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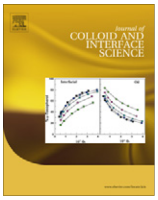

Rare earth element sorption onto hydrous manganese oxide: A modeling study

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ABSTRACT

Manganese oxides are important scavengers of rare earth elements (REE) in hydrosystems. However, it has been difficult to include Mn oxides in speciation models due to the lack of a comprehensive set of sorption reactions consistent with a given surface complexation model (SCM), as well as discrepancies between published sorption data and predictions using the available models. Surface complexation reactions for hydrous Mn oxide were described using a two surface site model and the diffuse double layer SCM. The specific surface area, surface side density, and pH_{zpc} were fixed to 746 m^2/g, 2.1 mmol/g, and 2.2, respectively. Two site types ($\equiv$XOH and $\equiv$YOH) were also used with pK_{a2} values of 2.35 ($\equiv$XOH) and 6.06 ($\equiv$YOH). The fraction of the high affinity sites was fixed at 0.36. Published REE sorption data were subsequently used to determine the equilibrium surface complexation constants, while considering the influence of pH, ionic strength, and metal loading. Log*K* increases from light REE to heavy REE and, more specifically, displays a convex tetrad effect. At low metal loading, the $\equiv$YOH site type strongly expresses its affinity toward REE, whereas at higher metal loading, the same is true for the $\equiv$XOH site type. This study thus provides evidence for heterogeneity in the distribution of the Mn oxide binding sites among REE.

1. Introduction

The distributions of rare earth elements (REEs) in natural waters have been intensively investigated for more than 40 years [1,2]. The absolute and relative concentrations of 14 stable REE have been determined in a variety of open ocean environments [3], estuaries [4], rivers [5], lakes [6], groundwaters [7], and hydrothermal fluids [8]. Although the complexation of hydrated trivalent REE with various inorganic anions (carbonate, hydroxide, sulfate, fluoride, and chloride) has been intensively studied [9], REE partitioning and fractionation between solution and relevant mineral surfaces are much less understood. To date, few studies have been dedicated to REE sorption onto mineral surfaces [10–15], and the most frequently used solids were Fe-oxyhydroxides [10,11,13–15]. REE sorption by amorphous ferric hydroxide was measured over a pH range of 3.5–9.0 and over a large ionic strength (IS) range. For a constant pH and individual REE, the magnitude of the estimated distribution coefficients differs by a factor of around 400. Although Mn-oxyhydroxides are as ubiquitous as Fe-oxyhydroxides and present high surface areas and a strong affinity for many elements [16], fewer studies have focused on REE adsorption by Mn-oxyhydroxides [10,13,17–19]. However, several studies have demonstrated that Mn-oxyhydroxides partly controlled REE fractionation and mobility in natural water. Thereby, they provided the evidence that a negative Ce anomaly in solution is developed through the oxidation/scavenging of Ce(III) onto the MnO_2 surface [10,17,19]. REE scavenging by ferromanganese nodules was also identified as a major process in controlling REE fractionation in seawater [8,20,21]. The lack of data for REE binding by Mn-oxyhydroxides may be attributed to the high variety of Mn-oxyhydroxide minerals and the heterogeneity of the published surface properties which complicate modeling studies. However, in order to accurately describe REE behavior, it is essential that REE binding to Mn-oxyhydroxides is quantitatively modeled. Many surface complexation models have been established to study and quantify cation sorption onto mineral surfaces. Each of them has their own solid–solution interface description, model parameters, and set of thermodynamic data, and many provide satisfactory fits to experimental data (e.g., [22]). Partially as a result of this model flexibility, ion sorption data on Mn-oxyhydroxides have been fit using a number of different surface complexation models (e.g., SCM). Thereby, a triple-layer SCM was used to evaluate and predict the surface complexation constants for hydrous manganese oxide (HMO) [23]. A variation on the constant capacitance model [24] was included in SCAMP to determine the model parameters for sorption on Mn-oxyhydroxides [25]. Crystallographic data were used as the basis for a new surface complexation model formulation [26]. More recently, Tonkin et al. [16] provided consistent surface complexation constants for several cations for a generic HMO

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and a diffuse double layer SCM for a system in which HMO is an important scavenger.

In this study, a quantitative SCM model for REE sorption by HMO at low substrate loadings (from 1.6 to 100 mg/L) was proposed using the generic HMO surface parameters provided by Tonkin et al. [16]. The REE-HMO binding constant was extrapolated using the linear free energy relationship (LFER) methodology and by fitting experimental data sets with the PhreePlot program [27]. Published experimental data cover an ionic strength range from 0 to 0.7 mol/L and a relatively wide pH range from 4 to 9 [10]. This model was further used to discuss the nature and importance of REE sorption by manganese oxyhydroxides in the open ocean.

2. Materials and methods

2.1. Surface complexation model description

The diffuse double layer SCM describes the sorption of solutes onto oxide surfaces. This model is the central component of the generalized two-layer model used to compile the database of surface reactions for hydrous Fe(III) oxide (HFO) provided by Dzombak and Morel [28]. In this work, the SCM was chosen because of its relative simplicity and its success in describing cation sorption to HMO [16]. Surface equilibrium reactions are written as combination sorption reactions (Eqs. (1)–(6) to specific hydroxyl sites on the oxide surface, to which a coulombic term that represents the electrochemical work of sorption is added. This coulombic term is calculated from the Gouy–Chapman electrical double layer theory and is included in the apparent equilibrium constants used by the model, $P = \exp(-F\psi/RT)$, where F is the Faraday constant, ψ is the electrostatic potential, r is the gas constant, and T is the absolute temperature.

$$\equiv \mathrm{X{-}OH} \Longleftrightarrow \equiv \mathrm{X{-}O^-} + \mathrm{H^+} \qquad \mathrm{K_{a2\equiv X-OH}} \tag{1}$$

$$\equiv \mathrm{Y{-}OH} \Longleftrightarrow \equiv \mathrm{Y{-}O^-} + \mathrm{H^+} \qquad \mathrm{K_{a2\equiv Y-OH}} \tag{2}$$

$$\equiv \mathrm{X{-}OH} + \mathrm{M}^{n+} \Longleftrightarrow \equiv \mathrm{X{-}OM}^{(n-1)+} + \mathrm{H^+} \qquad \mathrm{K_{\equiv X-OM}} \tag{3}$$

$$\equiv \mathrm{X{-}OH} + \mathrm{M}^{n+} + \mathrm{H_2O} \Longleftrightarrow \equiv \mathrm{X{-}OMOH}^{(n-2)+} + 2H^+ \quad \mathrm{K_{\equiv X-OMOH}} \tag{4}$$

$$\equiv \mathrm{Y{-}OH} + \mathrm{M}^{n+} \Longleftrightarrow \equiv \mathrm{Y{-}OM}^{(n-1)+} + \mathrm{H^+} \qquad \mathrm{K_{\equiv Y-OM}} \tag{5}$$

$$\equiv \mathrm{Y{-}OH} + \mathrm{M}^{n+} + \mathrm{H_2O} \Longleftrightarrow \equiv \mathrm{Y{-}OMOH}^{(n-2)+} + 2\mathrm{H^+} \quad \mathrm{K_{\equiv Y-OMOH}} \tag{6}$$

The HMO surface properties (specific surface area (SSA), surface site density, and acidity constants), REE-HMO stability constants, and concentration of a non-specifically adsorbing electrolyte solution are required. Data for HMO were obtained from Tonkin et al. [16] (Table 1). The SSA value input to the model fixed at 746 m^2/g is calculated and is therefore higher than the values determined by the BET-N_2 method, which range from 0.048 to 359 m^2/g [29]. The total HMO concentration of the surface sites (mol/g) was divided into fractions for the two site types (≡XOH and ≡YOH), which present high and low affinity for REE binding, respectively. REE sorption onto HMO is therefore simulated assuming that two types of sites are available on the oxide surface (Table 1). Modeling calculations were performed with PHREEQC and PhreePlot [27,30]. Three keyword data blocks are required to define the surface complexation data for a simulation: (i) SURFACE_MASTER_SPECIES, (ii) SURFACE_SPECIES, and (iii) SURFACE. The SURFACE_MASTER_SPECIES data block defines a binding site, named “Hmo” (HMO; [16]), with two binding sites, “Hmo_w” and “Hmo_s”, for the “weak” and “strong” binding sites. Inorganic speciation was then performed; the Nagra/PSI database [31] was used and updated including the same well-accepted stability constants at infinite dilution (25 °C) for the REE inorganic complexes (hydroxide, sulfate, and carbonate; [32–34]). As Bau and Koschinsky [35] proposed, Ce(III) is oxidized after its sorption onto oxyhydroxide, and therefore, only REE(III) were considered in the proposed SCM.

Table 1
SCM parameters for HMO [16].

pK_{a1}	pK_{a2}	SSA (m^2/g)	Total site density (mmol/g)	‘Strong’ site density (≡XOH) (mmol/g)	‘Weak’ site density (≡YOH) (mmol/g)
2.35	6.06	746	2.1	1.34	0.76

2.2. REE-HMO sorption stability constants

2.2.1. Extrapolation of the linear free energy relationship

The linear free energy relationship (LFER) or the correlation between the first hydrolysis constant for aqueous species and the corresponding surface complexation constant was used to estimate the sorption stability constant as has been previously done in numerous studies [16,28,36,37]. The LFER can be used to extend results from a limited data set to other metals. The REE-HMO stability constants were estimated by the same extrapolation method used by Tonkin et al. [16]. These authors observed that a LFER exists for HMO between $\log K_{\equiv \mathrm{XOMe}}$, $\log K_{\equiv \mathrm{XOMeOH}}$, $\log K_{\equiv \mathrm{YOMe}}$ and $\log K_{\equiv \mathrm{YOMeOH}}$ and the first hydrolysis (OH) constant for the metals ($\log K_{\mathrm{MeOH}}$).

However, Tonkin et al. [16] caution against assuming a LFER for all metals on HMO, notably with regard to the possible oxidation/scavenging mechanisms on the HMO surface. The estimated stability constant of REE binding to HMO is reported in Table 2. The first hydrolysis constant of REE, $\log K_{\mathrm{REE\text{-}OH}}$, is taken from the NIST database [38]. The REE-HMO stability constants extrapolated from the LFER methodology are listed in Table 3 with the REE-OH stability constant used for the calculation.

2.2.2. PhreePlot modeling

The pK_{a2}, α values, and published REE sorption data [10] were subsequently used to determine the equilibrium surface complexation constants for the whole REE series ([REE] = 125 μg/L; [HMO=δ-MnO_2] = 10 mg/L; room temperature; IS fixed with $NaNO_3$; no control of the CO_2 species). They were modeled using the computer program PhreePlot [27] and the Nagra/PSI database [31], which was modified to include the well-accepted infinite dilution (at 25 °C) of inorganic species [32,33]. Intrinsic constants for the surface complexation model were optimized by Powell’s nonlinear least squares method using PhreePlot’s fitting options. The REE-HMO stability constants are listed in Table 4. Only

Table 2
Stability constants used for the LFER established by Tonkin et al. [16].

	$\log K_{\mathrm{MeOH}}$	$\log K_{\equiv \mathrm{XOMe}}$	$\log K_{\equiv \mathrm{XOMeOH}}$	$\log K_{\equiv \mathrm{YOMe}}$	$\log K_{\equiv \mathrm{YOMeOH}}$
Ba	0.53	0.45	–	–	–
Ca	1.15	−1.5	–	–	–
Cd	3.92	−2.4	−8	−3.5	−8.5
Co	4.35	1	−3.9	–	–
Cu	6.5	0.85	−2.8	0.86	−5.7
Mg	2.56	−2.4	−7.7	–	–
Mn	3.41	1.2	−2.7	–	–
Ni	4.14	−0.48	−5	–	–
Pb	6.29	–	−0.86	3.4	−1.6
Sr	0.71	−1.6	−6.6	–	–
Zn	5.04	−0.01	−4.4	–	−7.6