The sorption of thorium (IV) and uranium (VI) to hematite in the presence of natural organic matter

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Received 24 September 1997; accepted 5 March 1998

Abstract

In most aquatic systems, natural organic acids constitute an important pool of trace-metal binding ligands. The effect of natural organic matter (NOM) on metal ion sorption to mineral surfaces is a complex function of the environment in which the mineral and ions reside, as well as the source, molecular weight distribution and composition of the NOM. In spite of the well-acknowledged importance of NOM in affecting metal-ion speciation and the widely-established use of surface complexation models to predict the behavior of metal ions in heterogeneous systems, little work has been reported on efforts to incorporate NOM into surface complexation models. In this paper we present experimental results for two such ternary (metal ion:metal oxide:NOM) systems, detailing: (1) U(VI):Suwannee river humic acid (HA):hematite; and (2) Th(IV):marine colloidal material (COM):hematite. Our objective is to describe overall ternary system behavior through the construction of a model composed of ‘binary’ subsystems (e.g. HA/hematite). In all cases, however, the postulation of ternary surface complexes is required to satisfactorily simulate ternary system behavior. We also describe the simulation of HA and COM as a suite of monoprotic acids with fixed pK_a values. This approach allows for the simultaneous simulation of both solution and surface reactions of NOM within a consistent chemical framework. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thorium; Uranium; Hematite; Natural organic matter; Modeling

1. Introduction

The fate of elements in aquatic systems is governed by a combination of two factors: (1) element speciation, and (2) the processes that act to transport those species. In most aquatic systems, species of natural organic matter (NOM) constitute an important pool of ligands for complexing trace metals and may dominate metal speciation under some conditions. While research on the complexation of trace metals by NOM, and NOM surrogates such as citric acid, has a rich representation in the literature, the role of NOM in the sorption of trace metals at the particle/solution interface is relatively poorly understood.
The advent of surface complexation models (SCMs) in the early 1970s (e.g. Schindler and Gamsjager [1]; Hohl and Stumm [2]) was crucial for two reasons: (1) it provided a framework for systematically evaluating the physical/chemical environment of particle surfaces; and (2), by the consideration of particles as ligands, SCMs engendered the inclusion of solution-phase and sorption reactions in a single computational framework (e.g. the MINEQL ‘family’ of computational engines). In spite of the ubiquitous presence of NOM in aquatic systems, and its well-documented ability to complex trace metals and to interact with particle surfaces, the inclusion of NOM as a component in surface chemical computations has proven to be somewhat elusive.

NOM results from the degradation of plants and animals and is ubiquitous to natural water systems. Total organic carbon (TOC) concentrations range from 0.5 ppm total organic carbon in groundwaters and marine systems, to over 20 ppm TOC in organic rich bog waters [3,4]. The NOM ‘problem’ is slippery, in large part, due to the widely-heterogeneous nature of NOM. Chemically, particulate (POC), dissolved (DOC) and colloidal (COC) organic carbon are composed of hundreds of compounds such as proteins, polysaccharides, lipids, humic acids and fulvic acids. A large fraction of macromolecular organic matter is heterogeneous in chemical composition, size and molecular weight, is polyelectrolytic, polyfunctional, polydisperse, internally porous and hydrated to a variable degree. In addition, its conformation is affected by pH and ionic strength. One of the most important properties of macromolecular NOM is its amphiphilic character: it contains both hydrophilic and hydrophobic parts. The polydispersity and organization (e.g. formation of aggregates or micelles) of natural particles and organic matter suggests that average chemical (e.g. complexation, acid–base or redox) and physical properties (e.g. age, residence time, exchange time) should be used with some degree of caution, and that property distribution spectra may more accurately reflect these characteristics.

2 The ratio of TOC to total organic matter concentration is approximately 1:2 based on 50 ± 5% elemental C [4,5].
that forms a basis for selection between different sorption processes or mechanisms.

The effect of organic acids on metal ion sorption to mineral surfaces depends on the components of the system, the molar ratio of the components [26] and, in some cases, the sequence in which the components are added to the system [27]. A variety of studies of metal ion sorption by mineral surfaces in the presence of organic ligands have been performed [28–35]. While a range of system behavior has been observed in these studies, in general, metal ion sorption is enhanced in the presence of organic ligands at low pH and decreased at high pH values. In many studies, model organic ligands have been used as surrogates for natural organic matter (e.g. [36,37]). The results of these studies have shown a correlation between the number and type of functional groups on the surrogate compounds and the extent of metal ion sorption to the metal oxide. Typically, with an increase in the number of functional groups there is a corresponding enhancement of metal ion binding to the mineral surface.

1.1. Models for simulating NOM chemistry and sorption

The inherent polyfunctional and heterogeneous nature of NOM molecules has made the modeling of metal complexation and mineral adsorption reactions difficult. In response to this complexity, a number of modeling approaches have been used to describe metal binding by NOM and NOM’s acid–base chemistry (see [38] and [39]). The modeling approaches differ primarily on two points: (1) the use of a discrete ligand versus a distribution of ligands to represent NOM; and (2) whether or not to explicitly consider electrostatics. When electrostatics are explicitly included, terms are invoked to account for the physical aspect of individual NOM molecules, including assumptions about shape (spherical or cylindrical), measured or assumed particle density, and measured particle size and molecular weight [40–45]. While the inclusion of electrostatics in model constructs may be more satisfying due to a closer correspondence to apparent physical reality, the need to determine values for model parameters that may or may not be known can limit their use. An alternative avenue is the discrete-ligand, non-electrostatic approach [38,46].

The approaches taken for modeling NOM sorption by mineral surfaces are not as chemically-explicit as are models for metal complexation by NOM. In most cases, NOM sorption by mineral surfaces has been described through the use of isotherms. The power of the surface complexation approach is that it provides a framework for linking solution- and surface-phase reactions. The molecular hypotheses upon which the various interfacial models are configured are founded on a number of assumptions, including sorbates as hard-sphere ions (e.g. Sposito, [47]). An apparent problem with extending surface complexation models to NOM sorption is that NOM, by its very nature, is a non-ideal sorbate: large, diffuse-charge molecules with hydrophobic and hydrophilic components. While surface complexation modeling of ‘model’ organic acid sorption to mineral surfaces is reasonably successful, applications of SCMs to NOM sorption have been few. Davis [28], for example, used a relatively simple approach to accurately describe the binding of NOM to alumina, and the binding of Cu(II) to alumina in the presence of NOM. The modeling consisted of a three-step process: (1) accounting for the adsorption of NOM to mineral surface, thereby creating a modified surface-ligand, (2) postulating ternary phase reactions for metal ions bound to dissolved NOM and sorbed to the modified surface-ligand; and (3) the determination of apparent \(K\) values for the two reaction types over range of pH values.

1.2. Modeling approach

Our objective is to describe overall (i.e. ‘ternary’) system behavior through the construction of a model composed of ‘binary’ subsystems. The flow of this paper follows the construction of the model, ternary system: (1) analysis of the properties of system components (i.e. NOM, actinide solution-phase speciation and hematite characterization); (2) the two-component (binary) systems (e.g. NOM/hematite); (3) ternary system (e.g. NOM/hematite/Th).
2. Materials

2.1. General

All reagents used in these experiments for pH adjustment, ionic strength adjustment, isotope separation, radiolabeling, etc., were analytical reagent grade or superior. All of the Th(IV) experiments were performed using Barnstead/Nanopure water. The uranium system experiments employed UV oxidized, ultra-low DOC Barnstead/Nanopure water (Easy-Pure UV) in a similar fashion. All of the teflonware, glassware, and plasticware used in these experiments was washed in Cole-Parmer MICRO Cleaning Solution and the appropriate water, soaked overnight in a 1% by mass NaOH solution and rinsed with water. The labware was then soaked overnight in a 10% by volume HCl solution, water rinsed at least three times and allowed to air dry. Prior to performing any experiments, the labware was soaked overnight in dilute NaClO₄ to pre-condition their internal surfaces.

2.2. Hematite

A monodisperse sol of spherical hematite was synthesized via the method specified by Penners and Koopal [53]. The size of the hematite was determined to be 65.7 ± 0.3 nm using dynamic light scattering with a Brookhaven Instruments Zeta-Plus Analyzer. A scanning electron microscope (data not shown) was employed to confirm the monodisperse and spherical nature of the hematite. Based on the average particle diameter and using a hematite density of 5.26 g/cm³, the specific surface area of the hematite was determined as 17.4 m²/g, assuming that the hematite is nonporous. A site density of 2.31 sites/nm², as advocated by Davis and Kent [54], provides a specific site concentration of 6.67 × 10⁻⁵ mol/g. Hematite was suspended in 0.001 M HClO₄ and stored at 4°C in amber glass.

2.3. Natural organic matter

Marine colloidal organic matter (COM), supplied by Peter Santschi of Texas A&M at Galveston, was isolated from the Gulf of Mexico surface waters (28°45’ N, 94°43’ W in 20 m of water, from the R/V Gyre) using tangential-flow ultrafiltration (10 000 Da to 0.45 μm). The desalted and freeze-dried COM was labeled with [¹⁴C]dimethylsulfate following Wolfinbarger and Crosby [55]. The unreacted label was removed by dialysis through Spectra/Por 7, 1000 MW cutoff membrane, purchased from Spectrum. Solutions were made to volume in Nanopure water and stored at 4°C in amber glass.

The Suwannee River Humic Acid (HA) was purchased from the International Humic Substances Society and was used without further purification. This humic substance has been exhaustively researched and characterized [56]. Solutions were made to volume in Easy-Pure water and stored at 4°C in amber glass.

2.4. Radionuclides

Two isotopes of each element were typically employed in these experiments. Thorium-234 was used in all thorium system experiments, as either a tracer or as the total Th(IV) component. This isotope was separated from uranyl (Unatural) acetate by ion exchange in our laboratory using Bio-Rad AG 1-X8 resin, ultra pure acids, and teflonware [57]. Where higher concentrations (10⁻⁹ M) of Th(IV) were required, ²³²Th as Th(NO₃)₄ was added. This isotope was obtained from the Johnson Matthey Catalogue Company as an ICP standard. The ²³⁴Th was measured by liquid scintillation counting (LSC) on a Packard 2500TR liquid scintillation analyzer or by gamma spectroscopy on a Canberra closed end coaxial well, Model GCW2523, high purity germanium detector.

In a similar fashion, the bulk of the U(VI) employed in the uranium system experiments was natural uranium, purchased as uranyl nitrate, UO₂(NO₃)₂, from Anderson Laboratories, Inc., as an ICP standard. To facilitate analysis by LSC on a Packard 2500TR, samples were spiked with ²³³U(VI) purchased from Isotope Products Laboratory. Standards for all four isotopes were prepared in acid (HNO₃ or HCl) and subsequently added as needed to each sample to provide the required total actinide concentrations (8.3 × 10⁻¹⁴ M or 10⁻⁹ Th(IV)₄ and 10⁻⁶ M U(VI)₂).
Table 1

<table>
<thead>
<tr>
<th>System</th>
<th>Hematite (g/l)</th>
<th>Ligand (mg/l)</th>
<th>Actinide (M)</th>
<th>pH range</th>
<th>Reaction time (h)</th>
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<tbody>
<tr>
<td>Th/Hem</td>
<td>3.37</td>
<td>–</td>
<td>8.3 × 10⁻¹⁴</td>
<td>1–8.5</td>
<td>12</td>
</tr>
<tr>
<td>COM/Hem</td>
<td>3.37</td>
<td>16.5</td>
<td>–</td>
<td>1–11</td>
<td>24</td>
</tr>
<tr>
<td>U/Hem</td>
<td>9</td>
<td>10</td>
<td>1 × 10⁻⁶</td>
<td>3–10</td>
<td>24</td>
</tr>
<tr>
<td>HA/Hem</td>
<td>9</td>
<td>10</td>
<td>–</td>
<td>3–10</td>
<td>48</td>
</tr>
<tr>
<td>Th/COM/Hem</td>
<td>3.37</td>
<td>16.5</td>
<td>8.3 × 10⁻¹⁴</td>
<td>1–10</td>
<td>36</td>
</tr>
<tr>
<td>U/HA/Hem</td>
<td>9</td>
<td>10</td>
<td>1 × 10⁻⁶</td>
<td>3–10</td>
<td>48</td>
</tr>
<tr>
<td>Th/COM</td>
<td>–</td>
<td>2–15</td>
<td>1 × 10⁻⁹</td>
<td>3.5</td>
<td>48</td>
</tr>
<tr>
<td>U/HA</td>
<td>–</td>
<td>4–100</td>
<td>1 × 10⁻⁶</td>
<td>4</td>
<td>48</td>
</tr>
</tbody>
</table>

3. Experimental protocols

3.1. Adsorption experiments

All adsorption experiments, i.e. two-component (binary) and three-component (ternary), were performed in batch fashion using polycarbonate Oak Ridge centrifuge tubes. The lids to these tubes were drilled (~ 3 mm hole) to allow for gas exchange; hence, all adsorption experiments were open to the environment to facilitate equilibration with atmospheric CO₂. In all of the batch experiments, the final solution volume and ionic strength (sodium perchlorate employed as background electrolyte) were fixed once the solution pH stabilized (12–24 h). Prior to stabilization, solution pH was adjusted with small volumes of HCl or NaOH. For solutions at pH values greater than 6.0, increasing volumes of NaHCO₃ were added to minimize equilibration times and pH drift [58]. The pH measurements for all experiments were made with Orion Ross combination electrodes. Prior to use, the electrodes were calibrated with NIST certified buffers (pH 4.00, 7.00 and 10.00). Sample pH values were recorded once the pH ceased to drift, which usually took 1–10 min. The samples were then placed on a shaker table in the dark and allowed to come to equilibrium. Kinetic experiments (data not included) were employed to provide appropriate equilibration times for each type of batch experiment. Experimental conditions are summarized in Table 1. After equilibration, the pH of the samples was measured, the solids were separated by centrifugation and aliquots of the supernatant liquid were taken for measurement. For the sorption experiments involving NOM, the HA concentration in the supernatant liquid was determined by measuring total organic carbon on a Shimadzu 500 TOC analyzer and the ¹⁴C labeled COM was measured by LSC on a Packard 2500TR.

Experimental conditions for the binary system reactions can be found in Table 1. The Th(IV)/hematite and marine COM/hematite experiments were performed at 6 ml total volume, whereas similar uranium/hematite experiments were performed at 10 ml total volume. In both instances the background electrolyte was 0.1 M sodium perchlorate, NaClO₄. A separate suite of experiments confirmed that the humic acid did not significantly coagulate and precipitate at low pH values over the 48 h equilibration time.

Ternary system experiments were performed in the same manner as the binary experiments. The conditions under which the experiments were performed may be found in Table 1.

3.2. Potentiometric titrations

All potentiometric titrations of COM, HA and hematite were performed in a nitrogen atmosphere at a constant temperature of 25 ± 0.1°C using an automated computer controlled titrimeter. Prior to being titrated, the hematite and COM samples were dialyzed against Easy-Pure water to remove any excess salt or acid. The HA was titrated without any additional purification. Appropriate aliquots of NaClO₄ and Easy-Pure water were added to bring the hematite, COM or HA sample volume to 50 ml and the desired ionic strength. For the COM and hematite, the samples were acidified and sparged.
with nitrogen gas (hematite-24 h, COM-1 h) to remove CO₂; the HA solutions were sparged but not acidified. Titrations were run from the initial pH to a pH of 10–10.5 and back to the starting pH with NaOH and HCl. The ionic strength was adjusted to the appropriate value and the titration sequence was repeated. This procedure was repeated a total of three or four times, resulting in data sets at three or four ionic strengths. Equilibrium for hematite and NOM titrations was defined to be when the pH drift was less than six repetitions at 0.1 mV/10 s (0.01 pH/min) and 0.05 mV/10 s (0.005 pH/min) between titrant additions, respectively.

### 3.3. Actinide/NOM complexation experiments

Two different methods were employed to measure the binding of the actinides to the NOM. The Th/COM system was examined by an ultra-filtration technique. The binding of U(VI) by HA was determined through the application of an ion exchange resin technique.

In a fashion similar to the thorium system binary experiments, the Th/COM binding studies were performed in polycarbonate Oak Ridge centrifuge tubes at a 6 ml final volume. The total Th(IV) concentration was $1 \times 10^{-9}$ M, the majority of that being $^{232}$Th. The COM concentration was varied from 2.45 mg/l to 14.7 mg/l. The solution final volume and ionic strength (using NaCl as a background electrolyte) were fixed once the solution pH of 3.5 was stabilized (12–24 h). The open system solutions were shaken in the dark for 48 h. The unbound Th(IV) was separated from the COM-bound Th(IV) via ultrafiltration (1000 MW cut off) using MPS® Micropartition devices from Amicon, Inc. Thorium was measured in the unfiltered Th/COM solution, in the solution passing the filter and in the fraction retained by the filter [59].

The uranium/HA batch experiments were performed with samples containing different amounts of HA with nominally 0.04 g of Dowex 50WX8 cation exchange resin in the Na⁺ form, $10^{-6}$ M uranium, $I = 0.1$ and pH 4. A sodium acetate solution (0.006 M) was used to buffer the pH. The samples were shaken in the dark for 48 h at which time 2 ml samples were taken for liquid scintillation analysis. The ratio of uranium in solution to uranium bound by the resin will increase as the concentration of HA increases. By using this relationship in comparison to samples without HA it is possible to determine the binding of U by the HA. These experiments and analysis are discussed in detail by Lenhart [60].

### 4. Modeling and results

The experimental results were evaluated and modeled in a stepwise manner. The data generated during the examination of the individual components were evaluated and simulated first. The results of the binary experiments were reviewed and modeled based on the information derived from the individual components. All of these data were employed in the construction of the ternary system simulations.

#### 4.1. Sorption of uranium and thorium by hematite

Fig. 1a, b present the results of experiments for U(VI) and Th(IV) sorption, respectively, to hematite suspended in 0.1 M NaClO₄ with solutions in equilibrium with atmospheric CO₂. Both Th(IV) and U(VI) exhibit rather steep fractional metal sorption ‘edges’ (the fraction of total metal sorbed as a function of pH). The positioning of the sorption edges at low pH values suggests the formation of relatively strong actinide:surface site complexes. The two edges can not be directly compared because of the marked differences in solid:solution ratios of the experimental conditions.

Simulations of the sorption of uranium and thorium by hematite are thoroughly discussed by Lenhart [60] and Murphy et al. [59], respectively. The simulations for U(VI) sorption onto hematite follows the two-site model that Waite et al. [58] have described for uranium binding to ferrihydrite, whereas the binding of Th(IV) only requires a one-site model. Hematite surface characteristics are given in Table 2. The values for hematite protolysis and electrolyte binding constants were
determined by applying the Triple Layer Model of Davis et al. [51], as modified by Hayes and Leckie [61], to potentiometric titration data compiled at $I = 0.006, 0.05$ and $0.5$ (Fig. 2). These hematite titration data were analyzed using the methodology suggested by Hayes et al. [62], with a site density of 2.31 sites/nm$^2$ as advocated by Davis and Kent [54] and Dzombak and Morel [63]; FITEQL (version 3.2; [52]) was the mathematical platform for data evaluation. A $\Delta pK_a$ value equal to 2.0 brackets the experimentally-determined value for $pH_{pzse}$ of 9.25. The best-fit simulation of the hematite titration data is shown in Fig. 2. The resulting FITEQL optimization for the surface protolysis and electrolyte binding constants is given in Table 3.

The distributions of solution-phase uranium and thorium species, for solutions in equilibrium with atmospheric CO$_2$, ($p$CO$_2$ = $10^{-3.5}$ atm) are presented in Fig. 3a and 3b, respectively. Th(IV)$_T$ and U(VI)$_T$ for the simulations are $8.3 \times 10^{-14}$ M and $1 \times 10^{-6}$ M, respectively. Values for U(VI) solution-phase complexes come from [64–66], as compiled in Lenhart [60]. It is evident from this diagram that there are primarily seven species which control the solution chemistry of uranium. The uranyl (UO$_2^{2+}$) and uranyl hydroxide (UO$_2$OH$^+$ and UO$_2$(OH)$_2$) species prevail at $pH < 6.5$ and four uranyl-carbonato species (UO$_2$CO$_3$$^0$, UO$_4$(CO$_3$)$_2$$^2-$, UO$_4$(CO$_3$)$_3$$^4-$, and (UO$_2$)$_2$CO$_3$(OH)$_2$$^-$) dominate at $pH > 6.5$. The sources for Th(IV) thermodynamic data are Baes...
Table 3
Hematite surface reactions: uranium system (from Lenhart and Honeyman, 1999 [69] unless stated otherwise)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log $K(I=0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{FeOH} + H^+ \rightarrow \text{FeOH}_2^+$</td>
<td>8.25$^a$</td>
</tr>
<tr>
<td>$\text{FeOH} = \text{FeO}^- + H^+$</td>
<td>-10.25$^a$</td>
</tr>
<tr>
<td>$\text{FeOH} + \text{Na}^+ = \text{FeO}^-$-Na$^+$ + H$^+$</td>
<td>-8.46$^a$</td>
</tr>
<tr>
<td>$\text{FeOH} + H^+ + \text{ClO}_4^- = \text{FeOH}_2^+\text{ClO}_4^-$</td>
<td>10.18$^a$</td>
</tr>
<tr>
<td>$\text{FeOH} + H_2\text{CO}_3 = \text{FeHCO}_3^- + H_2O$</td>
<td>6.00</td>
</tr>
<tr>
<td>$\text{FeOH} + H_2\text{CO}_3 = \text{FeCO}_3^- + H_2O + H^+$</td>
<td>-3.30</td>
</tr>
<tr>
<td>$\text{Fe}_6\text{(OH)}_2 + \text{UO}_2^{5+} = \text{Fe}_5\text{O}_2\text{UO}_2 + 2\text{H}^+$</td>
<td>-0.08$^7$</td>
</tr>
<tr>
<td>$\text{Fe}_6\text{(OH)}_2 + \text{UO}_2^{5+} + H_2\text{CO}_3 = -3.43$</td>
<td></td>
</tr>
<tr>
<td>$\text{Fe}_6\text{(OH)}_2 + \text{UO}_2^{5+} + H_2\text{CO}_3 = -12.14$</td>
<td></td>
</tr>
<tr>
<td>$\text{Fe}_6\text{O}_2\text{UO}_2(\text{CO}_3)_2 + 4\text{H}^+$</td>
<td></td>
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<tr>
<td>$\text{Fe}_6\text{O}_2\text{UO}_2(\text{CO}_3)_2 + 4\text{H}^+$</td>
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<td>$\text{Fe}_6\text{O}_2\text{UO}_2(\text{CO}_3)_2 + 4\text{H}^+$</td>
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<td>$\text{Fe}_6\text{O}_2\text{UO}_2(\text{CO}_3)_2 + 4\text{H}^+$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ From TLM fit of hematite titrations (Fig. 2).

and Mesmer [67] and Østhols et al. [68]. As is the case with U(VI), thorium carbonato species are dominant in the alkaline pH region, thorium hydroxy species in the circumneutral pH region and the free aquo ion only becomes dominant at pH values less than 4.

The binding of carbonate by hematite was simulated through the analysis of electrophoretic mobility data as discussed by Lenhart and Honeyman [69]. This simulation is predicated on the decrease in the $pH_{eig}$ of metal oxides in the presence of adsorbing anions as is thoroughly discussed by Stumm [70]. This analysis provides the constants for the formation of the monodentate inner-sphere carbonate surface species ($\text{FeHCO}_3^-$) and ($\text{FeCO}_3^-$) as suggested by FTIR results presented by Su and Suarez [71] for carbonate sorption to ferrihydrite. Reaction stoichiometry and equilibrium constants for these reactions are shown in Table 3.

Using the proton, electrolyte ion and carbonate binding constants (Table 3), the uranyl sorption data shown in Fig. 1a were simulated by postulating the formation of the inner-sphere uranyl species, $\text{Fe}_6\text{O}_2\text{UO}_2$ and $\text{Fe}_6\text{O}_2\text{UO}_2$, and an inner-sphere uranyl-carbonato species, $\text{Fe}_6\text{O}_2\text{UO}_2\text{CO}_3^2-$, after Waite et al. [58]. Following the approach of Waite et al. [58], the ratio of strong to weak sites was determined to be 1:325 [69]. To get a proper representation of the experimental data Lenhart and Honeyman [69] modeled the reaction with the charge of the carbonate in the uranyl-carbonato complex ($\text{Fe}_6\text{O}_2\text{UO}_2\text{CO}_3^2-$) in the $\beta$-plane. The FITEQL simulation of the uran-ium sorption data is represented by the solid line in 1a.

The thorium sorption data were simulated using a single surface reaction for thorium:

$$\text{FeOH} + \text{Th}^{4+} = \text{FeOHT}^{4+} \quad (1)$$

Fig. 3. Distributions of solution phase actinide species for solutions free of NOM and in equilibrium with atmospheric CO$_2$ are plotted versus pH, (a) fraction U(VI)$_1$ (10$^{-6}$ M); (b) fraction Th(IV)$_1$ (8.3 x 10$^{-14}$ M).
Table 4
Surface reactions: thorium system

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log $K$ ($I = 0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$OH + Th$^{4+}$ = Fe$_2$OHTH$^{4+}$</td>
<td>28.9*</td>
</tr>
<tr>
<td>Fe$_2$OH + HL$_1$ = FeL$_1$ + H$_2$O</td>
<td>9.24*</td>
</tr>
<tr>
<td>Fe$_2$OH + HL$_2$ = FeL$_2$ + H$_2$O</td>
<td>7.26*</td>
</tr>
<tr>
<td>Fe$_2$OH + HL$_3$ = FeOH$_2$L$_1$ + H$_2$O</td>
<td>7.51*</td>
</tr>
<tr>
<td>Fe$_2$OH + HL$_4$ = FeOH$_2$L$_4$ + H$_2$O</td>
<td>9.14*</td>
</tr>
<tr>
<td>Fe$_2$OH + HL$_4$ + Th$^{4+}$ = FeOThL$_4$ + 2H$^+$</td>
<td>23.73*</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
* Based on model fit of COM sorption edge.  
** Based on model fit of Th/hematite sorption.  
** Determined by fitting ternary thorium sorption edge.

in addition to the proton, electrolyte ion and carbonate sorption reactions for hematite (Tables 3 and 4). The observed proton stoichiometry (mols of protons released per mol of Th sorbed) could only be simulated through the postulation of a sorption reaction yielding no net release of protons. Simulation is shown as a solid line in Fig. 1b.

Unlike U(VI) sorption to hematite, Th was postulated to form a surface complex with one site type. It was demonstrated by Quigley et al. [72] that Th(IV) sorption by hematite, over nearly eleven orders of magnitude in sorption density, to within 10% of maximum sorption density, can be simulated by postulating a single reaction stoichiometry with a constant surface complexation equilibrium value. In the case of the data reported here, the concentration of hematite sites ($2.25 \times 10^{-4}$ M) is in large excess compared to total thorium ($8.3 \times 10^{-14}$ M). There is no reason to expect, under these conditions, that Th and U bind to the same site types.

The stoichiometry for reaction (1) is unusual but not unique. Dzombak and Morel [39], for example, suggest that highly-charged ions may sorb to neutral surface sites under conditions of low pH and low sorption density. Hayes [73] suggested that a delay between metal-ion binding to a metal-oxide surface and proton release from the surface is indicative of delocalized, interfacial protons. Gunneriusson et al. [74] postulate stoichiometry similar to Eq. (1) for the sorption of lead by goethite. They conclude that Pb(II) may be coordinated to more than one surface hydroxyl group without the release of the surface group’s proton. Finally, the work of van Riemsdijk et al. [75] has yielded surfaces that include a number of heterogeneous sites, including singly-, doubly- and triply-coordinated surface oxygens, providing the opportunity for developing relatively low proton coefficients for metal-ion sorption.

4.2. Approach for modeling reactions involving NOM

A primary objective of geochemical studies is to understand the behavior of environmental systems from a knowledge of their basic physico-chemical properties. One strategy to reach this goal is to use model surrogates for components of the environmental system under study. An example of this approach is the use of ‘model’ metal oxides (e.g. [1,2]) to evaluate interfacial models for metal binding to particle surfaces. More recently, relatively simple organic acids (e.g. [33–35]) have been employed to evaluate the general effect of NOM on metal speciation in heterogeneous systems containing inorganic particles. A problem with surrogates is the question of the extent to which they accurately represent the essential characteristics of the target environmental material.

The challenge of modeling the physico-chemical behavior of ‘real’ materials is to capture (i.e. represent) their essential characteristics in model formulations. In the case of NOM, our goal is to describe its acid/base-, metal binding- and surface chemical-properties in such a manner that: (1) a single conceptual model of NOM is adopted; and (2) the model is capable of yielding simulations of NOM behavior over a range of system conditions (e.g. pH, $I$, particle/NOM ratio, etc.). In our approach, we are trying to straddle the ground between strict correspondence to physico-chemical reality and modeling tractability.

In the modeling described below the chemical behavior of NOM is described using a discrete ligand approach advocated by several researchers [40,48,49] and as implemented by Westall et al. [50]. In their model, NOM is represented as ‘an assembly’ of monoprotic acids with assumed $pK$
values and without explicit correction for electrostatic effects. Several goals of Westall et al. coincide with the goals of this study:
1. The accurate representation of the experimental data over a range of system conditions. To a certain extent, the degree of model ‘correctness’ is expressed in the model’s predictive capability.
2. A small and orderly set of adjustable parameters. ‘Orderliness’ is established through the systematic construction of the composite chemical model (i.e. the ternary system) through parsimonious ‘fits’ of the sub-models to basic data sets. With respect to NOM, Westall et al. provide a framework for the comparison of heterogeneous materials with a minimum of adjustable parameters (i.e. acid concentrations).
3. Reasonable ease of use with general speciation models.
4. Insight into the physical nature of the interactions. It is unlikely, though possible, that a model that is fundamentally incorrect will be able to ‘predict’ the response of a system over a reasonably-wide range of system conditions. Clearly, modeling complex systems requires simplification. Our philosophy is that a model should be no more complicated than is necessary to accurately represent the experimental data over the required range of solution conditions. A chemically ‘reasonable’ model, even though a simplification of the target system, should be able to provide insight to system properties even if the model is not ‘microscopically’ accurate.

It is important at this point to highlight the departure of this study from the model of Westall et al. Westall et al., as stated above, propose that it is possible to describe NOM as a suite of discrete monoprotic acids. However, the physical relationship of the acid groups to the NOM ‘molecule’ is not specified. In our work we treat the acids as a suite of discrete ligands able to act independently of each other. This issue, the relationship between the acids groups and the NOM ‘molecule’, only becomes important when considering the role of the particle/water interface in speciation calculations and the interaction of NOM with particle surfaces. The development of a model considering NOM as a suite of discrete monoprotic acids has two consequences: (1) surface site/metal ion bridging by the ligand is prohibited; (2) because the ligands (i.e. the conjugate bases) are allowed to sorb independently of each other, the NOM fractionates as a function of pH.

Consequence 1: Clearly, metal-ion binding to particle surfaces that are coated (i.e. irreversibly occluded) by organic matter require the simulation of surface complexation as the formation of a particle/ligand/metal-ion complex. Indeed, studies of metal-ion sorption to metal oxides in the presence of organic acids such as citrate are often simulated as forming species such as \( \text{mm} \equiv \text{XLM} \), where \( \equiv \text{X} \) is a Lewis acid site and \( \text{L} \) and \( \text{M} \) is a generic ligand and metal-ion, respectively. However, there is little spectroscopic data to support such postulated species. On the other hand, metal/inorganic ligand complexes are usually postulated as forming surface complexes of the form \( \equiv \Delta \text{XLM} \). There is no reason to believe that our hypothetical organic monoprotic organic ligands should be treated differently from similar inorganic ligands.

Consequence 2: NOM sorptive fractionation is known to occur as a function of molecular weight \([16,24]\); there is no reason to believe that NOM will not be fractionated to some degree as a function of pH.

4.3. Determination of proton reactions for Suwannee river humic acid (HA) and marine colloidal organic matter

The approach of Westall et al. [38] was adopted for the evaluation of the HA and COM. This method can be employed using the equilibrium chemical model FITEQL (Version 3.2 [52]) for the optimization of model constants. This process models the acid–base characteristics of a polyprotic substance using a spectrum of discrete monoprotic acids with defined \( pK \) values. Corrections for the electrostatic energy associated with natural macromolecules are not explicitly included in this approach. Instead, it includes an electrolyte association term \( (K_{Na}) \) to implicitly represent the electrostatic energy. The structure and reactivity
of NOM ‘molecules’ are complex and the methodology employed here does not presume correspondence to a strict physical or chemical model of natural organic matter. However, this approach allows for a consistent evaluative framework when simulating the interactions of disparate fractions of natural organic matter with metal oxide surfaces and ions [60].

For the pH range encompassed by the data in this study (pH 3–10), we chose to represent the NOM ‘molecule’ as a suite of either four or five discrete, monoprotic ligands with pK<sub>a</sub> values ranging from 2 to 10. The concentration of each of these individual ligands, as well as the K<sub>Na</sub> term, was determined by fitting the potentiometric titration data shown in Fig. 4a and 4b for HA and COM, respectively. The values for the parameters determined from the FITEQ model simulation of titration data represented in Fig. 5a.

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Table 5
Humic acid solution reactions (from Lenhart and Honeyman, 1999 [69])

<table>
<thead>
<tr>
<th>Reaction</th>
<th>T&lt;sub&gt;H&lt;/sub&gt; (mmol/g)&lt;sup&gt;*&lt;/sup&gt;</th>
<th>Log K (I = 0)&lt;sup&gt;*&lt;/sup&gt;</th>
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* Determined from FITEQ model simulation of titration data represented in Fig. 5a.

Table 6
Colloidal organic matter solution-phase reactions

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<th>Reaction</th>
<th>T&lt;sub&gt;H&lt;/sub&gt; (mmol/g)&lt;sup&gt;*&lt;/sup&gt;</th>
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<td>1.23</td>
<td></td>
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</tbody>
</table>

* Determined from FITEQ model simulation of titration data represented in Fig. 5b.
* From Murphy et al. [59].
Fig. 5. The fraction of NOM adsorbed onto hematite as a function of pH, with all samples in equilibrium with atmospheric CO$_2$ and $I = 0.1$ (NaClO$_4$). Symbols represent experimental data and lines represent model fit values, (a) humic acid at 10 mg/l ($5.35 \times 10^{-5}$ mol sites/l) adsorbing to 9 g/l hematite ($6.0 \times 10^{-4}$ mol sites/l); (b) COM at 16 mg/l ($2.02 \times 10^{-5}$ mol sites/l) adsorbing to 3.37 g/l hematite ($2.25 \times 10^{-4}$ mol sites/l).

4.4. Adsorption of HA and COM to hematite

Fig. 5 presents pH/fractional HA and COM sorption onto hematite. The results of these binary experiments can not be compared directly due to the different conditions, e.g. solid/solution ratio, under which the data were collected. However, in both cases, the NOM sorption behavior is characterized by cation-like sorption at low pH values and broad sorption ‘envelopes’. In addition, HA and COM exhibit anion-like behavior at high pH values. Such sorption behavior is commonly observed with complex natural polyelectrolytes [18,20,24,76].

In our methodology for simulating the sorption of NOM by metal oxides, we expand on the discrete ligand approach previously used to account for metal and proton binding by NOM to include the formation of ligand-exchange and electrostatic-attraction surface complexes of NOM with hematite. With this approach, the same ligands that are assumed to react with components in solution are also postulated to form surface complexes with surface hydroxyl groups on metal oxides. This method again allows us to use a consistent method to handle large, complex NOM 'molecules', using a small and orderly set of adjustable parameters.

The HA sorption data spans a pH range of 3 to 10. Correspondingly, five ligands, $L_1$, $L_2$, $L_3$, $L_4$ and $L_5$, with $pK$ values of 2, 4, 6, 8 and 10, respectively, were invoked. $L_1$, $L_2$ and $L_3$ are postulated to represent ‘carboxylic’ functional groups and $L_4$ and $L_5$ represent ‘phenolic’ groups. A ligand exchange reaction has most commonly been used to simulate the sorption of acidic carboxyl groups to metal oxide surfaces [77]; whereas for more basic phenolic groups an outer-sphere electrostatic reaction has been advocated [78]. Using these simplifications, and the Na$^+$ binding reaction, a ligand exchange reaction for the ‘carboxyl’ groups ($L_1$, $L_2$ and $L_3$) and outer-sphere electrostatic attraction reactions for the ‘phenolic’ groups ($L_4$ and $L_5$) were used to inverse model the sorption data [60]. This approach distributes the charge of the humic acid between the surface plane (0-plane) for ligands $L_1$, $L_2$, and $L_3$ and the inner Helmholtz plane ($\beta$-plane) for ligands $L_4$ and $L_5$. Employing this approach, Lenhart [60] was able to simulate the sorption of both Suwannee river HA and FA over a range of ligand concentrations using the same set of binding constants.

In a similar fashion, the COM sorption was simulated by postulating four ligands: $L_1$, $L_2$, $L_3$, and $L_4$ with $pK$ values of 4, 6, 8, and 10, respectively. The ligands are operationally-defined as ‘carboxyl’ ($L_1$ and $L_2$) and ‘phenolic’ ($L_3$ and $L_4$) groups, based on their $pK$ values. As with the
simulation of the HA sorption data, the FITEQL simulation of COM sorption to hematite was based on two different types of reactions: a ligand exchange reaction for the ‘carboxyl’ groups (L₁ and L₂) and an outer-sphere electrostatic attraction reaction for the ‘phenolic’ groups (L₃ and L₄) (e.g. Schindler [78]).

The ligand sorption reactions and surface complex formation constants are presented in Tables 3 and 4 for the uranium and thorium ternary systems, respectively. Note that the macromolecular organic matter was conceptualized and simulated as a suite of discrete ligands and that these ligands were considered to act independently during sorption. Further details can be found in Lenhart [60] and Murphy et al. [59].

4.5. Complexation of actinides to natural organic matter

The data collected using the ion exchange resin technique for the analysis of U(VI) binding with HA was evaluated using a non-linear least squares method [60]. The simulation of the resin data was integrated with the discrete ligand approach for describing HA. In a simplification of the simulation [60], only monodentate reactions between the uranyl ion (UO₂⁺) and the model ligands L₂ and L₃ forming the species UO₂L₂ and UO₂L₃ are included in Table 5. The log K values for the reactions with HL₂ and HL₃ are 2.39 and 1.63, respectively. Fig. 6a shows the simulated fractional distribution of U(VI) including the model uranyl complexes with ligands L₂ and L₃. It is not necessary to include the ligands L₁, L₄ and L₅ to get an adequate representation of the data from [60]; consequently, these model ligands were excluded from binding U(VI). This simulation is beyond the scope of this paper and will be discussed in a forthcoming manuscript. It is important to note that the uranyl ligand complexes dominate until circumneutral pH values.

The complexation of Th(IV) with COM functional groups was determined by ultrafiltration separation using a 1000 Da membrane to separate the ‘free’ actinide from that bound to the COM. This method allows the partitioning to be measured without altering solution conditions or concentrations of the free actinide. The fraction of Th(IV) complexed with the COM was evaluated in the same manner as U(VI). This simulation required only the formation of a complex between the COM model ligand, L₁, and Th⁴⁺ forming the species ThL₁⁺. Fig. 6b shows the fractional distribution of Th(IV) for a system containing 10⁻⁹ M Th(IV) and 16.5 mg/l COM. Thorium-ligand complexes, other than those formed with L₁, are negligible below circumneutral pH values, under which the thorium/COM complexation was examined. The value of log K for this reaction is 7.01. Note that the effect of NOM on thorium speciation is less dramatic than for the case of U(VI) and HA.

Fig. 6. Distributions of solution phase actinide species in the presence of NOM and in equilibrium with atmospheric CO₂, (a) fraction UT (10⁻⁶ M) in the presence of 10 mg/l HA (5.35 × 10⁻⁵ mol sites/l); (b) Fraction ThT (8.3 × 10⁻¹⁴ M) in the presence of 16 mg/l COM (2.02 × 10⁻⁵ mol sites/l).
4.6. Uranium and thorium sorption in ternary systems

Fig. 7a and 7b present the data for pH/fractional actinide sorption onto hematite in the absence (open symbols) and presence (filled symbols) of NOM. In addition, the figures display the model simulations for these systems having invoked ternary equations (solid lines) and without invoking ternary equations (dotted lines). In both the U/HA/hematite and the Th/COM/hematite systems, ternary equations are required to provide an accurate simulation of the data.

The effects of adding 10 ppm HA to systems with $10^{-6}$ M uranium at ionic strength 0.1, 9 g/l hematite and pH 3–10 are shown in Fig. 7a. Generally, in the cation-like region, the addition of HA enhances U(VI) sorption relative to the HA-free system. However, in the anion-like region, the sorption of U(VI) in the presence of HA is slightly less than that observed in the HA-free system. In similar experiments (data not shown), Lenhart [60] has demonstrated that the effect is more pronounced at lower solid/solution ratios. These results are consistent with Payne et al. [79] who observed similar phenomena for the adsorption of uranium onto hydrous ferric oxide in the presence of NOM.

The postulation of two ternary surface complexes was required to simulate the ternary system data, as discussed by Lenhart and Honeyman [69]. As shown in Fig. 6a, the dominant solution-phase species in the region of ‘enhanced’ U(VI) sorption are the hypothetical UO$_2$L$_2^+$ and UO$_2$L$_3^+$ complexes. These species were invoked in the formation of the ternary surface complexes ($\equiv$FeOH-UO$_2$L$_2^+$ and $\equiv$FeOH-UO$_2$L$_3^+$) as shown in Table 3. Different representations of species with the ligands L$_2$ and L$_3$ were unable to improve model fits [69].

As with U(VI) ternary system, Th(IV) sorption to hematite is enhanced at low pH values, relative to the COM-free system. Under these conditions, 3.37 g/l hematite, $10^{-9}$ M Th(IV)$_T$ and 16.5 mg/l COM; the COM has a relatively large impact on Th(IV) sorption to hematite. Simulations of the ternary system data required the postulation of a single ternary surface complex, ($\equiv$FeOThL$_2^{2+}$). However, there is no redistribution of Th(IV) in the circumneutral to alkaline pH range from the formation of non-sorbing Th/COM complexes. In essence, hematite surface sites out-compete the COM ligands for complexation with Th(IV).
5. Conclusions

In this paper we present a methodology for describing the complex interactions of metal ions with mineral surfaces in the presence of NOM. The chosen approach treats NOM as a suite of discrete monoprotic acids with defined pH values. By treating NOM in this manner, we are able to include NOM as a component in both solution and surface reactions, thereby allowing for the simulation of complex ternary systems within a consistent chemical and thermodynamic framework. The viability of treating NOM in this manner is presented by successfully simulating two completely disparate systems: Th(IV)/hematite/marine COM and U(VI)/hematite/Suwannee river HA. In both systems, the approach is to first describe the properties of the individual components (NOM, hematite and metal), followed by the binary combinations (metal/NOM, NOM/hematite and metal/hematite), and concluding with the ternary systems (metal/NOM/hematite). By treating systems in this manner, it is possible to describe the ternary system in terms of its component parts, allowing for the simulation of the observed enhanced sorption of both thorium and uranium at acidic pH values, as well as, the failure of the NOM to affect enhanced desorption at alkaline pH values. The objective of simulating ternary system behavior as the sum of just the binary systems was not achieved. Ternary reactions have to be invoked to model the actinide/NOM/hematite systems.

Acknowledgements

This research was supported by the National Science Foundation (OCE-9416088), the U.S. Department of Energy, the U.S. Geological Survey and the Colorado School of Mines. The comments and questions from two anonymous reviewers are appreciated.

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