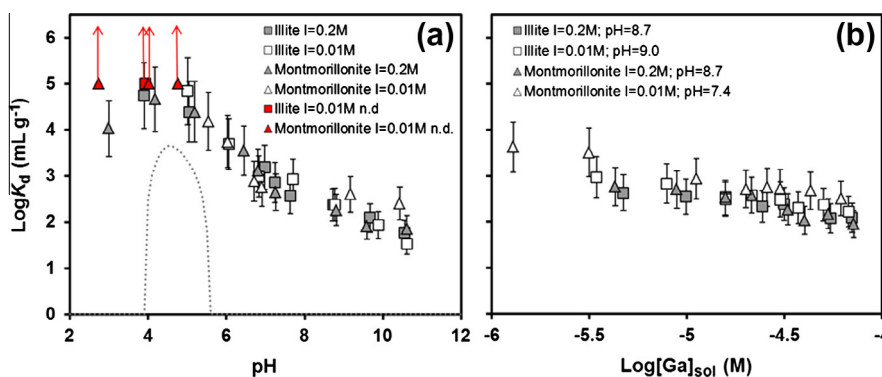


Fig. 2. (a) Ga sorption as a function of pH and (b) Ga sorption isotherms on montmorillonite and illite (1 g L^{-1}). Red points refer to the minimum $\text{Log}K_d$ values according with the detection limit (real $\text{Log}K_d$ undetermined due to non-detected $[\text{Ga}]_{\text{sol}}$). The dotted line refers to apparent $\text{Log}K_d$ due to Ga precipitation simulated in absence of clay ($I = 0.01 \text{ M}$, $[\text{Ga}]_{\text{tot}} = 4 \times 10^{-5} \text{ M}$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

Summary of sorption reactions and constants used in the developed Ga sorption model on illite and montmorillonite colloids.

Ga–Na exchange reaction and selectivity coefficients		
Reaction		Log K_{SEL}
$3\text{Clay}(\text{Na}) + \text{Ga}^{3+} \leftrightarrow \text{Clay}(\text{Ga}) + 3\text{Na}^+$	Illite	3.4 ^a
	Montmorillonite	3.0 ^a
Ga surface complexation reactions and constants on the edge sorption sites		
Reactions	Log K	$\equiv S^{\text{S}}$
$\equiv\text{SOH} + \text{Ga}^{3+} \xrightarrow{K_{s,0}} \equiv\text{SOGa}^{2+} + \text{H}^+$	0.15	3.23
$\equiv\text{SOH} + \text{Ga}(\text{OH})^{2+} \xrightarrow{K_{s,1}} \equiv\text{SOGa}(\text{OH})^+ + \text{H}^+$	–0.88	1.68
$\equiv\text{SOH} + \text{Ga}(\text{OH})_2^+ \xrightarrow{K_{s,2}} \equiv\text{SOGa}(\text{OH})_2^0 + \text{H}^+$	–1.03	1.45
$\equiv\text{SOH} + \text{Ga}(\text{OH})_3^0 \xrightarrow{K_{s,3}} \equiv\text{SOGa}(\text{OH})_3^- + \text{H}^+$	–0.42	2.4
$\equiv\text{SOH} + \text{H}^+ + \text{Ga}(\text{OH})_4^- \xrightarrow{K_{s,4}} \equiv\text{SOH}_2\text{Ga}(\text{OH})_4$	11.6 ^a	12.0 ^a

All data refer to infinite dilution; Log K_{SEL} values should be considered as indicative, given the high uncertainty of the experimental data at acidic pH.^a Estimated values from the experimental data in this work.**Table 4**

Estimation of the complexation constants for Ga cationic species applying the LFER equations on alumina and silica.

i	Log $K_{h,i}$	LFER equation for silanol sites (Righetto et al., 1991)	Log $K_{S^{\text{W}},i-1}$	LFER equation for aluminol sites (Hachiya et al., 1984)	Log $K_{S^{\text{F}},i-1}$
1	–2.85	$\text{Log } K_{S^{\text{W}},0} = 2.00 + 0.65\text{Log } K_{h,1}$	0.15	$\text{Log } K_{S^{\text{F}},0} = 6.02 + 0.98\text{Log } K_{h,1}$	3.23
2	–4.43	$\text{Log } K_{S^{\text{W}},1} = 2.00 + 0.65\text{Log } K_{h,2}$	–0.88	$\text{Log } K_{S^{\text{F}},1} = 6.02 + 0.98\text{Log } K_{h,2}$	1.68
3	–4.66	$\text{Log } K_{S^{\text{W}},2} = 2.00 + 0.65\text{Log } K_{h,3}$	–1.03	$\text{Log } K_{S^{\text{F}},2} = 6.02 + 0.98\text{Log } K_{h,3}$	1.45
4	–3.72	$\text{Log } K_{S^{\text{W}},3} = 2.00 + 0.65\text{Log } K_{h,4}$	–0.42	$\text{Log } K_{S^{\text{F}},3} = 6.02 + 0.98\text{Log } K_{h,4}$	2.4

at lower ionic strength (0.01 M), as befits to ionic exchange mechanism.

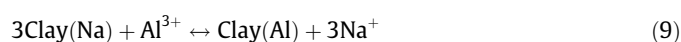
Log K_{d} values between pH 8.5 and 11, where sorption is approximately constant, suggest the saturation of the sorption sites. Isotherms (Fig. 2b) can give more information about saturation process at basic pH. The sorption tendency in the isotherms of illite and montmorillonite was very similar, presenting a slightly negative slope, which is likely due to the starting of the edge sites saturation.

3.3. Adsorption data modelling

Based on previous studies and the experimental data in this work, the following interactions were considered as possible sorption reactions for the modelling procedure: (a) the exchange of Ga cationic species, (b) the complexation of cationic and neutral Ga species on weak sites and strong sites and (c) the complexation of anionic Ga species on weak sites and strong sites.

3.3.1. Ga exchange

The fit of the experimental data at very acidic conditions, where Ga sorption presented high dependence on the ionic strength, required the consideration of the Na–Ga³⁺ ionic exchange. The corresponding exchange reaction, formulated according with the Eq. (2), is referred in Table 3. The possible competence of the cations Al³⁺ in solution for the exchange positions was taken into account including the following exchange reaction:



A value of Log $K_{\text{SEL}}^{\text{Al}}$ of 1.0 was used for illite (Bradbury and Baeyens, 2005a). Selectivity coefficient data for Al are not available for Na–montmorillonite. We made the assumption of similar exchange behaviour of illite and montmorillonite and Log $K_{\text{SEL}}^{\text{Al}}$ of 1.0 is also used for montmorillonite. The measured Al concentrations of 1.0×10^{-5} M and 1.9×10^{-6} M in solution in illite and montmorillonite suspensions (pH 3), respectively, were used for the calculations.

Selectivity constants $K_{\text{SEL}}^{\text{Ga}}$ (Eq. (3)) were estimated considering the Ga sorption data at the lower pH. Given the high uncertainty of this data, the estimated values should be considered as indicative. The estimated Log K_{SEL} were 3.4 and 3.0, for illite and montmorillonite, respectively (Table 3). Log K_{SEL} reported in the literature for the exchange reactions of Na by other trivalent cations as Eu(III) and Am(III) on illite and montmorillonite are between 1.9 and 2.9 (Bradbury and Baeyens, 2005b, 2009a,b; Gorgeon, 1994). According with the estimated values of $K_{\text{SEL}}^{\text{Ga}}$, Ga is more selectively retained on illite and montmorillonite by ionic exchange.

3.3.2. Complexation of cationic and neutral Ga species

It was considered that the complexation of cationic and neutral species (i.e. Ga³⁺, Ga(OH)²⁺, Ga(OH)₂⁺ and Ga(OH)₃) occurs by means of inner sphere mononuclear complexes. The corresponding reactions, formulated according with the Eq. (7), are summarized in Table 3. These reactions are in agreement with previous studies in alumina and silica (Lin et al., 1997; Pokrovsky et al., 2004) that suggest that Ga complexing reactions imply a proton release. They are also in agreement with different studies in oxides and carbonates that indicate that Ga very likely adsorbs forming mononuclear complexes, which was supported by EXAFS evidences in FeOOH (Persson et al., 2006) and by the modelling of experimental data in SiO₂, Al₂O₃, CaCO₃, MgCO₃ and MnO₂ (Lin et al., 1997; Pokrovsky et al., 2004).

The complexation constants of the cationic and neutral Ga species on weak and strong sites were estimated from the Ga hydrolysis constants, applying the LFER theory. LFER equations were determined for aluminol and silanol groups (on gibbsite and quartz respectively by Hachiya et al., 1984, and Righetto et al., 1991), which are the main functional groups in clays. Weak sites ($\equiv S^{\text{W}}$) and strong sites ($\equiv S^{\text{F}}$) on illite and montmorillonite (Section 2.4.2.2) were not associated with specific functional groups. However, an analogy can be observed between the weak and strong sites (e.g. Baeyens and Bradbury, 1997) and the silanol and aluminol groups identified on 2:1 clays (Stadler and Schindler, 1993), as was already suggested by Strawn et al. (2004).

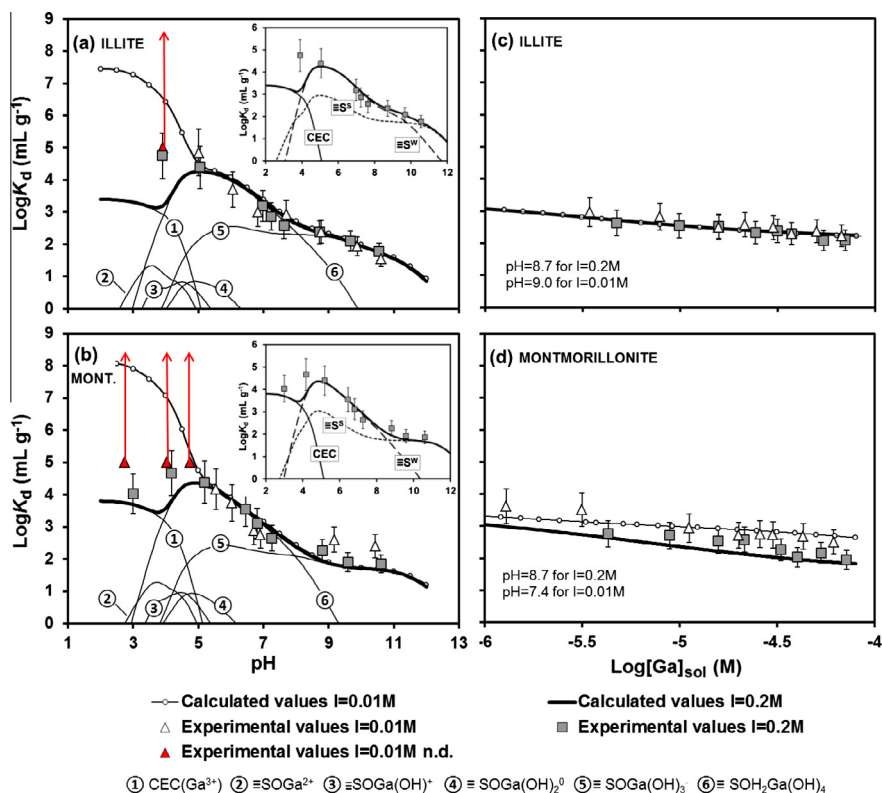


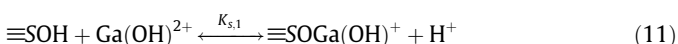
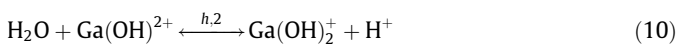
Fig. 3. Simulation of Ga sorption on clay colloids using the developed model (Table 3). (a) Ga sorption as a function of pH on illite and (b) on montmorillonite; (c) Ga sorption isotherms on illite and (d) on montmorillonite. Lines labelled with 1, 2, 3, 4, 5, 6 correspond to the simulation of the specific species at $I = 0.2$ M. Lines labelled with $\equiv S^S$, $\equiv S^W$ and CEC correspond to the simulation of the specific site at $I = 0.2$ M.

For the application of the LFER equations in this work, strong sites were related to aluminol groups ($\equiv S^S \approx \equiv AlOH$), given that both present high reactivity and low density on 2:1 clays (Chisholm-Brause et al., 2001), and weak sites were related to silanol groups ($\equiv S^W \approx \equiv SiOH$).

The density of aluminol sites deduced from the ideal structure of the 2:1 clays is estimated to be the 30–50% of the silanol site density (Tertre et al., 2006; Tourmassat et al., 2004; Zarzycki and Thomas, 2006). The ratio reported between strong and weak site is lower (Table 1). This is probably because the total aluminol sites are not available for ion sorption. Hence, weak and strong sites would correspond to the silanol and aluminol sites accessible for ions.

LFER equations were estimated for strong sites of montmorillonite and illite by Bradbury and Baeyens (2005b) and Bradbury and Baeyens (2009b) ($\log K_{S,i-1} = 8.1 + 0.83 \log K_{h,i}$; $\log K_{S,i-1} = 7.9 + 0.83 \log K_{h,i}$) and they are not very different to LFER equations in aluminol groups (Table 4). However, LFER equations for the total weak sites were not determined, and weak sites are strictly necessary to explain the sorption at the relatively high concentration used in this study (4×10^{-5} M Ga).

The calculation of the complexation constants was performed as indicated in Table 4. The hydrolysis reaction of each species is associated to its complexing reaction, for example:



Both reactions (10) and (11) imply a proton release and the Ga association with an oxygen atom ($HO-$ or $\equiv SO-$, respectively). This estimation system was applied previously for modelling of Pu,

Am(III), Th(IV) or Np(V) complexation (Alonso and Degueldre, 2003; Degueldre and Bolek, 2009; Degueldre and Kline, 2007; Degueldre et al., 1994).

The estimated constants for cationic and neutral species ($K_{S^W,0}$, $K_{S^W,1}$, $K_{S^W,2}$, $K_{S^W,3}$, $K_{S^S,0}$, $K_{S^S,1}$, $K_{S^S,2}$ and $K_{S^S,3}$) are established as fixed parameters in the modelling.

At this point of the modelling, including the complexation reactions of cationic and neutral species and the $Ga^{3+}-Na^+$ exchange reaction, the model would not be able to explain well the experimental data (see Supplementary Material). The simulation predicts Ga precipitation around pH 5 but the amount of precipitated Ga is not enough to explain the high K_d values observed (see Supplementary Material). This indicates that some process is not being taken into account.

3.3.3. Complexation of the anionic species

the complexation of the anion $Ga(OH)_4^-$ could play an important role in the Ga sorption on illite and montmorillonite, given that $Ga(OH)_4^-$ dominates the aqueous speciation at $pH > 5$ (Fig. 1). Despite illite and montmorillonite present net negative charge at all pH conditions, anions can interact with the protonated edge sites. In previous studies (Persson et al., 2006; Pokrovsky et al., 2004), the Ga sorption on different oxides and carbonates (MnO_2 , $FeOOH$, $CaCO_3$, $MgCO_3$) was attributed mainly to the reaction between the $Ga(OH)_4^-$ anion and the protonated hydroxyl groups on the surfaces. Therefore, the next step of the modelling procedure was to include the complexation reaction of $Ga(OH)_4^-$, formulated according with the Eq. (8) and presented in the Table 3.

The calculation of the corresponding complexation constants on weak and strong sites ($K_{S^W,4}$, $K_{S^S,4}$) was not possible by the application of the LFER theory and they were estimated by fit of the experimental data and presented in the Table 3.

All the sorption reactions and constants used in the model are summarized in Table 3. The simulation of the experimental data indicates that the developed model is able to predict Ga sorption on montmorillonite and illite over the wide range of conditions considered in this study, as is illustrated in Fig. 3.

All the parameter used in the model were fixed with the exception of $\text{Log}K_{s,4}$ for the complexation reaction of $\text{Ga}(\text{OH})_4^-$ on the edges sites and the selectivity coefficients K_{SEL} . Thus, the application of the LFER theory in aluminol and silanol groups allowed to strongly reduce the number of fitting parameters.

3.4. Results implications

Fig. 3 shows the simulations of Ga sorption as a function of pH (Fig. 3a and b) and the simulations of the Ga isotherms (Fig. 3c and d) on illite and montmorillonite colloids using the developed model (Table 3). In addition, Fig. 3a and b detail the contribution of each sorbed species to the total Ga sorption. Fig. 3a-Inset and Fig. 3b-Inset detail the contribution of the different types of sorption sites (CEC, weak and strong sites) to the Ga sorption.

The simulations predict (Fig. 3a and b) that Ga does not precipitate at all the pH range studied. Precipitation would be hampered by the complexation reaction of $\text{Ga}(\text{OH})_4^-$, which was required for the adequate fit of the experimental data (see Supplementary Material). Hence, the modelling strongly suggests that clay colloids favour Ga sorption preventing the Ga precipitation, as was observed by (Persson et al., 2006; Pokrovski et al., 2002) in presence of goethite and silica, respectively. Even so, spectroscopic studies are necessary to confirm this hypothesis.

The simulations indicate that the contribution of the different Ga surface species is very similar on illite (Fig. 3a) and montmorillonite (Fig. 3b). In both clays, the main surface species implicated on Ga sorption are $\text{CEC}(\text{Ga}^{3+})$, $\equiv\text{SO}(\text{GaOH})_3^-$ and $\equiv\text{SOH}_2(\text{GaOH})_4$. At ionic strength 0.2 M, Ga^{3+} exchange predominates at pH below 3.8, $\text{Ga}(\text{OH})_4^-$ complexation predominates between pH 3.8 and 7.9 and $\text{Ga}(\text{OH})_3$ complexation predominates at pH higher than 7.9.

Fig. 3a-Inset and Fig. 3b-Inset allow to identify that weak sites ($\equiv\text{S}^{\text{W}}$) are the main responsible of the Ga sorption between pH 3.8 and 7.9 and strong sites ($\equiv\text{S}^{\text{S}}$) are the main responsible at pH higher than 7.9. Sorption peak at pH ~ 5 is due to the coincidence at this point of the weak sites still protonated ($\equiv\text{S}^{\text{W}}\text{OH}_2^+$, Table 1) and the presence of the anion GaOH_4^- in solution (Fig. 1b).

4. Conclusions

Ga shows very similar sorption behaviour on illite and montmorillonite colloids. Sorption is strongly dependent on pH (with decreasing tendency as pH increases) and dependent on ionic strength only at very acidic conditions.

The Ga sorption modelling on montmorillonite and illite has been carried out, for the first time. Ga sorption was modelled taking into consideration ionic exchange and surface complexation on weak and strong sites on the clay edges. According with the developed model, Ga sorption on both clays can be explained on the basis of three main reactions: Ga^{3+} exchange at very acidic conditions (pH < ~ 3.8); $\text{Ga}(\text{OH})_4^-$ complexation on the weak sites in acidic-neutral conditions (between pH ~ 5.2 and pH ~ 7.9); and $\text{Ga}(\text{OH})_3$ complexation on strong sites at basic conditions (pH > ~ 7.9).

The application of the LFER theory allowed to strongly reduce the number of free parameters for the modelling procedure and predicted low relevance of Ga^{3+} , $\text{Ga}(\text{OH})_2^+$ and $\text{Ga}(\text{OH})_2^+$ complexation on the overall Ga sorption.

The developed model suggests that the presence of montmorillonite and illite colloids could prevent the Ga precipitation through its sorption, which has to be confirmed by spectroscopic evidences.

From the experimental data and the developed model in this study, we can conclude that conditions of mildly acidic pH and low ionic strength favour very high Ga sorption on montmorillonite and illite. However, considerable Ga sorption occurs from pH 3 to pH 11 independently on the ionic strength. This can have contradictory implications on the Ga movement through the geosphere. On one hand, higher Ga sorption on clays implies higher retention in the solid phase. On the other hand, low saline waters (low ionic strength) and non-extremely acidic pH, which are conditions favourable for high Ga sorption, also favour clay colloids stability (Laaksoharju and Wold, 2005; Missana et al., 2003; Novich and Ring, 1984). Hence, under these conditions, montmorillonite and illite colloids should be considered as a potential via of Ga migration in the natural systems.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apgeochem.2013.10.015>.

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