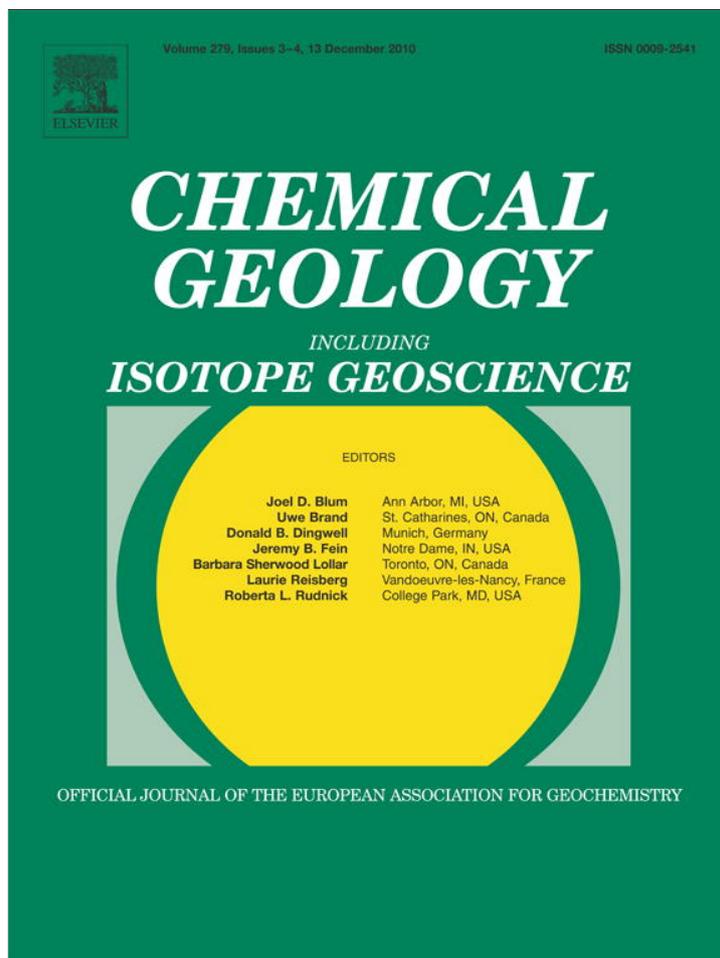


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Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Research paper

Rare earth elements adsorption onto Carrizo sand: Influence of strong solution complexation

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ARTICLE INFO

Article history:

Received 6 April 2010

Received in revised form 21 September 2010

Accepted 13 October 2010

Editor: J.D. Blum

Keywords:

Rare earth elements

Adsorption

Solution complexation

CO₂ partial pressure

Humic substance

Carrizo sand

ABSTRACT

To better understand the mobility and transport of rare earth elements (REE) in groundwater flow systems, the influence of carbonate ions as well as humic substances on REE adsorption onto Carrizo Aquifer sand was investigated as a function of CO₂ partial pressures (P_{CO_2}), pH, ionic strength, and initial REE concentrations. Batch adsorption experiments were carried out at room temperature ($23^\circ \pm 1^\circ \text{C}$) in a glove box under different P_{CO_2} (i.e., $0 < P_{\text{CO}_2} \leq 10^{-1.3}$ atm). Our experiments show that carbonate ions can either increase or decrease REE adsorption depending on the carbonate ion concentrations or the initial REE concentrations. More specifically, the degree that REEs are adsorbed onto the aquifer sand is inversely related to the amount of carbonate species of REEs. For example, an increase of P_{CO_2} from 0 to $10^{-3.5}$ atm, or the presence of carbonate ions in low initial REE concentrations (e.g., 10 $\mu\text{g}/\text{kg}$), generally result in enhanced REE adsorption, owing to the low amount of carbonate species of REEs in solution. With further increase of P_{CO_2} at constant pH (7) and dissolved REE concentrations, solution complexation of REEs with carbonate ions increases and readily outcompetes mineral surface sites for REEs, leading to less REE adsorption. In addition, our experiments show that in the presence of carbonate ions, increasing pH from neutral pH to more alkaline pH leads to decreases in REE adsorption. The presence of humic substances can also either increase or decrease REE adsorption, depending on the pH range of the solution. Humic substances enhance REE adsorption at acidic pH range (i.e., $\text{pH} < 4$) and decrease REE adsorption when pH is above 4. Ionic strength has a negligible effect on REE adsorption in dilute solutions, and only when ionic strength was increased to 0.1 M was a decrease in REE adsorption noticeable.

REE adsorption onto Carrizo sand can be successfully described by a model that considers both surface complexation and surface exchange reactions. Specifically, the modeling studies point out the important role that surface exchange reactions play in REE adsorption onto Carrizo sand at high REE loading conditions (i.e., high initial REE concentration at low solid/solution ratio). Model calculations show that strong solution complexation of dissolved REEs with carbonate ions competes for uncomplexed REE ions, $[\text{Ln}^{3+}]_f$, where Ln is any of the lanthanides, and thus decreases REE adsorption at high P_{CO_2} levels ($> 10^{-2.3}$ atm) or at high pH (> 8.0). Model calculations also indicate that competition between Na^+ and uncomplexed REE ions, $[\text{Ln}^{3+}]_f$, for exchange sites results in less REE adsorption at high ionic strength (e.g., $I = 0.1$ M). Both experimental and modeling studies show that REE adsorption onto Carrizo sand is strongly influenced by REE solution complexation reactions, which are sensitive to P_{CO_2} levels, pH, and the amount and type of solution complexing ligands.

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1. Introduction

Rare earth elements (REEs) are widely recognized by geochemists as useful geotracers in the study of many geological processes (e.g., Goldberg et al., 1963; Kay and Gast, 1973; Hanson, 1980; Elderfield and Greaves, 1982; Cullers and Graf, 1984; Smedley, 1991; Sholkovitz et al., 1993; Johannesson et al., 1997a,b; Dia et al., 2000; Möller et al., 2000), and also as chemical analogues of the radioactive actinides (e.g., Choppin, 1983, 1989; Krauskopf, 1986; Silva and Nitsche, 1995).

Concerning REE geochemistry in mineral–water interaction, numerous studies have been carried out to investigate REE adsorption onto individual oxide and silicate minerals as well as onto bulk sediments and rocks (Aagaard, 1974; Byrne and Kim, 1990; Koeppenastrop and DeCarlo, 1992, 1993; Benedict et al., 1997; Bau, 1999; Kawabe et al., 1999a,b; Bradbury and Baeyens, 2002; Coppin et al., 2002; Davranche et al., 2004, 2005, 2008; Quinn et al., 2004, 2006a,b; Tang and Johannesson, 2005a; Tertre et al., 2005, 2008; Piasecki and Sverjensky, 2008). For experiments conducted at circumneutral pH with simple synthetic, dilute solutions that lack strong complexing ligands like carbonate ions or dissolved organic matter, heavy REEs (HREE) are preferentially adsorbed onto solid mineral phases compared to light REEs (LREE; e.g., Aagaard, 1974; Bau, 1999; Kawabe et al., 1999a;

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Coppin et al., 2002; Quinn et al., 2004, 2006a; Tang and Johannesson, 2005a; Tertre et al., 2005, 2008). By contrast, for experiments conducted with seawater (e.g., Byrne and Kim, 1990; Koeppenkastrup and DeCarlo, 1992, 1993) or synthetic groundwaters with aqueous complexing ligands (e.g., Benedict et al., 1997), LREEs are preferentially adsorbed onto the solid mineral phases compared to HREEs. The opposite REE adsorption patterns are attributed to solution complexation of REEs with carbonate ions in seawater or synthetic groundwaters, which is further supported by REE adsorption experiments conducted with solutions “doped” with carbonate ions (e.g., Kawabe et al., 1999b; Quinn et al., 2006b). These experiments also clearly show that HREEs are preferentially removed from solution by adsorption for aqueous solutions that lack strong solution complexing ligands, whereas LREEs are preferentially removed by adsorption from solutions doped with carbonate ions. Furthermore, REE adsorption experiments in the presence of humic substance (HS; e.g., Davranche et al., 2004, 2005, 2008) indicate that the degree of fractionation across the REE series that results from adsorption depends on the concentrations of HS in solution. Therefore, the adsorption of REE to mineral surfaces in natural water systems is demonstratively influenced by solution complexation.

Because groundwater is the principal source of drinking water in the United States (and globally; Solley et al., 1993; Fetter, 1999), the ability to accurately predict the fate and transport of heavy metals and radionuclides in aquifers is critical. For example, it is generally agreed that the interaction of groundwater with buried radioactive waste is the most likely release mechanism for many radionuclides, including transuranics, into the environment (Glynn, 2003; Davis et al., 2004). Although the REEs are not typically considered groundwater contaminants because they occur naturally and are generally not radioactive, studying their geochemistry in groundwater flow systems is important from the standpoint of developing an understanding of how the chemically analogous transuranics (e.g., Am, Cm, and Cf) behave in groundwater–aquifer systems. Likewise, careful study of REE adsorption to aquifer mineral surfaces can provide important insight into the mechanisms and processes that control adsorption of radioactive transuranics in the environment. Previously, we collected groundwater samples along a flow path in the Carrizo Sand aquifer in south Texas, measured REE concentrations in these groundwaters, and investigated how the geochemistry (i.e., concentrations, fractionation patterns, and speciation) of dissolved REEs change as groundwater geochemistry evolves along the flow path (Tang and Johannesson, 2006). We also conducted batch adsorption experiments of the REEs onto Carrizo sand under atmospheric conditions and developed a surface complexation model for REE adsorption onto Carrizo sand (Tang and Johannesson, 2005a). To more fully understand the mobility and the transport of REEs in groundwater flow systems, in this study, we directly investigate the influence of varying partial pressure of carbon dioxide gas (P_{CO_2}) levels at constant pH (i.e., 7) on REE adsorption onto Carrizo sand. In addition, we also examine the influence of dissolved organic matter on REE adsorption onto Carrizo sand as organic ligands are known to strongly complex REEs in natural waters (Tang and Johannesson, 2003; Johannesson et al., 2004; Sonke and Salters, 2006; Pourret et al., 2007).

Studying the adsorption of REEs and other trace elements (e.g., uranium) at high P_{CO_2} is important for a number of reasons, including: (1) carbonate ions are known to form strong solution complexes with these and other trace elements (Cantrell and Byrne, 1987; Lee and Byrne, 1993; Johannesson et al., 1996; Luo and Byrne, 2004); (2) P_{CO_2} in aquifers commonly reaches values of 10^{-2} to $10^{-1.3}$ atm and may increase along flow paths in some aquifers (Hem, 1985; Davis and Curtis, 2003; Davis et al., 2004); and (3) interest in sequestering CO_2 in deep aquifers may change the in situ P_{CO_2} of these aquifers, possibly affecting heavy metal mobilization. For example, to address issues related to global warming by reducing the amount of CO_2 in the atmosphere, a process called geologic sequestration is suggested to

capture CO_2 at stationary sources and to inject it through a well into underground geological formations such as declining oil fields and saline aquifers (Knauss et al., 2005). However, the increase in P_{CO_2} level could influence the mobility of heavy metals and radionuclides in aquifers. Thus, direct investigation of the influence of varying P_{CO_2} level on REE adsorption onto aquifer sediments might also provide important information about the potential environmental effects caused by geologic sequestration of carbon dioxide (CO_2).

In this contribution, we present the results of batch adsorption experiments under different CO_2 partial pressures (i.e., $0 < P_{\text{CO}_2} \leq 10^{-1.3}$ atm) or in the presence of dissolved organic matter and discuss the results qualitatively. All experimental data are included as an electronic annex file. These data resulting from the batch adsorption experiments under different CO_2 partial pressures are subsequently quantitatively modeled to expand the robustness of the surface complexation model of Tang and Johannesson (2005a).

2. Materials and methods

2.1. Materials

All Teflon® bottles and other laboratory vessels used in the study were first cleaned using trace element clean procedures (Tang and Johannesson, 2005a). The background electrolyte solutions used for batch experiments consisted of 0.1 M, 0.01 M, or 0.001 M NaCl solutions made up in doubly-deionized, ultrapure water (18.2 M Ω cm, Millipore™). A 10 ppm or 100 ppm multi-element REE standard solution (SPEX CertiPrep, Inc., NJ) was used to adjust the initial REE concentrations of reaction solutions. An Accumet® accuCap combination pH electrode (Catalog no. 13-620-130), calibrated at room temperature ($23^\circ \pm 1^\circ \text{C}$) with NIST certified buffer solutions (pH 4.00, 7.00, and 10.00), was used to measure pH. All the experiments were conducted at room temperature ($23^\circ \pm 1^\circ \text{C}$).

Natural sand samples used in our experiments were collected from outcrop in the recharge area of the Eocene Carrizo Sand aquifer in southeastern Texas. The Carrizo sand aquifer has been described previously (Tang and Johannesson, 2005b, 2006). Certified standard grade N_2 gas mixed with appropriate CO_2 content (i.e., 0%, 0.5%, 2%, and 5%, respectively) was purchased from Airgas, Inc. Suwannee River fulvic acid (FA) standard (IHSS Code 1S101F) was purchased from the International Humic Substances Society, and synthetic humic acid (HA) was purchased from Sigma-Aldrich® (Aldrich™ H16752). No purification was conducted for FA or HA before use in our experiments.

2.2. Experimental procedure

Batch experiments were conducted in a class 100 laminar flow hood open to laboratory air or in a protector glove box (Model 5080000, Labconco Corp.). For the experiments done in the glove box, the reaction solutions were bubbled with certified standard grade N_2 gas mixed with various CO_2 contents. The pH of the solution was monitored and adjusted if necessary with either 0.1 M HCl or 0.1 M NaOH before mixing with the sand and was allowed to drift during the adsorption experiment. When the pH of the solution was stable for several hours at the target pH value, the solution was assumed to be equilibrated with the N_2 – CO_2 atmosphere within the glove box. As shown in Table 1, for experiments with the same initial pH values, the concentrations of carbonate ions in the solution are expected to increase with increasing P_{CO_2} levels. The P_{CO_2} levels in our reaction solutions ranged from 0 to $10^{-1.3}$ atm, which covers the P_{CO_2} range of 10^{-3} to $10^{-1.6}$ atm in actual groundwaters from the Carrizo Sand Aquifer (Tang and Johannesson, 2005b).

The sand/solution ratio used in our batch experiments is 25 g/L. In our previous experiments (Tang and Johannesson, 2010) a higher sand/solution ratio of 1000 g/L was used. The substantially lower sand/

Table 1

The PHREEQC-calculated concentrations of carbonate ions [CO₃²⁻] in 0.01 M NaCl solutions, which are equilibrated with the N₂-CO₂ atmospheres of various P_{CO₂} levels at T = 23 °C and pH = 7.

log P _{CO₂} (atm)	-3.5	-2.3	-2	-1.7	-1.3
[CO ₃ ²⁻] (M)	3.3 × 10 ⁻⁸	5.3 × 10 ⁻⁷	1.1 × 10 ⁻⁶	2.1 × 10 ⁻⁶	5.6 × 10 ⁻⁶
[HCO ₃ ⁻] (M)	5.4 × 10 ⁻⁵	8.6 × 10 ⁻⁴	1.7 × 10 ⁻³	3.5 × 10 ⁻³	8.8 × 10 ⁻³

solution ratio used in the current experiments reflects the fact that REEs are initially released from the aquifer sand upon reaction with the aqueous solution (Tang and Johannesson, 2010). Specifically, when Carrizo sand was reacted with a sodium bicarbonate/carbonate aqueous solution at pH = 9.6 (i.e., 14.41 mM NaHCO₃ + 2.8 mM Na₂CO₃), the amount of La, Gd, and Lu released from Carrizo sand was 5.2 × 10⁻³, 1.6 × 10⁻³ and 1.7 × 10⁻⁴ µg/g of the sand. These values correspond to roughly 5.2 µg, 1.6 µg, and 0.17 µg of La, Gd, and Lu, respectively, being released to a 1 L solution for a sand/solution ratio of 1000 g/L, but only 0.13 µg, 0.04 µg, and 4 ng of La, Gd, and Lu, respectively, being released to a 1 L solution for a sand/solution ratio of 25 g/L. Therefore, the lower sand/solution ratio minimizes potential artifacts originating from leaching REEs from Carrizo sand during the initial portion of the adsorption experiments. Similar observations have been reported for U in batch adsorption experiments (Davis et al., 2004).

2.2.1. Kinetic experiments

Previously, we found that a period of 12 h was required to attain stationary state for REE adsorption onto Carrizo sand for a sand/solution ratio of 1000 g/L exposed to laboratory air (Tang and Johannesson, 2005a). Because we chose a lower sand/solution ratio (25 g/L) for our current studies of REE adsorption, the kinetic experiments were redone at the lower sand/solution ratios. Here, a set of the REE solutions (20 mL) containing all 14 naturally occurring lanthanides and Carrizo sand (0.5 g) was prepared in 30 mL Teflon® bottles in a class 100 laminar flow hood open to laboratory air. The background electrolyte solution used is 0.01 M NaCl. The initial concentration of each REE in the solution was adjusted to 10 µg/kg. To avoid the potential of mineral dissolution, the initial pH of the solution was adjusted to 8.3 with 0.1 M NaOH before mixing with the sand. The mixtures were shaken on a VWR Mini shaker for 1 hour (h), 2 h, 4 h, 8 h, 12 h, 1 day (d), 2 d, 3 d, 4 d, 5 d, 10 d, and 15 d, respectively. After shaking, the mixtures were immediately filtered through 0.45 µm polyethersulfone membrane filters (Whatman Inc.), acidified to pH < 2 with ultrapure nitric acid (Seastar Chemicals, baseline), and stored cold (i.e., 4 °C) until analysis.

2.2.2. REE adsorption

An initial series of batch experiments was conducted to evaluate the effect of the P_{CO₂} levels in the reaction solutions on REE adsorption onto Carrizo sand. Specifically, 0.5 g of Carrizo sand and 20 mL of REE solutions of various concentrations (see discussion later) were mixed in 30 mL Teflon® bottles, and subsequently shaken on a VWR Mini shaker for 5 days in the glove box under: (1) pure N₂ atmosphere; (2) laboratory air; (3) N₂ + 0.5% CO₂; (4) N₂ + 2% CO₂; and (5) N₂ + 5% CO₂. Again, the background electrolyte solution used is 0.01 M NaCl. The initial pH of the solution was kept at 7.0 before mixing with the sand. For each P_{CO₂} level, the batch adsorption experiments were run for five different initial REE concentrations (i.e., 10 µg/kg, 50 µg/kg, 100 µg/kg, 500 µg/kg, and 1 mg/kg). After attaining stationary state as determined by the kinetic experiments (see previous discussion), the mixtures were subsequently filtered through 0.45 µm polyethersulfone membrane filters (Whatman Inc.), acidified to pH < 2 with ultrapure nitric acid (Seastar Chemicals, baseline), and stored cold (i.e., 4 °C) until analysis.

A second series of batch experiments was conducted to investigate the effect of pH on REE adsorption onto Carrizo sand. In these experiments, the concentration of each REE in the initial 0.01 M NaCl electrolyte solution were held constant at 100 µg/kg, and the pH was

varied from 4 to 9. These experiments were conducted in equilibrium with: (1) laboratory air; (2) N₂ + 0.5% CO₂; and (3) N₂ + 2% CO₂.

To evaluate the effect of ionic strength, a third series of batch experiments were conducted under laboratory air at initial concentration of 100 µg/kg for each REE, varying initial pH values, and using 0.001 M or 0.1 M NaCl background electrolyte solutions. A fourth series of batch experiments were also conducted under laboratory air conditions at pH 7, varying REE concentrations from 10 µg/kg to 1 mg/kg, and either using a 0.001 M or 0.1 M NaCl background electrolyte solution.

Finally, to evaluate the effect of dissolved organic ligands on REE adsorption, a fifth series of experiments were conducted under laboratory air at initial concentration of 100 µg/kg for each REE and initial pH values varying from 4 to 9 using a 0.01 M NaCl background electrolyte solution “doped” with 10 mg/L Suwannee River FA or 10 mg/L Aldrich HA.

2.3. Modeling method

The geochemical model PHREEQC for windows (version 2.15.02) and the default database of PHREEQC were used to perform modeling calculations. Data to describe the thermodynamics and speciation of aqueous REEs were added into the default database. Stability constants for aqueous REE complexes are the same as we used in a solution complexation model (Tang and Johannesson, 2003). Thus, the source of these stability constants for aqueous REE complexes can be found in Tang and Johannesson (2003). A surface complexation model for REE adsorption onto Carrizo sand developed at low REE loading conditions (i.e., low initial REE concentration at high solid/solution ratio; Tang and Johannesson, 2005a) was applied to this study. Description of surface complexation model and model parameters can be found in Tang and Johannesson (2005a). To account for additional surface reactions at high REE loading condition (i.e., high initial REE concentration at low solid/solution ratio), surface exchange reactions are also included in the model (see details in Section 3.3).

2.4. Analysis

REE concentrations in all batch adsorption solutions were determined at Tulane University using a magnetic sector inductively-coupled plasma mass spectrometer (ICP-MS; Thermo Finnigan MAT Element 2) and following procedures discussed previously (Johannesson et al., 2004, 2005; Tang and Johannesson, 2005b, 2006). Briefly, the ICP-MS was calibrated using a series of REE calibration standards of known concentrations that were prepared from the Clartas PPT® certified reference multi-element solution (SPEX CertiPrep, Inc., NJ). 10 ppb of indium was added to all samples, including the standard solutions, as an internal standard to correct for instrumental drift. To improve the analysis, an Apex inlet system (Elemental Scientific Inc., Omaha, NE) was used. The Apex inlet system increases the sensitivity of the ICP-MS analysis and provides a means to analyze concentrated, corrosive samples and those containing organic solvents (Elemental Scientific Inc., Omaha, NE, 2007).

The REE isotopes ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷¹Yb, and ¹⁷⁵Lu were used to quantify the REEs in the extraction samples. Quality control monitoring was performed by measuring several multi-REE standard solutions (Accu Trace™ Reference, 10 mg/L, USA). The detection limit was 1 ng/kg for all the REEs. The relative standard deviation (RSD) for the repeated analyses was better than 5% for the majority of the REEs.

3. Results

3.1. Kinetic experiments

The kinetic experiments (Fig. 1) indicate that a large fraction of each REE was rapidly adsorbed onto Carrizo sand, which is similar to

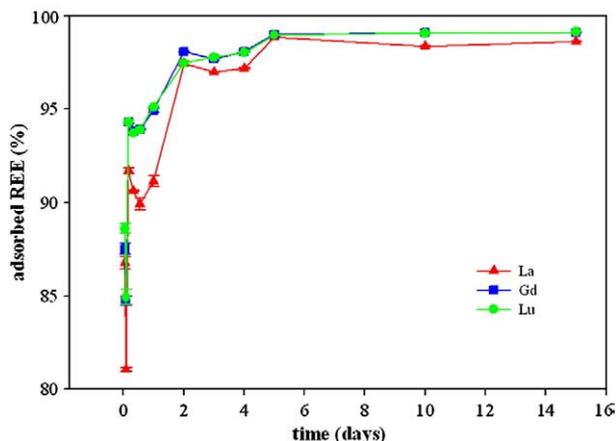


Fig. 1. REE adsorption onto Carrizo sand as a function of time. Initial concentration of each REE is 10 $\mu\text{g/kg}$ (57–72 nM depending on atomic number). Background electrolyte solution is 0.01 M NaCl solution. Initial pH=8.3. These kinetic experiments were conducted in a Class 100 Laminar flow bench and were thus open to the laboratory air. Error bars represent three multiple analyses, the majority of which are smaller than the symbols employed.

our previous results (Tang and Johannesson, 2005a). However, adsorption stationary state is not attained in the current kinetic experiment until a period of approximately 5 days, which is

substantially longer than the 12 h stationary state period noted by Tang and Johannesson (2005a). Again, we attribute the longer adsorption stationary state period for the current experiments to the substantially lower sand/solution ratio employed (25 g/L) compared to our previous study (1000 g/L). Consequently, a shaking time of 5 days was used in all subsequent REE adsorption experiments in the current study. The kinetic experiments also indicate that, when initial concentration of each REE was 10 $\mu\text{g/kg}$, >80% of each REE was adsorbed within 1 h and almost all (>98%) REEs were adsorbed onto Carrizo sand after the 5 day stationary state period. Because of the strong adsorption of the REE, we note that for REE concentrations less than 10 $\mu\text{g/kg}$, it was difficult to detect small variations in the amount of each REE adsorbed. Thus, higher REE concentrations (from 10 $\mu\text{g/kg}$ to 1 mg/kg) were used in subsequent experiments in order to obtain detectable differences when high percentage of REEs is adsorbed.

3.2. REE adsorption

3.2.1. REE adsorption behavior across the lanthanide series

When REE adsorption experiments are conducted in the glove box under a pure N_2 atmosphere, or outside the glove box under the ambient laboratory air, our data show REE adsorption onto Carrizo sand generally increases with increasing atomic number across the lanthanide series (Fig. 2). These data indicate that in the absence of strong complexing ligands in solution, HREEs are preferentially adsorbed relative to MREEs and LREEs. Such adsorption behavior of

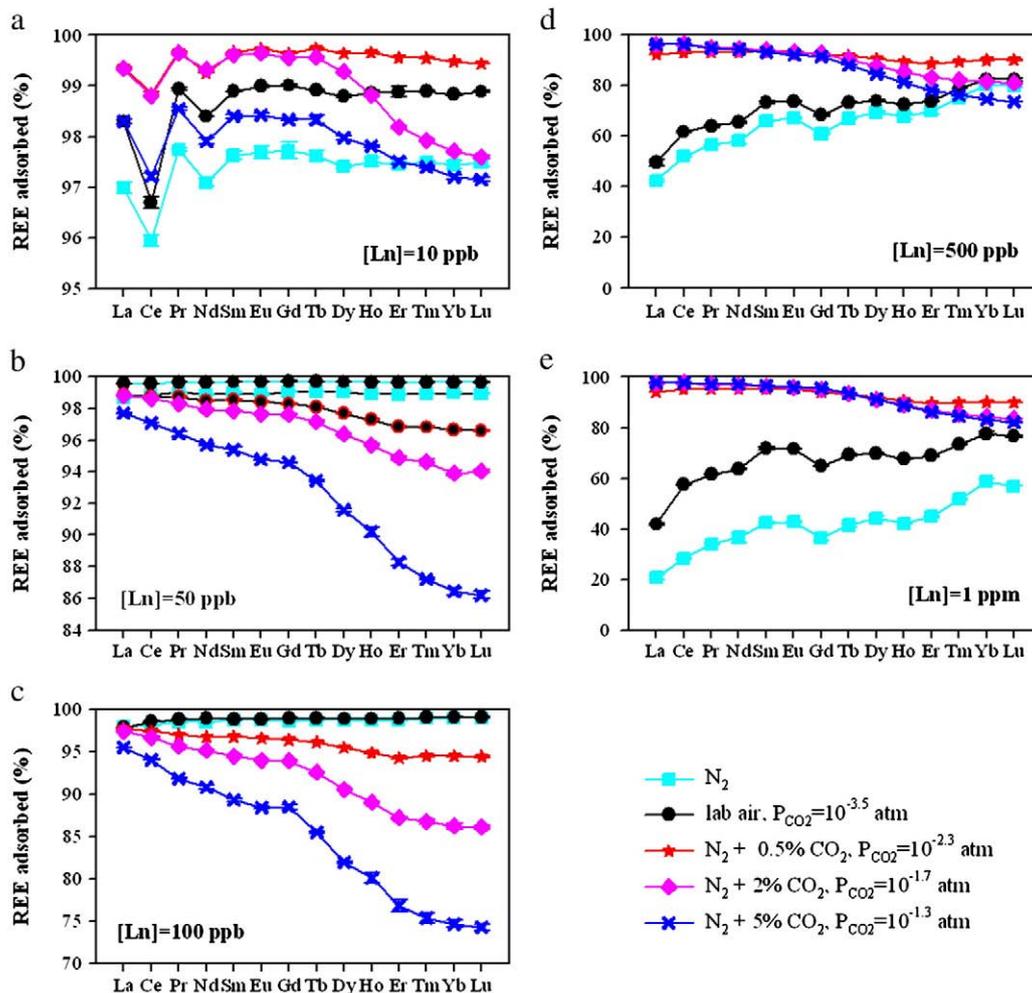


Fig. 2. REE adsorption across the REE series as a function of the atomic number. For all solutions, even those with high P_{CO_2} , initial pH was adjusted to 7. Background solution is 0.01 M NaCl solution. [Ln] denotes the initial concentration of each REE in solution. Note that the scale of the ordinate for panels (a) through (e) varies substantially. Error bars represent three multiple analyses, the majority of which are smaller than the symbols employed.

the REEs is consistent with our previous studies where HREEs exhibit greater adsorption to Carrizo sand than LREEs and MREEs for experiments conducted under laboratory air condition (Tang and Johannesson, 2005a). Moreover, as the initial solution concentrations of the REEs increase, the degree of preferential adsorption of the HREEs relative to the LREEs also increases (see Fig. 2d, e). However, when the P_{CO_2} level increases to $10^{-2.3}$ atm or above (i.e., the $\text{N}_2 + 0.5\% \text{CO}_2$, $\text{N}_2 + 2\% \text{CO}_2$, and $\text{N}_2 + 5\% \text{CO}_2$ experiments), LREEs are preferentially adsorbed onto Carrizo sand compared to HREEs such that the slope of the REE adsorption pattern becomes more negative with increasing P_{CO_2} levels (Fig. 2). Consequently, changing P_{CO_2} levels in groundwater systems can fractionate the REEs in solution by influencing the relative amount of each REE adsorbed to aquifer sands.

3.2.2. Effect of P_{CO_2} on REE adsorption

An increase in the P_{CO_2} level from 0 (i.e., pure N_2) to $10^{-3.5}$ atm (i.e., laboratory air) promotes an increase in REE adsorption onto Carrizo sand for all studied initial REE concentrations (Fig. 2). This P_{CO_2} effect is more substantial when the concentrations of REEs in the initial solution are relatively high (i.e., 500 $\mu\text{g}/\text{kg}$ or 1 mg/kg) and the percentage of each REE adsorbed is comparatively low (see Fig. 2d, e). Moreover, for initial solutions with REE concentrations of 10 $\mu\text{g}/\text{kg}$ (Fig. 2a), REE adsorption onto Carrizo sand initially increases with increasing P_{CO_2} level up to $10^{-2.3}$ atm (i.e., $\text{N}_2 + 0.5\% \text{CO}_2$), and then the amount of HREE adsorbed decreases as the P_{CO_2} level is raised to higher values (i.e., $\text{N}_2 + 2\% \text{CO}_2$). At an even higher P_{CO_2} level ($\text{N}_2 + 5\% \text{CO}_2$) for the 10 $\mu\text{g}/\text{kg}$ REE solutions, the amounts of LREE and MREE adsorbed onto Carrizo sand also decrease (relative to the $\text{N}_2 + 2\% \text{CO}_2$ experiment), approaching similar adsorption amounts to those measured for the pure N_2 atmosphere (Fig. 2a). Therefore, to summarize the results for the 10 $\mu\text{g}/\text{kg}$ REE solutions, an increase of the P_{CO_2} level from 0 to $10^{-2.3}$ atm leads to an overall increase in REE adsorption onto Carrizo sand, followed by a small decrease in the amount of HREEs adsorbed, and a subsequent decrease in the amount of MREEs and LREEs adsorbed as P_{CO_2} is increased to $10^{-1.3}$ atm. However, when the concentration of each REE in the initial solution is 50 $\mu\text{g}/\text{kg}$ or above, the increase of the P_{CO_2} level from $10^{-2.3}$ atm to $10^{-1.3}$ atm corresponds to a much larger decrease in the amount of REEs adsorbed, especially for the HREEs (Fig. 2b, c, d, and e). Indeed, the amount of Lu and Yb adsorbed decreases from approximately 100% under laboratory air conditions to roughly 75% adsorbed for $P_{\text{CO}_2} = 10^{-1.3}$ atm for the 100 $\mu\text{g}/\text{kg}$ solutions (Fig. 2c). In contrast, for the initial solutions where the REE concentrations are 500 $\mu\text{g}/\text{kg}$ or greater, the relative amount of each REE adsorbed onto Carrizo sand is larger for experiments conducted in equilibrium with high P_{CO_2} levels (i.e., $\text{N}_2 + 0.5\% \text{CO}_2$, $\text{N}_2 + 2\% \text{CO}_2$, or $\text{N}_2 + 5\% \text{CO}_2$) than for those experiments conducted in equilibrium with pure N_2 or laboratory air (see Fig. 2d, e). Below we demonstrate that these observations can be explained by the precipitation of rare earth element carbonates at high P_{CO_2} levels.

The effect of P_{CO_2} on REE adsorption onto Carrizo sand is also shown as a function of pH in Fig. 3. Specifically, the adsorption edge for the REEs shifts towards higher pH values as the P_{CO_2} increases from $10^{-3.5}$ atm (i.e., the ambient laboratory air) to $10^{-1.7}$ atm (i.e., $\text{N}_2 + 2\% \text{CO}_2$). Indeed, the adsorption edge shifts by approximately 1 pH unit as P_{CO_2} increases from $10^{-3.5}$ atm to $10^{-1.7}$ atm. Furthermore, for $P_{\text{CO}_2} > 10^{-2.3}$ atm (i.e., $\text{N}_2 + 0.5\% \text{CO}_2$), the amount of REE adsorbed decreases as pH increases above 7 (Fig. 3). The decrease in the amount of REE adsorption with increase in P_{CO_2} is especially substantial for the HREEs (Fig. 3). For each experiment shown in Fig. 3, the REE concentration in the initial solution was 100 $\mu\text{g}/\text{kg}$ for each REE in a background electrolyte solution of 0.01 M NaCl.

3.2.3. Effect of pH on REE adsorption

At $P_{\text{CO}_2} = 10^{-3.5}$ atm (i.e., ambient laboratory air), REE adsorption increases with increasing pH, such that the majority of each REE initially in solution is adsorbed between pH 4 and 5 (Fig. 3). However,

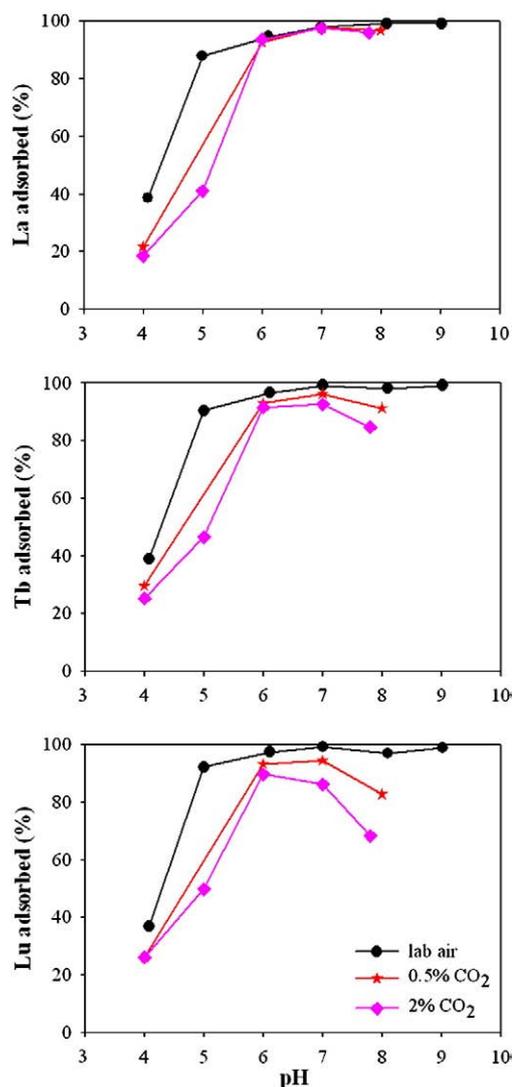


Fig. 3. Adsorption edges for La, Tb, and Lu onto Carrizo sand for solutions in equilibrium with laboratory air ($P_{\text{CO}_2} = 10^{-3.5}$ atm), 0.5% CO_2 ($P_{\text{CO}_2} = 10^{-2.3}$ atm), and 2% CO_2 ($P_{\text{CO}_2} = 10^{-1.7}$ atm). Initial concentration of each REE is 100 $\mu\text{g}/\text{kg}$. Background electrolyte solution is 0.01 M NaCl solution. Error bars are smaller than the symbols.

as mentioned above, at P_{CO_2} levels of $10^{-2.3}$ atm (i.e., $\text{N}_2 + 0.5\% \text{CO}_2$) and $10^{-1.7}$ atm (i.e., $\text{N}_2 + 2\% \text{CO}_2$), REE adsorption initially increases with increasing pH and then decreases for $\text{pH} > 7$. The subsequent desorption of previously adsorbed REE that occurs as pH increases is especially notable for the HREEs (e.g., compare Lu with La; Fig. 3). At the higher P_{CO_2} levels, the maximum La adsorption occurs at $\text{pH} \approx 7$, whereas Lu, and to a lesser extent Tb, exhibit maximum adsorption at $\text{pH} \approx 6$.

3.2.4. Effect of ionic strength on REE adsorption

In addition to the P_{CO_2} effect, REE adsorption onto Carrizo sand is also affected by ionic strength (i.e., concentration of the background NaCl electrolyte; Fig. 4). For $P_{\text{CO}_2} = 10^{-3.5}$ atm and at ionic strengths of 0.001 M and 0.01 M, REE adsorption increases dramatically as pH increases from 4 to 6 (i.e., ~40% adsorbed at pH 4 to >90% adsorbed at pH 6), reaching a plateau close to 100% adsorbed at $\text{pH} > 7$ (Fig. 4). However, at an ionic strength of 0.1 M, the amount of each REE adsorbed is markedly decreased, especially for the LREEs for a given $\text{pH} < 8$ compared to the more dilute solutions. The adsorption edges for La, Tb, and Lu exhibit much shallower slopes relative to the more dilute solutions. The amount of HREEs adsorbed does not approach 100% at ionic strength of 0.1 M until $\text{pH} \approx 8.3$. Furthermore, at $\text{pH} 8.3$,

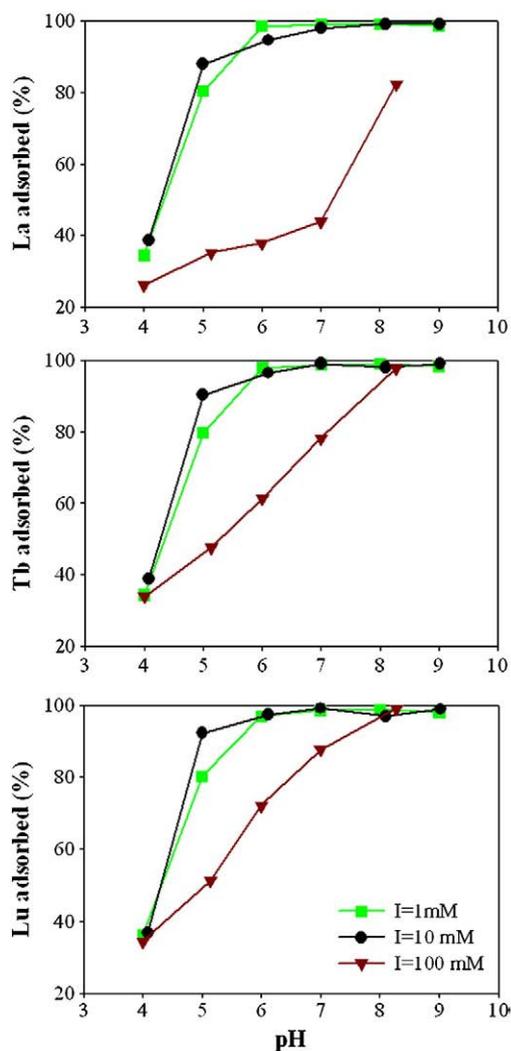


Fig. 4. Adsorption edges for La, Tb, and Lu onto Carrizo sand for different ionic strength solutions ($I=0.001$ M, 0.01 M, and 0.1 M). Background electrolyte solution is NaCl, initial concentration of each REEs is 100 $\mu\text{g}/\text{kg}$, and $P_{\text{CO}_2}=10^{-3.5}$ atm (i.e., laboratory air). Error bars are smaller than the symbols.

only about 80% of initial La in solution has been adsorbed with the remaining 20% still in solution even at this alkaline pH.

Our previous investigation (Tang and Johannesson, 2005a) showed that an increase in ionic strength from 0.002 M to 0.01 M was insufficient to affect REE adsorption behavior. As alluded to above, this behavior is confirmed by the results of our new experiments, which exhibit no discernable difference in REE adsorption edges onto Carrizo sand for ionic strengths between 0.001 M and 0.01 M (Fig. 4). Clearly, however, a 10-fold increase in ionic strength from 0.01 M to 0.1 M shifts the adsorption edge for individual REEs to substantially higher pHs, especially for LREEs. The greater effect that high ionic strength has on LREEs is further demonstrated in Fig. 5 where the amount of La, Tb, and Lu adsorbed onto Carrizo sand are shown as a function of the initial REE concentration in solution and ionic strength. As shown in Fig. 5, decreasing ionic strength from 0.01 M to 0.001 M does not influence REE adsorption, whereas increasing ionic strength from 0.01 M to 0.1 M decreases the amount of each of these REEs that are adsorbed onto Carrizo sand. The decrease of REE adsorption is especially prominent for solutions with higher initial REE concentrations (i.e., $[\text{Ln}]=500$ $\mu\text{g}/\text{kg}$ or 1 mg/kg; Fig. 5). Again, the effect of ionic strength on REE sorption is most pronounced for the LREEs.

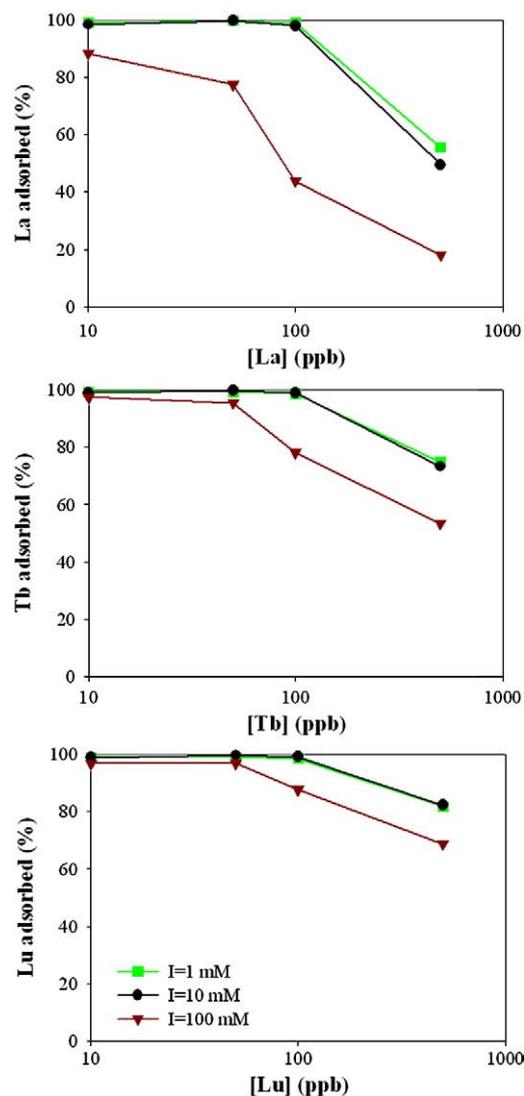


Fig. 5. REE adsorption as a function of initial REE concentration as well as ionic strength. The initial pH of each solution was 7 and $P_{\text{CO}_2}=10^{-3.5}$ atm (i.e., laboratory air). Error bars are smaller than the symbols.

3.2.5. Effect of initial REE concentration on REE adsorption

As shown in Fig. 5, at ionic strength = 0.001 M or 0.01 M, almost all of each REE studied (i.e., La, Tb, and Lu) is adsorbed onto Carrizo sand when initial concentration of each REE in solution is ≤ 100 $\mu\text{g}/\text{kg}$ for pH = 7. As the concentration of REE in the initial solution is increased to 500 $\mu\text{g}/\text{kg}$ for each REE, the amount of each REE adsorbed onto Carrizo sand decreases. The effect of increased REE concentration is especially substantial for the LREEs (Fig. 5).

3.2.6. Effect of humic substance on REE adsorption

The presence of dissolved organic matter substantially increases the amount of each REE (i.e., La, Tb, and Lu) adsorbed at low pH (i.e., pH = 4; Figs. 6, 7). However, for pH ≥ 5 , the effect of adding dissolved organic matter to the batch adsorption solutions is to substantially decrease the amount of La, Tb, and Lu adsorbed onto Carrizo sand compared to the experimental solution lacking dissolved organic matter (Figs. 6, 7). Moreover, in the case of the experiments conducted with 10 mg/kg of Suwannee River FA in solution, the amount of each REE adsorbed onto Carrizo sand decreases with increasing pH, and this effect is more pronounced for the HREEs (Tb, Lu) than for the LREEs (La; Fig. 6). For example, at pH 4 and 9.5, approximately 80% and 65%, respectively, of La is adsorbed onto

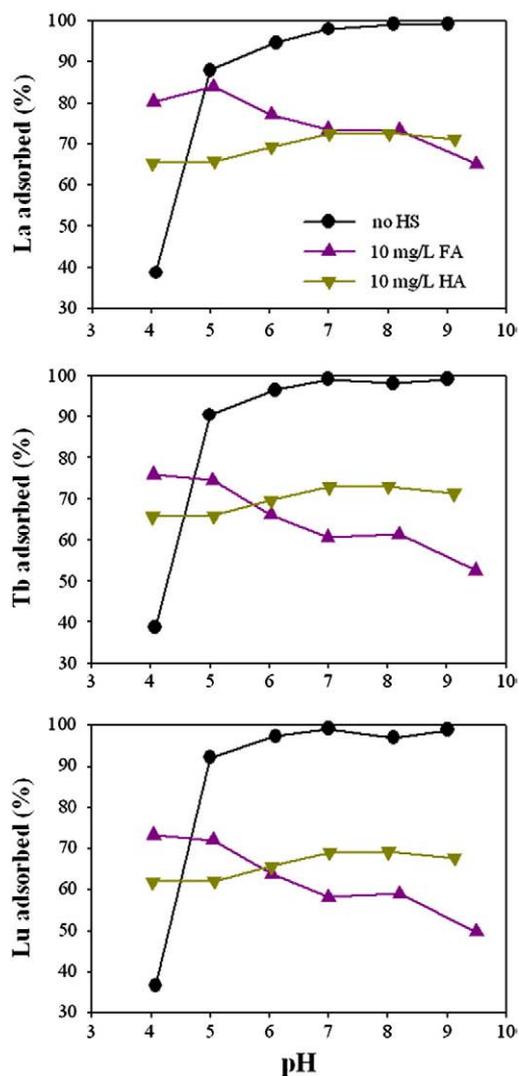


Fig. 6. Influence of humic substances on REE adsorption. Initial concentration of each REE = 100 $\mu\text{g}/\text{kg}$. $P_{\text{CO}_2} = 10^{-3.5}$ atm (i.e., laboratory air). Background electrolyte solution is 0.01 M NaCl solution. FA is Suwannee River fulvic acid, whereas HA represents Aldrich humic acid. Error bars are smaller than the symbols.

Carrizo sand in the presence of Suwannee River FA, whereas for these same pH values, 75% and ~50%, respectively, of Lu is adsorbed. In comparison, the relative change in the amount of each REE adsorbed onto Carrizo sand in the presence of 10 mg/kg of Aldrich HA is relatively minor, although in each case, the amount of La, Tb, and Lu adsorbed increases slightly (less than a 10% change in the amount adsorbed) with increasing pH (Fig. 6).

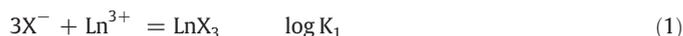
In addition to HS influencing the amount of each REE adsorbed onto Carrizo sand, the two different types of HS employed in our experiments differentially affected REE adsorption across the REE series (Fig. 7). Specifically, relatively more of the MREEs (i.e., Sm and Eu) are adsorbed onto Carrizo sand compared to LREEs and HREEs from initial solutions containing Aldrich HA. As a consequence, the relative amount of each REE adsorbed onto Carrizo sand for solutions containing Aldrich HA exhibit a MREE-enriched pattern across the REE series (Fig. 7). Please note that this MREE-enriched pattern for REE adsorption is similar to the MREE-enriched pattern exhibited by the apparent stability constants or the apparent partition coefficients for REE complexation with humic acids measured in laboratory experiments at REE/DOC molar ratios $>10^{-3}$ (Fig. 8; Yamamoto et al., 2005, 2010; Pourret et al., 2007; Marsac et al., 2010). In contrast, for initial

solution containing Suwannee River FA, the LREEs are preferentially adsorbed onto Carrizo sand relative to the MREEs and HREEs (Fig. 7).

3.3. Modeling results

In our previous experiments (Tang and Johannesson, 2005a), REE adsorption onto Carrizo sand was investigated at low REE loading (i.e., the solid/solution = 1000 g/L and initial concentration = 10 or 100 ppb for each REE). From these experiments we developed an initial surface complexation model for REE adsorption onto Carrizo sand. However, when this model developed at low REE loading conditions was directly applied to our new batch adsorption experiments that were conducted at relatively high REE loading conditions (i.e., the solid/solution = 25 g/L and initial concentration of each REE ranging from 10 ppb to 1 ppm), the model was able to reproduce trends in the experimental data when the initial concentration of each REE was 10 ppb, but under-predicted REE adsorption onto Carrizo sand when the initial concentration of each REE increased from 50 ppb to 1 ppm. These observations suggest that surface complexation reactions are sufficient to describe REE adsorption at low REE loading conditions, but not at high REE loading conditions. For example, potentiometric titrations of Carrizo sand by Tang and Johannesson (2005a) indicate that 0.5 g of Carrizo sand used in each of our new adsorption experiments has total surface sites of 5.95×10^{-7} mol ($1.19 \mu\text{mol}/\text{g} \times 0.5 \text{ g}$). However, when the initial concentration of each REE in the new batch experiments was 1 ppm, the total amount of adsorbed REEs was measured to be 7.34×10^{-7} mol and 1.19×10^{-6} mol for experiments conducted under the pure N_2 atmosphere and under the laboratory atmosphere, respectively. Consequently, at high initial REE concentrations, the amount of surface sites is insufficient for complete adsorption of the REEs in our new batch experiments. Therefore, additional surface exchange reactions must be included into the model in order to correctly describe REE adsorption at high REE loading conditions.

Moreover, ionic strength effects observed in our new batch experiments also supports the addition of surface exchange reactions in order to explain REE adsorption at high REE loading conditions. It is well known that increasing ionic strength decreases the activity coefficient of dissolved ions in solution. At the same time, increasing ionic strength decreases the double layer thickness and thus results in stronger surface complexation of cations with surface sites. Therefore, cation sorption onto mineral surfaces via surface complexation alone is insensitive to ionic strength (Dzombak and Morel, 1990). Tertre et al. (2008) presented a model that included both surface complexation and surface exchange reactions can successfully describe REE adsorption onto basaltic rock at different ionic strengths. Thus, we suggest that the lower amount of each REE adsorbed onto Carrizo sand at high ionic strength (i.e., 0.1 M; Figs. 4 and 5) likely involves other surface reactions such as surface exchange, which is more sensitive to the variation of ionic strength than surface complexation alone. In this study, we introduce the following surface exchange reaction into our model to account for additional surface reactions:



where X^- is the exchange master species defined in the default database of PHREEQC and Ln^{3+} is any uncomplexed REE ion in solution. Again, in the model calculations, we used the same model parameters estimated by Tang and Johannesson (2005a) for the surface complexation reactions. The amount of REEs removed from solution by exchange reactions, however, was estimated as the difference between the total amount of each REE removed from the initial solutions as determined by our experimental measurements and the amount of REEs removed from solution by surface complexation that is predicted by the surface complexation model of Tang and Johannesson (2005a). Then, based on the estimated

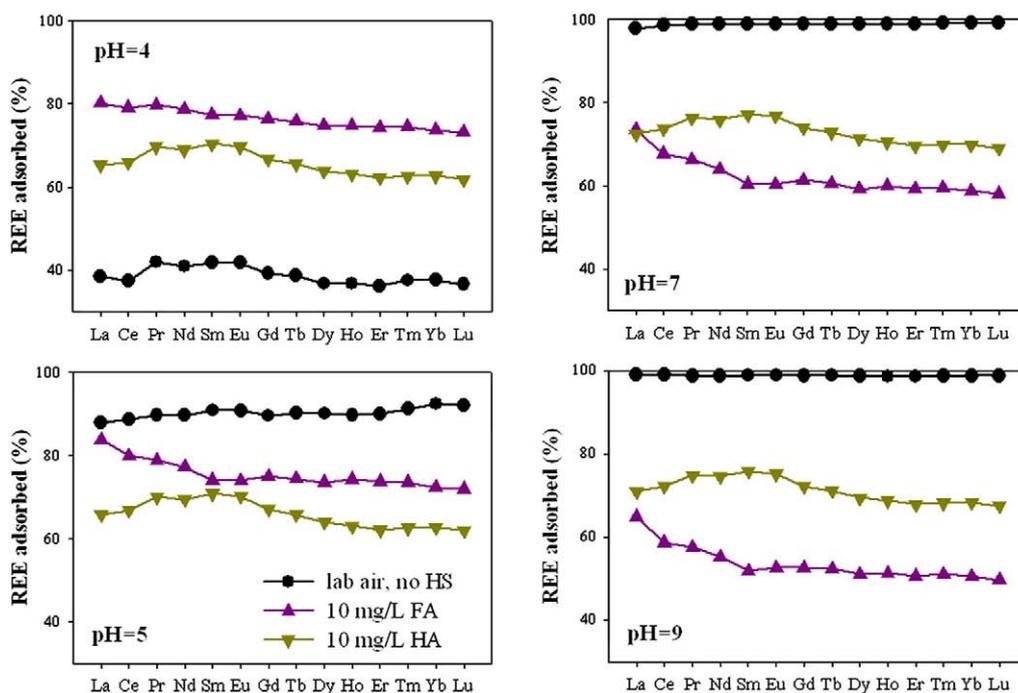


Fig. 7. Influence of humic substances (Suwannee River FA and Aldrich HA) on the patterns of REE adsorption across the lanthanide series. Initial concentration of each REE = 100 µg/kg and $P_{CO_2} = 10^{-3.5}$ atm (i.e., laboratory air). Background electrolyte solution is 0.01 M NaCl solution. Error bars are smaller than the symbols.

amount of the REE removed from solution by exchange reactions, we subsequently adjusted the amount of exchange sites or the exchange constant, K_1 , for each REE exchange reaction to recover our experimental data.

By holding the exchange constant, K_1 , in reaction (1) constant and varying the amount of the exchange sites, X , we were able to

reproduce the experimental results for REE adsorption conducted under a N_2 atmosphere for different initial REE concentrations and a solid/solution of 25 g/L (Fig. 9). The amount of exchange sites required to account for additional REE adsorption at different REE loadings are listed in Table 2. The exchange constants for REE exchange reactions are listed in Table 3.

Subsequently, the model parameters determined for experiments conducted under a N_2 atmosphere were then applied to experiments conducted at a constant pH of 7.0 but different P_{CO_2} levels. Tang and Johannesson (2005a) reported that additional adsorption of REE carbonate complexes is only required for $pH > 7.3$ at low REE loading. However, without considering the additional adsorption of REE carbonate complexes, the model slightly under-predicts the amount of each REE adsorbed onto Carrizo sand for our new batch experiments conducted at different P_{CO_2} levels and a constant pH of 7.0, suggesting that additional adsorption of REE carbonate complexes is also required to describe REE adsorption behavior in the presence of carbonate ions at high REE loading, even when pH is below 7.23. Consequently, adsorption of both carbonate complexes ($LnCO_3^+$) and dicarbonate complexes ($Ln(CO_3)_2^-$) of REEs onto Carrizo sand was considered in the model. According to our model calculations, at high REE loading, strong surface sites on Carrizo sand were occupied by uncomplexed REE ions, $[Ln^{3+}]_f$, leaving weak surface sites for surface binding of aqueous REE carbonate complexes and dicarbonate complexes. Thus, in this study, only weak surface sites were considered for the adsorption of aqueous REE carbonate species as follows:

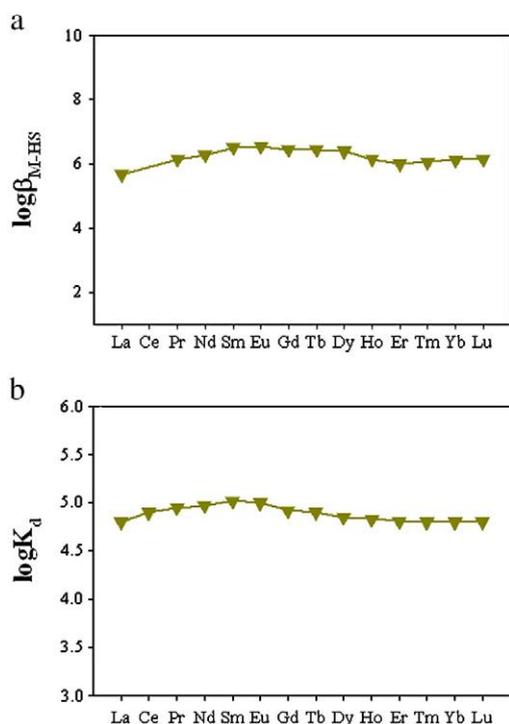
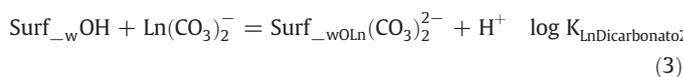


Fig. 8. Patterns of REE complexation with humic acids (HA): (a) the pattern of the apparent stability constants for REE–HA complexes determined using solvent extraction at REE–HA = 3.0×10^{-3} mol/equiv. and $I = 0.1$ M (Yamamoto et al., 2010); (b) the pattern of the apparent partition coefficients for REE–HA complexes measured at REE/DOC molar ratio = 2.73×10^{-2} (Marsac et al., 2010).

Conditional surface complexation constants ($K_{Ln\text{Dicarbonato2}}$) for $Ln(CO_3)_2^-$ adsorption onto weak surface sites used in the current model were previously estimated by Tang and Johannesson (2005a). For the current modeling, we estimated conditional surface complexation

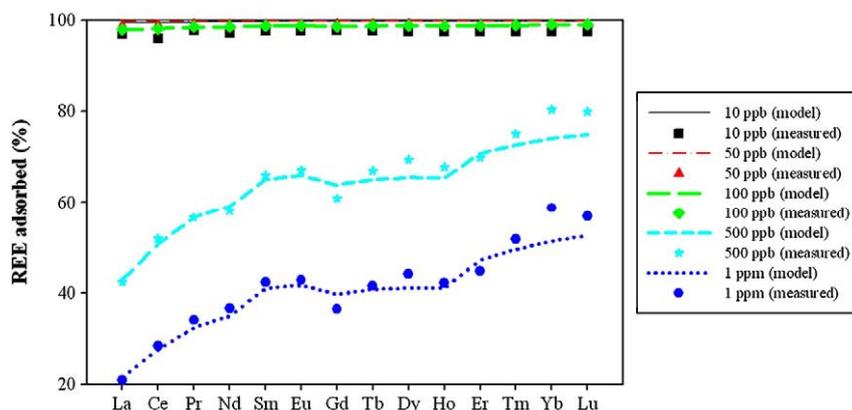


Fig. 9. Model results for REE adsorption onto Carrizo sand under a N₂ atmosphere at pH = 7.0 and initial concentration ranging from 10 ppb to 1 ppm for each REE. Experimental data are shown by symbols and model calculations are shown by lines. Error bars are smaller than the symbols.

Table 2

The amount of exchange sites required to account for additional REE adsorption onto Carrizo sand at different initial concentration of each REE.

Initial concentration of each REE	10 ppb	50 ppb	100 ppb	500 ppb	1 ppm
Amount of exchange site (mol)	7.5×10^{-8}	3.9×10^{-7}	6.13×10^{-7}	1.7×10^{-6}	2.1×10^{-6}

constants ($K_{Ln\text{carbonato}}$) for carbonate complexes of REEs onto weak sites of Carrizo sand (see Table 3). Through our model calculations, we found that, at pH 7.0, one additional term Surf_wOLnCO₃ is sufficient to describe REE adsorption at different P_{CO_2} levels when the initial concentration of each REE was 50 ppb or higher, whereas both Surf_wOLnCO₃ and Surf_wOLn(CO₃)₂²⁻ are required when the initial concentration of each REE in solution was 10 ppb. Fig. 10 presents the model results for batch experiments conducted at different P_{CO_2} levels with initial concentrations of 100 ppb for each REE and pH = 7.0.

The model was further applied to batch experiments conducted under the ambient laboratory atmosphere at different pH as well as different ionic strengths. The model predicted that the amount of REEs removed from solution by surface complexation was essentially the same at pH 4 and pH 5. Thus, the difference in REE adsorption between pH 4 and pH 5 shown in Figs. 3 and 4 is mainly due to exchange reactions. To correctly describe the pH effect on exchange reactions, the following proton exchange reaction is also included in our model:



Table 3

Conditional constants (K_1) for REE exchange reactions as well as conditional surface complexation constants ($K_{Ln\text{carbonato}}$) for carbonate complexes of REEs onto weak sites of Carrizo sand as Surf_wOLnCO₃, where w refers to weak sites.

REE	log K_1	log $K_{Ln\text{carbonato}}$
La	3.34 ± 0.11	-1.77 ± 0.21
Ce	3.44 ± 0.07	-1.57 ± 0.23
Pr	3.51 ± 0.08	-1.53 ± 0.18
Nd	3.54 ± 0.07	-1.50 ± 0.15
Sm	3.65 ± 0.04	-1.47 ± 0.16
Eu	3.67 ± 0.03	-1.49 ± 0.16
Gd	3.62 ± 0.06	-1.54 ± 0.14
Tb	3.60 ± 0.04	-1.56 ± 0.14
Dy	3.61 ± 0.06	-1.61 ± 0.14
Ho	3.62 ± 0.05	-1.67 ± 0.14
Er	3.65 ± 0.08	-1.67 ± 0.16
Tm	3.73 ± 0.07	-1.61 ± 0.06
Yb	3.76 ± 0.09	-1.47 ± 0.08
Lu	3.77 ± 0.08	-1.44 ± 0.06

The conditional proton exchange constant for the above reaction (K_4) was estimated to be $10^{-3.3}$ by difference in total REE adsorption between pH 4 and pH 5 (Figs. 3 and 4). As shown in Fig. 11, the model parameters estimated from our new batch experiments are applicable to a wider pH range as well as a wider ionic strength range than our previous estimates from Tang and Johannesson (2005a). The model calculations also indicate that pH affects the adsorption of aqueous REE carbonate complexes. More specifically, no additional adsorption of aqueous REE carbonate complexes was required to describe REE adsorption onto Carrizo sand for $pH \leq 5$. However, one additional term, Surf_wOLnCO₃, is necessary to describe REE adsorption for $5 \leq pH \leq 8$, and two additional terms, Surf_wOLnCO₃ and Surf_wOLn(CO₃)₂²⁻, are required for $pH > 8$. Our model calculations also indicate that, when ionic strength was increased from 0.01 M to 0.1 M, the amount of each REE adsorbed was significantly decreased by competition between uncomplexed REE ions, [Ln³⁺]_F, and Na⁺ for exchange sites.

4. Discussion

4.1. Solubility control of REEs by carbonates

As shown in both Figs. 2 and 5, for experiments conducted under pure N₂ or laboratory air, the percentage of REEs adsorbed onto Carrizo sand generally decreased as the concentrations of REEs in the initial solution increased. The same general inverse relationship between decreasing amounts of REEs adsorbed with increasing solution concentrations of REEs is also observed for those experiments conducted in equilibrium with atmospheres composed of N₂ + 0.5% CO₂, N₂ + 2% CO₂, or N₂ + 5% CO₂, and where the initial concentration of each REE is 100 µg/kg or less (Fig. 2a–c). However, when the initial concentration of each REE is 500 µg/kg or greater, the batch adsorption experiments suggest that the amount of REE adsorption appears to actually increase for those experiments conducted at $P_{CO_2} \geq 10^{-2.3}$ atm (i.e., in equilibrium with N₂ + 0.5% CO₂, N₂ + 2% CO₂, or N₂ + 5% CO₂; Fig. 2d, e). The apparent increase in REE adsorption for these experiments with high initial REE concentrations suggests that in addition to adsorption, other geochemical reactions or processes also removed REEs from solutions during these experiments. For the experiments conducted in equilibrium with atmospheres composed of N₂ + 0.5% CO₂, N₂ + 2% CO₂, or N₂ + 5% CO₂, the amount of apparent adsorption of each REE from the solution with

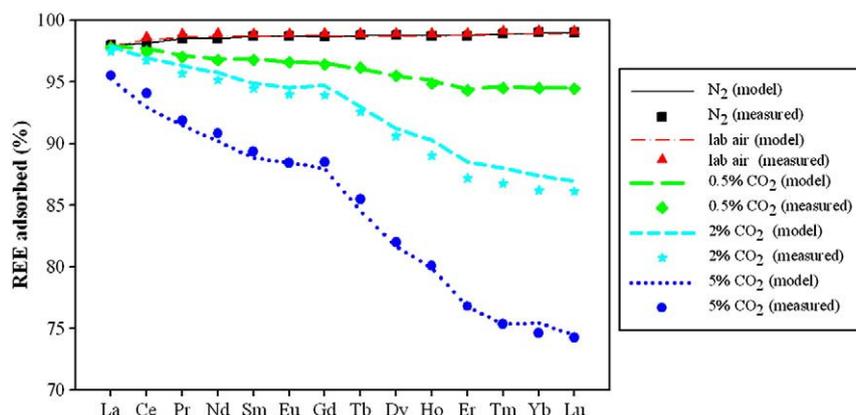


Fig. 10. Model results for REE adsorption onto Carrizo sand at pH = 7.0, initial concentration of each REE = 100 ppb, and P_{CO_2} ranging from 0 to $10^{-1.3}$ atm. Experimental data are shown by symbols and model calculations are shown by lines. Error bars are smaller than the symbols.

initial concentration of 500 $\mu\text{g}/\text{kg}$ for each REE is essentially the same as that from the solution with initial concentration of 1000 $\mu\text{g}/\text{kg}$ for each REE (Fig. 2d, e). Considering the fact that REE carbonate precipitates or co-precipitates (i.e., $\text{Ln}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$) are highly insoluble (Table 4; Smith and Martell, 1976; Firsching and Mohammadzadel, 1986), we suggest that the actual initial concentration of each REE for these experiments is limited by the solubility of REE carbonate precipitates/co-precipitates. As shown in Table 4, for initial

concentration of 500 $\mu\text{g}/\text{kg}$ for each REE and $P_{CO_2} = 10^{-2.3}$ atm (i.e., $\text{N}_2 + 0.5\% \text{CO}_2$), the calculated activity products (AP) for REE carbonates in a 0.01 M NaCl background solution at 25 °C and pH = 7 are remarkably similar to the solubility products (K_{sp}) for REE carbonate salts at infinite dilution (i.e., $I = 0$ M). The similarity in the AP and K_{sp} indicates that our experimental solutions containing a concentration of 500 $\mu\text{g}/\text{kg}$ for each REE and $P_{CO_2} = 10^{-2.3}$ atm are likely at equilibrium with these REE carbonate precipitates. Moreover, when the initial concentration of each REE is increased to 1 mg/kg or the P_{CO_2} increases to $10^{-1.7}$ or $10^{-1.3}$ atm, the calculated AP values also increase such that the experimental solutions become supersaturated with respect to REE carbonate salts (Table 4). Consequently, evaluation of the AP of the experimental solutions provides evidence that REE carbonate precipitates/co-precipitates may limit the maximum initial REE concentrations in the reaction solutions. Thus, the high calculated percentage of REEs absorbed shown in Fig. 2d and e for experiments conducted in equilibrium with atmospheres composed of $\text{N}_2 + 0.5\% \text{CO}_2$, $\text{N}_2 + 2\% \text{CO}_2$, or $\text{N}_2 + 5\% \text{CO}_2$ likely reflects both REE adsorption onto Carrizo sand as well as the precipitation/co-precipitation of REE carbonates in these batch reactors.

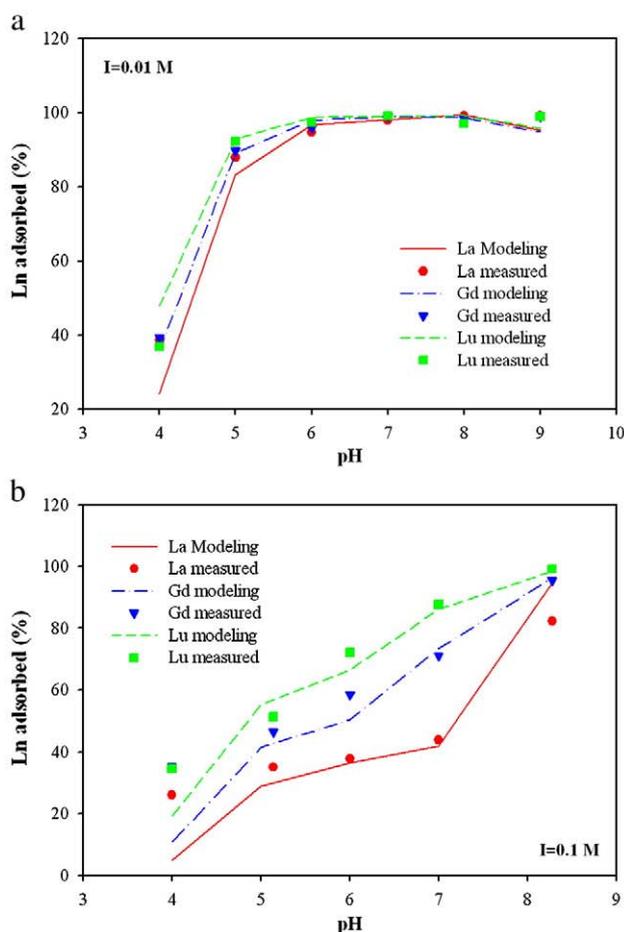


Fig. 11. Model results for REE adsorption onto Carrizo sand under an ambient laboratory atmosphere at an initial concentration for each REE = 100 ppb and pH varying from 4 to 9. Background solution is a 0.01 M NaCl solution in Panel (a) and is a 0.1 M NaCl solution in Panel (b). Error bars are smaller than the symbols.

4.2. Role of exchange reactions in REE adsorption

In our previous study of REE adsorption onto Carrizo sand (Tang and Johannesson, 2005a) a simple surface complexation model was

Table 4

Solubility products (reported as pK_{sp}^0) for REE carbonates at zero ionic strength and 25 °C. Also presented are calculated activity products (reported as $-\log \text{AP}$) for REE carbonates in 0.01 M NaCl background solutions at 23 °C and pH = 7.0: (a) initial concentration of each REE = 500 $\mu\text{g}/\text{kg}$ and $P_{CO_2} = 10^{-2.3}$ atm and (b) initial concentration of each REE = 1000 $\mu\text{g}/\text{kg}$ and $P_{CO_2} = 10^{-1.3}$ atm.

pK_{sp}^0	Smith and Martell (1976)	Firsching and Mohammadzadel (1986)	$-\log \text{AP}$	
			(a)	(b)
$\text{La}_2(\text{CO}_3)_3$	33.4	29.91	31.64	29.59
$\text{Ce}_2(\text{CO}_3)_3$	–	–	32.00	30.19
$\text{Pr}_2(\text{CO}_3)_3$	–	33.19	32.23	30.56
$\text{Nd}_2(\text{CO}_3)_3$	33.0	34.10	32.32	30.69
$\text{Sm}_2(\text{CO}_3)_3$	32.5	34.41	32.65	31.16
$\text{Eu}_2(\text{CO}_3)_3$	32.3	35.03	32.71	31.26
$\text{Gd}_2(\text{CO}_3)_3$	32.2	35.45	32.58	31.08
$\text{Tb}_2(\text{CO}_3)_3$	–	34.86	32.73	31.39
$\text{Dy}_2(\text{CO}_3)_3$	31.5	33.97	32.92	31.63
$\text{Ho}_2(\text{CO}_3)_3$	–	32.80	32.93	31.71
$\text{Er}_2(\text{CO}_3)_3$	–	28.25	33.06	31.90
$\text{Tm}_2(\text{CO}_3)_3$	–	31.58	33.20	32.14
$\text{Yb}_2(\text{CO}_3)_3$	31.1	31.67	33.44	32.31
$\text{Lu}_2(\text{CO}_3)_3$	–	32.16	33.37	32.34

adequate to describe REE adsorption at low REE loading (i.e., the solid/solution = 1000 g/L and initial concentration of each REE = 10 or 100 ppb). However, the same model under-predicts the amount of REE adsorption at the high REE loadings used in the current study (i.e., the solid/solution = 25 g/L and initial concentration of each REE ranging from 10 ppb to 1 ppm). When surface exchange reactions are also included in the model, however, the model predictions are in good agreement with the experimental results. The agreement between the experiment and model results is accommodated by an increase in the amount of exchange sites with increase in REE loading (see Table 2). Our model studies indicate that at low REE loading conditions (i.e., low initial REE concentration at high solid/solution ratio), REE adsorption onto Carrizo sand mainly occurs via surface complexation reactions. However, at high REE loading conditions (i.e., high initial REE concentration at low solid/solution ratio), both surface complexation and exchange reactions occur during REE adsorption onto Carrizo sand. Moreover, with the increase in REE loading, exchange reactions apparently play a more important role as more exchange sites are required to account for REE adsorption (see Table 2).

Our model studies further indicate that exchange reactions also play an important role in REE adsorption onto Carrizo sand at high ionic strengths. According to our model calculations, activity coefficients of uncomplexed REE ions, $[Ln^{3+}]_F$, decreased at high ionic strength (i.e., 0.1 M) but the amount of REEs removed by surface complexation reactions was essentially the same owing to the stronger coulombic force at high ionic strength. In contrast, the amount of REEs removed by exchange reactions significantly decreased at high ionic strength because fewer exchange sites are available for REEs at high ionic strength owing to increased competition from more abundant ions (e.g., Na^+). For example, for REE adsorption at low ionic strength ($I=0.01$ M) and experimental conditions of $pH=5$, initial concentration = 100 ppb for each REE, and $P_{CO_2} = 10^{-3.5}$ atm, the model predicts that ~7.8% of the exchange sites were occupied by Na^+ ions, ~83% of La was removed from solution by exchange reactions, and only 0.21% of La was removed from solution by surface complexation reactions. In contrast, at higher ionic strength ($I=0.1$ M) and the same experimental conditions, ~53.2% of the exchange sites were occupied by Na^+ ions, ~28.8% of La was removed from solution by exchange reactions, and 0.22% of La was removed from solution by surface complexation reactions. Thus, these model results indicate that surface complexation of the REEs is insensitive to variations in ionic strength, and further, the lower amounts of REE adsorption that occurs with increasing ionic strength chiefly reflects the loss of available exchange sites for uncomplexed REE ions, $[Ln^{3+}]_F$, owing to increased competition from more abundant ions like Na^+ .

4.3. Role of P_{CO_2} in REE adsorption

Consistent with previous studies (e.g., Quinn et al., 2006b), REE adsorption at pH 7 initially increases when P_{CO_2} slightly increases from 0 to $10^{-3.5}$ atm, but then decreases with further increase in P_{CO_2} (Fig. 2). Our model calculations (also see Quinn et al., 2006b) indicate that in addition to the adsorption of the uncomplexed REE ion, $[Ln^{3+}]_F$, onto mineral surfaces, aqueous complexes such as carbonate complexes $[LnCO_3^-]$ and/or $[Ln(CO_3)_2^-]$ can also be adsorbed. Consequently, a slight increase of P_{CO_2} from 0 to $10^{-3.5}$ atm will lead to the formation of REE carbonate complexes in solution, a fraction of which will adsorb onto Carrizo sand (see Section 3.3), leading to an increase in the total amount of REEs adsorbed. With further increases in P_{CO_2} ($\geq 10^{-2.3}$ atm), the amount of each REE complexed with carbonate ions in solution increases. Again, the increase in the amount of solution complexation of the REEs with carbonate ions in our experiments reflects the fact that the experimental solutions were equilibrated with the various N_2 - CO_2 atmospheres within the glove

box, while holding the pH of the solution constant at 7 using 0.1 M NaOH. Consequently, the increase in P_{CO_2} of the experimental atmosphere within the glove box leads to more CO_2 dissolution into the solutions, and subsequent increase in the concentrations of bicarbonate and carbonate ions under the constant, circumneutral pH conditions of the solutions (Table 1). The increase in HCO_3^- and CO_3^{2-} ions in solutions leads to a greater percentage of the REEs being complexed with carbonate ions (e.g., Lee and Byrne, 1993; Johannesson and Lyons, 1994; Luo and Byrne, 2004).

The model calculations (Section 3.3) indicate that uncomplexed REE ions, $[Ln^{3+}]_F$, are the dominant species of each REE that adsorbs onto Carrizo sand, and the total amount of REEs adsorbed onto Carrizo sand subsequently decreases with increasing P_{CO_2} above $10^{-2.3}$ atm. The implication of the experimental and modeling results to the mobility of REEs in actual groundwater-aquifer systems is that, when pH is buffered by rock-water reactions, an increase in the total dissolved carbonate ion concentration will favor REE migration due to solution complexation of REEs with carbonate ions.

4.4. Role of pH in REE adsorption

According to previous studies (Davis and Kent, 1990; Dzombak and Morel, 1990), sorption curves for cations typically exhibit S-shapes, such that, cation sorption gently increases with increasing pH at low pH values, steeply increases within a narrow pH range (i.e., the “adsorption edge”), and then gradually approaches a plateau at higher pH values. The REEs exhibit similar adsorption behavior as a function of pH for experiments conducted at relatively low ionic strength (i.e., $I=0.001$ or 0.01 M) and in the absence of strong solution complexing ligands such as carbonate ions and dissolved organic matter (Figs. 3, 4 and 6). However, the effect of pH on REE adsorption is apparently “buffered” at high ionic strength (i.e., $I=0.01$ M; Fig. 4). Specifically, for a 0.1 M NaCl background electrolyte solution, the amount of REE adsorbed onto Carrizo sand decreases for pH between 4 and 8 compared to dilute solutions (Fig. 4). Our observations of the decrease of REE adsorption at high ionic strength are consistent with previous results for REE sorption onto basaltic rock (Tertre et al., 2008). The model calculations suggest that this “buffering” effect is mainly due to competition between Na^+ and uncomplexed REE ions, $[Ln^{3+}]_F$, for exchange sites at high ionic strength in our solutions.

In the presence of strong solution complexing ligands, the role of pH in REE adsorption is complex. For example, for the experimental solutions in equilibrium with $N_2 + 0.5\% CO_2$ or $N_2 + 2\% CO_2$ atmospheres (Fig. 3), REE adsorption is decreased slightly compared to experiments conducted in equilibrium with laboratory air. This is because REEs are adsorbed mainly as uncomplexed REE ions, $[Ln^{3+}]_F$, as indicated by our model calculations. Strong solution complexation of dissolved REEs with carbonate ions under $N_2 + 0.5\% CO_2$ or $N_2 + 2\% CO_2$ atmospheres decreases the amount of uncomplexed REE ions, $[Ln^{3+}]_F$, and thus decreases REE adsorption. Moreover, as pH increases from 4 to 8, the amount of the REEs (i.e., La, Tb, and Lu) adsorbed initially increases for all REEs up to pH ~6, and then decreases with further increasing pH (Fig. 3). The main reason for this pH effect is that the fraction of each REE complexed with carbonate ions in solution increases with increasing pH such that REE carbonate complexes predominate for $pH > 6.0$ as indicated by our model calculations.

Furthermore, in the presence of FA in solution, REE adsorption generally decreases with increasing pH , whereas REE adsorption slightly increases with increasing pH in the presence of HA (Fig. 6). The different pH effect on REE adsorption observed in the NaCl solutions doped with FA or HA is probably due to different adsorption behavior of REE-FA complexes and REE-HA complexes onto Carrizo sand (see discussion later). Nonetheless, we point out that compared to solutions containing no humic substances, the presence of HS in solution also inhibits REE adsorption onto Carrizo sand when pH is above 5 (Fig. 6).

The geochemical implication of our results concerning the role of pH in REE adsorption is that although increasing pH promotes REE adsorption, the composition of the aqueous solution, and in particular, the concentrations of ligands that can form strong aqueous complexes with the REEs (e.g., CO_3^{2-} , organic ligands) can act to decrease REE adsorption onto mineral surface sites. The reactivity of these ligands towards REEs will increase as pH increases promoting deprotonation of HS and dissociation of carbonic acid. Consequently, in natural groundwater systems where carbonate complexes or organic complexes with low molecular weight DOC such as FA dominate dissolved REE speciation, an increase of pH above 7 would inhibit REE adsorption or promote desorption of REEs, thus favoring the migration of dissolved REEs in the aquifer.

4.5. Role of ionic strength in REE adsorption

Tang and Johannesson (2005a) reported no ionic strength effect on REE adsorption onto Carrizo sand from solutions with ionic strength within the range of 0.002–0.01 M. Previously, we attributed the lack of any discernable ionic strength effect on REE adsorption to an insufficient change of ionic strength in our experiments. The results presented here for 0.001 M and 0.01 M ionic strength are also in agreement with the observations of Tang and Johannesson (2005a). However, when ionic strength is increased to 0.1 M, adsorption of REEs onto Carrizo sand is decreased compared to the amount of REE adsorbed for lower ionic strength solutions (Figs. 4, 5). As discussed above, high ionic strength appears to “buffer” the role of pH in REE adsorption, such that the REE adsorption edge is subdued, only gradually increasing with increasing pH (Fig. 4). The suppressed adsorption edge observed at high ionic strength is in remarkable contrast to the steep adsorption edge for REEs that occurs between pH 4 and 5 at low ionic strength. Consequently, the amount of each REE adsorbed onto Carrizo sand from high ionic strength solution ($I=0.1$ M) is substantially less than the amount adsorbed from low ionic strength solutions ($I=0.001$ and 0.01 M) at any given pH between ~4 and 8. Indeed, for the high ionic strength solution, 100% adsorption of dissolved REE is attained at pH values between 8 and 9, whereas the same amount of adsorption is attained at pH between 6 and 7 for the low ionic strength solutions (Fig. 4). The model calculations suggest that the decrease of REE adsorption at high ionic strength chiefly reflects the decrease in surface exchange sites available for REE surface exchange reactions owing to the increase in competitive solute concentrations (e.g., Na^+) that accompanies increasing ionic strength.

The geochemical implication of our results is that in natural aquifer–groundwater systems with dilute waters of low ionic strength, the amount of REEs adsorbed onto aquifer mineral surface sites will not be affected by slight changes in the concentrations in the major dissolved solutes. However, when saline natural waters, such as seawater, mixes with fresh waters as occurs in subterranean estuaries (Moore, 1999), or via anthropogenically-induced seawater-intrusion into coastal aquifers, our data suggest that REE adsorption onto aquifer mineral surface sites will be inhibited compared to the case including only fresh groundwater. Consequently, in coastal aquifers where terrestrial-sourced groundwaters of meteoric origin mix with recirculating saline waters originating in the ocean, REE adsorption onto aquifer mineral surfaces and/or particle surfaces will be less significant than in low ionic strength fresh waters. According to our modeling studies, this is because less exchange sites are available for REEs at high ionic strength. Our studies imply that introduction of saline waters into coastal aquifers by either natural processes such as recirculation of saline, marine groundwater, or from seawater-intrusion by over-pumping of coastal wells, could induce REE desorption from aquifer mineral surface sites, adding to the flux of REEs to the coastal oceans (e.g., Johannesson and Burdige, 2007; Johannesson et al., 2008).

4.6. Role of humic substance in REE adsorption

Adsorption of humic substances onto mineral substrates is stronger in acidic waters than in neutral to high pH waters, such that the adsorption of humics generally decreases with increasing pH (Ledin et al., 1994; Lippold et al., 2005; Wan and Liu, 2006). Therefore, in the presence of humic substances, REE adsorption onto mineral surface sites is enhanced in the acidic pH range due to the additional adsorption of humic-bound REEs. However, with increasing pH, the presence of humic substances in the experimental solutions decreases REE adsorption because of desorption of humic substance as pH increases, along with the associated humic-bound REEs (Ledin et al., 1994; Lippold et al., 2005; Wan and Liu, 2006; Lippold and Lippmann-Pipke, 2009). The pH range where humic substances enhance REE adsorption is influenced by the solid materials, concentrations of humic substances, and ionic strength (Ledin et al., 1994; Lippold et al., 2005; Wan and Liu, 2006). Our results show that for Carrizo sand, both HA and FA at concentrations of 10 mg/L enhance REE adsorption at pH of 4, but results in lower amounts of REE adsorption when pH is above 5 (Figs. 6, 7). Thus, in the Carrizo sand aquifer where groundwater pH ranges from ~6 to 8.5 (Tang and Johannesson, 2005b, 2006), complexation of REE with humic substances would be expected to favor the migration of dissolved REEs.

Note that the pH-dependence of the influence of HA and FA on REE adsorption differs as described above (Fig. 6). In the presence of FA, REE adsorption generally decreases with increasing pH, whereas in the presence of HA, REE adsorption increases slightly, albeit the amount adsorbed changes by less than 10%, with increasing pH (Fig. 6). We submit that the difference in REE adsorption in the presence of FA and HA is due to the differences in: (1) the solution complexing capacity of FA and HA for dissolved REEs and (2) the various primary adsorption species (i.e., uncomplexed REE ions vs. humic-bound REE complexes). As evidence, we present the REE adsorption patterns across the REE series at different pH for REEs bound to fulvic acid and REEs complexed with humic acid (Fig. 7). In the presence of HA, REE adsorption patterns are remarkably consistent with the patterns exhibited by the apparent stability constants or the apparent partition coefficients of REE–HS complexes measured in laboratory experiments at REE/DOC molar ratios $>10^{-3}$ (Fig. 8; Yamamoto et al., 2005, 2010; Pourret et al., 2007; Marsac et al., 2010). Whereas in the presence of FA, REE adsorption patterns are essentially opposite to the patterns of the apparent stability constants or the apparent partition coefficients of REE–HA complexes (Fig. 8). These differences in the relative adsorption of REEs across the REE series in the presence of FA and HA suggest that REE solution complexation with these organic ligands strongly influences the primary adsorption species. Because HA has a stronger complexing capacity than FA for dissolved REEs (Sonke and Salters, 2006; Tang and Johannesson, 2010), REE adsorption chiefly involves the adsorption of the humic-bound, REE complexes in the presence of HA, whereas REE adsorption is dominated by adsorption of uncomplexed REE ions, $[\text{Ln}^{3+}]_f$, for the experimental solutions containing FA. Therefore, REE adsorption patterns in the presence of HA agree with the species distribution of HA-bound REEs, but REE adsorption patterns in the presence of FA are contrary to the species distribution of FA-bound REEs. It has been suggested that REE–humate complexation (HA) increases with increasing pH (Sonke and Salters, 2006; Pourret et al., 2007). Thus, REE adsorption should increase with increasing pH in the presence of HA but decrease in the presence of FA (Fig. 6).

5. Summary

This work investigates the influence of strong solution complexation on REE adsorption by natural aquifer materials from the Carrizo Sand aquifer of Texas. Our results indicate that in the absence of

strong solution complexation, REEs are strongly adsorbed onto Carrizo sand at neutral to high pH, and REE adsorption generally increases with increasing atomic number across the REE series. Increasing the P_{CO_2} level from 0 to $10^{-3.5}$ atm (i.e., laboratory air) enhances REE adsorption but does not fractionate the REE. However, when the P_{CO_2} level is increased above $10^{-2.3}$ atm (i.e., $\text{N}_2 + 0.5\% \text{CO}_2$) while holding pH constant at 7, REE solution complexation with dissolved carbonate ions substantially decreases REE adsorption, with REE adsorption generally decreasing from LREEs to HREEs across the REE series, in accord with the increasing strength of REE–carbonate complexes with increasing atomic number (e.g., Luo and Byrne, 2004). For acidic pH (i.e., $\text{pH} < 4$) and in the presence of dissolved humic substances, REE adsorption onto Carrizo sand increases due to the additional adsorption of humic-bound REEs. However, for $\text{pH} > 5$, humic substances decrease REE adsorption onto Carrizo sand. The different pH-dependence of HA and FA influence on REE adsorption observed in our results suggests that the primary adsorption species of REEs are HA-bound complexes in the presence of HA and are uncomplexed REE ions, $[\text{Ln}^{3+}]_{\text{F}}$, in the presence of FA.

Our results indicate that the role of pH on REE adsorption is also influenced by strong solution complexation. In the absence of strong solution complexation, REE adsorption increases with increasing pH and approaches a plateau near 100% adsorption when pH is above 7. However, in the presence of relatively high carbonate ions (i.e., $P_{\text{CO}_2} > 10^{-2.3}$ atm, $[\text{CO}_3^{2-}] = 5.3 \times 10^{-7}$ mol/kg) or FA and at neutral or high pH, the increase of pH leads to a decrease in REE adsorption. In the presence of HA, increasing pH only slightly increases REE adsorption.

Our results also indicate that for fresh, natural waters, a slight increase of ionic strength (0.001 to 0.01 M) will not affect REE adsorption on natural sand. However, if ionic strength is increased to 0.01 M, REE adsorption is inhibited compared to the low ionic strength solutions. In addition, the proportion of REEs adsorbed onto Carrizo sand generally decreases with the initial REE concentrations.

The geochemical modeling studies indicate that REE adsorption onto Carrizo sand mainly occurs via surface complexation at low REE loading condition (i.e., low initial REE concentration at high solid/solution ratio), whereas at high REE loading condition (i.e., high initial REE concentration at low solid/solution ratio), both surface complexation and surface exchange reactions are important processes that transfer REEs from solution to mineral surfaces of Carrizo sand. With the increase in REE loading, surface exchange apparently plays a more important role in the REE adsorption process. Our modeling studies also indicate that surface complexation is insensitive to the variations of ionic strength, and instead, the ionic strength effects observed in experiments presented in this contribution are best explained by competition between Na^+ and uncomplexed REE ions, $[\text{Ln}^{3+}]_{\text{F}}$, in solution for available surface exchange sites. Model calculations show that REEs are mainly adsorbed as uncomplexed REE ions, $[\text{Ln}^{3+}]_{\text{F}}$, but carbonate species of dissolved REEs can also be adsorbed onto Carrizo sand. Thus, the presence of carbonate ions can either increase or decrease REE adsorption depending on the amount of aqueous REE carbonate complexes.

Supplementary materials related to this article can be found online at doi:10.1016/j.chemgeo.2010.10.011.

Acknowledgments

We are especially thankful to Dr. L. Douglas James, Hydrologic Sciences program director for NSF hydrologic sciences for making the study possible as part of NSF grant EAR-0805331 to Karen H. Johannesson. We are grateful to Dr. D. Grimm of Tulane University's Coordinated Instrumentation Facility for her assistance in running the ICP-MS. Thoughtful and constructive comments from Dr. Joel D. Blum, Dr. Emmanuel Tertre, and an anonymous reviewer are appreciated.

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