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Abstract- Competitive mechanisms between rare earth elements (REE) and aluminium for humic acid (HA) binding were investigated by combining laboratory experiments and modeling to evaluate the effect of Al on REE-HA complexation. Results indicates that Al^{3+} competes more efficiently with heavy REE (HREE) than with light REE (LREE) in acidic (pH=3) and low REE/HA concentration ratio conditions providing evidence for the Al high affinity for the few HA multidentate sites. Under higher pH - 5 to 6 - and high REE/HA conditions, Al is more competitive for LREE suggesting that Al is bound to HA carboxylic rather than phenolic sites. PHREEQC/Model VI Al-HA binding parameters were optimized to simulate precisely both Al binding to HA and Al competitive effect on REE binding to HA. REE-HA binding pattern could only be simulated reasonably well in the whole experimental conditions studied only if ΔLK_{1A} was optimized (i.e. the parameter controlling width of the distribution of log K around log K_{MA}, the median value). The present study provides fundamental knowledge on Al binding mechanisms to HA. Aluminium competitive effect on other cations binding to HA depends clearly on its affinity for carboxylic, phenolic or chelate ligands, which is pH dependent. Under circumneutral pH conditions in natural waters, Al should lead to LREE-depleted patterns since Al is not expected to bind efficiently neither to HA phenolic groups nor to strong HA multidentate groups. As deduced from the behavior of Al species, other potential competitor cations are expected to have their own competitive effect on REE-HA binding. Therefore, in order to reliably understand and model REE-HA pattern variations in natural waters, a precise knowledge of the exact behavior of the different REE competitor cations is required. Finally, this study highlights the ability of the REE to be used as a "speciation probe" to precisely describe cation interactions with HA as here evidenced for Al.

Keywords: rare earth elements, aluminium, competition, complexation, humic acid, PHREEQC, Model VI.

1. INTRODUCTION

Lanthanides represent a group of 14 naturally occurring elements, commonly denoted as rare earth elements (REE), which bind strongly to natural dissolved organic matter (DOM) (Takahashi et al., 1997; Viers et al., 1997; Dia et al., 2000; Tang and Johannesson, 2003; Johannesson et al., 2004; Gruau et al., 2004; Davranche et al., 2005; Sonke and Salters, 2006; Pourret et al., 2007a; Pédrot et al., 2008; Marsac et al., 2010; Yamamoto et al., 2010). The unique property of REE is their chemically coherent behavior in natural systems. The regular variations of their chemical behavior along the series can generate DOM/solution partition coefficient (K_d) patterns with specific shapes depending on the binding conditions (i.e. the nature of the functional group involved). REE binding to humic acid (HA) experiments conducted under variable REE/HA ratios (defined as the REE to carbon molar ratio) and pH conditions exhibit changes in K_d^{REE} pattern indication that REE can bind to different type of HA sites (Marsac et al., 2011). More precisely, REE-HA binding experiments under acidic and low REE/HA conditions yielded K_d^{REE} patterns showing an increase of heavy REE (HREE) as compared to light REE (LREE). This feature is involved by the REE binding to HA few strong sites that are similar to chelate ligands such as EDTA and have more affinity for HREE than LREE (Sonke and Salters, 2006; Marsac et al., 2010; Yamamoto et al., 2010). Experiments conducted at high REE/HA conditions showed K_d^{REE} pattern with an increase for the middle REE (MREE) specific of REE binding with carboxylic ligands such as acetic acid (Tang and Johannesson, 2003; Pourret et al., 2007b). This downward MREE concavity was suggested to be developed through the REE binding with abundant and weak HA carboxylic sites. This K_d^{REE} pattern dependence to REE/HA and involved HA binding site was

successfully modeled by Marsac et al. (2011) using the specific humic-ion binding model (Model VI) developed by Tipping (1998). The modeling approach suggest that at high REE/HA conditions, although LREE are dominantly (>80%) bound to carboxylic sites, a majority of HREE (>80%) are bound to phenolic and carboxy-phenolic sites (Marsac et al., 2011). The experimental and modeling results raise therefore the possibility that REE could be used as a tool to determine which of the carboxylic, phenolic or chelate functional groups are implicated in the binding of a given cation by HA. All cations able to compete with REE for HA binding could not only involve a quantitative decrease of the complexed REE bound to HA but also modify the REE-HA K_d pattern depending on their respective affinity for carboxylic, phenolic or chelate HA sites. Conversely, variations of the REE-HA K_d pattern patterns observed in presence of a competitive cation could provide additional clues to explain why REE pattern variations occur in natural, organic-rich waters (Marsac et al., 2010, and references therein).

In this respect, aluminium (Al) is of particular interest. Aluminium is abundant in natural, organic-rich waters, specifically acidic water, with Al^{3+} activity up to around 10^{-3} mol L^{-1} (Tipping, 2005). Moreover, Al has strong affinity for HA and is thus a strong competitor for cations-HA binding including REE (Bidoglio et al., 1991; Tanizaki et al., 1992; Takahashi et al., 1997; Dupré et al., 1999; Kinniburgh et al., 1999; Pinheiro et al., 2000; Tipping et al., 2002; Lippold et al., 2005). The competitive binding of Al and the whole REE group has not been experimentally studied. A common belief is that Al is preferentially bound to strong HA sites and is therefore a stronger competitor for HREE than for LREE. As a consequence, Al should induce a relative decrease of HREE in the K_d^{REE} pattern (Yamamoto et al., 2010; Tang and Johannesson, 2010; Marsac et al., 2011). However, this stronger competition of Al for HREE is opposite to Tipping et al. (2002) parameters of Model VI describing Al and REE

91 binding to HA. The ΔLK_2 parameter that defines the strength of HA multidentate sites are
92 $\Delta LK_2(Al) < \Delta LK_2(LREE) < \Delta LK_2(HREE)$. Therefore, Model VI predicts a stronger
93 competitive effect of Al on LREE than on HREE.

94 In the present study, REE-Al-HA binding experiments were performed simultaneously
95 on the 14 naturally occurring REE over a range of metal loading and pH conditions. The aim
96 of this work is threefold: i) to experimentally investigate the competitive effects of Al on REE
97 complexation by HA in conditions that highlight the competition with the few strong
98 multidentate and phenolic groups, respectively; ii) to evaluate the ability of PHREEQC/Model
99 VI to predict the experimental data and to improve the quality of the modeling; iii) to test the
100 ability of the REE to be used as a fingerprint of the mechanisms of Al binding to HA.

101 ## 2. MATERIALS AND METHODS

102 All chemicals used were of analytical grade, with all experimental solutions being
103 prepared with doubly-deionised water (Milli-Q system, Millipore™). Synthetic REE solutions
104 were prepared from a nitrate REE standard (10 mg L^{-1}, Accu Trace™ Reference Standard).
105 Polyethylene containers used to get REE-HA complexation equilibrium were all previously
106 soaked in 10% Ultrapure HNO_3 for 48h at 60°C, then rinsed with deionised water for 24h at
107 60°C. All experiments were performed at room temperature, i.e. 20°C ± 2.

108 ### 2.1. Humic acid

109 Purified humic acid (HA) was obtained from synthetic Aldrich humic acid (Aldrich™,
110 H1, 675-2). The purification was performed with the protocol of Vermeer et al. (1998), except
111 that a tangential ultrafiltration step was added to remove any possible HA molecules <10 kDa
112 using a Labscale TFF system equipped with a Pellicon XL membrane (PLCGC10,
113 Millipore™). Humic acid was freeze-dried and stored in a glass container. Prior to use,

purified HA was solubilized overnight in a solution of 0.01 M NaCl at pH = 10 to ensure complete dissolution (Vermeer et al., 1998). The pH was adjusted to 3 in the HA suspensions, which were then filtered at 0.2µm to remove any potential precipitate and therefore to ensure studying the same HA fraction in any experiments performed even at higher pH. The dissolved organic carbon (DOC) concentration of the filtrates was then measured to assess the true HA concentration of the experimental suspensions.

2.2. Experimental set-up of the REE and Al binding to HA

A standard batch equilibrium technique was used to study the competitive effect of Al on REE binding by HA. The fourteen REE and Al were simultaneously added to HA suspension set in a 10^{-2} M (NaCl) electrolyte solution. Experimental suspensions were stirred for 48 h to reach equilibrium according to the protocol defined by Pourret et al. (2007b). The pH was monitored regularly with a combined Radiometer Red Rod electrode, calibrated with WTW standard solutions (pH 4 and 7). The accuracy of pH measurements was ±0.05 pH units. At equilibrium (48 h), 10 mL of the suspension were sampled and ultra-filtered at 5 kDa to separate the REE-HA and Al-HA complexes from the remaining inorganic REE and Al. Ultrafiltrations were carried out by centrifuging the suspension aliquots through 15 mL centrifugal tubes equipped with permeable membranes of 5 kDa pore size (Vivaspin 15RH12, Sartorius). All the membranes used were first washed with 0.15 mol L^{-1} HCl, then rinsed twice with ultrapure water to minimize contamination. Centrifugations were performed using a Jouan G4.12 centrifuge with swinging bucket rotor at 3000g for 30 min. The purification step that consists in removing HA fractions <10 kDa ensures that no organic molecules pass through the 5 kDa membrane at this stage of the experiments. All experiments were performed in triplicate.

Two types of REE-Al competition experiments were performed. The first type was performed at pH 3, under low REE/HA ($\sum$[REE] = 1 µM; DOC = 9 mg L^{-1}; REE/HA = 1.2 10^{-3} molREE/molC) and variable Al concentration (0 to 20 µM) conditions. Under these conditions, REE should be preferentially bound to HA by means of the few strong multidentate sites occurring on them. The competition with Al for these sites, if occurring, should result in a relative HREE depletion of log K_d^{REE} pattern (see above). This first series of experiments was limited to pH 3 since higher pH values do not allow keeping measurable amounts of REE in solution, due to the low REE/HA effect. The second series of experiments was performed at variable pH ranging from 3 to 6, using higher REE/HA ($\sum$[REE] = 10 µM; DOC = 6.7 mg L^{-1}; REE/HA = 2 10^{-2} molREE/molC) and equal REE-Al concentrations ($\sum$[REE] = [Al] = 10 µM). Reference experiments without Al were performed for comparison. Due to higher REE/HA, REE are expected to be preferentially complexed by carboxylic and phenolic functional groups in this second series of experiments, with an expected increase of the phenolic/carboxylic ratio with increasing pH due to the higher proton dissociation constant of phenolic groups (Marsac et al., 2011). Thus, this second series of experiments was designed to provide information about the ability of Al to compete REE for binding with HA phenolic sites. Speciation calculations carried out with PHREEQC showed that all inorganic REE occur as free aqueous REE^{3+} species in the two series of experiments (Tang and Johannesson, 2003; Pourret et al., 2007a; Marsac et al., 2010). The situation is different for Al that can form hydroxide species and precipitate as $Al(OH)_{3(s)}$ in our experimental condition. Stability constants between Al and hydroxides were taken from minteq.v4 database. Aluminium activity was controlled by the precipitation of $Al(OH)_3$, following the reaction:

$$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O \qquad K_{SO} \qquad (1)$$

The REE complexation with HA is described using the apparent partition coefficient K_d, as follows:

$$K_d(Ln_i) = \frac{\mu g Ln_i \text{ adsorbed } L^{-1}/g \text{ DOC}}{\mu g Ln_i^{3+} mL^{-1}} \quad (2)$$

where Ln_i = La to Lu.

2.3. Solution analysis

Rare earth elements and Al concentrations were determined with an Agilent Technologies™ HP4500 ICP-MS instrument. Ultrafiltrate, containing Al and REE inorganic species, were injected directly after adding HNO_3 to a concentration of 0.37 N. The initial suspensions were also analyzed to determine precisely total cation concentrations for each experiment. The suspensions were first digested with sub-boiled nitric acid (HNO_3 14 N) at 100°C, and then resolubilized in HNO_3 0.37 N after complete evaporation, to avoid interferences with organic carbon during mass analysis by ICP-MS. Quantitative analyses were performed using a conventional external calibration procedure. Three external standard solutions with REE and Al concentrations similar to the analyzed samples were prepared from a multi-REE and an Al standard solution (Accu Trace™ Reference, 10 mg L^{-1}, USA). Indium (In) was added to all samples as an internal standard at a concentration of 0.87 µmol L^{-1} (100 ppb) to correct for instrumental drift and possible matrix effects. Indium was also added to the external standard solutions. Calibration curves were calculated from measured REE/In and Al/In intensity ratios. As established from repeated analyses of multi-REE standard solution (Accu Trace™ Reference, USA) and the SLRS-4 water standard, the instrumental error on REE and Al analysis were below 3 and 5 %, respectively.

Dissolved organic carbon concentrations were determined using a Shimadzu 5000 TOC analyzer. The accuracy of DOC concentration measurements is estimated at ± 5%, as determined by repeated analysis of freshly prepared standard solutions (potassium biphtalate).

2.4. PHREEQC/Model VI

Humic ion-Binding Model VI (hereafter referred to as Model VI) is a model developed by Tipping (1998), which is implemented in the geochemical code WHAM 6. This model was recently introduced into the PHREEQC (version 2) developed by Parkhurst and Appelo (1999) for the entire REE series to improve REE-HA binding description, in particular by removing the linear relationship between log K_{MA} and log K_{MB} (Marsac et al., 2011). PHREEQC (version 2) is a computer code based on an ion-association aqueous model, which was designed to perform speciation and saturation-index calculations in waters.

The humic-ion binding Model VI was developed by Tipping (1998). A thorough description of Model VI can be found in Tipping (1998). The model is a discrete binding site model which takes electrostatic interactions into account. Eight sites are considered and divided into an equal number of type A sites (the weak acidic sites, commonly associated with carboxylic functional groups) and type B sites (the strong acidic sites, commonly associated with phenolic functional groups). There are n_A (mol g^{-1}) type A sites and $n_A/2$ type B sites. Proton binding is described by the two median intrinsic constants (pK_A or pK_B) and two parameters defining the spread of the equilibrium constants around the median (ΔpK_A or ΔpK_B). The intrinsic equilibrium constants for metal ions (e.g. La^{3+} or Al^{3+}) and their first hydrolysis product (e.g. $LaOH^{2+}$ or $AlOH^{2+}$) binding are defined by two median constants (log K_{MA} and log K_{MB}), together with parameters that define the spread of the values around the medians (ΔLK_{1A} and ΔLK_{1B}). By considering the results from many datasets, a universal average value of ΔLK_1 was obtained for all cations (2.8), where $\Delta LK_1 = \Delta pK_A - \Delta LK_{1A} =$

206 ΔpK_B - ΔLK_{1B} (appendix in Tipping et al., 2011). Some of the type A and type B
207 monodentate sites can form bi- and tridentate sites. The stability constants of these bi- and
208 tridentate sites are defined by the sum of the log K values of the monodentate sites of which
209 they are constituted. Cation-HA binding can occur through carboxylic groups (CG), carboxy-
210 phenolic groups (CPG) or phenolic groups (PG). A small part of the stability constants of
211 multidentate groups are increased by the ΔLK_2 parameter, the so-called "strong binding site
212 term" (Tipping, 1998). ΔLK_2 is attributed to the chelation effect or the participation of
213 ligands, such as the nitrogen-containing groups. Marsac et al. (2011) showed that to
214 accurately simulate REE-HA binding, ΔLK_2 parameter had to be optimized independently for
215 carboxylic (ΔLK_{2C}) and phenolic groups (ΔLK_{2P}). In the present paper, sites whose stability
216 constants with a cation depend on ΔLK_2 will be denoted as “strong multidentate sites”. An
217 electrical double layer, where only counter-ions can accumulate, is also defined in the model.
218 The double layer thickness is set by the Debye-Hückel parameter $\kappa = (3.29 \times 10^9 \times I^{1/2})^{-1}$
219 (Appelo and Postma, 2005). The distribution of ions between the diffuse layer and the bulk
220 solution is calculated by a simple Donnan model. Intrinsic equilibrium constants are corrected
221 by the Boltzmann factor that depends on HA surface area which was determined to be equal
222 to 19000 m^2/g at ionic strength of 0.01 (Marsac et al., 2011). In this study, HA was defined as
223 the SOLUTION_MASTER_SPECIES, SOLUTION_SPECIES and PHASES in the
224 PHREEQC database. The 80 types of site considered by Model VI to bind REE, Al and their
225 respective first hydrolysis products were defined as SURFACE_MASTER_SPECIES, and
226 their respective stability constants as SURFACE_SPECIES in the PHREEQC database. Al
227 hydroxide precipitation was also taken into account by defining $Al(OH)_3$(ha) - noted "ha" for
228 the experiments carried out in the presence of HA - in the PHASES block of PHREEQC
229 database. Aluminium activity was controlled by the precipitation of $Al(OH)_3$, following eq. 1.

With ultrafiltration at 5 kDa, Al-HA amount and precipitated as hydroxides cannot be separately measured. The calculated amount of Al present in the fraction > 5kDa is defined therefore by:

$$Al > 5\ kDa = Al(OH)_{3(s)} + Al\text{-}HA \quad (4)$$

As a preliminary study, Al specition in the fraction > 5kDa was simulated from pH = 3 to pH = 6 in conditions comparable to our experiments (i.e. [DOC] = 6.7 mg L^{-1}; [Al] = 10 µM; IS = 0.01 M of NaCl). Simulation were performed using Model VI Al-HA binding parameters determined by Tipping et al. (2002) and Log K_{SO} = 9 (eq. 1), which correspond to a 48h equilibrated $Al(OH)_{3(s)}$ (IUPAC, Stability Constants Database). Results are presented in Figure 1 and show that Al^{3+} binding to HA is dominant at pH < 5. $AlOH^{2+}$ binding to HA ranges between 10% and 40% for pH > 4. $Al(OH)_{3(s)}$ precipitates from pH = 5 and represents 60% of simulated Al in the fraction > 5kDa at pH = 6.

Errors between experiments and simulations were quantified by the root mean square error of the regression (rmse), i.e. the sum of the squares of the differences between observed and calculated log υ, where υ is the amount of REE bound to HA per gram of dissolved organic carbon (DOC). To consider a fit as to be of good quality, two conditions had to be fulfilled, namely: i) that the total rmse calculated from the whole experimental conditions and REE were low, and ii) that the rmse values calculated for the fourteen REE were sufficiently close to each other.

3. RESULTS

3.1. Experimental Al competitive effect on REE-HA binding

Figure 2 illustrates Al influence on log K_d^{REE} patterns at pH = 3 and low REE/HA (= 1.2 10^{-3}). For [Al] = 0, REE-HA pattern increases regularly from La to Lu occurring through

253 preferential binding of REE to the low density strong multidentate sites with higher affinity
254 for HREE than for LREE (Yamamoto et al., 2010; Marsac et al., 2010). The presence of 1 μM
255 of Al strongly decreases the amount of REE bound to HA, while changing the log K_d^{REE}
256 patterns which increases for MREE (MREE downward concavity). The Al concentration rise
257 from 1 to 20 μM decreases the amount of REE bound to HA, but does not influence the log
258 K_d^{REE} pattern which remains essentially identical to that of the [Al] = 1 μM experiment.
259 Therefore, Al appears to compete more efficiently with HREE than LREE in these
260 experiments, suggesting that Al has a higher affinity for strong multidentate sites. Because
261 less strong sites are available, REE bind mainly to weaker HA sites present in higher
262 concentration. At pH 3, the main REE-HA binding sites are thus carboxylic ligands whose
263 stability constants increase for MREE.

264 Figure 3a presents the percentage of REE bound to HA for [Al] = 0 and 10 μM for the
265 experiments conducted at high REE/HA ($2\ 10^{-2}$) and variable pH (3 to 6). Without Al, around
266 30% of REE are bound to HA at pH = 3, a value that reaches 95% at pH = 6. The presence of
267 Al in equal amount than REE decreases the proportion of REE bound to HA. This decrease is
268 not uniform: Al competitive effect on REE-HA binding appears stronger between pH 4 and 5
269 than for lower pH. For pH > 5, $Al(OH)_{3(s)}$ precipitation might occur (fig. 1), decreasing
270 dissolved Al concentration and competition effect on REE-HA binding. Figure 3b compares
271 the log K_d^{REE} patterns at pH = 3, 4.5 and 6 for the REE-HA and REE-Al-HA experiments. As
272 previously observed at high REE/HA and whatever the pH can be, REE-HA experiments
273 result in log K_d^{REE} patterns with a MREE downward concavity, specific of the predominant
274 binding REE with weak, high density carboxylic HA sites (Tang and Johannesson 2003;
275 Pourret et al., 2007b; Marsac et al., 2010, and references therein). With Al, the LREE/HREE
276 balance is progressively modified with the increasing pH. At pH = 3, the competitive effect of

Al is more pronounced for the HREE than for the LREE, and at pH = 6, Al displaces more strongly LREE than HREE (Fig. 3b). The corresponding change of the log K_d^{REE} pattern from a log K_d^{REE} pattern presenting a MREE downward concavity at pH = 3 to a log K_d^{REE} pattern slightly increasing for HREE at pH = 6 might be indicative of the type of HA sites bound to Al and REE. At pH=3 with Al, the HREE depletion suggests the preferential binding of Al to the few strong multidentate HA sites as for low REE/HA. Conversely, the LREE depletion or HREE enrichment at pH = 6 might be due to the inability of Al to bind to HA phenolic sites. Marsac et al. (2011) showed that about 80% of HREE are bound to HA phenolic and carboxy-phenolic groups (i.e. phenol-containing groups) at pH=6. Conversely, at pH = 6, 80% LREE are bound to HA carboxylic groups. Therefore, Al appears to be a strong competitor of REE bound to COOH groups (i.e. mainly the LREE) than REE bound to phenol-containing groups (i.e. mainly the HREE). In turn, $Al(OH)_n^{(3-n)}$ species - which are the dominant Al species at pH = 6 - present stronger affinity for carboxylic groups than for phenolic groups.

3.2. Al and REE speciation modeling with PHREEQC/Model VI

Our experiments at pH = 3, low REE concentrations and varying Al concentrations show that Al^{3+} is a stronger competitor for HREE than LREE. In these conditions HREE are mainly bound to strong multidentate sites whose stability constant with REE depends on ΔKL_2. This behaviour can not be simulated with Tipping et al. (2002) parameters for Al-HA binding and Marsac et al. (2011) parameters for REE-HA binding in Model VI, as illustrated on Figure 4a (dotted lines) for the experiment at low REE/HA, pH = 3 and [Al] = 20 µM. Indeed here, $\Delta KL_2(Al^{3+})$ is very low (=0.46) and is, therefore, defined as a LREE competitor rather than a HREE one. Consequently, Al-HA binding parameters in Model VI must be re-evaluated. PHREEQC/Model VI requires the simultaneous adjustment of four parameters to

300 describe Al binding by HA, namely: log K_{MA} (for carboxylic groups), log K_{MB} (phenolic),
301 ΔLK_{2C} (strong multi-carboxylic) and ΔLK_{2P} (strong multi-phenolic) which can generate a
302 high degree of uncertainty on each parameter when individually taken. The Al-HA binding
303 parameters cannot be directly fitted from the Al-HA concentration since the possible presence
304 of $Al(OH)_{3(s)}$ in the >5 kDa fraction prevents the experimental quantification of Al-HA
305 concentration (Figure 1). However, the Al competitive effects on REE-HA binding pattern
306 and REE-HA concentrations provide important constraints on Al-HA binding parameters.

307 New Al-HA binding parameters in Model VI where determined by a data fitting
308 procedure, which consist in minimizing the RMSE. First, Al^{3+} parameters were determined
309 with our experiments at pH = 3, where other Al chemical species binding to HA and the
310 precipitation of $Al(OH)_{3(s)}$ can be neglected (Fig. 1). To define Al^{3+} as a stronger competitor
311 for HREE, log $K_{MB}(Al^{3+})$ and $\Delta LK_{2P}(Al^{3+})$ (6.20 and 5.00, respectively) were determined
312 higher or close to the values for Lu (5.23 and 5.11, respectively) since Lu presents the highest
313 log K_{MB} and ΔLK_{2P}. The log $K_{MA}(Al^{3+})$ was determined equal to 3 close to log K_{MA}(Lu)
314 (3.16), which is the lowest log K_{MA} in the REE series. Because ΔLK_{2C} are similar for every
315 REE and range from 2.01 and 2.31 for La and Lu, respectively, $\Delta LK_{2C}(Al^{3+})$ was determined
316 equal to 1 to limit Al^{3+} competitive effect on LREE at low pH. Parameter values for Al-HA
317 binding are summarized in table 1. The newly optimized Al-HA binding parameters improve
318 the REE data fits at low REE/HA and pH = 3, compared with Tipping et al. (2002) parameter,
319 as illustrated for [Al] = 20 µM on Figure 4a (dash-dotted line). Simulations at higher pH were
320 performed setting log K_{MA} and log K_{MB} for $AlOH^{2+}$ equal to Al^{3+}, according to Tipping et al.
321 (1998). However, to limit Al competition with HREE between pH 5 and 6, ΔLK_{2C} and ΔLK_{2P}
322 for $AlOH^{2+}$ were set equal to 0. Log K_{SO} was also optimized and was found equal to 9.3,
323 which is closed to the literature data (i.e. log K_{SO} =9, IUPAC, Stability Constants Database).

RMSE for REE was equal to 0.07, which is low and should indicate a good fit. Figure 4b presents experimental and simulated percentage of each REE bound to HA at pH = 6. It shows that Al competitive effect on REE-HA binding is underestimated in these conditions (dash-dotted line). Furthermore, the stronger competitive effect on LREE than on HREE can not be reproduced. To improve the simulation of Al competitive effect on REE at pH > 4.5, a higher value of log K_{MA} for $AlOH^{2+}$ than for Al^{3+} would be required (not shown), which is not thermodynamically consistent.

As shown previously on REE-HA sorption edge (figure 3a), Al competitive effect on REE-HA binding is low at pH < 4 and become stronger at pH > 4. From a modelling point of view, this behaviour could be explained by different ΔLK_{1A} for Al and REE. Indeed, ΔLK_{1A} represents the spread of stability constants between a cation and HA carboxylic groups around log K_{MA} value. An increase of this spread decreases Al stability constants with half of HA carboxylic groups, presenting the lower pK_a and log K with REE, and increases it for the second half. Therefore, an increase of ΔLK_{1A} would lead to a decrease of Al-HA binding at low pH and to an increase of Al-HA binding at high pH, accompanied with the corresponding competitive effect on REE-HA binding. Model VI parameters for Al^{3+} determined above were used as initial values for data fitting. Log K_{MA} and log K_{MB} for $AlOH^{2+}$ were set equal to Al^{3+} ones but ΔLK_{2C} and ΔLK_{2P} were set equal to 0 for $AlOH^{2+}$. The best fit was obtained with ΔLK_{1A} (Al) = 2.7, against -0.7 as determined by Tipping et al. (1998) for every cation (i.e. ΔpK_a - ΔLK_{1A} = 2.8). The modification of ΔLK_{1A} implied some modification of other parameters (log K_{MA} = 3.3, log K_{MB} = 6.0 and ΔLK_{2C} = 3) as presented in table 1. The fit can be considered of good quality because RMSE for REE is equal to 0.06. These parameters for Al-HA binding allow simulating reasonably well REE-HA patterns at pH = 3 and low REE concentration (Figure 4a, line) but also at pH = 6 and [REE] = [Al] (Figure 4b, line). Figure 5

348 presents the fraction of Al > 5kDa versus the pH. The new parameters for Al can also
349 simulate reasonably well Al-HA binding.

350 ## 4. DISCUSSION

351 The present study shows that Model VI Al-HA binding parameters have to be modifying
352 to be able to describe Al competitive effect on REE-HA binding. To test their reliability, the
353 new Model VI parameters for Al-HA binding determined in the present study were used to
354 simulate the experiments of (i) Kinniburgh et al. (1999), who studied Al-HA binding between
355 pH = 4 and 4.5 at various total Al concentration and (ii) Weng et al. (2002), who studied Al-
356 HA binding when HA is in contact with gibbsite between pH = 3.1 and 7. The conditions
357 studied by these authors provide a good test for the present Al parameters because they differ
358 strongly from our experiments. Figure 6 presents modeled versus experimental results of the
359 amount of Al bound to HA (in mol/kg). Our data at low REE/HA, pH = 3 and varying Al
360 concentrations are also presented. Data are close to the 1:1 line, showing a relatively good fit.
361 The total RMSE for Al in our experiments, Kinniburgh et al. (1999), and Weng et al. (2002)
362 is equal to 0.04. Therefore, the present Model VI Al-HA binding parameters derived from our
363 REE-Al competitive experiments allow simulating Al-HA binding in a wide range of pH and
364 Al to HA concentration ratio.

365 To date, Al competitive effect on cation-humics binding was generally studied at pH < 5
366 (Mota et al., 1996, Kinniburgh et al., 1999; Pinheiro et al., 2000). Model VI parameters for
367 Al-HA binding determined by Tipping et al. (2002) can reproduce reasonably well
368 experimental results. However, with these parameters at pH = 6, Al-HA binding is not strong
369 enough to limit $Al(OH)_{3(s)}$ precipitation and Al competitive effect on other cations, such as
370 REE, is also limited (Fig. 4b). Furthermore, the present experimental results clearly show that

371 Al-HA interactions occur mainly by carboxylic HA sites rather than by phenolic HA sites.
372 Therefore, the chemical mechanisms defined by Tipping et al.'s (2002) set of Al-HA
373 parameters is not precise enough to simulate cation competition for HA binding under
374 environmental conditions. The new parameters determined in the present study describe more
375 precisely the mechanisms of Al binding to HA. Under the circumneutral pH conditions
376 characteristic of most natural waters, Al is therefore expected to be a significant competitor of
377 trace metals and radionuclides presenting a high binding affinity for HA carboxylic groups as
378 compared to phenolic groups such as LREE.

379 Numerous studies established that dissolved organic matter (DOM) controls the REE
380 speciation in natural, organic-rich waters (Bidoglio et al., 1991; Takahashi et al., 1997; Viers
381 et al., 1997; Dia et al., 2000; Johannesson et al., 2004; Gruau et al., 2004; Davranche et al.,
382 2005; Pourret et al., 2007a; Pédrot et al., 2008). Laboratory experiments here performed as
383 well as previous studies meanwhile established that HA binding has the potential of
384 fractionating REE depending on the involved HA binding sites and REE/HA ratio (Sonke and
385 Salters, 2006, Pourret et al., 2007b; Yamamoto et al., 2010; Marsac et al., 2010; 2011). For
386 low REE/HA, when REE-HA binding occurs mainly through strong multidentate sites, REE
387 patterns of natural, organic-rich waters are expected to show a progressive increase from La to
388 Lu. By contrast, when REE-HA binding is dominated by weak carboxylic sites (i.e. for high
389 REE/HA), patterns are expected to exhibit a MREE downward concavity (Yamamoto et al.,
390 2010; Marsac et al. 2010). By compiling data from natural, organic-rich waters, Marsac et al.
391 (2010) recently showed that REE patterns effectively displayed variations that could be partly
392 due to the REE/HA (or metal loading) effect. The true occurrence of this effect is however
393 challenged by other mechanisms able to potentially fractionate REE. The competitive effect
394 generated by other cations such as Al and Fe is one of possible mechanisms (Tang and

395 Johannesson, 2010). Yamamoto et al. (2010) suggested that even low concentrations of Al
396 and Fe could delete the above “low REE/HA” fractionation process. The experiments at pH 3
397 and low REE/HA reported in the present study show that Al competition has effectively the
398 potential of limiting the higher HREE-HA binding confirming this suggestion. However, at
399 pH > 5, the contrary is observed. Aluminium occurrence decreases LREE binding to HA.
400 Therefore, these results show that the Al binding to HA in circumneutral waters could
401 promote HREE enrichment in the dissolved fraction (i.e. < 0.2 μM) due to HREE higher
402 affinity for HA binding as compared to that of LREE. In other words, Al competition with
403 REE at circumneutral pH enhances the metal loading effect on REE-HA pattern.

404 The present study confirms that the REE-HA pattern depends on the REE speciation on
405 HA and can be used as a fingerprint of the dominant HA binding sites in given pH or
406 REE/HA conditions. Modification of REE speciation on HA - and thus in REE-HA pattern -
407 is expected to occur not only in response to variations of REE/HA ratio but, to the occupation
408 of HA sites by competitor cations, such as Al. Marsac et al. (2011) suggested that different
409 effects on REE-HA pattern are anticipated depending on the affinity of competitor cations for
410 carboxylic and phenolic sites. At pH > 5, the competitive effect of Al, occurring mainly for
411 LREE, confirms this hypothesis. Up to now, predictions of REE speciation in natural,
412 organic-rich waters were performed using Model VI (or the previous version Model V), using
413 generic parameters for other cations (Tang and Johannesson, 2003; Pourret et al., 2007b).
414 These predictions could only give information about the total amount of REE displaced by the
415 competitor cation but, not on the competition effect on the 14 REE taken individually.
416 Generic cation-HA binding parameters commonly used in Model VI are those determined
417 initially by Tipping (1998) applying a linear relationship between carboxylic and phenolic
418 parameters. The cations present therefore the same relative affinity for HA carboxylic and

phenolic functional groups. Even if this assumption gives satisfactory modeling results for competitive experiments between two cations (Tipping, 1998; Peters et al., 2001; Tipping et al., 2002), the present REE-Al competition study shows that these generic parameters are not mechanistically sufficient to describe the effects of cation competition on REE pattern. To use geochemical models as a reliable tool to describe REE patterns in natural, organic rich-waters, a more accurate description of the different competitor cations binding behavior with HA is clearly required. In this perspective, further experimental studies of cation-REE competitive binding to HA are required, which might in turn take benefit of the "REE fingerprint" set up in this and previous studies to further highlight the complex mechanisms involved in cation binding to HA.

5. CONCLUSION

The competition experiments between REE and Al show different Al competition effects depending on the pH and the REE/HA ratio. Under acidic (pH = 3) and low REE/HA conditions, Al^{3+} as the dominant Al species compete more strongly with HREE than with LREE. Therefore, Al^{3+} has high affinity for the few amount of HA strong multidentate sites. Under higher pH ranging from 5 to 6 and higher REE/HA conditions, the competition is more pregnant with meaning for LREE than for HREE, suggesting a strong interaction of Al with HA carboxylic groups. PHREEQC/Model VI Al-HA binding parameters were optimized to simulate precisely both Al binding to HA and its competitive effect on REE. REE-HA binding pattern could only be simulated reasonably well in the whole experimental conditions studied only if ΔLK_{1A} was optimized (i.e. the parameter controlling width of the distribution of log K around log K_{MA}, the median value). The present study provides fundamental knowledge on Al binding mechanisms to HA. Aluminium competitive effect on other cations binding to HA depends clearly on its affinity for carboxylic, phenolic or chelate ligands,

443 which is pH dependent. From our experimental results, we can conclude that, the presence of
444 Al should enhance the metal loading effect on REE-HA pattern (i.e. an increase from LREE
445 to HREE) since Al is not expected to bind efficiently neither to HA phenolic groups nor to the
446 low amount of HA strong multidentate groups. As deduced from the different behavior
447 depicted by the different Al species, other potential competitor cations are expected to have
448 their own competitive effect on REE-HA binding. Therefore, a precise knowledge of the exact
449 behavior of the different REE competitor cations is required in order to reliably understand
450 and model REE-HA pattern variations in natural waters. Finally, the REE-HA patterns
451 resulting from Al competition were used as a probe to evaluate Al ability to bind to different
452 HA sites (carboxylic, phenolic or chelate ligands). This ability of the REE to be used as a
453 "speciation probe" could be applied to other cations in order to precisely describe their
454 interactions with HA.
455
456 **Acknowledgments**. We thank Pr. Johnson Haas (AE), Dr. Jianwu Tang and two anonymous
457 reviewers for their important comments. This research was funded by the French ANR,
458 through the "Programme Jeunes Chercheuses - Jeunes Chercheurs: SURFREE (Rare earth
459 elements partitioning at solid-water interface: Impact on REE geochemical behaviour and
460 tracing properties)".
461

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552

Table and Figure Captions

Table 1. log K_{MA}, log K_{MB}, ΔLK_{2C} and ΔLK_{2P} for Al^{3+} and $AlOH^{2+}$ determined by Tipping et al. (2002) and fitted from the present experimental data using PHREEQC/Model VI adjusting or not the parameter ΔLK_{1A}. (*) In the present study ΔLK_{2C} and ΔLK_{2P} for $AlOH^{2+}$ were set equal to 0.

Figure 1. Preliminary modeling study of Al speciation in the fraction > 5kDa (i.e. Al-HA + $Al(OH)_{3(s)}$) calculated with PHREEQC/Model VI for [DOC] = 6.7 mg L^{-1}, [Al] = 10 µM, IS = 0.01 M (NaCl) and pH ranging from 3 to 6. Model VI Al-HA binding parameters were determined by Tipping et al. (2002).

Figure 2. log K_d^{REE} patterns for REE, Al competitive binding to HA experiments at pH 3 and low REE/HA ratios (1.2 10^{-3} molREE/molC) for [Al] = 1 and 20 µM. Error bars represent standard deviation from triplicates (can be hidden by symbols).

Figure 3. REE-HA binding for high REE/HA experiments: (a) effect of Al concentration on the % of REE bound to HA relative to pH. (b) log K_d^{REE} patterns with and without Al relative to pH.

Figure 4. REE percentage bound to HA from experimental data and simulation using PHREEQC/Model VI, either in using Tipping et al. (2002) parameters for Al-HA binding (dotted line), optimized parameters without optimizing ΔLK_{1A} (dash-dotted line) or optimizing ΔLK_{1A} (line). (a) refers to the experiment conducted at pH 3, low REE/HA and

577 [Al] = 20 μM, whereas (b) refers to the experiment performed at pH = 6, high REE/HA and
578 with Σ[REE] = [Al] = 10 μM.
579
580 **Figure 5.** Comparison between experimental and simulated percentage of Al present
581 in the > 5 kDa fraction for experiments at Σ[REE] = [Al] = 10μM, [DOC] = 6.7 mg L^{-1} and
582 pH 3-6.
583
584 **Figure 6.** Comparison between experimental and simulated amount of Al bound to
585 HA, using optimized PHREEQC/Model VI Al-HA parameters, for literature data and the
586 present study data at pH 3 and low REE/HA.
587
588

589

Parameters for Al^{3+} and $AlOH^{2+}$	Tipping et al. (2002) $\Delta LK_{1A} = -0.7$	Present study $\Delta LK_{1A} = -0.7$	Present study $\Delta LK_{1A} = 2.7$ (adopted)
Log K_{MA}	2.60	3.00	3.30
Log K_{MB}	7.66	6.20	6.00
$\Delta LK_{2C}^{(*)}$	0.46	1.00	3.00
$\Delta LK_{2P}^{(*)}$	0.46	6.00	6.00

590

591

592 **Table 1**

593

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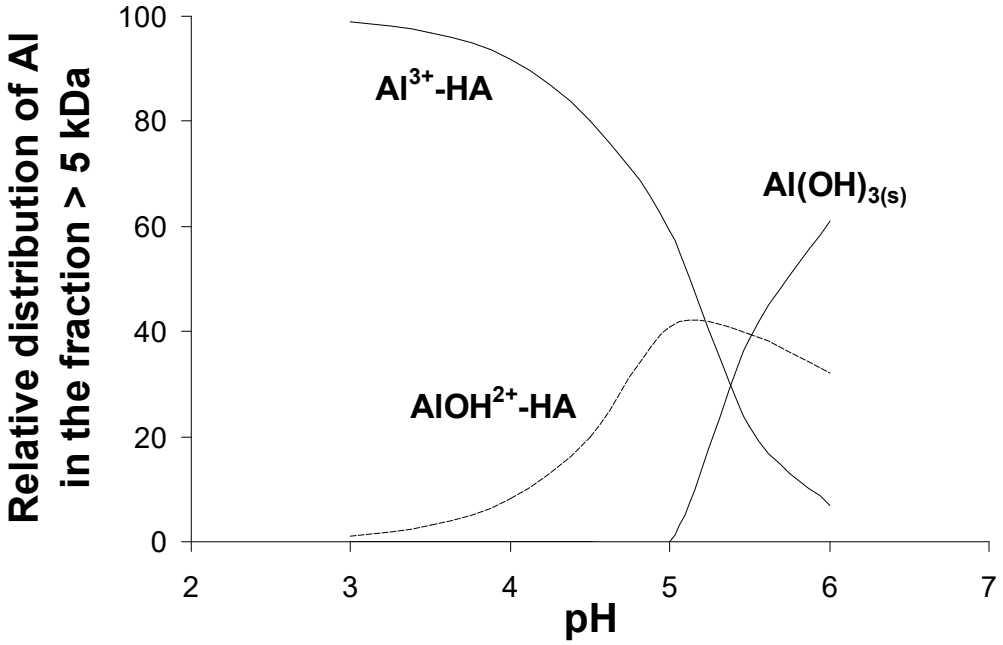

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596 **Figure 1**

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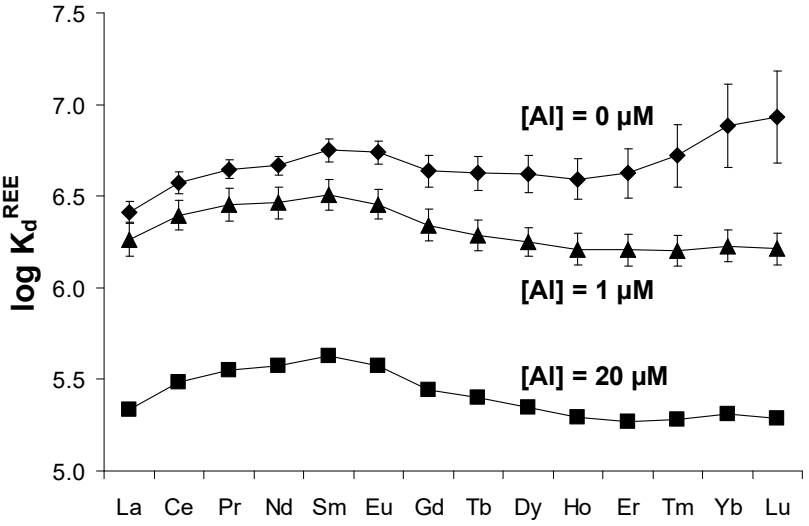

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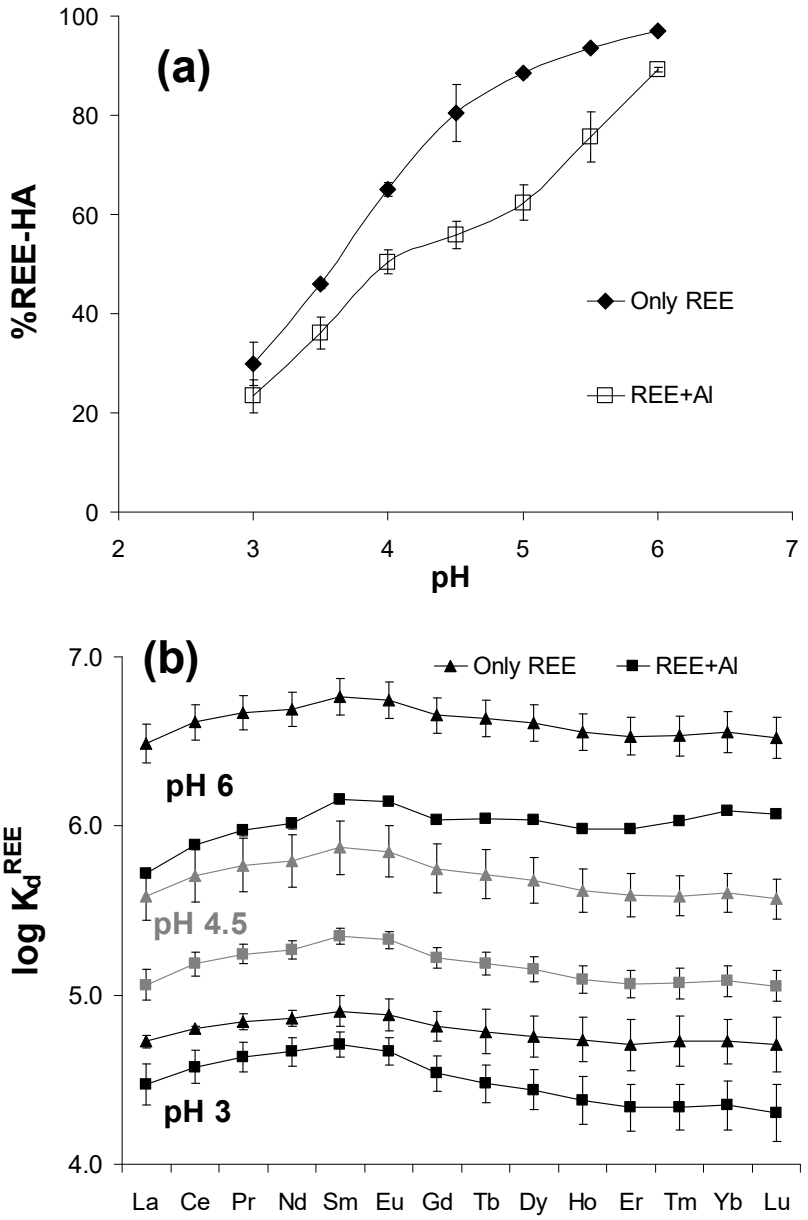
601 **Figure 2**



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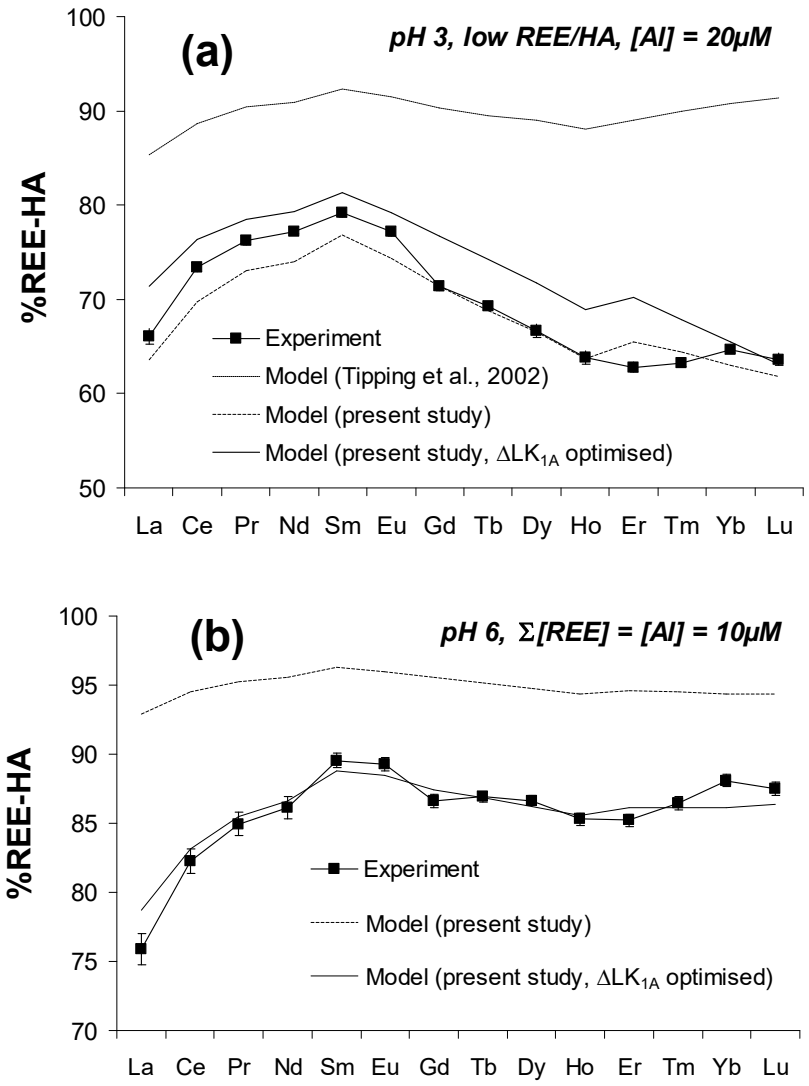

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606 **Figure 4**

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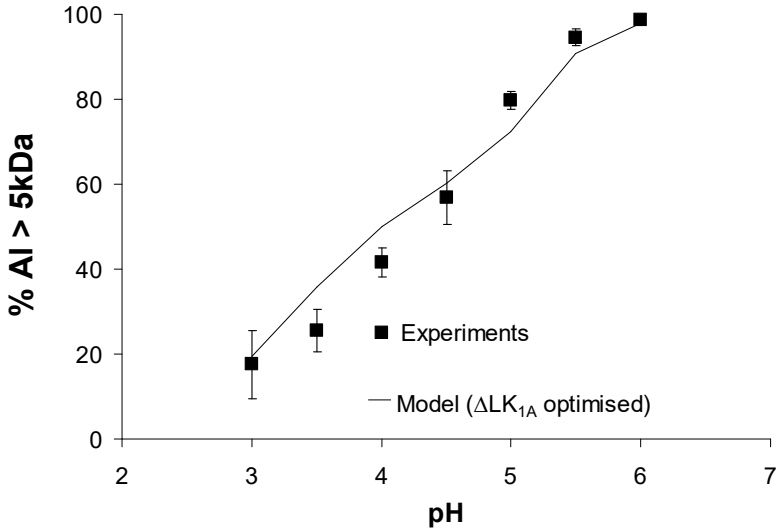

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610 **Figure 5**

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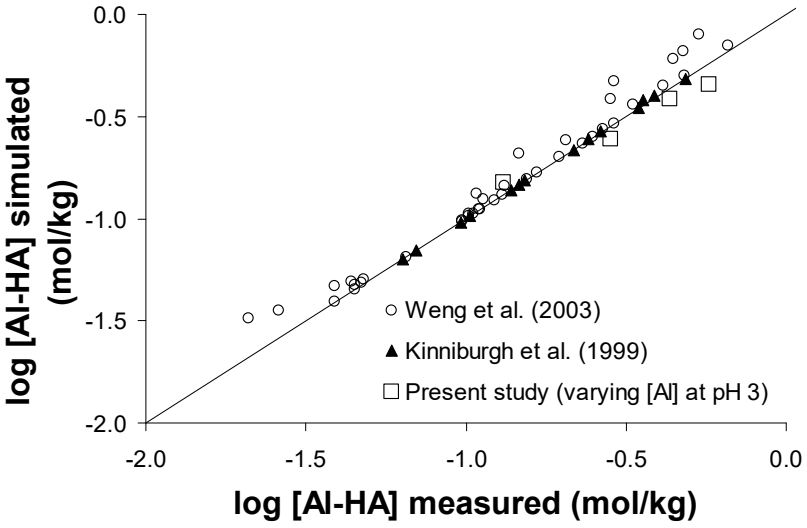

613

614 **Figure 6**