



# COMPETITIVE BINDING OF REE TO HUMIC ACID AND MANGANESE OXIDE: IMPACT OF REACTION KINETICS ON DEVELOPMENT OF CERIUM ANOMALY AND REE ADSORPTION

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**COMPETITIVE BINDING OF REE TO HUMIC ACID AND  
MANGANESE OXIDE: IMPACT OF REACTION KINETICS  
ON DEVELOPMENT OF CERIUM ANOMALY AND REE  
ADSORPTION**

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**Abstract**

The competitive binding of rare earth elements (REE) to purified humic acid (HA) and  $\text{MnO}_2$  was studied experimentally using various HA/ $\text{MnO}_2$  ratios over a range of pH (3 to 8).  $\text{MnO}_2$ , humic acid and REE solutions were simultaneously mixed to investigate the kinetics of the competitive reactions. Aqueous REE-HA complex is the dominant species whatever the experiment time, pH and HA/ $\text{MnO}_2$  ratio. The value of the distribution coefficients between  $\text{MnO}_2$  and solution ( $\log K_d^{\text{REE/MnO}_2}$ ) increases with the HA/ $\text{MnO}_2$  ratio, indicating that part of the REE-HA complexes are adsorbed onto  $\text{MnO}_2$ . The development of a Ce anomaly appears strongly limited in comparison with inorganic experimental conditions. Throughout the experimental run time, for HA/ $\text{MnO}_2$  ratios of less than 0.4,  $\text{MnO}_2$  acts as a competitor leading to a partial dissociation of the REE-HA complex. The majority of the dissociated REE is readsorbed onto the  $\text{MnO}_2$  surface. The readsorption of REE is expressed by an increased Ce anomaly on the  $\log K_d^{\text{REE/MnO}_2}$  pattern as well as a change in shape of the coefficient distribution of REE between soluble HA and solution pattern ( $\log K_d^{\text{REE/HA}}$  decrease for the heavy rare earth elements – HREE). Thus, REE are not only bound to  $\text{MnO}_2$  as a REE-HA complex, but also as REE(III). Moreover, the competition between HA and  $\text{MnO}_2$  for REE binding is shown to be higher at low pH (<6) and low DOC/Mn ratio. This study partially confirms previous work that demonstrated the control of REE adsorption by organic matter, while shedding more light on the impact of pH as well as complexation reaction competition on long-term REE partitioning between solid surface and organic solutions. The latter point is important as regards to REE speciation under conditions typical of rock and/or mineral alteration.

**Key-words-** rare earth elements, humic acid,  $\text{MnO}_2$ , kinetics, competition, complexation, dissociation.

## 1. Introduction

Organic matter has recently been shown to be one of the key factors controlling rare earth element (REE) speciation in aquatic environments such as shallow groundwaters, surface waters and soil solutions. This fundamental role has been studied by direct techniques including ultrafiltration, electrochemical measurements of organic-rich waters (Tanizaki et al., 1992; Viers et al., 1997; Dupré et al., 1999; Dia et al., 2000; Ingri et al., 2000; Johannesson et al., 2004) and laboratory studies and model calculations (Tang and Johansson (2003); Sonke and Salters, 2006; Yamamoto et al., 2005; Pourret et al, 2007a). The dominantly organic speciation of REE has several consequences on the distribution and behaviour of these elements in aquatic environments. REE organic complexation suppresses the development of a Ce anomaly and limits the REE adsorption onto Fe- and Mn-oxides. Recently, Davranche et al. (2004 and 2005) designed laboratory experiments to study the impact of REE organic complexation during REE adsorption onto potential oxidative surfaces of HFO (hydrous ferric oxide) as well as  $\text{MnO}_2$ . These authors introduced REE in the form of REE-humate complex into a suspension of oxidative solid. Their studies demonstrated (i) a strong decrease of REE adsorption onto  $\text{MnO}_2$ , (ii) a suppression of the tetrad effect and (iii) a suppression of the Ce anomaly, when REE occurs as REE-humate complexes. These authors (*op. cit.*) attributed such phenomena to an anionic adsorption process mediated by organic matter (adsorption by the humate side of the REE-humate complex) as well as the fact that REE cannot behave independently from each other since they are collectively bound to the humate molecule. Concerning these data, Davranche et al. (2005) state that Ce anomalies may not be a reliable proxy of redox conditions in organic-rich waters or in precipitates formed in equilibrium with waters rich in humic substances. However, REE in soils, soil solutions and aquatic systems draw their source from rocks and rock-forming minerals subjected to weathering/alteration processes (e.g., Sholkovitz, 1995; Gaillardet et al., 2003). The chemical reactions involved in

these processes are mainly hydrolysis inducing the release of REE as free REE(III) species. In this context, released REE are likely to be complexed by the ligands occurring in solution, including carbonate, sulphate, soluble organic matter, colloids and the solid surfaces. The distribution of REE between all these different ligands is therefore controlled by complexation stability constants, reactions kinetics, element concentrations and physico-chemical parameters (pH, Eh and T°). Furthermore, natural environments are often non steady-state systems, requiring kinetic approaches to determine more realistic chemical speciation of elements (Sekaly et al., 1999; Xue et al., 2001; Guthrie et al., 2003; Wang et al., 2005). Therefore, there are two main drawbacks in Davranche et al. (2004 and 2005) conclusion that REE organic complexation suppresses the oxidative scavenging of Ce and limits REE adsorption onto MnO<sub>2</sub>. Firstly, these authors do not take into account the respective kinetics of REE complexation reaction by organic matter and MnO<sub>2</sub> and, secondly, the REE-humate complex is completely stabilized before its interaction with MnO<sub>2</sub>. Kawabe et al. (1999) and Ohta and Kawabe (2000) noted similar suppression of Ce anomalies with both REE and REE(III)-carbonate complexes during adsorption onto FeOOH. They suggested that the Ce anomaly did not develop because Ce(III) complexation with carbonate was faster than Ce(III) oxidation kinetics. Thus, the key question concerning Ce anomaly suppression and, more generally, the REE partitioning between surface solid and organic solution is the rate at which REE are complexed by MnO<sub>2</sub> and organic matter, respectively. If oxidation and adsorption kinetics were faster than organic complexation, a Ce anomaly could nevertheless develop, despite the presence of organic matter, and a high amount of REE could be adsorbed onto MnO<sub>2</sub>. Another concern is the stability of the REE-humate complex. Rate et al. (1993) indicated that reactions necessary to stabilize cation-humate complex take place at least after 24 h. Several authors have also provided evidence that the time-dissociation of cation-humate complexes in the presence of a ligand competitor depends on the prior contact time between cations and organic molecules (Rate et al., 1993; Geckeis et al., 2002; Wang et al., 2005).

Under the experimental conditions used by Davranche et al. (2004 and 2005), organic REE complexes were completely stabilized before contact with  $\text{MnO}_2$ . Thus,  $\text{MnO}_2$  could not destabilize the REE-humate complex. Clearly, the natural environment could be different when REE occurs in contact with organic matter and solid surface at the same time. Therefore, the conditions prevailing in nature need to be experimentally explored.

In this study, competitive kinetic experiments were carried out to assess the impact of the competitive kinetic reaction between  $\text{MnO}_2$  and humic acid for REE complexation on Ce anomaly development and REE adsorption. The experiments were performed with  $\text{MnO}_2$  and purified humic acid in the presence of all 14 REE occurring simultaneously. To allow kinetic competition,  $\text{MnO}_2$ , humic acid and REE solutions were prepared separately and mixed together simultaneously. The REE phases included organic and/or inorganic REE bound to  $\text{MnO}_2$  surface, REE complexed to aqueous humic acid and soluble REE in the inorganic solution. Each of these phases was separated using a combination of filtration/ultrafiltration techniques. Two series of experiments were designed to allow the determination of the respective roles of humic acid/ $\text{MnO}_2$  ratio and pH.

## 2. Materials and methods

All chemicals used were of analytical grade, and all the experimental solutions were prepared with doubly deionised water (MilliQ system, Millipore™). Complexes were prepared in polyethylene containers previously soaked in 10 % Ultrapure  $\text{HNO}_3$  for 48 h at 60 °C, then rinsed with MilliQ water for 24 h at 60 °C to remove all possible REE contamination sources. Synthetic REE solutions were prepared from nitrate REE standards (10 ppm, Accu Trace™ Reference Standard). All experiments were carried out at room temperature, i.e. 20 °C  $\pm$  2.

### 2.1. Humic acid

Purified humate, referred to below as HA (humic acid), was obtained from synthetic Aldrich™ humic acid (Aldrich™, H1, 675-2) following the protocol described by Vermeer et al. (1998). The HA sample was freeze-dried and stored in a glass container at room temperature. HA obtained was ash free and in its protonated form, with the following elemental composition (in weight percent): C = 55.8 %, O = 38.9 %, H = 4.6 %, N = 0.6 %. REE concentrations REE in HA were below the detection limit of ICP-MS measurement (i.e. below 1 ppt). HA has a mean molecular weight of 23 kDa (Vermeer et al., 1998). Prior to use, the freeze-dried humate was resuspended overnight in an 0.001 mol L<sup>-1</sup> NaCl electrolyte solution at pH = 10, to ensure complete dissolution of the sample (Davranche et al., 2004 and 2005).

### 2.2. Manganese oxide

Synthetic MnO<sub>2</sub> (Aldrich) was used in the adsorption experiments. The solid structure was analysed by X-Ray diffraction (XRD) on a Siemens D5000 diffractometer. The principal *d* spacing indicated a pyrolusite (MnO<sub>2</sub>) structure. The total surface site number of MnO<sub>2</sub> was estimated using the solid CEC (Cation Exchange Capacity) and determined following the cobaltihexammine method, ISO 11260 (AFNOR, 1994). Ions bound with the solid surface are exchanged with cobaltihexammine ions, and the CEC is the concentration of cobaltihexammine ions eliminated from the solution. Five g of solid MnO<sub>2</sub> were mixed with 10 mL of 0.017 M cobaltihexammine solution for 3 h. The suspension was then centrifuged and the concentration of cobaltihexammine ion remaining in solution was measured at 470 nm with an Uvikon Biotek Instruments UV spectrophotometer. The analyses indicated that the MnO<sub>2</sub> used in this study has a CEC of 70 meq/100g.

Surface acidity constants were determined from potentiometric titrations of  $5\text{g.L}^{-1}$  of solid with NaOH (0.1 M) and  $\text{HNO}_3$  (0.1 M), in 0.1 M NaCl solution as the supporting electrolyte (Davranche et al., 2003). Titrations were carried out with a Metrohm 794 DMS Titrimo apparatus equipped with a Metrohm combined (3 M KCl) glass electrode. Measured acidity constants ( $\text{pK}_{\text{a}1} = 7.89$  and  $\text{pK}_{\text{a}2} = 3.65$ ) yielded a  $\text{pH}_{\text{zpc}}$  equal to 5.8, a value that falls within the reported  $\text{pH}_{\text{zpc}}$  range for  $\text{MnO}_2$  (i.e. 4.5 to 7.8; Langmuir, 1997).

### 2.3. Adsorption/Complexation procedures

*Inorganic REE adsorption onto  $\text{MnO}_2$ .* These series of experiments were carried out to provide the inorganic reference baseline necessary to interpret the data obtained during the experiments with organic matter. REE adsorption onto  $\text{MnO}_2$  was carried out in batch reactor, in which 100 mL of  $10^{-3}\text{M}$  NaCl solution were prepared with 5 ppb of each REE (e.g., 36 nmol.L<sup>-1</sup> La to 28.6 nmol.L<sup>-1</sup> Lu) and 100 mg.L<sup>-1</sup> of  $\text{MnO}_2$ . The pH was adjusted to the experimental value used, in the pH range from 3 to 8, by adding 0.1N  $\text{HNO}_3$  or 0.1N NaOH. Experimental solutions were stirred for 48 h (the equilibrium time was determined from preliminary kinetic experiments) to allow equilibration and partitioning of REE between the aqueous solution and  $\text{MnO}_2$ . Suspension aliquots of about 10 mL were sampled at steady state and filtered through 0.2  $\mu\text{m}$  cellulose acetate filters (Sartorius). The REE concentration of the filtrate was analysed to determine the concentration of REE in solution. The amount of REE adsorbed onto  $\text{MnO}_2$  was obtained by subtracting the REE concentration left in solution from the initial REE concentration taking into account sampling-induced volume variations as previously established elsewhere (Davranche et al., 2004, 2005; Pourret et al., 2007b).

*Experiments on REE complexation competition between humate and  $\text{MnO}_2$ .* All reactants were prepared separately and mixed together simultaneously to allow a detailed simulation of



the competition between humate and  $\text{MnO}_2$  for REE complexation over time. Therefore, three  $10^{-3}$  M NaCl solutions were prepared with HA, REE and  $\text{MnO}_2$ . Their pH were adjusted to 5 by adding  $\text{HNO}_3$  0.1N. The pH value of 5 was chosen for comparison with previous published data on the adsorption of REE-humate complexes onto  $\text{MnO}_2$  (Davranche et al., 2005). The three solutions were then mixed together to provide a suspension containing  $100 \text{ mg.L}^{-1}$  of  $\text{MnO}_2$ , 5 ppb of each REE (e.g.,  $36 \text{ nmol.L}^{-1}$  La to  $28.6 \text{ nmol.L}^{-1}$  Lu) and 2.5, 10, 20 and  $40 \text{ mg.L}^{-1}$  of HA. All competition-experiments were performed in duplicate or triplicate. The pH was monitored periodically with a pH-meter and re-adjusted to 5, when necessary, by addition of 0.1 N  $\text{HNO}_3$  or 0.1 N NaOH. Suspension aliquots of 10 mL were sampled immediately to determine the initial concentration of REE and HA in suspension. In addition, 15 mL of aliquot suspension were regularly sampled and filtered at  $0.2 \text{ }\mu\text{m}$ , yielding a retentate representing the inorganic or organic (as REE-HA complexes) REE fraction complexed with  $\text{MnO}_2$ . 10 mL of this sample were immediately digested for REE analysis, while the remaining 5 mL were stored for DOC analysis. An additional 10 mL volume was sampled and ultra-filtered at 10 kDa to separate the REE complexed with HA or  $\text{MnO}_2$  from the remaining inorganic REE. Ultrafiltrations were carried out by centrifuging the 10 mL solution samples through 15 mL centrifugal tubes equipped with permeable membranes of 10 kDa pore size (Millipore Amicon Ultra-15). All centrifugal filter devices were washed and rinsed with  $0.1 \text{ mol L}^{-1}$  HCl and Milli-Q water two times before use to minimize contamination. Centrifugations were performed using a Jouan G4.12 centrifuge with swinging bucket rotor at  $3000 \text{ g}$  for 30 min. This allowed the  $\text{MnO}_2$ - and HA-REE complexes to be quantitatively separated from uncomplexed inorganic REE species. The selectivity of the 10 kDa membrane with regard to the REE-HA complexes was checked by monitoring the DOC contents of the ultrafiltrates. Results show that the latter were systematically lower or equal to blank values (below 0.1 ppm). Possible adsorption of inorganic REE species onto the membrane or onto cell walls was also monitored. Inorganic REE solutions of given REE concentration were

ultrafiltered several times. Results showed that 100% of the REE present in solution were recovered in the ultrafiltrates, demonstrating that none of the REE was adsorbed, either on the membranes or on the walls of the cell devices. Moreover, to verify that no  $\text{MnO}_2$  colloids were present in the  $0.2\mu\text{m}$  filtrate. Mn concentration was systematically analysed in each fractions ( $<0.2\mu\text{m}$  and  $<10\text{ kDa}$ ). The concentration obtained was systematically lower than 1% of the total Mn and equal in each fraction, indicating that Mn is not under colloidal form but under free inorganic species.

The amount of (organic and/or inorganic) REE complexed with  $\text{MnO}_2$  corresponds to the difference between the initial REE concentration and the remaining REE concentration in the  $<0.2\mu\text{m}$  filtrate, while the amount complexed with aqueous HA corresponds to the difference between the REE concentration in the  $<0.2\mu\text{m}$  filtrate and the  $<10\text{ kDa}$  ultrafiltrate.

Finally, to simulate the role of pH in the competition between HA and  $\text{MnO}_2$  for REE binding, the same protocol as previously described was performed from pH 3 to 8 for a HA/ $\text{MnO}_2$  ratio=0.1. Suspension aliquots were sampled after 48 h for comparison with the inorganic reference experiments (section 2.3).

## 2.5. REE and dissolved organic matter analysis

REE concentrations were determined with an Agilent Technologies TM HP4500 ICP-MS instrument. Quantitative analyses were performed using a conventional external calibration procedure. Three external standard solutions with REE concentrations similar to the analysed samples were prepared from a multi-REE standard solution (Accu Trace<sup>TM</sup> Reference,  $10\text{ mg.L}^{-1}$ , USA). Indium was added to all samples as an internal standard at a concentration of  $0.87\mu\text{mol.L}^{-1}$  (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/indium 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 analysis in our laboratory is below 3 %. Organic samples used for REE determination were all immediately digested with sub-boiled nitric acid (HNO<sub>3</sub> 14 N) at 100°C, then resolubilized in HNO<sub>3</sub> 0.4 N after complete evaporation, to avoid interferences with organic matter during mass analysis by ICP-MS for the organic experiment samples.

Dissolved organic carbon concentrations were determined at Rennes University 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).

(ICPMS REE detection limits and chemical blank reproducibility can be found in the supplementary file).

### 3. Results

(All experimental data can be found in the supplementary file)

The complexation behaviour of REE onto the MnO<sub>2</sub> surface and/or HA is described using the apparent partition coefficient  $K_d$ , expressed as follow:

$$K_d^{REE/MnO_2} = \frac{\mu g \text{ (Adsorbed REE)}^a / g \text{ Mn oxide}}{\mu g.mL^{-1} \text{ (Aqueous REE)}^a} \quad (1)$$

$$K_d^{REE/HA} = \frac{\mu g \text{ ( Adsorbed REE)}^b / g \text{ Aqueous HA}}{\mu g.mL^{-1} \text{ (Inorganic aqueous REE)}^b} \quad (2)$$

(Adsorbed REE)<sup>a</sup> represents the concentration of REE adsorbed onto MnO<sub>2</sub> obtained by subtracting REE concentrations left in solution after filtration at 0.2 μm from the initial REE concentration. (Aqueous REE)<sup>a</sup> corresponds to the REE concentration left in solution after filtration at 0.2 μm. (Adsorbed REE)<sup>b</sup> represents the concentration of REE complexed with aqueous HA, and is calculated by subtracting the REE concentrations left in solution after

filtration at 0.2  $\mu\text{m}$  and the inorganic REE concentration in the 10-kDa ultrafiltrate. (Inorganic aqueous REE)<sup>b</sup> corresponds to the inorganic REE concentration in the 10-kD ultrafiltrate. Considering this method of calculation, REE adsorbed on the  $\text{MnO}_2$  surface could occur either, as inorganic REE or, as REE-HA complexed species.

Ce anomalies on  $\log K_d^{\text{REE}}$  patterns are determined as follows:

$$Ce / Ce^* = \frac{\log(K_d^{\text{Ce}})}{\frac{1}{2} [\log(K_d^{\text{La}}) + \log(K_d^{\text{Pr}})]} \quad (3)$$

Finally, DOC partitioning between  $\text{MnO}_2$  and solution are converted into apparent partition coefficients using:

$$K_d^{\text{DOC/MnO}_2} = \frac{\mu\text{g DOC adsorbed/g Mn oxide}}{\mu\text{g.mL}^{-1} \text{ DOC in solution}} \quad (4)$$

### 3.1. Impact of HA/ $\text{MnO}_2$ ratio on competition between HA and $\text{MnO}_2$ for REE binding.

(Reproducibility of  $\log K_d^{\text{REE/HA}}$  and  $\log K_d^{\text{REE/MnO}_2}$  can be found in the supplementary file.)

*Kinetics.* Figure 1 presents the time-series variation of  $\log K_d^{\text{REE/MnO}_2}$  and  $\log K_d^{\text{REE/HA}}$  (HA not adsorbed at solid surface) for La, Gd and Lu as well as  $\log K_d^{\text{DOC/MnO}_2}$  for HA/ $\text{MnO}_2$  ratios of 0.4, 0.1 and 0.025. Time-series variations of  $\log K_d^{\text{REE/MnO}_2}$  reveal that a pseudo-equilibrium was reached before 10 h (Fig.1). Previous studies by Davranche et al. (2005) provide evidence that, when REE are initially present as REE-humate complexes, a pseudo-equilibrium is attained more slowly after about 10 days (see Fig. 6 in Davranche et al., 2005). Therefore, a pseudo-steady state is reached more rapidly when REE are introduced as free species in solution.

For a given HA/ $\text{MnO}_2$  ratio, REE partition coefficients are higher for aqueous HA than on  $\text{MnO}_2$ . This result suggests that REE are more complexed to HA than  $\text{MnO}_2$ , whatever the initial concentration of HA in the solution. However,  $\log K_d^{\text{REE/MnO}_2}$  decreases

progressively with the HA/MnO<sub>2</sub> ratio. At 72 h,  $\log K_d^{La/MnO_2}$  yields values of 3.68, 3.16 and 2.50 for ratios of 0.4, 0.1 and 0.025, respectively. This contrasts strongly with the behaviour of  $\log K_d^{REE/HA}$ , which remains nearly constant. At 72 h,  $\log K_d^{La/HA}$  is at around 7.65, 7.70 and 7.61, for ratios of 0.4, 0.1 and 0.025, respectively. This implies that, when initial HA concentration is high compared to MnO<sub>2</sub>, a greater amount of REE could be adsorbed onto the MnO<sub>2</sub> surface, probably as REE-HA complex, since values of  $\log K_d^{REE/MnO_2}$  and  $\log K_d^{DOC/MnO_2}$  are closely similar for ratios of 0.4 and 0.1. Furthermore, Fig. 1 displays lower and higher amounts of adsorbed DOC for HA/MnO<sub>2</sub> ratios of 0.025 and 0.4, respectively. Several studies have shown that, in a ternary system composed of cations, organic matter and solid surface, the cation adsorption was not only enhanced compared with the corresponding binary system but also with the organic matter concentration, generally for low pH (Xiangke et al., 2000; Christl and Kretzschmar 2001; Wu et al., 2003).

A slight decrease of  $\log K_d^{REE/HA}$  appears vs. time (Fig.1), with  $\log K_d^{La/HA}$ , for example, showing values of 7.61 and 7.38 at 8h and 72 h, respectively, for a HA/MnO<sub>2</sub> ratio of 0.025. The decrease is even more pronounced for HREE (heavy rare earth elements), with  $\log K_d^{Lu/HA} = 7.15$  and 6.76 at 8 and 72 h, respectively. This decrease occurs simultaneously with a slight increase of  $\log K_d^{REE/MnO_2}$ , with  $\log K_d^{La/MnO_2} = 2.48$  and 2.52 and  $\log K_d^{Lu/MnO_2} = 2.38$  and 2.52 for ratio= 0.025 at 8 and 72 h, respectively. The  $\log K_d^{REE/HA}$  decrease is related to a decreasing HA/MnO<sub>2</sub> ratio, suggesting that a more important partial dissociation of the REE-HA complex is occurring when MnO<sub>2</sub> is in high amount as compared to that of HA.

Log  $K_d^{REE}$  patterns in each compartment. In Fig. 2a, Log  $K_d^{REE/MnO_2}$  patterns are nearly flat except for the occurrence of a Ce anomaly for HA/MnO<sub>2</sub> ratios of 0.1 and 0.025. Davranche et al. (2005) reported the same type of pattern when REE was initially present as REE-humate complex. They interpreted this pattern shape as reflecting the anionic adsorption of the REE-humate complex onto the MnO<sub>2</sub> surface. As illustrated in Fig. 2a and Fig. 3, where Ce anomaly variations are expressed as Ce/Ce\*, the Ce anomaly increases with decreasing HA/MnO<sub>2</sub> ratio and increasing time. Moreover, the Ce anomaly develops rapidly in the first hour, for experiments conducted with a HA/MnO<sub>2</sub> ratio of 0.025, and after 10h for experiments conducted with ratios of 0.1 and 0.2. Furthermore, at these three HA/MnO<sub>2</sub> ratios, the amplitude of the Ce anomaly is time-dependent. No steady state was reached at 72h. Although the experiment at ratio = 0.2 continued until 288 h (data not shown here), there was no observed stabilization of the Ce-anomaly value (Ce/Ce\* = 1.033 at 288 h). Such a result differs markedly from the study by Davranche et al. (2005), who report no development of Ce anomaly, even after 20 days of experiment run-time (Fig. 5, in Davranche et al. (2005)).

The log  $K_d^{REE/HA}$  patterns presented in Fig. 2b show a slight increase in LREE log  $K_d^{REE/HA}$  (light rare earth element) and decrease in HREE log  $K_d^{REE/HA}$  on each pattern. However, the pattern obtained for HA/MnO<sub>2</sub> = 0.4 is flatter. This type of pattern is different from the patterns for the REE-humate complex obtained by Davranche et al. (2005) and Pourret et al. (2007b). The present patterns exhibit downward-concave and convex shapes in the MREE for the HA fraction and the solution, respectively. The decrease observed for HREE is counterbalanced by the HREE concentration increase in the dissolved inorganic REE pattern. The discrepancy in HREE slopes between the patterns displayed in Figs. 2b and 2c is due to the fact that the REE pattern in HA fraction is expressed in log  $K_d$ , while the REE pattern in solution is expressed in ppb. In Fig. 4, Gd/Yb ratio is plotted versus time for a HA/MnO<sub>2</sub> ratio of 0.1. The Gd/Yb ratio calculated from log  $K_d^{REE/HA}$  increases with time;

Gd/Yb = 1.03 and 1.08 at  $t = 1$  h and 168 h, respectively. On the contrary, the Gd/Yb ratio calculated from the inorganic REE concentration in solution decreases with time; Gd/Yb = 0.6 and 0.27 at  $t = 1$  h and 168 h, respectively. The variation of Gd/Yb ratio with time suggests that the HREE  $\log K_d^{REE/HA}$  decrease observed on  $\log K_d^{REE/HA}$  patterns results from a transfer towards the inorganic solution of part of the HREE complexed to HA.

### 3.2. Impact of pH on competition between HA and MnO<sub>2</sub> for REE adsorption (HA/MnO<sub>2</sub> ratio = 0.1 and $t = 48$ h)

Experimental data are illustrated in Fig. 5 for four REE (La, Ce, Gd and Lu). Figure 5a represents  $\log K_d^{REE/MnO_2}$  as a function of pH, without HA in solution. REE adsorption onto MnO<sub>2</sub> is strongly dependent on pH with, for example,  $\log K_d^{La/MnO_2}$  ranging from 2.36 to 5.88 when pH increases from 3 to 8. De Carlo et al. (1998) and Ohta and Kawabe (2001) observed the same pH dependence. As can be seen, Ce is more strongly adsorbed than the other REE. Figure 5b illustrates the  $\log K_d^{REE/MnO_2}$  and  $\log K_d^{REE/HA}$  values for four REE (La, Ce, Gd and Lu) as well as  $\log K_d^{DOC/MnO_2}$ . Comparison of Figs. 5a and 5b provides evidence that the presence of HA strongly decreases the  $\log K_d^{REE/MnO_2}$  at high pH, with  $\log K_d^{La/MnO_2}$  displaying values of 5.88 and 3.67 at pH 8 without and with HA, respectively. Whatever the pH is, a major part of each REE is complexed with HA; e.g.  $\log K_d^{La/MnO_2} = 3.67$  and  $\log K_d^{La/HA} = 7.73$  at pH 8. Thus,  $\log K_d^{REE/HA}$  is also pH-dependent, with REE being more easily complexed to HA at alkaline than at acidic pH. However, we can observe a slight decrease in the  $\log K_d^{REE/HA}$  value with increasing pH; e.g.  $\log K_d^{La/HA} = 8.07$  and 7.73 at pH 6 and 8, respectively. This decrease develops along with an increase in the adsorption of REE onto MnO<sub>2</sub> (Fig. 6b). Several studies on the adsorption of organic matter onto solid surface have shown that the value of  $\log K_d^{DOC/MnO_2}$  decreases with increasing pH (Gu et al., 1994;

Vermeer et al., 1997; Avena and Koopal, 1999). As a result, and in contrast to the experiment performed at pH 5, the ratio of  $\log K_d^{\text{DOC/MnO}_2}$  to  $K_d^{\text{REE/MnO}_2}$  deviates from 1 over the pH range concerned indicating that REE and HA are not entirely bound to each other when adsorbed onto the MnO<sub>2</sub> surface. Figure 6 presents the patterns of  $\log K_d^{\text{REE/MnO}_2}$  without HA, as well as the  $\log K_d^{\text{REE/HA}}$  and  $\log K_d^{\text{REE/MnO}_2}$  for the competitive complexation experiment under three pH conditions (4, 6 and 8) at 48 h. As expected,  $\log K_d^{\text{REE/MnO}_2}$  patterns without HA exhibit a Ce anomaly that decreases with increasing pH (Fig. 6a).  $\log K_d^{\text{REE/HA}}$  patterns exhibit two types of shape, (i) a relatively flat shape and (ii) a shape characterized by HREE  $\log K_d^{\text{REE/HA}}$  value decrease, such as developed in the  $\log K_d^{\text{REE/HA}}$  pattern obtained at pH 5 for the various HA/MnO<sub>2</sub> ratios (Figs. 2b and 6b). Fig. 7 illustrates the evolution of the Gd/Yb ratio relative to pH for the competitive complexation experiment. The evolution of Gd/Yb ratio on HA reflects the HREE  $\log K_d^{\text{REE/HA}}$  value decrease. At low pH, when low amounts of REE are complexed by HA, the ratio is equal to ~1, namely, no HREE  $\log K_d^{\text{REE/HA}}$  decrease occurs. From pH 4 to 5, the ratio increases to an average value of 1.045, and decrease takes place. At higher pH, the value of Gd/Yb ratio decreases, while the shape of the  $\log K_d^{\text{REE/HA}}$  pattern becomes flat once again. These results suggest that HREE  $\log K_d^{\text{REE/HA}}$  value decrease on the  $\log K_d^{\text{REE/HA}}$  patterns occurs only over a limited pH range (pH = 3-6).

#### 4. Discussion

As previously suggested by Davranche et al. (2004 and 2005), the present data provide evidence that REE organic complexation results in a decrease of the REE adsorption onto



MnO<sub>2</sub> and a strong limitation of the development of a Ce anomaly at the mineral surface. However, we point out here two significant differences compared with previous studies: (i) the Ce anomaly develops through time and with decreasing HA/MnO<sub>2</sub> ratio, (ii) some of the REE-HA complexes are unstable, and are dissociated through time in the presence of MnO<sub>2</sub>.

#### 4.1. Slowdown and reduction in the development of Ce anomalies

Figures 2a and 3 provide evidence that the development of a Ce anomaly at the MnO<sub>2</sub> surface is strongly attenuated with increasing HA/MnO<sub>2</sub> ratio. In previous studies, Davranche et al. (2004 and 2005) investigated the impact of HA complexation on REE adsorption onto MnO<sub>2</sub> and HFO (hydrous ferric oxide). In their experiments, REE were complexed to HA prior to contact with the solid surfaces. When comparing the organic experiments with the inorganic experiments, these authors either observed only very weakly positive Ce anomalies on the log  $K_d^{REE/MnO_2}$  pattern or no anomaly at all (see Figs. 5 and 7 in Davranche et al., 2005). To interpret their data, they proposed two hypotheses. Firstly, under their experimental conditions, the REE-HA complex was adsorbed at the MnO<sub>2</sub> or HFO surface by an anionic adsorption mechanism. REE-HA was then absorbed by the humate side of the complex. Therefore, Ce was not in direct contact with the potential oxidative MnO<sub>2</sub> or HFO surface, so Ce(III) was unlikely to be oxidized into Ce(IV). Secondly, different REE could not behave independently from each other in the organic experiments since they were collectively bound to humate molecules. In this way, the Ce anomaly is unable to develop, simply due to the binding of the entire REE pool to humate. Davranche et al (2004 and 2005) based their two hypotheses on the fact that log  $K_d^{REE/MnO_2} / \log K_d^{DOC/MnO_2}$  ratios were close to 1.0 at pH 5 and 7.5, suggesting that REE and HA remain bound to each other during adsorption of the REE-HA complexes onto the MnO<sub>2</sub> and HFO surfaces. However, the new experimental dataset presented here provides a distinct interpretive framework. Even if the Ce anomaly is greatly

attenuated compared with inorganic experiments (Davranche et al., 2005), a slight Ce anomaly is developed whose amplitude increases with time and decreasing HA/MnO<sub>2</sub> ratio (Fig. 3). Moreover, competitive experiments conducted as a function of pH demonstrate that both  $\log K_d^{\text{REE/MnO}_2}$  and  $\log K_d^{\text{DOC/MnO}_2}$  values are quite different relative to the pH and for low HA/MnO<sub>2</sub> ratios as well. Therefore, REE and HA are not entirely bound to each other when adsorbed onto the MnO<sub>2</sub> surface (Fig. 6b). Linked with the time-dependent development of the Ce anomaly (Fig. 3), this observation suggests that (i) part of Ce adsorbed onto MnO<sub>2</sub> is directly in contact with the surface and is therefore oxidized by MnO<sub>2</sub> and (ii) there is a time-dependent ‘source’ of Ce in the suspension, which becomes oxidized in Ce(IV). As shown above in Fig.1,  $\log K_d^{\text{REE/HA}}$  decreases with time and decreasing HA/MnO<sub>2</sub> ratio. This decrease indicates a dissociation of the REE-HA complex with time. The inorganic Ce required for the development of a Ce anomaly on MnO<sub>2</sub> likely draws its source from dissociation of the organic complex. Moreover, Figs. 2a and 3a indicate a dissociation of the REE-HA complex that increases with increasing HA/MnO<sub>2</sub> ratio. The amount adsorbed from the dissociation of the REE-HA complex is easily accessible if we consider the time when the Ce anomaly appears as the reference time after which readsorption occurs (readsorption of inorganic REE). However, it is impossible to assess the amount of REE bound as inorganic and/or REE-HA complex in the first stage of the experiment. Consequently, calculations can only yield the proportion of inorganic REE that is adsorbed onto MnO<sub>2</sub> from the dissociation of inorganic REE-HA complexes (Tables 1 and 3). For the experiment at HA/MnO<sub>2</sub>= 0.1 and pH 5, Table 1 reports the proportion of Ce bound to each phase of the suspension and the proportion of inorganic Ce supplied by Ce-HA complex dissociation and readsorbed onto MnO<sub>2</sub>. The data show a time-dependent increase of the inorganic Ce bound onto MnO<sub>2</sub>, supplied by dissociation of the organic complex, which represents from 16.2 % to 32.3 % of all the Ce adsorbed onto MnO<sub>2</sub> at 8 h and 72 h,

respectively. At 72 h, this proportion corresponds to 5.6 % of the total Ce present in the suspension.

#### 4.2. REE-HA complex dissociation

Another major result of the present study is the evidence of a dissociation of the REE-HA complex with time and with decreasing HA/MnO<sub>2</sub> ratio. Table 2 presents the proportion of REE dissociated from REE-HA complex, the proportion of REE dissociated from REE-HA complex and reabsorbed onto MnO<sub>2</sub>, as well as the proportion of REE dissociated from REE-HA complex and removed to the inorganic solution during the experiment with HA/MnO<sub>2</sub> = 0.025. These data imply that most of the dissociated REE is readsorbed onto the MnO<sub>2</sub> surface. LREE exhibit higher readsorption than HREE: 98.9% for La as against 95.8% for Lu. By contrast, in the inorganic solution, the LREE make up a lower proportion than HREE: 1.1 % for La as against 4.2% for Lu. This contrasted behaviour of HREE and LREE is recorded in the shapes of the log  $K_d^{REE}$  and dissolved inorganic REE patterns (Fig.1).

Several authors have proposed that a cation-humate (natural or synthetic) complex could be dissociated in the presence of a competitive ligand (Rate et al., 1993; Geckeis et al., 2002; Artinger et al. 2002; Monsallier et al. 2003; Wang et al., 2005). Generally, the competitors used in these studies were chelating resins (Chelex 100 Biorad), ligands (metallochromic ligands, PAR) or cation exchanger resin (Dowex 50, HYPHAN). All these authors have established that humate complex dissociation is time-dependent, showing that dissociation of the cation-humate complex decreases with increasing reaction time. By studying the dissociation of an Eu-humate and Am-humate complex in the presence of a resin, Geckeis et al. (2002) and Wang et al. (2005) demonstrated that Eu and Am shift from a fast to a slow dissociation species with increasing time. Rate et al. (1993), Geckeis et al. (2002), Monsallier et al. (2003) and Wang et al. (2005) investigated the influence of predissociation

cations and humate contact time, pH of solution and humate initial concentration on the dissociation time. Rate et al. (1993) and Geckeis et al. (2002) showed that a longer duration of cation-humate pre-equilibration decreases the complex dissociation. They suggested a complex ripening process where, after an initial sorption step, the cations migrate to stronger binding sites or move to inner sites of the macromolecular structure of the humic molecule. Rate et al. (1993) further showed that long-term reaction between cation and humate may induce molecular conformation changes that can influence the dissociation reaction rate. Concerning the influence of pH, Rate et al. (1993) demonstrated that complex dissociation falls sharply between pH 5 and 7, in contrast to Monsallier et al. (2003) and Wang et al. (2005), who showed an enhancement of the dissociation of Eu-humate and Am-humate complex between pH 3 and 6. Monsallier et al. (2003) attributed their result to different humic colloid structures for the different pH values. Finally, Rate et al. (1993) and Monsallier et al. (2003) provided evidence that increasing the humic concentration decreases the cation-humate complex dissociation rate. Regarding the influence of these parameters on dissociation, and hence the stability of the cation-humate complex, Rate et al. (1993) inferred that thermodynamic complex stability is more determinant in complex dissociation than non-diffusive processes.

The present experimental set-up may be regarded as similar to that of previous cited studies. HA represents the humic molecule, REE the cation and  $\text{MnO}_2$  can be considered as the competitive ligand. The present experiments were designed to study the kinetics of REE binding to HA and  $\text{MnO}_2$ , and therefore all reactants were added simultaneously. While a major proportion of the REE appears to be immediately complexed to HA, the complex is not immediately stabilized thermodynamically due to the competitive presence of  $\text{MnO}_2$ . REE could be dissociated from the earlier-formed REE-humate complex, and then readsorbed partly onto  $\text{MnO}_2$ . Experiments conducted as a function of HA/ $\text{MnO}_2$  ratio show that the dissociation-redistribution process increases with decreasing HA/ $\text{MnO}_2$  ratio, i.e. with

decreasing HA concentration, as demonstrated by Rate et al. (1993) and Monsallier et al. (2003). The  $\log K_d^{\text{REE/HA}}$  pattern for the competitive experiment (Fig. 6) and the variation of Gd/Yb ratio (Fig. 7), both represented as function of pH, show that HREE  $\log K_d^{\text{REE/HA}}$  decrease is not developed for pH >6. Such decrease is characteristic of HREE dissociation from the REE-HA complex, implying that the dissociation increases up to pH 6 and decreases thereafter. Therefore, this new dataset agrees with the results of Monsallier et al. (2003) and Wang et al (2005). These latter authors demonstrated an increase in complex dissociation between pH 3 and 6, while Rate et al. (1993) obtained a dissociation decrease between pH 5 and 7.

The last point concerns the quantitative redistribution of the REE between MnO<sub>2</sub> and inorganic solution. As expected by the dissociation process, the major part (about 98%) of the REE dissociated from REE-HA is readsorbed onto the MnO<sub>2</sub> surface. However, a difference in behaviour appears between LREE and HREE, the latter being more efficiently removed to inorganic solution (Table 2). A possible explanation could be that REE-MnO<sub>2</sub> adsorption constants are higher for LREE than HREE, thus inducing a higher concentration of HREE in solution. In the literature, there are no REE-MnO<sub>2</sub> adsorption constants available for the whole REE series. However, experiments of REE adsorption or coprecipitation with MnO<sub>2</sub> have provided some evidence that HREE are more effectively adsorbed than LREE onto the MnO<sub>2</sub> surface (Koeppenkastrop and De Carlo, 1992; De Carlo et al., 1998; Bau, 1999; Ohta and Kawabe, 2001; Davranche et al., 2005). Moreover, Quinn et al. (2006) recently provided a data-set of REE-HFO complexation constants, showing that  $\log \beta_{\text{HFO}}^{\text{REE}}$  increases with the REE atomic number. In view of the above considerations, some other explanations are required. For instance, HREE could be complexed with an inorganic ligand that allows its stabilisation in the inorganic solution. The experimental conditions in our study involve very few possible ligands, in fact only Cl<sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. The stability constants of REE-Cl<sup>2+</sup>

complexes show lower values with increasing atomic number of the REE, thus excluding the role of  $\text{Cl}^-$  as a stronger HREE complexant (Wood et al., 1990). In the literature, HREE enrichment in solution has often been interpreted in terms of a preferential carbonate complexation (Millero, 1992; Lee and Byrne, 1993; Johansson et al., 1996). However, in the present study, even if each experiment was performed under atmospheric conditions, the pH value of 5 rules out a significant complexation of HREE by carbonate. Wood et al. (1990) calculated the distribution of Eu among the various carbonate and bicarbonate complexes as a function of carbonate activity, proposing that Eu speciation is dominated by the free Eu(III) form at pH 5. Consequently, further investigations are required to explain the distribution of HREE between  $\text{MnO}_2$  surface and inorganic solution.

#### 4.3. Implications regarding Ce and REE adsorption when organic matter occurs

The results demonstrate that, as previously observed by Davranche et al. (2004 and 2005), the REE adsorption onto  $\text{MnO}_2$  decreases with respect to inorganic experiments. Nevertheless, the adsorption rate is not totally controlled by the REE-HA adsorption. Experiments performed as a function of pH provide evidence that  $\log K_d^{\text{REE/MnO}_2}$  is not directly linked to  $\log K_d^{\text{DOC/MnO}_2}$ . This is supported by the results given on Fig. 1c, where  $\log K_d^{\text{REE/MnO}_2}$  values are slightly higher than  $\log K_d^{\text{DOC/MnO}_2}$ . Such a discrepancy indicates that a significant amount of REE is bound to the  $\text{MnO}_2$  surface as REE(III) inorganic species. However, the increase of  $\log K_d^{\text{REE/MnO}_2}$  and the lack of large Ce anomalies with increasing HA/ $\text{MnO}_2$  ratio also implies that part of the REE occurs as REE-HA complexes themselves adsorbed onto the solid surface. Thus, REE are not only sorbed onto  $\text{MnO}_2$  as inorganic species but also as REE-HA complexes. We performed calculations to estimate the amount of REE bound onto  $\text{MnO}_2$  as REE-HA and as inorganic species in the experiment at pH 5 with

an HA/MnO<sub>2</sub> ratio of 0.01 (Table 3). At 72 h, a non-negligible proportion of REE is bound in an inorganic form onto MnO<sub>2</sub>, at the expense of REE-HA dissociation, i.e. between 13.5 % for La and 32.5 % for Ce, representing 1.9 to 5.7 % of the total REE in suspension, respectively. Experiments conducted as a function of pH reveal that competition between HA and MnO<sub>2</sub> increases with the pH value. However, even if MnO<sub>2</sub> appears to compete with HA for REE complexation, the major part of the REE remains as a soluble REE-HA complex, i.e. 82.5% at 72h for La, in the experiment conducted at pH= 5 with HA/MnO<sub>2</sub> ratio = 0.01. In the suspension, REE speciation is thus dominated by organic complexed species. It is important to note that the role of soluble REE organic complexation could become less dominant with increasing pH (Fig. 5 b).

However, in the context of ongoing solid alteration processes (in soils, or aquifers) where REE are released in a soluble inorganic form, the present work provides evidence that REE speciation will be dominated by organic complexation and also partially by solid adsorption. As a function of pH and organic matter/solid surface ratio, an increasing proportion of REE might be sorbed, particularly as ionic species. This latter point is of major importance. The present study implies that the development of a Ce anomaly can be limited but not entirely suppressed in organic-rich solution as suggested previously, according to the pH conditions and organic matter/oxidative surface ratio. Therefore, we could raise the question of whether the HA/MnO<sub>2</sub> ratios used in the experiments are comparable with natural conditions. To address this question, DOC/Mn ratios were calculated from 16 natural soil samples (Alfisols, Aridisols, Inceptisols, Mollisols and Ultisols), using the estimated Mn concentrations (mg.kg<sup>-1</sup>) in Mn oxide form and the DOC concentrations (mg.kg<sup>-1</sup>) provided in Jiang et al. (2005). DOC/Mn ratio varies from 0.3 to 11.9. The HA/MnO<sub>2</sub> ratios used in the present experiments are expressed in terms of DOC/Mn ratio, with values varying between 3.6 and 0.2. The mechanism described here could therefore potentially occur in natural

environments. However, the competition between HA and  $\text{MnO}_2$  for REE complexation will be more markedly expressed on the REE patterns for low DOC/Mn ratio and pH from 3 to 6.

A decrease of REE adsorption onto  $\text{MnO}_2$  is observed in the presence of organic matter, while the development of a Ce anomaly is effectively limited but not suppressed. Therefore, the present study leads to the same restriction on the use of the Ce anomaly as a redox proxy as previously stated by Davranche et al. (2005). However, the new experimental dataset sheds more light on these surface processes, by allowing us to assess the impact of pH and competition between complexation reactions. The formation and dissociation of REE-HA complexes are indeed both pH-dependent. Increasing the pH decreases the concentration of REE-HA complexes in solution and favours the sorption reaction onto  $\text{MnO}_2$ . Indeed, the dissociation of REE-HA complexes is at a maximum in the 3 to 6 pH range, implying that solid surfaces behave as a competitive ligand especially over this pH range. Furthermore,  $\text{MnO}_2$  and HA competition for REE binding not only influences the REE distribution between the solution and the relevant solid but also the kinetics of the adsorption and dissociation reactions, and hence the development of a Ce anomaly. As a result, in the experiment carried out for 288 h (results not shown here), the amplitude of the Ce anomaly never reached a steady state, meaning that REE-HA dissociation and inorganic REE readsorption onto  $\text{MnO}_2$  were still occurring at that time. This last point raises questions on the impact of such mechanisms in the context of a long-term rock or mineral alteration. What will be the amplitude of the Ce anomaly? Will the amount of adsorbed REE at the solid surface always remain negligible compared to the amount of REE complexed with organic matter?

Finally, the present dataset provides evidence that complexation mechanisms are involved depending on the initial REE chemical species present.



## 5. Conclusions

Experimental studies of the kinetic competition between HA and MnO<sub>2</sub> for REE complexation were carried out using a combination of filtration/ultrafiltration techniques to study the impact on Ce anomaly development and REE fractionation. REE speciation is dominated by the REE-HA complex. Accordingly, in contrast with inorganic conditions, there is a decrease in the amount of REE adsorbed by MnO<sub>2</sub> and the development of a Ce anomaly is strongly limited as previously shown by Davranche et al. (2005). Nevertheless, for the tested HA/MnO<sub>2</sub> ratios below 0.4, the present data show that MnO<sub>2</sub> acts as a competitor able to induce a slight dissociation of the REE-HA complex. Most of the dissociated REE is subsequently readsorbed onto the MnO<sub>2</sub> surface, and this readsorption is recorded by an increase in development of the Ce anomaly, despite the overall REE organic speciation. Moreover, the increase of  $\log K_d^{\text{REE/MnO}_2}$  with increasing HA/MnO<sub>2</sub> ratio also indicates that REE are partially bound to HA, which is itself adsorbed onto the solid surface. Consequently, the REE are adsorbed onto MnO<sub>2</sub> surfaces as REE(III) and REE-HA complex. The processes described in this study are pH-dependent. At alkaline pH, the REE-HA complex becomes less dominant and dissociation does not occur since no modification is observed in the shape of the REE-HA pattern. The competition for REE complexation between HA and MnO<sub>2</sub> is more intensive at low DOC/Mn ratio and pH from 3 to 6.

The present study corroborates Davranche et al. (2004 and 2005) conclusions regarding the use of Ce anomalies as a redox proxy in paleoenvironments. However, this new dataset highlights the importance of (i) competition between ligands for REE binding and (ii) pH control on REE distribution. When the REE-HA complex is not stabilized, the presence of competitive surface could induce dissociation of the organic complex and a redistribution of the REE between the solid surface and the inorganic solution. This would not only lead to modifications of the solution composition but also the REE pattern in solution, which itself

exhibits a negative Ce-anomaly. Moreover, the competition between HA and  $\text{MnO}_2$  involves a drastic slowdown of the reaction kinetics, inducing at long-term modification of the REE distribution as well as an increase in the amplitude of the Ce-anomaly. The process described above should play a major role when REE are released in the form of inorganic REE(III) species, notably during rock alteration/weathering. When present in free ionic form, REE are available for complexation with each ligand occurring in solution. As shown in this study, the kinetics of the complexation reactions and the stability of the complexes so formed will impose the REE speciation at equilibrium.

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## Tables and figure captions

Table 1

Ce distribution in each phase of the suspension, estimate of Ce involved in anomaly development and amount of inorganic Ce adsorbed onto  $\text{MnO}_2$ , for the experiment with  $\text{HA}/\text{MnO}_2$  ratio = 0.1 and  $\text{pH}=5$ .

Table 2

Proportions of (i) REE dissociated from REE-HA complex, (ii) REE reabsorbed onto  $\text{MnO}_2$  and (iii) REE removed to the inorganic solution. Percentages are calculated for the competition experiment with  $\text{HA}/\text{MnO}_2$  ratio = 0.025 between 1 and 72 h.

Table 3

Proportions of REE adsorbed onto  $\text{MnO}_2$  irrespective of their chemical form, as well as proportions of inorganic REE adsorbed onto  $\text{MnO}_2$  and inorganic REE readsorbed onto  $\text{MnO}_2$ , with respect to the total amount of REE resulting from dissociation of the REE-HA complex. Calculations are presented for the competition experiment with  $\text{HA}/\text{MnO}_2$  ratio = 0.1,  $\text{pH} = 5$  and  $t = 72$  h.

Fig. 1. Time variation of  $\log K_d^{\text{REE}}$  on  $\text{MnO}_2$  and aqueous HA (not adsorbed on  $\text{MnO}_2$ ) and  $\log K_d^{\text{DOC}}$  on  $\text{MnO}_2$  for a mixture of HA, REE (5 ppb) and  $\text{MnO}_2$  ( $100\text{mg.L}^{-1}$ ) at  $\text{pH} 5$ , as a function of the  $\text{HA}/\text{MnO}_2$  ratio, a)  $R = 0.4$ , b)  $R = 0.1$  and c)  $R = 0.025$ . Errors bars correspond to  $\sigma$  for three replicates; error bars are generally smaller than the symbol size.



Fig. 2. Log  $K_d^{REE}$  patterns for a)  $MnO_2$ , b) aqueous HA and NaCl solution, c) REE concentration (ppb) in solution at pH 5. Values plotted vs. increasing atomic number within REE series after 72h of experiment for three HA/ $MnO_2$  ratios ( $R = 0.4, 0.1$  and  $0.025$ ).

Fig. 3. Time variation of Ce anomaly expressed as  $Ce/Ce^*$  in the mixture of  $MnO_2$  and HA at pH 5 for four HA/ $MnO_2$  ratios ( $R = 0.4, 0.2, 0.1$  and  $0.025$ ). Ce anomalies were calculated from log  $K_d$  values. Error bars corresponds to s for three replicates, error bars are generally smaller than the symbol size.

Fig. 4. Gd/Yb ratio versus time calculated from log  $K_d^{REE/HA}$  and soluble inorganic REE concentrations for HA/ $MnO_2$  ratio = 0.1

Fig. 5. Variation of log  $K_d^{REE}$  versus pH a) on  $MnO_2$  and b) aqueous HA (not adsorbed on  $MnO_2$ ) and log  $K_d^{DOC}$  on  $MnO_2$  in a mixture of HA, REE (5 ppb) and  $MnO_2$  ( $100 \text{ mg.L}^{-1}$ ) for HA/ $MnO_2$  ratio = 0.1.

Fig.6. Patterns of a) log  $K_d^{REE/MnO_2}$  without HA, b) log  $K_d^{REE/HA}$  and log  $K_d^{REE/MnO_2}$  for competitive complexation experiments at three pH values (4, 6 and 8) with 48 h equilibration-time.

Fig. 7. Gd/Yb ratio versus pH, calculated from log  $K_d^{REE/HA}$  for competitive complexation of REE between HA ( $10 \text{ mg.L}^{-1}$ ) and  $MnO_2$  ( $100 \text{ mg.L}^{-1}$ ).

Time (h)	Ce adsorbed onto MnO <sub>2</sub> *	Ce bound to aqueous HA (%)	Inorganic Ce in solution (%)	inorganic Ce readsorbed onto MnO <sub>2</sub> from Ce-HA dissociation/total adsorbed Ce** (%)	Ce involved in Ce anomaly development/total Ce concentration** (%)
1	8.1	91.6	0.3	-	-
3	11.8	88.0	0.2	-	-
8	14.1	85.9	0.5	16.2	2.3
24	14.3	85.6	0.1	17.4	2.5
48	16.5	83.4	0.1	28.6	4.7
72	17.4	82.5	0.1	32.3	5.6

\*: Ce bound as inorganic species and/or Ce-HA complexes

\*\* : % Ce involved in development of the Ce anomaly, calculated with respect to % Ce bound to MnO<sub>2</sub> at 3 h, just prior to development of the Ce anomaly and Ce-HA

$$\text{dissociation.}(\% = \frac{[\text{Ce}]_{\text{adsorbed onto MnO}_2}^{\text{t=x}} - [\text{Ce}]_{\text{adsorbed onto MnO}_2}^{\text{t=3}}}{[\text{Ce}]_{\text{adsorbed onto MnO}_2} \text{ or } [\text{Ce}]_{\text{total}}} * 100)$$

Table 1

	REE dissociated from REE-HA complex/ REE total concentration (%)	REE readsorbed onto MnO <sub>2</sub> / REE dissociated from REE-HA (%)	REE removed to inorganic solution/ REE dissociated from REE-HA (%)
La	7.9	98.9	1.1
Ce	11.3	99.1	0.9
Pr	8.4	99.0	1.0
Nd	7.4	98.1	1.9
Sm	8.6	99.1	0.9
Eu	8.6	99.0	1.0
Gd	6.8	98.9	1.1
Tb	7.5	98.8	1.2
Dy	7.0	98.2	1.8
Ho	6.8	98.6	1.3
Er	6.8	97.5	2.4
Tm	6.8	96.9	3.0
Yb	6.9	96.2	3.8
Lu	7.0	95.8	4.2

Table 2

	REE bound to MnO <sub>2</sub> (%)	Inorganic REE adsorbed onto MnO <sub>2</sub> from the REE-HA complex dissociation/ total adsorbed REE* (%)	Inorganic REE readsorbed from the REE-HA complex dissociation/ REE total concentration (%)
La	13.9	13.5	1.9
Ce	17.7	32.3	5.7
Pr	14.6	22.4	3.3
Nd	14.7	17.5	2.6
Sm	13.1	17.4	2.3
Eu	12.8	25.5	3.3
Gd	13.5	25.9	3.5
Tb	12.0	20.5	2.5
Dy	10.7	19.3	2.1
Ho	11.7	21.1	2.5
Er	11.8	16.8	2.0
Tm	11.9	17.0	2.0
Yb	12.0	13.8	1.7
Lu	12.1	13.6	1.6

\*: percent of inorganic REE adsorbed onto MnO<sub>2</sub>, calculated with respect to percent of REE

bound to MnO<sub>2</sub> at 3 h, just prior to development of Ce anomaly and REE-HA dissociation,

$$\left( \% = \frac{[\text{REE}]_{\text{adsorbed onto MnO}_2}^{\text{t=x}} - [\text{REE}]_{\text{adsorbed onto MnO}_2}^{\text{t=3}}}{[\text{REE}]_{\text{adsorbed onto MnO}_2} \text{ or } [\text{REE}]_{\text{total}}} * 100 \right)$$

Table 3

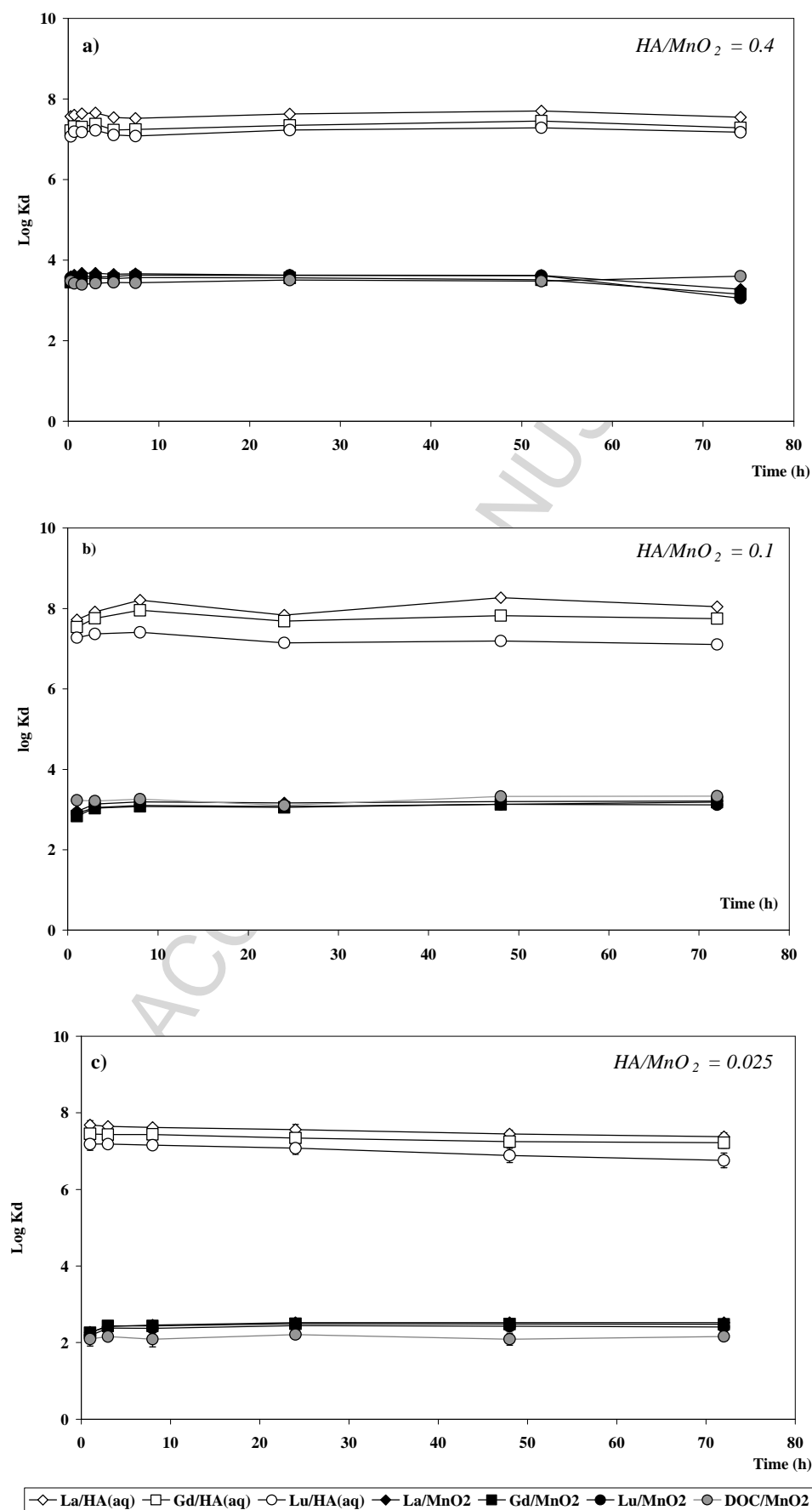


Fig. 1

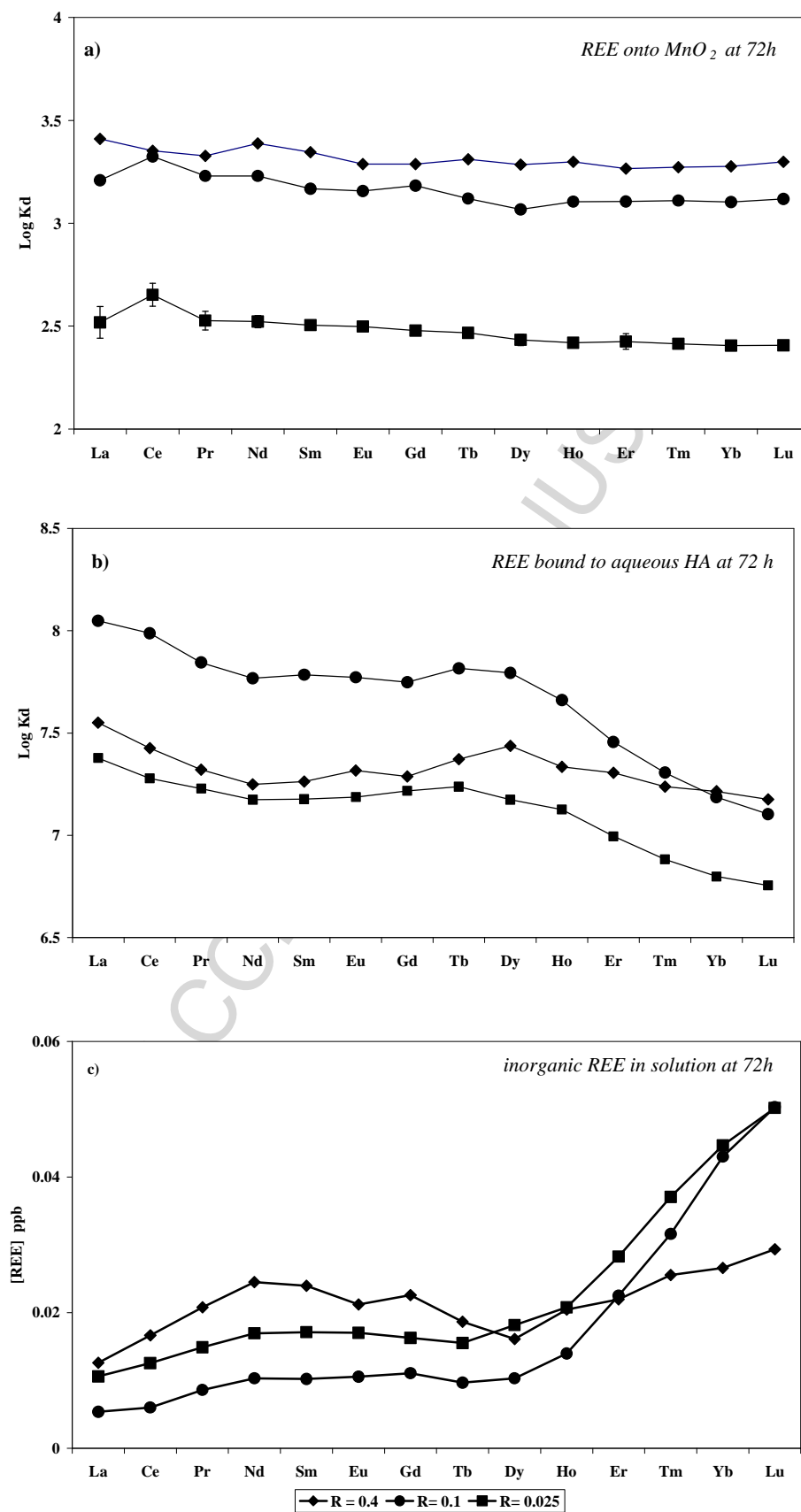


Fig. 2

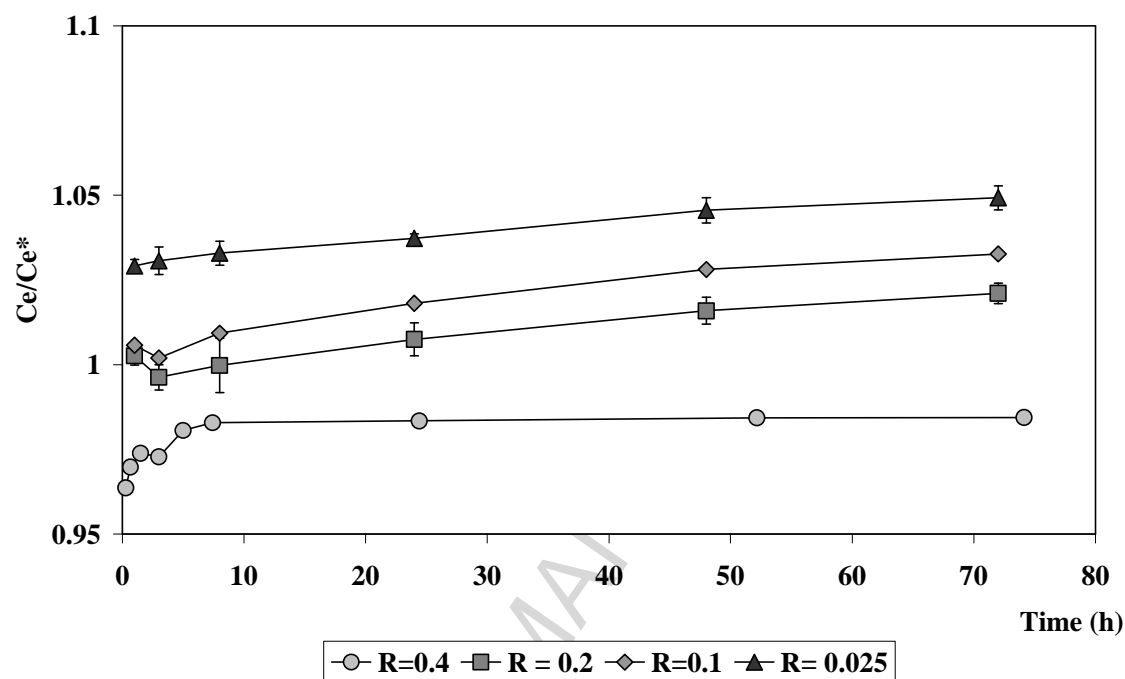


Fig. 3

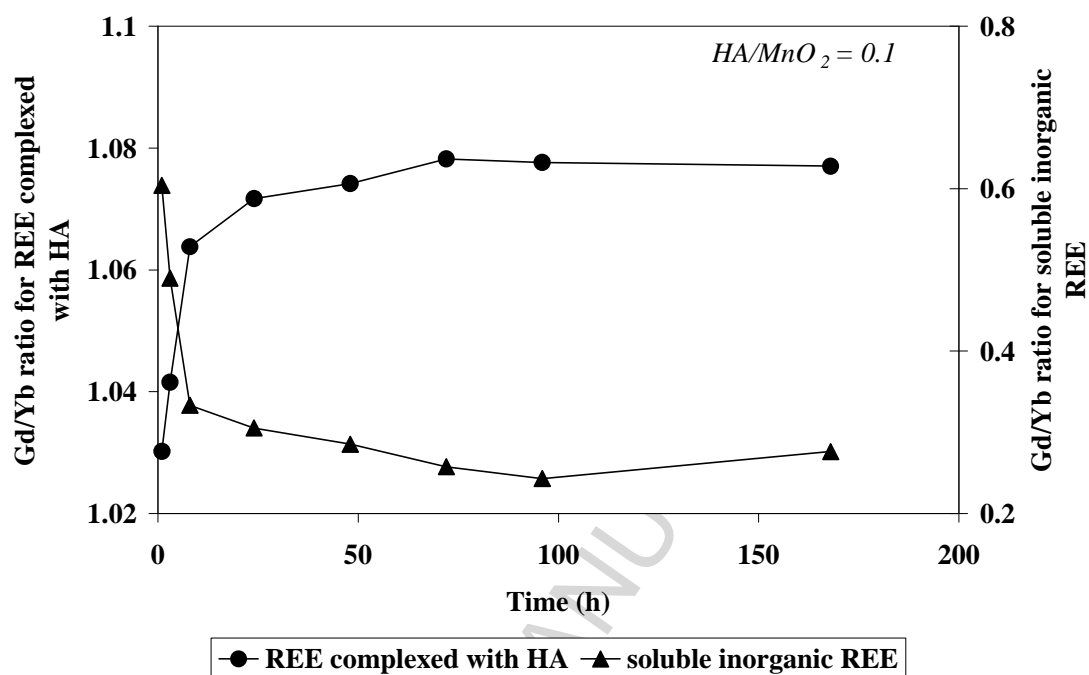


Fig. 4



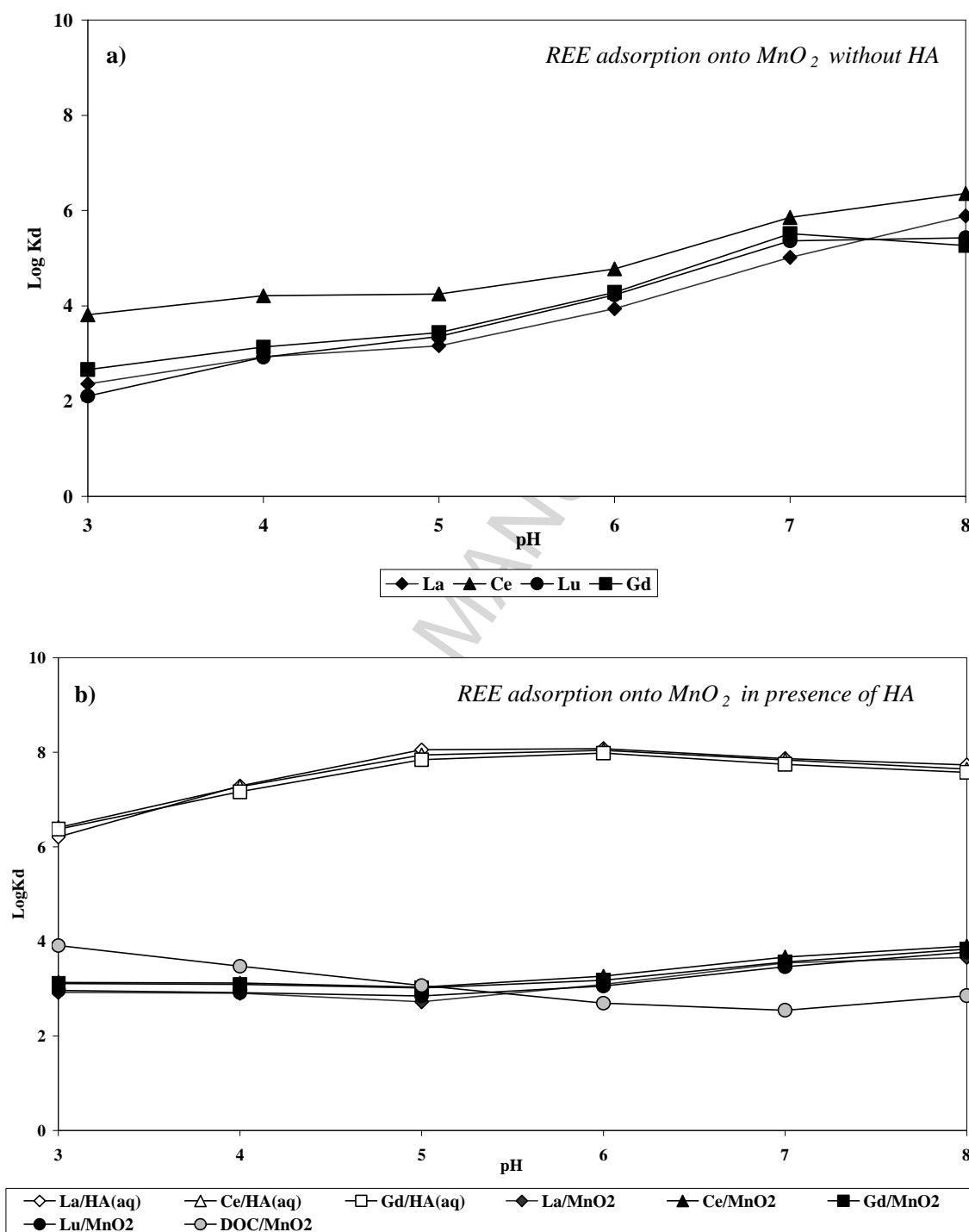


Fig. 5

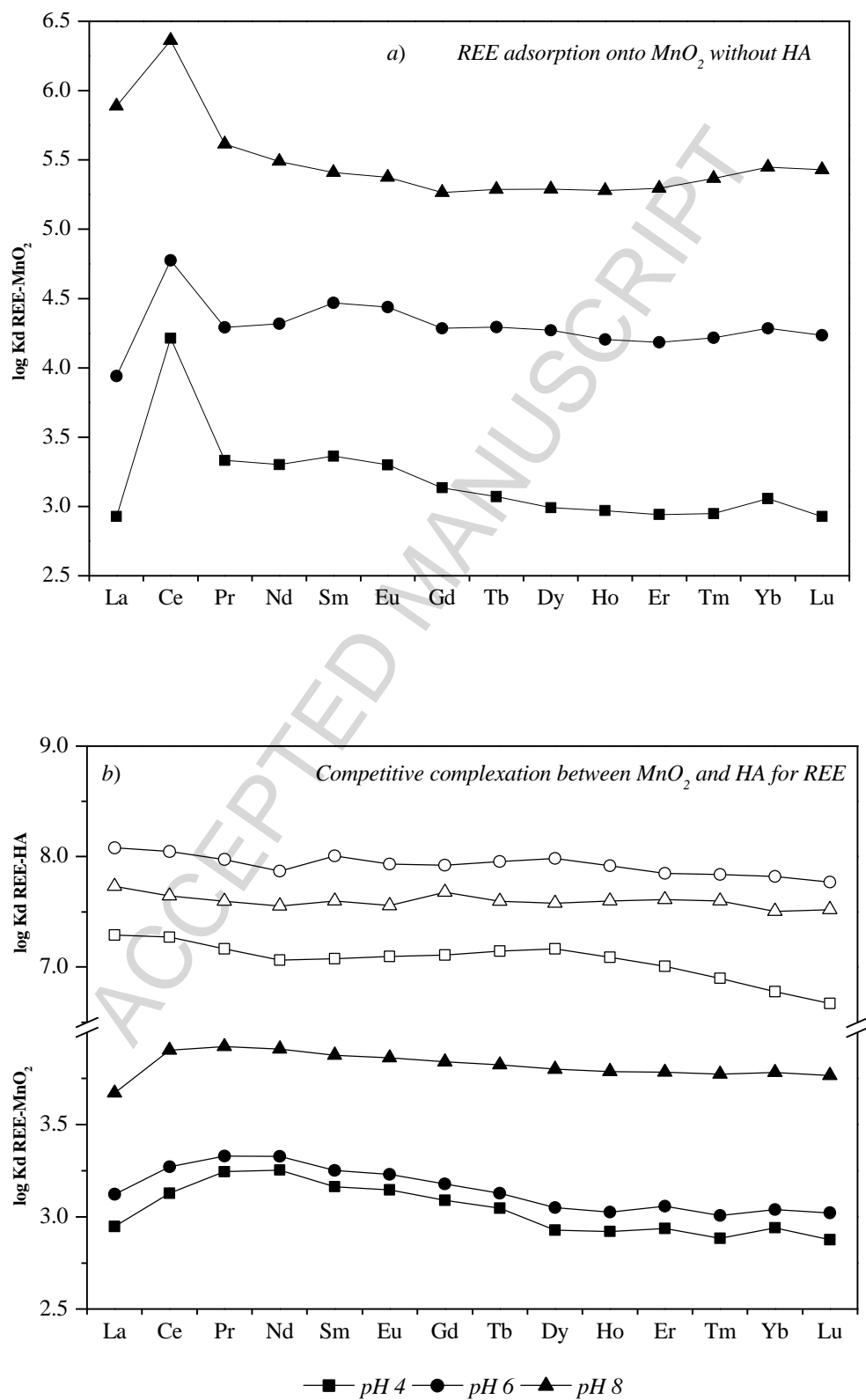


Fig.6

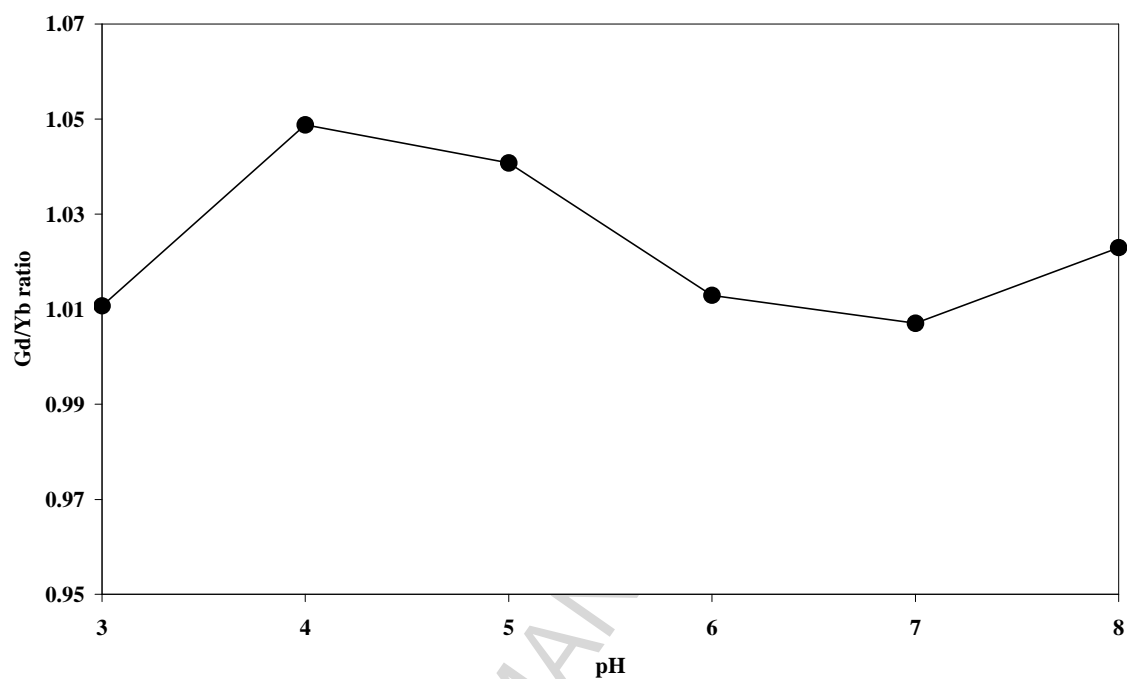


Fig. 7