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Influence of solution and surface chemistry on yttrium and rare earth element sorption

Kelly Ann Quinn
University of South Florida

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Influence of Solution and Surface Chemistry on Yttrium and Rare Earth Element Sorption

by

Kelly Ann Quinn

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
College of Marine Science
University of South Florida

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Keywords: iron, pH, carbonate, ionic strength, ICP-MS

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<td>HREE</td>
<td>heavy rare earth elements</td>
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<tr>
<td>ICP-MS</td>
<td>inductively-coupled plasma mass spectrometer</td>
</tr>
<tr>
<td>ID-TIMS</td>
<td>isotope dilution thermal ionization mass spectrometry</td>
</tr>
<tr>
<td>INAA</td>
<td>instrumental neutron activation analysis</td>
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<tr>
<td>LREE</td>
<td>light rare earth elements</td>
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<tr>
<td>MREE</td>
<td>middle rare earth elements</td>
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<td>NASC</td>
<td>North American Shale Composite</td>
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<tr>
<td>PAAS</td>
<td>Post-Archean Average Australian Shale</td>
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<td>SCM</td>
<td>surface complexation model</td>
</tr>
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<td>YREE</td>
<td>yttrium and the rare earth elements</td>
</tr>
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<td>$iK_S$</td>
<td>distribution coefficient, defined as $iK_S = [MS_i]_T/([M^{3+}]_S \times [S_i])$, where the subscript S can be Fe, Al, Ga, or In</td>
</tr>
<tr>
<td>$[MS_i]_T$</td>
<td>total concentration of sorbed YREE</td>
</tr>
<tr>
<td>$[M^{3+}]_S$</td>
<td>concentration of a free hydrated YREE ion</td>
</tr>
<tr>
<td>$[S_i]$</td>
<td>concentration of sorptive solid substrate</td>
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<td>$iK^T_{Fe}$</td>
<td>distribution coefficient expressed in terms of total YREE concentration in solution, defined as $iK^T_{Fe} = [MS_i]_T/ (M_T \times [Fe^{3+}]_S)$</td>
</tr>
<tr>
<td>$M_T$</td>
<td>total concentration of YREE in solution</td>
</tr>
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<td>$[Fe^{3+}]_S$</td>
<td>concentration of precipitated iron</td>
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<td>$iK'_{Fe}$</td>
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<td>$M_{SW}$</td>
<td>total concentration of YREE in seawater</td>
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<td>$I$</td>
<td>ionic strength</td>
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<tr>
<td>$Q_{PH}$</td>
<td>slope of the linear regression of $log , iK_{Fe}$ with respect to pH</td>
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<td>$Q_l$</td>
<td>slope of the linear regression of $log , iK_{Fe}$ with respect to ionic strength</td>
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<td>$log , iK_{Fe}(pH , 0, , I = 0)$</td>
<td>intercept of the linear regression of $log , iK_{Fe}$</td>
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<td>$s\beta_n$</td>
<td>stability constant for free YREE sorption by surface hydroxyl groups, defined as $s\beta_n = ([S-FeO_d(OH)_{3-d}M^{3-n}] \times [H^+]^n)/ ([M^{3+}] \times [S-Fe(OH)_3])$ where S− represents the bulk solid</td>
</tr>
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<td>$sK_1$</td>
<td>ferric hydroxide surface protonation constant, defined as $sK_1 = [S - Fe(OH)_2^+] \times ([S - Fe(OH)_3] \times [H^+]$)</td>
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$sK_2$ ferric hydroxide surface deprotonation constant, defined as

$$sK_2 = \frac{[S - Fe(OH)_3^-] \times [H^+]}{[S - Fe(OH)_2^+]^3}$$

$\text{CO}_3^2\beta_i$ stability constant for sorption of YREE-carbonate complexes, defined as

$$\text{CO}_3^2\beta_i = \frac{[S - FeO(OH)_2^+ MCO_3^0] \times [H^+]}{([\text{MCO}_3^+] \times [S - Fe(OH)_3^-])}$$

$i\beta_n$ stability constant of the $n^{th}$ complex of metal M with solution ligand $L_i$, defined as

$$i\beta_n = \frac{[M(L_i)^n]}{[M^{3+}] \times [L_i]^n}$$

where $L_i$ can be $\text{CO}_3^{2-}$, $\text{OH}^-$, $\text{F}^-$, $\text{HCO}_3^-$, etc.

$\text{CO}_3^2\beta_n$ YREE complexation constant with carbonate expressed in terms of total bicarbonate concentrations, defined as

$$\text{CO}_3^2\beta_n = \frac{\left([\text{M(CO}_3^{3-2n}] \times [H^+]^n\right)}{([\text{M}^{3+}] \times [\text{HCO}_3^-]^n)}$$

$\Delta H_n^0$ enthalpy
Influence of Solution and Surface Chemistry on Yttrium and Rare Earth Element Sorption

Kelly Ann Quinn

ABSTRACT

The sorption behavior of yttrium and the rare earth elements (YREEs) was investigated using a variety of hydroxide precipitates over a range of solution conditions. Experiments with amorphous hydroxides of Al, Ga, and In were conducted at constant pH (~6.0) and constant ionic strength (I = 0.01 M), while YREE sorption by amorphous ferric hydroxide was examined over a range of ionic strength (0.01 M \leq I \leq 0.09 M), pH (3.9 \leq \text{pH} \leq 7.1), carbonate concentration (0 M \leq \text{[CO}_3^{2-}]_T \leq 150 \mu M), and temperature (10^\circ C \leq T \leq 40^\circ C). Sorption results were quantified via distribution coefficients, expressed as ratios of YREE concentrations between the solid and the solution, and normalized to concentrations of the sorptive solid substrate. Distribution coefficient patterns for Al, Ga, and In hydroxides were well correlated with the pattern for YREE hydrolysis. In contrast, amorphous ferric hydroxide developed a distinct pattern that was different than those for Al, Ga, and In precipitates but similar to the pattern predicted for natural marine particles.

YREE sorption was shown to be strongly dependent on pH and carbonate concentration, significantly dependent on temperature, and weakly dependent on ionic strength. Distribution coefficients for amorphous ferric hydroxide (\(iK_{Fe}\)) were used to develop a surface complexation model that contained (i) two equilibrium constants for sorption of free YREE ions (M^{3+}) by surface hydroxyl groups, (ii) one equilibrium constant for sorption of YREE carbonate complexes (MCO_3^+), (iii) solution complexation constants for YREE carbonates and bicarbonates, (iv) a surface protonation constant for amorphous ferric hydroxide, and (v) enthalpies for M^{3+} sorption. This quantitative model...
accurately described (i) an increase in $iK_{Fe}$ with increasing pH, (ii) an initial increase in $iK_{Fe}$ with increasing carbonate concentration due to sorption of $\text{MCO}_3^+$, in addition to $\text{M}^{3+}$, (iii) a subsequent decrease in $iK_{Fe}$ due to increasing YREE complexation by carbonate ions (especially extensive for the heavy REEs), and (iv) an increase in $iK_{Fe}$ with increasing temperature.
1. Introduction

Yttrium and the fourteen stable rare earth elements (YREEs) are extensively used to study geochemical processes in all types of natural water (e.g., rivers, estuaries, and the ocean). The YREEs are ideal tools to explore fundamental aqueous reactions because they form a coherent series of elements whose chemical properties display small but systematic changes with increasing atomic number. This chemical coherence is due to the gradual filling of their $4f$ electron shell. Because outer electrons ($n = 5, 6$) shield this inner shell, there are only minor differences in the chemical reactivity along the series. The empty ($\text{La}^{3+}$), half-filled ($\text{Gd}^{3+}$), and completely filled ($\text{Lu}^{3+}$) $4f$ electron shells have increased stability and therefore may display anomalous behavior relative to the rest of the YREE series (e.g., de Baar et al., 1991; McLennan, 1994). The dominant systematic change that is observed in YREE chemical properties, such as solution complexation, is caused by the decrease in ionic radius with increasing atomic number, which is known as the lanthanide contraction. Table 1.1 lists the ionic radii of the YREEs, along with their atomic numbers and atomic weights.

As can be seen in Table 1.1, Y has an ionic radius almost equal to that of Ho and, therefore, the two elements are expected to display similar geochemical behaviors. It has been shown though that Y resembles a variety of REEs in its complexation characteristics (e.g., Moeller, 1963, 1972; Moeller et al., 1965; Byrne and Lee, 1993; Liu and Byrne, 1995). Because the $4f$ orbitals of the REEs influence bonding, the REEs display enhanced covalency compared to Y (Siekierski, 1981; Borkowski and Siekierski, 1992). This delocalization of $f$ orbitals in the REEs causes Y to behave as a light pseudolanthanide when complexing with soft ligands (e.g., organics). On the other hand, Y approaches the chemical behavior of Ho when participating in ionic interactions with hard ligands (e.g., carbonate).
Table 1.1. Some basic YREE properties, including name, symbol, atomic number (Z), atomic weight, and trivalent ionic radius for coordination number 6 (Shannon, 1976).

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Z</th>
<th>Atomic weight (g/mole)</th>
<th>Ionic radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>yttrium</td>
<td>Y</td>
<td>39</td>
<td>88.9059</td>
<td>0.900</td>
</tr>
<tr>
<td>lanthanum</td>
<td>La</td>
<td>57</td>
<td>138.9055</td>
<td>1.032</td>
</tr>
<tr>
<td>cerium</td>
<td>Ce</td>
<td>58</td>
<td>140.115</td>
<td>1.01</td>
</tr>
<tr>
<td>praseodymium</td>
<td>Pr</td>
<td>59</td>
<td>140.9077</td>
<td>0.99</td>
</tr>
<tr>
<td>neodymium</td>
<td>Nd</td>
<td>60</td>
<td>144.24</td>
<td>0.983</td>
</tr>
<tr>
<td>promethium</td>
<td>Pm</td>
<td>61</td>
<td>(145)</td>
<td>-</td>
</tr>
<tr>
<td>samarium</td>
<td>Sm</td>
<td>62</td>
<td>150.36</td>
<td>0.958</td>
</tr>
<tr>
<td>europium</td>
<td>Eu</td>
<td>63</td>
<td>151.96</td>
<td>0.947</td>
</tr>
<tr>
<td>gadolinium</td>
<td>Gd</td>
<td>64</td>
<td>157.25</td>
<td>0.938</td>
</tr>
<tr>
<td>terbium</td>
<td>Tb</td>
<td>65</td>
<td>158.9254</td>
<td>0.923</td>
</tr>
<tr>
<td>dysprosium</td>
<td>Dy</td>
<td>66</td>
<td>162.50</td>
<td>0.912</td>
</tr>
<tr>
<td>holmium</td>
<td>Ho</td>
<td>67</td>
<td>164.9304</td>
<td>0.901</td>
</tr>
<tr>
<td>erbium</td>
<td>Er</td>
<td>68</td>
<td>167.26</td>
<td>0.890</td>
</tr>
<tr>
<td>thulium</td>
<td>Tm</td>
<td>69</td>
<td>168.9342</td>
<td>0.880</td>
</tr>
<tr>
<td>ytterbium</td>
<td>Yb</td>
<td>70</td>
<td>173.04</td>
<td>0.868</td>
</tr>
<tr>
<td>lutetium</td>
<td>Lu</td>
<td>71</td>
<td>174.967</td>
<td>0.861</td>
</tr>
</tbody>
</table>

Another property that makes the YREEs a good probe of geochemical processes is oxidation state. All YREEs are present as trivalent ions in natural waters, with Ce and Eu also existing in the tetravalent and divalent states, respectively. Oxidation of Ce, which results in the formation of an insoluble oxide (CeO₂), rapidly occurs in the upper water column of the ocean (e.g., Goldberg et al., 1963; de Baar et al., 1983; German et al., 1995; Alibo and Nozaki, 1999). Processes that convert dissolved Ce³⁺ to particulate Ce⁴⁺ include biologically mediated oxidation (Moffett, 1990, 1994a,b) and abiotic oxidation on the surfaces of Mn oxides (Koeppenkastrop and De Carlo, 1992; Sholkovitz et al., 1994). Reduction of Eu, on the other hand, generally occurs at high temperatures and pressures, such as those found in hydrothermal fluids (e.g., Michard et al., 1983; German et al., 1990; Klinkhammer et al., 1994). The anomalous behaviors of Ce and Eu caused by redox reactions are quantified via Ce and Eu anomalies, defined as:

\[
\text{Ce anomaly} = \frac{3C_{en}}{2L_{an} + N_{dn}} \text{ or } \frac{2C_{en}}{L_{an} + P_{rn}}
\]  

(1.1)

and
Eu anomaly = $\frac{2E_{\text{un}}}{(S_{\text{m}} + G_{\text{dn}})}$, \hspace{1cm} (1.2)

where the subscript $n$ represents shale-normalized concentrations. Depletions or enrichments of either element relative to neighboring elements yield values less than 1 (negative anomalies) or greater than 1 (positive anomalies).

Differences in the ionic radii and the oxidation states of the YREEs lead to mass fractionation, defined by Byrne and Sholkovitz (1996) as “the variation in the relative lanthanide concentrations through biogeochemical reactions.” This fractionation in natural samples can be masked by the effect of the Oddo-Harkins Rule, which holds that elements with an even atomic number are more cosmogenically abundant than those with an odd atomic number. As an example of this odd-even pattern, Figure 1.1 shows the YREE abundances in a seawater sample (Zhang and Nozaki, 1996). To remove this saw-tooth distribution, samples are normalized to a chosen reference material, which is typically shale for samples obtained in the marine environment (Figure 1.1). As discussed by Piper (1974), REE patterns of marine samples more closely resemble the pattern of shale than that of chondrite, the preferred reference material for normalization of terrestrial rocks and minerals. Shale also represents the upper continental crust (Taylor and McLennan, 1985), which is considered to be the principal source material for REEs to the ocean.

Several different shale values in the literature have been used for normalization, including (i) mean shale, an average of the North American, European, and Russian shale composite (Haskin and Haskin, 1966; Piper, 1974; de Baar et al., 1985a), (ii) North American Shale Composite (NASC), an average of 40 shales mainly from North America (Haskin et al., 1968; Gromet et al., 1984; Goldstein and Jacobsen, 1988), and (iii) Post-Archean Average Australian Shale (PAAS), an average of 23 shales from Australia (Nance and Taylor, 1976; McLennan, 1989). Table 1.2 lists the YREE abundances (ppm and µmol/kg) in these three shales. By calculating anomalies in a manner similar to that shown in equations (1.1) and (1.2), Alibo and Nozaki (1999) showed for several seawater samples that the magnitude and direction (positive or negative) of the anomaly for all REEs, except La and Ce, varied depending on the shale values used in the normalization.
Figure 1.1. (A) Dissolved YREE concentrations (pmol/kg) at a depth of 689 m in the Pacific Ocean (Zhang and Nozaki, 1996). (B) Shale-normalized pattern of the seawater sample shown in panel A using the PAAS values given in Table 1.2 (McLennan, 1989).

This indicates that interpretations of anomalies must be made cautiously. Despite the variation in specific anomalies, the major features of shale-normalized patterns described below are maintained with different reference shales.

As can be seen in Figure 1.1, the YREEs display a shale-normalized pattern in seawater that is enriched in heavy REEs (HREEs) relative to light REEs (LREEs). Additionally, there is a pronounced Ce depletion relative to La and Pr creating a large
Table 1.2. YREE abundances (ppm and µmol/kg) in mean shale (Haskin and Haskin, 1966), NASC (Haskin et al., 1968), and PAAS (McLennan, 1989).

<table>
<thead>
<tr>
<th></th>
<th>Mean shale</th>
<th></th>
<th>NASC</th>
<th></th>
<th>PAAS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppm</td>
<td>µmol/kg</td>
<td>ppm</td>
<td>µmol/kg</td>
<td>ppm</td>
<td>µmol/kg</td>
</tr>
<tr>
<td>Y</td>
<td>36</td>
<td>405</td>
<td>27</td>
<td>304</td>
<td>27</td>
<td>304</td>
</tr>
<tr>
<td>La</td>
<td>41</td>
<td>295</td>
<td>32</td>
<td>230</td>
<td>38.2</td>
<td>275</td>
</tr>
<tr>
<td>Ce</td>
<td>83</td>
<td>592</td>
<td>73</td>
<td>521</td>
<td>79.6</td>
<td>568</td>
</tr>
<tr>
<td>Pr</td>
<td>10.1</td>
<td>71.7</td>
<td>7.9</td>
<td>56.1</td>
<td>8.83</td>
<td>62.7</td>
</tr>
<tr>
<td>Nd</td>
<td>38</td>
<td>263</td>
<td>33</td>
<td>229</td>
<td>33.9</td>
<td>235</td>
</tr>
<tr>
<td>Pm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sm</td>
<td>7.50</td>
<td>49.9</td>
<td>5.7</td>
<td>37.9</td>
<td>5.55</td>
<td>36.9</td>
</tr>
<tr>
<td>Eu</td>
<td>1.61</td>
<td>10.6</td>
<td>1.24</td>
<td>8.16</td>
<td>1.08</td>
<td>7.11</td>
</tr>
<tr>
<td>Gd</td>
<td>6.35</td>
<td>40.4</td>
<td>5.2</td>
<td>33.1</td>
<td>4.66</td>
<td>29.6</td>
</tr>
<tr>
<td>Tb</td>
<td>1.23</td>
<td>7.74</td>
<td>0.85</td>
<td>5.35</td>
<td>0.774</td>
<td>4.87</td>
</tr>
<tr>
<td>Dy</td>
<td>5.50</td>
<td>33.8</td>
<td>5.8</td>
<td>35.7</td>
<td>4.68</td>
<td>28.8</td>
</tr>
<tr>
<td>Ho</td>
<td>1.34</td>
<td>8.12</td>
<td>1.04</td>
<td>6.31</td>
<td>0.991</td>
<td>6.01</td>
</tr>
<tr>
<td>Er</td>
<td>3.75</td>
<td>22.4</td>
<td>3.4</td>
<td>20.3</td>
<td>2.85</td>
<td>17.0</td>
</tr>
<tr>
<td>Tm</td>
<td>0.63</td>
<td>3.73</td>
<td>0.50</td>
<td>2.96</td>
<td>0.405</td>
<td>2.40</td>
</tr>
<tr>
<td>Yb</td>
<td>3.53</td>
<td>20.4</td>
<td>3.1</td>
<td>17.9</td>
<td>2.82</td>
<td>16.3</td>
</tr>
<tr>
<td>Lu</td>
<td>0.61</td>
<td>3.49</td>
<td>0.48</td>
<td>2.74</td>
<td>0.433</td>
<td>2.47</td>
</tr>
</tbody>
</table>

negative Ce anomaly. The HREE enrichment and Ce depletion increase with depth in the ocean and also increase from the Atlantic Ocean to the Pacific Ocean (Byrne and Sholkovitz, 1996, and references therein). As described above, Ce exhibits anomalies due to its active redox chemistry. For elements not influenced by redox transformations, several descriptions of the processes that control the fractionation between HREEs and LREEs in seawater have been considered over the past 40 years.

Following one of the first measurements of REE concentrations in seawater, Goldberg et al. (1963) suggested that the HREE enrichment may be due either to increasing stability of solution complexes across the REE series or differential sorption by solids. Høgdahl et al. (1968) proposed that REE fractionation may be caused either by redox reactions along with differential mineral uptake or by differential solubility due to variations in ionic radius. However, it was anticipated (Moeller et al., 1965; Høgdahl et al., 1968) that neither process would be effective for the REEs in seawater. Basing their
interpretation on the proposition that REE distributions are determined by the suspended matter in natural waters, Kolesov et al. (1975) stated that the relative abundances of the REE depend on the composition of the suspended matter, the formation of REE solution complexes with organic and inorganic ions, and REE solubility. Despite the fact that these initial studies were unable to establish the cause of fractionation, they were able to provide relatively accurate descriptions of the overall REE fractionation pattern (i.e., Figure 1.1).

In addition to measuring REE concentrations in seawater, Goldberg et al. (1963) measured concentrations in a manganese nodule and suggested that incorporated REE were precipitated directly from seawater. Several studies were subsequently performed with oceanic ferromanganese nodules to determine the mechanism of REE incorporation into nodules (Elderfield et al., 1981, and references therein), but some researchers also used these studies to look at REE fractionation in seawater. Based on observations that REE concentrations in ferromanganese nodules from depths greater than approximately 3500 m display a mirror-image pattern relative to seawater, Piper (1974) suggested that formation of deep-water nodules fractionates the REE and therefore could be responsible for the observed seawater fractionation pattern. Piper (1974) concluded that the mechanism controlling the fractionation might involve REEs being released from dissolving biogenic tests and then being coprecipitated with Fe and Mn phases. Elderfield et al. (1981) agreed with Piper (1974) that REE fractionation may be controlled by the formation of nodules but suggested that the pattern reflects the relative proportions of Fe-rich and P-rich carrier phases in the nodule, with the Fe-rich phase producing the inverted seawater pattern.

REE concentration determinations in seawater experienced a hiatus of several years as methods more precise than instrumental neutron activation analysis (INAA) were developed to measure picomolar YREE concentrations. Compared to the REE chemical yield averaging about 90% in the work of Goldberg et al. (1963), de Baar improved the analysis of seawater by INAA, demonstrating a chemical yield of 100% and precision of 2–5% (1σ) (de Baar et al., 1983, 1985a,b). A major advancement came with the use of isotope dilution thermal ionization mass spectrometry (ID-TIMS) by Elderfield and
Greaves (1982), which increased the precision and sensitivity of measurements to typically ± 1% (2σ). Over the next couple of years, additional measurements of REE concentrations in the ocean were interpreted as being indicative of fractionation during YREE scavenging by marine particulate matter (Elderfield and Greaves, 1982; de Baar et al., 1983; Klinkhammer et al., 1983). It was also proposed that since HREEs form more stable solution complexes in seawater, LREEs would be preferentially removed by the scavenging process (Elderfield and Greaves, 1982; de Baar et al., 1983; Klinkhammer et al., 1983). Referring to the steady state scavenging model of Schindler (1975) and Balistrieri et al. (1981), de Baar et al. (1985b) stated that REE fractionation occurs during the “equilibration of REE(III) between inorganic complexes in solution and surface sites on small suspended particles”. The work of de Baar et al. (1985a,b) may have been the first to explicitly attribute YREE fractionation in seawater to the competition between solution chemistry and surface chemistry.

At the time of the de Baar et al. publications, YREE surface complexation characteristics were unknown and little was known about YREE solution complexation. Despite the fact that equilibrium constants had not yet been measured for REE solution complexes, Turner et al. (1981) assessed the speciation of trivalent REEs in seawater based on linear free-energy relationships for divalent metals. Using the observed correlation between the stability constants of carbonate and oxalate complexes for divalent metals, Turner et al. (1981) calculated that at a free carbonate ion concentration of $10^{-4.50}$ M, the fraction of free ion in seawater decreased along the REE series from 38% for La to 5% for Lu, while the fraction of carbonate complexes ($3MCO_3^-$ only) generally increased from 22% for La to 81% for Yb. The remaining fraction of REEs was attributable to a combination of hydroxide, chloride, and sulfate complexes with fluoride complexes only accounting for approximately 1% of the total for each individual REE (Turner et al., 1981). Based on the fact that carbonate dominated the speciation of REEs in seawater, most of the initial studies involving YREE solution complexation focused on the carbonate ion.

Initially, carbonate complexation constants were measured for individual REE, including La (Ciavatta et al., 1981), Eu (Lundqvist, 1982), Ce (Ferri et al., 1983), and Y
(Spahiu, 1985). Since these four studies were interested in groundwater speciation, experiments were performed at ionic strengths between 0.3 M and 3 M. In order to determine constants appropriate to seawater and also to improve the correlation used by Turner et al. (1981), Cantrell and Byrne (1987a) measured carbonate and oxalate stability constants for Ce, Eu, and Yb at an ionic strength of 0.68 m. It was shown that $\text{M(CO}_3\text{)}^2_-,\text{ along with MCO}_3^+$, are the dominant species for REEs in seawater (Cantrell and Byrne, 1987a), which significantly altered the speciation scheme of Turner et al. (1981). Using the measured carbonate stability constants for Ce, Eu, and Yb, along with those estimated for the remaining REEs via a quadratic function in atomic number, Cantrell and Byrne (1987a) calculated that at a total carbonate ion concentration of $10^{3.86}$ m (free concentration = $10^{4.71}$ m, using the ion pairing model of Millero and Schreiber, 1982), the fraction of carbonate complexes ($\text{MCO}_3^+$ and $\text{M(CO}_3\text{)}^2_-$) increased along the YREE series from 86% for La to 98% for Lu, while the fraction of free ion decreased from 7% for La to 0.3% for Lu.

Over the next several years, additional measurements of carbonate complexation were carried out to further improve this speciation scheme, although the majority of studies involved only Eu (Thompson and Byrne, 1988; Chatt and Rao, 1989; Rao and Chatt, 1991). Since shale-normalized REE patterns in seawater exhibit an anomaly at Gd (de Baar et al., 1985b, 1991), Lee and Byrne (1993) determined carbonate complexation constants for Gd and its neighbors, Eu and Tb, as well as representative light and heavy REEs (Ce and Yb). In addition to demonstrating the “Gd-break” in the series, they also estimated carbonate stability constants for the other REEs using the measured constants plus multiple linear regression analyses. By measuring carbonate stability constants for Y and Gd and then comparing the resulting Y and REE solution chemistries, Liu and Byrne (1995) showed that the solution complexation behavior of Y closely resembles that of Tb.

The introduction of inductively-coupled plasma mass spectrometry (ICP-MS) allowed the entire YREE series to be studied simultaneously, greatly improving the understanding of comparative YREE aquatic geochemistry relative to perspectives that are gained by measurements of individual elements. Liu and Byrne (1998) determined carbonate stability constants for the entire YREE series by solvent exchange and ICP-MS. Stability
constants for elements such as Ce, Eu, Gd, Tb, and Yb, which had been examined previously, were in good agreement with prior results. A plot of YREE carbonate complexation constants versus atomic number showed (i) a general increase from La to Lu, (ii) a negative anomaly at Gd, and (iii) a close relationship between Y and Eu (Liu and Byrne, 1998). Using adsorptive exchange analysis, Kawabe et al. (1999a) and Ohta and Kawabe (2000) also determined carbonate complexation constants for the entire YREE series. However, their results were 1.0 – 1.5 log units higher than essentially all previously determined values obtained using a variety of techniques. In order to better constrain the results, Luo and Byrne (2004) utilized potentiometry to measure YREE carbonate stability constants. This work showed excellent agreement with the solvent exchange results of Liu and Byrne (1998).

YREE behavior in natural waters has become increasingly well characterized through inclusion of YREE stability constant results for a variety of solution ligands, including bicarbonate (Luo and Byrne, 2004), fluoride (Schijf and Byrne, 1999; Luo and Byrne, 2000; Luo and Millero, 2004), hydroxide (Klungness and Byrne, 2000), chloride (Luo and Byrne, 2001), and sulfate (Schijf and Byrne, 2004). Using the above-referenced solution complexation constants, YREE speciation for seawater can be calculated at pH 8.2 and a total bicarbonate concentration of 2 mM. Figure 1.2 shows the fraction of each species as log ([ML]/M_T), where M represents a YREE ion and L represents a solution ligand. It can be seen that the results do not differ much from those of Cantrell and Byrne (1987a).

In contrast to the extensive studies on inorganic complexation, little is known about YREE solution complexation with natural organic matter. Byrne and Li (1995) summarized YREE complexation constants with 101 organic ligands, which were obtained from the compilations of Critical Stability Constants by Martell and Smith (1974, 1977, 1982) and Smith and Martell (1975, 1989). More specific studies have determined YREE complexation constants with acetate (e.g., Kolat and Powell, 1962; Wood et al., 2000) and oxalate (e.g., Schijf and Byrne, 2001). These investigations have
utilized a variety of well-characterized organic ligands that may not accurately represent the complex properties of natural organic matter, which consists of humic acids, fulvic acids, and other biologically-derived material. Relatively few YREE binding constants with natural humic substances have been measured, and studies usually were conducted only for individual elements (see electronic annex of Sonke and Salters, 2006). Tang and Johannesson (2003) used the published data for Eu, Tb, and Dy plus linear free-energy relationships with the stability constants of lactic and acetic acids to estimate equilibrium constants for the entire YREE series. Combining these estimated constants with the Humic Ion-Binding Model V (Tipping, 1994), Tang and Johannesson (2003) predicted that organic matter dominates YREE speciation in circumneutral-pH river waters and organic-rich groundwaters (dissolved organic carbon > 0.7 mg/L). To improve future calculations of YREE speciation in natural waters, Sonke and Salters (2006) determined humic substance binding constants for the entire YREE series.
In addition to complexation by organic and inorganic solution ligands, the other dominant process controlling YREE distributions in natural waters is scavenging, or the sorptive removal of dissolved elements from solution by particles (Goldberg, 1954; Goldberg et al., 1963; Balistrieri et al., 1981; Bruland, 1983; Fowler and Knauer, 1986). YREEs are scavenged in estuaries, where freshwater and seawater mix, by the formation of colloids (Sholkovitz, 1976, 1992; Sholkovitz and Elderfield, 1988). In the upper ocean, YREEs are predominantly scavenged by particles and particle coatings, which are composed of either organic matter or Fe oxides (Balistrieri et al., 1981; Hunter, 1983). Below approximately 300 m, concentrations of YREEs in seawater may also be controlled by YREE phosphate coprecipitation (Jonasson et al., 1985; Byrne and Kim, 1993; Liu and Byrne, 1997; Liu et al., 1997).

Before direct measurements were possible, the sorptive behavior of marine particulates was modeled based on the residence time of an element (Schindler, 1975). Two different methods were used for this modeling: (i) relative concentrations of dissolved YREEs were estimated using surface and solution complexation constants, and then compared to actual measurements, and (ii) surface complexation constants were estimated from shale-normalized YREE concentrations and solution complexation constants that had been directly measured. For the first method, the relevant surface groups and associated complexation constants were not well known, so either YREE hydrolysis constants (Balistrieri et al., 1981; Erel and Morgan, 1991; Erel and Stolper, 1993) or YREE complexation constants with dissolved monocarboxylic acids (Byrne and Kim, 1990) were used in the calculation. For the second method, Lee and Byrne (1993) and Byrne and Sholkovitz (1996) used the most accurate YREE ocean concentrations and solution complexation constants that were available at the time to calculate surface stability constants. These modeling efforts are described in more detail in Section 2.2.

There have been relatively few measurements of REE concentrations in marine particulates, either sinking (Murphy and Dymond, 1984; Masuzawa and Koyama, 1989; Fowler et al., 1992; Tachikawa et al., 1997; Lerche and Nozaki, 1998) or suspended (Bertram and Elderfield, 1993; Sholkovitz et al., 1994; Alibo and Nozaki, 1999; Tachikawa et al., 1999; Kuss et al., 2001). The shale-normalized REE patterns obtained
in these studies show various degrees of enrichment in either HREEs (Murphy and Dymond, 1984; Kuss et al., 2001) or LREEs (Fowler et al., 1992; Tachikawa et al., 1997, 1999), while some show an enrichment in middle REEs (MREEs) (Lerche and Nozaki, 1998; Alibo and Nozaki, 1999). In addition, Ce anomalies are both negative (Murphy and Dymond, 1984; Kuss et al., 2001) and positive (e.g., Sholkovitz et al., 1994; Tachikawa et al., 1997), and change with depth (Tachikawa et al., 1999) or particle flux (Fowler et al., 1992). The observed pattern variations may be caused by differences in (i) the shale values used for normalization, (ii) the chemical methods used for leaching and/or digestion, and (iii) particle properties, such as composition, size, and sinking velocity. Because multiple parameters can influence compositional results, comparisons between different studies are difficult.

In one of the first measurements of REE concentrations in sinking particles, Murphy and Dymond (1984) observed shale-normalized REE patterns similar to seawater (i.e., HREE enrichment and negative Ce anomaly). In sharp contrast, the shale-normalized REE patterns of Masuzawa and Koyama (1989) were flat with positive Ce anomalies. Masuzawa and Koyama (1989) attributed their observations to the preferential removal of Ce, along with Mn, from seawater by settling particles. Although their patterns were quite different, Murphy and Dymond (1984) and Masuzawa and Koyama (1989) both determined that the total REE flux increases with depth, possibly due to ongoing sorption of REEs by the sinking particles. Using regressions between measured REE concentrations and percentages of end member components, Murphy and Dymond (1984) calculated that 30–60% of the REE flux comes from the biogenic component, which is dominant in the upper water column and decreases with depth. The remainder of the total flux was considered to be detrital, gradually increasing with depth and becoming dominant in deeper water (Murphy and Dymond, 1984).

Both of the above studies were performed during a single time period and could not be used to draw any conclusions about temporal variations in particle fluxes. By using automated time-series sediment traps, Fowler et al. (1992) were able to observe changes in shale-normalized patterns of sinking particles due to rapid variations in particle flux associated with the crash of a phytoplankton bloom. In the course of the Fowler et al.
observations, REE patterns of particles remained flat with negative Ce anomalies throughout the water column. In comparison, when particle fluxes were lower, REE patterns of particles were flat in surface waters and developed LREE enrichments and positive Ce anomalies with depth. Fowler et al. (1992) concluded that slowly sinking particles are more effective at scavenging REEs, especially LREEs and Ce, compared to fast sinking particles. This same effect of vertical flux on REE sorption was observed by Tachikawa et al. (1997) in their comparison between a mesotrophic site with large dust fluxes and an oligotrophic site with lower fluxes and greater LREE enrichments.

Measuring REE concentrations in suspended particles, Bertram and Elderfield (1993) determined that < 5% of the total REE in seawater is in particulate form, except for Ce, for which ≤ 20% of the total is particulate. Since the REE patterns of dissolved/particulate ratios resembled the shale-normalized pattern of seawater, Bertram and Elderfield (1993) suggested that particulate REEs are composed mainly of detrital matter. Sholkovitz et al. (1994) increased the understanding of marine particulate behavior by performing a series of three chemical digestions on suspended particles. The first digestion used acetic acid to remove the surface coatings, which consisted of organic matter and Mn oxides. The acetic acid digest, containing 50–70% of the REEs and the main fraction of Mn, had a shale-normalized REE pattern that was the mirror-image of seawater (i.e., LREE enrichment and positive Ce anomaly). The second digestion, which involved strong acids, and the third digestion, which was carried out in a digestion bomb, both contained the major fraction of Al and Fe, indicating a detrital composition. The shale-normalized patterns for the strong acid and bomb digests were relatively flat, which is consistent with a detrital source. Based on these three digestions, Sholkovitz et al. (1994) concluded that REEs are removed from seawater and fractionated by surface coatings, with Mn oxyhydroxides possibly controlling Ce oxidation and the preferential removal of LREEs compared to HREEs.

Despite using a sequential digestion method similar to Sholkovitz et al. (1994), Lerche and Nozaki (1998) observed shale-normalized patterns for sinking particles that had a MREE enrichment in all three digests. In addition, the Ce anomaly changed from negative in the acetic acid digest to unity in the acid leach to positive in the residual
fraction. Lerche and Nozaki (1998) suggested that the adsorbed REEs are altered into a more refractory solid phase prior to or during particle sinking. The differences between the results of Sholkovitz et al. (1994) and Lerche and Nozaki (1998) indicate that the sorptive behavior of marine particulates is not yet fully understood.

One of the major challenges in particulate REE studies is determining the association between the REEs and a specific carrier phase since particle composition can vary throughout the ocean. Several studies used observations of particulate Mn, Al, and Fe concentrations, which represent inorganic carrier phases, to infer relationships with the REEs (Masuzawa and Koyama, 1989; Sholkovitz et al., 1994; Tachikawa et al., 1997, 1999). Kuss et al. (2001) extended this by also measuring concentrations of particulate organic carbon (POC), CaCO3, and opal, which are considered to be biogenic YREE carrier phases in suspended matter. Through linear regression analyses of YREE concentrations versus carrier phase values, Kuss et al. (2001) demonstrated strong fractionation between HREEs and LREEs for each particulate fraction. Y and the HREEs were strongly correlated with POC and Mn, indicating that organic ligands form stronger complexes with increasing REE atomic number and that Mn may be associated with biogenic matter rather than oxyhydroxides. On the other hand, the LREEs were strongly correlated with Al and to a lesser extent Fe, which indicates a crustal or clay origin and some sorption onto an Fe-oxide phase.

Since marine particles are composed of several different phases (e.g., Fe-Mn oxides, aluminosilicates, organic matter, etc.), surface complexation constants for discrete phases, which are similar to solution complexation constants, cannot be determined from the above-mentioned studies. In order to accurately model YREE distributions in natural waters, a better understanding of YREE interactions with particle surfaces must be gained through observations of YREE associations with pure phases. To supplement the extensive database on YREE solution complexation, an increasing number of studies have been devoted to examination of YREE surface chemistry. Investigations of YREE sorption have utilized a variety of pure substrates, such as alumina (e.g., Fairhurst et al., 1995; Marmier et al., 1997; Rabung et al., 2000), silica (e.g., Kosmulski, 1997; Takahashi et al., 1998; Marmier et al., 1999), rutile (e.g., Ridley et al., 2005), sand (e.g., Tang and
Johannesson, 2005), organics (e.g., Bingler et al., 1989; Stanley and Byrne, 1990), clays (e.g., Bradbury and Baeyens, 2002; Coppin et al., 2002; Rabung et al., 2005), manganese oxides (e.g., Bidoglio et al., 1992; De Carlo et al., 1998; Davranche et al., 2005), and iron oxides (e.g., Koeppenkastrop and De Carlo, 1992; Bau, 1999; Ohta and Kawabe, 2001). Because iron is ubiquitous in natural waters and is the main substrate used in the present research, the following discussion will principally focus on YREE sorption by a variety of forms of particulate iron.

Some of the first studies involving REE sorption by iron(III) hydroxide and oxide were interested in preconcentration and decontamination of radionuclides. Musić et al. (1979) and Musić and Ristić (1988) showed that REE sorption in low ionic strength solutions ($\leq 0.15$ M) increased as the pH increased from 4 to 7. The pH-adsorption edges for Ce, Gd, and Yb were very similar (Musić and Ristić, 1988), suggesting a lack of fractionation. Although they described the reactions involved in REE sorption, neither investigation modeled the process or related the results to seawater.

Early investigations of REE sorption in seawater showed that LREEs are preferentially removed by most solids compared to HREEs, which leads to fractionation (Byrne and Kim, 1990; Koeppenkastrop et al., 1991; Koeppenkastrop and De Carlo, 1992). Despite the fact that surface complexation appeared to be stronger for LREEs, differences among various solids were observed. Silica phases were unique in their sorption behavior because they displayed a greater affinity for HREEs, except when covered by a thin organic film, which enhanced LREE sorption (Byrne and Kim, 1990). Koeppenkastrop and De Carlo (1992) observed that REE sorption by crystalline goethite was weaker than sorption by amorphous iron oxyhydroxide, but that goethite created stronger fractionation between the LREEs and the HREEs. In addition, the residual seawater pattern from these experiments resembled the shale-normalized REE pattern in the ocean (Koeppenkastrop and De Carlo, 1992).

As was discussed earlier, seawater contains numerous solution ligands that compete with surfaces for free YREE ions. To determine YREE surface complexation constants, any effects from this strong solution complexation must be removed. YREE sorption onto amorphous ferric hydroxide in simple synthetic solutions without complexing ligands has
been investigated over a range of pH (3.5 – 9.0), ionic strength (0.0 – 0.7 M), and substrate loading (i.e., $\Sigma [\text{REE}] / [\text{Fe}^{3+}]_T$; 0.004 – 0.4) (De Carlo et al., 1998; Bau, 1999; Kawabe et al., 1999b; Ohta and Kawabe, 2001). These studies showed that in the absence of solution complexation, HREEs are preferentially removed from solution but the magnitudes of estimated distribution coefficients for individual YREEs, at constant pH, varied by as much as a factor of 400.

Similar to Musić et al. (1979) and Musić and Ristić (1988), De Carlo et al. (1998) and Bau (1999) observed an increase in YREE sorption with increasing pH. In addition to increasing YREE sorption with increasing pH, Bau (1999) reported that the relative magnitudes of YREE sorption (i.e., fractionation patterns) vary with pH. The pH dependence of YREE sorption can be described via a surface complexation model (SCM), which provides a thermodynamic explanation for the competitive complexation of H$^+$ and dissolved metal ions by surface hydroxyl groups (Schindler and Stumm, 1987; Dzombak and Morel, 1990). Several investigations of REE sorption have utilized a SCM to interpret the sorptive behavior of individual REEs, such as Eu sorption onto hematite (Rabung et al., 1998a) and sorption of La and Yb by hematite and goethite (Marmier et al., 1997; Marmier and Fromage, 1999). As discussed by Rabung et al. (1998a), comparisons between these investigations are difficult due to distinct differences in data interpretations along with SCM variations. By utilizing three different SCMs to interpret the same data, however, Marmier and Fromage (1999) showed that the diffuse layer model and the constant capacitance model yielded similar results and, at low loading, a non-coulombic SCM could satisfactorily model La sorption data. Since the SCM was applied to only a few individual REEs, variations in YREE sorption patterns with pH (Bau, 1999) were not addressed in these studies.

In addition to modeling YREE sorption in terms of pH, the effect of solution complexation on YREE sorption needs to be included in SCMs. Stanley and Byrne (1990) examined REE sorption in seawater by *Ulva lactuca* L., a macroalga, over a range of carbonate concentrations. The variation in their calculated solution complexation intensity for Gd (i.e., ratio of free to total Gd) was much greater than the variation in their observed Gd solid/solution distribution coefficients. Stanley and Byrne (1990) suggested
that this difference may be due to the sorption of complexed solution species such as GdCO$_3^+$, in addition to sorption of free dissolved metal (Gd$^{3+}$), at high degrees of solution complexation. On the other hand, Koeppenkastrop and De Carlo (1993) proposed that dissolved REEs dissociate from carbonate ligands before being sorbed as free ions onto a solid. Their conclusion was based on the observation that carbonate complexation slowed the rate of uptake of Eu by iron oxide in seawater. Kawabe et al. (1999a) and Ohta and Kawabe (2000) examined YREE sorption by amorphous ferric hydroxide in the absence and presence of carbonate ($0 \leq [\text{HCO}_3^-] \leq 12$ mM). Their results showed that distribution coefficients increased along the YREE series in the absence of carbonate but this trend reversed when carbonate was present in solution. As was already stated, Ohta and Kawabe (2000) used their distribution coefficient results to calculate carbonate complexation constants, which displayed a consistent pattern across the YREE series but were at least an order of magnitude greater than most literature data.

Based on this review of YREE aqueous geochemistry, the aim of my dissertation is to examine the influence of solution and surface chemistry on YREE sorption in aqueous solutions. My project has three main goals. The first goal is characterization of YREE sorption by the freshly precipitated hydroxides of iron(III), aluminum, gallium, indium, and scandium. These experimental results will show whether different amorphous precipitates have similar or unique sorption patterns. Comparison of distribution coefficient patterns for different solids with YREE solution complexation constant patterns allows assessment of the extent to which complexation properties of surface functional groups can be described in terms of solution complexation characteristics. The results of this assessment will be discussed in Chapter 2. The second goal of my project is characterization of the pH and ionic-strength dependence of YREE sorption by amorphous ferric hydroxide. An SCM will be constructed from distribution coefficient measurements obtained over a wide range of conditions. The results will then be used for general predictions of environmental YREE behavior. This topic will be discussed in Chapter 3. My third goal is characterization of the influence of carbonate complexation on YREE sorption by amorphous ferric hydroxide in simple aqueous solutions. Combining SCM parameters and previous characterizations of YREE carbonate
complexation constants, predictions of YREE sorption in the presence of carbonate can be compared to experimental observations. An especially important issue here is whether YREE sorption behavior can be described solely in terms of sorbed M$^{3+}$ ions, or whether sorption of solution complexes such as MCO$_3^+$ must also be considered. Chapter 4 will be devoted to the results of this objective. Finally, Chapter 5 will briefly describe observations from YREE sorption experiments performed with amorphous ferric hydroxide over a range of temperatures.

My studies will lead to a quantitative model of YREE sorption by an environmentally important sorptive substrate, amorphous ferric hydroxide, and, in general, an improved quantitative model of YREE removal from seawater by marine particles. Since the processes that control YREE distributions in seawater are known to influence all metals in the ocean, this work will provide a better understanding of the general nature of metal cycling in the ocean.
2. Comparative Scavenging of Yttrium and the Rare Earth Elements in Seawater:

Competitive Influences of Solution and Surface Chemistry

The following chapter has been peer-reviewed and published essentially in this form:

2.1 Abstract

Distribution coefficients were obtained for yttrium and the rare earth elements (YREEs) in aqueous solutions containing freshly precipitated hydroxides of trivalent cations (Fe$^{3+}$, Al$^{3+}$, Ga$^{3+}$, and In$^{3+}$). Observed patterns of log $i_KS$ – where $i_KS = [MS_i][M^{3+}]^{-1}[S_i]^{-1}$, [MS$_i$] is the concentration of a sorbed YREE, [M$^{3+}$] is the concentration of a free hydrated YREE ion, and [S$_i$] is the concentration of a sorptive solid substrate (Fe(III), Al, Ga, In) – exhibited similarities to patterns of YREE solution complexation constants with hydroxide ($\beta_{1}$) and fluoride ($\beta_{1}$), but also distinct differences. The log $i_KS$ pattern for YREE sorption on Al hydroxide precipitates is very similar to the pattern of YREE hydroxide stability constants ($\beta_{1}$) in solution. Linear free-energy relationships between log $i_KS$ and log $\beta_{1}$ showed excellent correlation for YREE sorption on Al hydroxide precipitates, good correlation for YREE sorption on Ga or In hydroxide precipitates, yet poor correlation for YREE sorption on Fe(III) hydroxide precipitates. Whereas the correlation between log $i_KS$ and log $\beta_{1}$ was generally poor, patterns of log ($i_KS/\beta_{1}$) displayed substantially increased smoothness compared to patterns of log $i_KS$. This indicates that the conspicuous sequence of inflections along the YREE series in the patterns of log $i_KS$ and log $\beta_{1}$ is very similar, particularly for In and Fe(III) hydroxide precipitates.

While the log $i_KS$ patterns obtained with Fe(III) hydroxide precipitates in this work are quite distinct from those obtained with Al, Ga, and In hydroxide precipitates, they are
in good agreement with patterns of YREE sorption on ferric oxyhydroxide precipitates reported by others. Furthermore, our log $\log K$ patterns for Fe(III) hydroxide precipitates bear a striking resemblance to predicted log $\log K$ patterns for natural surfaces that are based on YREE solution chemistry and shale-normalized YREE concentrations in seawater.

Yttrium exhibits an itinerant behavior among the REEs: sorption of Y on Fe(III) hydroxide precipitates is intermediate to that of La and Ce, while for Al hydroxide precipitates Y sorption is similar to that of Eu. This behavior of Y can be rationalized from the propensities of different YREEs for covalent vs. ionic interactions. The relatively high shale-normalized concentration of Y in seawater can be explained in terms of primarily covalent YREE interactions with scavenging particulate matter, whereby Y behaves as a light REE, and primarily ionic interactions with solution ligands, whereby Y behaves as a heavy REE.

2.2 Introduction

One of the major objectives of chemical oceanography is to gain an understanding of the processes that control the concentrations and distributions of elements in the oceans. Yttrium and the fourteen stable rare earth elements are of unique value in this regard because of the coherence in their chemical properties. Chemical characteristics of the trivalent rare earth elements are sufficiently similar that this coherence is intermediate to that of isotopes of a single element on the one hand and elements in the same group (column) of the Periodic Table on the other. On account of this, the oceanic abundances of rare earth elements, like isotopes, are generally described in a comparative manner. In the same sense that the pattern of a fingerprint, rather than any quantitative aspect, is uniquely informative, abundance patterns of yttrium and the rare earth elements (YREEs) provide sensitive measures of environmental processes.

Although in all seawater below a certain depth the YREEs are near their solubility limits with respect to mixed-YREE phosphate precipitates (Byrne and Kim, 1993; Liu and Byrne, 1997; Liu et al., 1997), it is generally thought that scavenging processes – sorptive removal of elements from the water column by sinking particles (Goldberg,
1954; Goldberg et al., 1963; Balistrieri et al., 1981; Bruland, 1983) – play a dominant role in shaping both the absolute and relative abundances of YREEs in the oceans. In previous work (Byrne and Kim, 1990), the single-box residence time model of Schindler (1975) was used to derive a simple equation that describes relative YREE abundances in seawater:

\[
\log \left( \frac{A_M}{(dA_M/dt)} \right) = \log \left( \frac{(M_T/[M^{3+}])}{(M_S/[M^{3+}])} \right) + \text{constant},
\]

(2.1)

where brackets [ ] denote the solution concentration of a chemical species, \( A_M \) is the total amount (mol) of metal M in seawater and \( dA_M/dt \) is its oceanic input (or removal) rate at steady state. The ratio \( A_M/(dA_M/dt) \) on the left hand side of equation (2.1) constitutes the equivalent of shale-normalized YREE concentrations in seawater or, alternatively, the residence times of individual YREEs with respect to their total oceanic input (or removal). It is very important to note that the two sides of equation (2.1) are offset by a constant, independent of M, that incorporates several poorly known quantities related to the surface characteristics, concentrations, and residence times of sorbing particles (Byrne and Kim, 1990).

On the right hand side of equation (2.1), the numerator denotes the extent (intensity) of solution complexation for metal M, where \( M_T \) represents the total dissolved metal concentration. The denominator denotes the affinities of particle surfaces for free metal ions \( M^{3+} \) in solution, where \( M_S \) represents the total sorbed metal concentration. Thus, equation (2.1) predicts that shale-normalized YREE concentrations in seawater can be described as a direct competition between solution ligands and surface ligands for free hydrated metal ions.

The solution complexation term, \( M_T/[M^{3+}] \), in equation (2.1) can be written as a summation over the contributions from all YREE solution complexes in seawater:

\[
\frac{M_T}{[M^{3+}]} = \sum_{i,n} (1+i\beta_n[L_i]^n),
\]

(2.2)

where \( i\beta_n \) are stability constants of the \( n^{th} \) complex of metal M with solution ligand \( L_i \):

\[
i\beta_n = \frac{[M(L_i)_n]}{[M^{3+}][L_i]^n}.
\]

(2.3)
Stability constants appropriate to seawater and freshwater have been determined for YREE complexation with fluoride (Schijf and Byrne, 1999; Luo and Byrne, 2000), chloride (Luo and Byrne, 2001), sulfate (Schijf and Byrne, 2004), hydroxide (Klungness and Byrne, 2000), and bicarbonate and carbonate (Liu and Byrne, 1998; Luo and Byrne, 2004).

The surface complexation term (\(M_S/[M^{3+}]\)) in equation (2.1) can be written as a summation over different types of surface complexation sites:

\[
\frac{M_S}{[M^{3+}]} = \sum_i (iK_S [S_i]), \tag{2.4}
\]

where \(iK_S\) is the affinity of surface ligand \(S_i\) for element \(M\):

\[
iK_S = \frac{[MS_i]}{[M^{3+}][S_i]} . \tag{2.5}
\]

The concentration \([S_i]\) of surface ligands in a solution, natural or synthetic, is expressed in the same units as solution ligands but, of course, denotes moles of particulate ligands per kilogram of solution. The quantity \(iK_S\) can be interpreted (as it will be here) as a distribution coefficient, where the ratio \([MS_i]/[S_i]\) is calculated as the sorbed metal concentration per mole of solid substrate (since the exact type and density of surface ligands are unknown). We will occasionally distinguish these distribution coefficients by replacing the subscript \(S\) with the chemical symbol of the trivalent cation in the hydroxide precipitate (e.g., \(iK_{Ga}\) for YREE sorption on Ga hydroxide).

The properties of \(iK_S\) relevant to natural marine surfaces are much less well understood than the properties of YREE complexation by solution ligands. Most prior work on YREE scavenging (Murphy and Dymond, 1984; Koeppenkastrop et al., 1991; Fowler et al., 1992; Koeppenkastrop and De Carlo, 1993; Sholkovitz et al., 1993; Schijf et al., 1994; Bau et al., 1996; Lerche and Nozaki, 1998) involved measurements of YREE distributions between seawater and particulate matter and, as such, did not provide true estimates of \(iK_S\) as defined in equation (2.5). Direct measurements of \(iK_S\) are becoming increasingly common (Bau, 1999; Ohta and Kawabe, 2000, 2001). However, measurements of \(iK_S\) with a variety of particle surfaces are sufficiently scarce that the quality of such data is uncertain. Thus, additional \(iK_S\) data are valuable for assessing the
quality of previous $K_S$ characterizations and extending such characterizations to different types of surfaces.

Two indirect methods have been used to model the sorptive characteristics of natural marine particles. In the first case, linear free-energy relationships of the form

$$\log_1 K_S = a \times \log_{\text{OH}} \beta_1 + b,$$

(2.6)

where $a$ and $b$ are constants and $\beta_1$ is the YREE hydroxide stability constant in solution, have been used to estimate $K_S$ behavior based on YREE solution complexation behavior (Schindler, 1975; Balistrieri et al., 1981; Erel and Morgan, 1991). As another means of evaluating the YREE sorptive characteristics of natural marine particles, Lee and Byrne (1993) and Byrne and Sholkovitz (1996) used equation (2.1) to estimate average $K_S$ values for marine particles based on (i) high-precision shale-normalized YREE concentrations in seawater and (ii) the best solution complexation constant data available at the time. Figure 2.1 shows a comparison of the Byrne and Sholkovitz (1996) $K_S$ estimates and direct $K_{Fe}$ measurements obtained by Bau (1999) for YREE sorption on ferric oxyhydroxides at pH ~ 6. The patterns shown in Figure 2.1 are quite distinct from the pattern of $\log_{\text{OH}} \beta_1$ (Klungness and Byrne, 2000) and exhibit an intriguing similarity that has not been previously noted.

In this work, we compare the YREE sorptive characteristics of a number of freshly precipitated trivalent metal hydroxides at pH ~ 6, namely Fe(OH)$_3$, Al(OH)$_3$, Ga(OH)$_3$, In(OH)$_3$, and Sc(OH)$_3$. The resulting $K_S$ data are discussed using the two approaches described above: linear free-energy relationships with $\beta_1$, and comparison with $K_S$ estimates derived from observations of shale-normalized YREE concentrations plus independently measured YREE solution complexation constants. In addition, $K_S$ data are discussed in terms of relative YREE ionicities with respect to solution and surface complexation (Martell and Hancock, 1996).

2.3 Materials and Methods

Experiments were performed to study YREE sorption on a number of trivalent metal hydroxides, which were precipitated directly from an acidic solution containing the
trivalent metal and all YREEs by increasing the pH with ammonia. Five separate experiments were performed. Solid substrates included Fe(III) hydroxide (a known strong YREE scavenger), hydroxides of the trivalent Group 13 elements Al, Ga, and In, and hydroxides of the YREE-like element Sc.

All chemical manipulations were performed inside a class 100 clean air laboratory or laminar flow bench. Trace metal-clean water (Milli-Q water) was produced with a Millipore (Bedford, MA) purification system. Teflon and polypropylene laboratory materials and polycarbonate filter membranes were cleaned by soaking in HCl or HNO₃.
for at least one week, followed by several thorough rinses with Milli-Q water. Certified 1.000 M hydrochloric acid was purchased from Sigma-Aldrich (St. Louis, MO), and TraceMetal Grade nitric acid from Fisher Scientific (Pittsburgh, PA). A YREE stock solution, containing 66.7 ppm of each YREE in 2% HNO$_3$, was prepared from single element ICP standards (SPEX CertiPrep, Metuchen, NJ). Salts of the trivalent metals were purchased from Sigma-Aldrich, except aluminum, for which an existing laboratory ICP standard was used (10,000 ppm in 10% HCl), and iron, which was purchased from Fisher Scientific as a ferric chloride solution (40% w/v in HCl). Indium was obtained as nitrate pentahydrate and scandium as chloride hexahydrate. Anhydrous gallium chloride was shipped in an ampoule under argon. All salts were of 99.999% purity with respect to metal content and were used as received. Scandium chloride was added directly to the experimental solution. The other salts were dissolved in a small quantity of Milli-Q water (gallium chloride under an argon atmosphere) and then diluted to a known volume with Milli-Q water, adding concentrated HCl or HNO$_3$ as necessary, to make concentrated stock solutions of the trivalent metals.

At the beginning of each experiment, a pH standard (pH 3.0, 0.001 M HCl) was prepared in 0.01 M NH$_4$NO$_3$ to match the ionic strength, I, of the experimental solution, which was calculated as I = 0.014 ± 0.002 M. The experimental solution consisted of 100 µM of the trivalent metal and 23.3 ppb of each YREE (total combined YREE concentration 2.36 µM) in 0.01 M HCl, HNO$_3$, or NH$_4$NO$_3$. Both solutions were equilibrated in a Teflon wide-mouth bottle inside a jacketed beaker thermostated at T = (25.0 ± 0.1)°C, and continuously stirred with a Teflon-coated ‘floating’ stir bar. The experimental solution was continuously bubbled with ultra-pure N$_2$, which had been passed through an in-line trap (Supelco, Bellafonte, PA) that removed all traces of CO$_2$. The pH of the experimental solution was expressed on the free hydrogen ion concentration scale. It was monitored regularly by comparison with the pH standard, using a Ross-type combination pH electrode (No. 810200) connected to a Corning 130 pH meter in the absolute millivolt mode. Linearity and Nernstian behavior of the electrode were verified by titrating a 0.3 M NaCl solution with concentrated HCl.
After an equilibration period of at most 24 hours, a sample was taken at the initial solution conditions (pH 2, no YREE sorption) to determine the total YREE concentrations, \( M_T \), for calculation of the distribution coefficients, \( iK_S \). Precipitation of hydroxides was subsequently initiated by raising the pH of the experimental solution to about 6.0 with careful additions of 1 M NH\(_4\)OH from a Gilmont micro-dispenser. The onset of precipitation was often accompanied by the appearance of finely dispersed solids in the solution and by slow fluctuations in the pH. Once a pH of about 6.0 was established, samples were taken with a pipette at fixed time intervals, increasing from minutes to hours to days. Two separate samples were taken each time. One sample was filtered from a polypropylene syringe through a Nuclepore filter membrane (polycarbonate, 0.10 µm pore size) mounted in a polypropylene filter holder. Five mL were used to rinse the syringe and membrane, and discarded. The next 5 mL were collected in a polypropylene centrifuge tube. The second sample was centrifuged at about 4,000 rpm for one hour in a Centra-4B centrifuge (International Equipment Company, Needham Heights, MA). In every experiment, except the one with Fe(III), the concentration of the trivalent metal was increased to 1 mM after the first set of samples had been withdrawn. The pH was then readjusted to 6.0 to induce further precipitation of hydroxides and a second set of samples was collected. Experiments with 100 µM In, Al, and Ga, did not always produce a visible precipitate, although YREE sorption was observed. The experiments with 1 mM of these metals resulted in stronger YREE sorption and more precise \( iK_S \) data. Higher concentrations of Fe(III) were not required because \( \log iK_{Fe} \) is substantially larger than \( \log iK_S \) values for In, Al, and Ga. As a consequence, YREE sorption can be observed at lower substrate concentrations using Fe than is the case for In, Al, and Ga.

The filtered samples and the supernatant of the centrifuged samples were diluted 5-fold with 1% HNO\(_3\), and a small amount of internal standard solution containing equal amounts of In, Cs, and Re was added. For the In experiment, the In of the internal standard was replaced with Rh. The resulting mixtures were analyzed for YREE with an Agilent Technologies 4500 Series 200 inductively-coupled plasma mass spectrometer (ICP-MS). Solutions were introduced into the ICP-MS with a Babington-type PEEK
nebulizer and a double-pass (Scott-type) quartz spraychamber, Peltier-cooled to T = 2°C. During instrument tuning, the formation of oxide and double-charged ions was minimized with a 10 ppb Ce solution. MO⁺ and M²⁺ peaks were always less than 1% and 3% of the corresponding M⁺ peak, respectively, and correction for this effect proved unnecessary. YREE concentrations were calculated from linear regressions of four standards (0.5, 1, 2, and 5 ppb). A 1% HNO₃ solution was run before and after the calibration line, to serve as a blank and to rinse the instrument after the highest standard. In addition, after each autosampler position, Milli-Q water was aspirated for 10 s followed by a 1% HNO₃ wash solution for 30 s, to rinse the outside of the autosampler probe and the sample introduction system. All standards and solutions were injected in triplicate. Ion counts were corrected for minor instrument drift by normalizing ⁸⁹Y to ¹¹⁵In (or ¹⁰⁵Rh), ¹³⁹La–¹⁶¹Dy to ¹³³Cs, and ¹⁶³Dy–¹⁷⁵Lu to ¹⁸⁷Re. The HP ChemStation software does not allow a mass-dependent correction by interpolation between internal standards, yet a constant check on the validity of the drift correction was performed by comparing the Dy concentrations calculated from ¹⁶¹Dy and ¹⁶³Dy, which were usually equal to within 2%. Blanks were generally below the instrument quantitation limit (0.01 ppb).

Scandium concentrations were measured in samples from the Sc experiment, after an additional 10- or 100-fold dilution, to verify that precipitation had occurred, because no visible solids were observed at any time and no YREE sorption could be detected. Since a suitable internal standard for Sc had not been added to the samples, Sc concentrations were determined with a semi-quantitative ICP-MS method, using a solution containing 100 ppb each of Be, Mg, Co, In, Bi, and U as a reference. To correct for any difference in matrix between the samples and the reference, the sample response curve was normalized to the concentrations of the internal standards (0.25 or 2.5 ppb In, Cs, and Re). The accuracy of this semi-quantitative method is approximately 10%.

Distribution coefficients were calculated using equation (2.5) and [M³⁺] = Mₜ, which is a valid approximation, since the concentration of solution species other than [M³⁺] was generally negligible ([MOH²⁺]/[M³⁺] ≲ 0.03; [M³⁺]/Mₜ ≳ 0.97) for our experimental conditions (pH ~ 6). The concentration of surface ligands [Sₜ] was set equal to the molar
concentration of precipitated metal (100 µM for Fe(III) and 1 mM for Al, Ga, and In). The concentration of sorbed YREE, \([\text{MS}_i]\), was calculated as the difference of the total initial concentration of each YREE measured at pH 2 and the concentration of each YREE in the filtrates at pH ~ 6.0.

**2.4 Results and Discussion**

**2.4.1 Comparative \(\log iK_S\) Results**

The \(iK_S\) results obtained with freshly precipitated Fe(III), Al, Ga, and In hydroxides are shown in Figure 2.2. In the Sc experiments, no YREE sorption could be detected at all, even though measurement of the dissolved Sc concentration confirmed that precipitation of Sc hydroxides was complete within a few hours.

**Figure 2.2.** \(\log iK_S\) results from filtered samples. (A) 100 µM Fe(OH)₃ (Table B.2). (B) 1 mM In(OH)₃ (Table A.3). (C) 1 mM Al(OH)₃ (Table A.1). (D) 1 mM Ga(OH)₃ (Table A.2).
Distribution coefficient patterns are highly consistent over periods of time between 15 minutes and as much as 141 hours. Solution pH in the Fe(III) and In experiments varied within a range of 0.1 pH units and only small changes were observed in the absolute magnitudes of log \( \log K_S \). In contrast, pH varied over a range of approximately 0.36 in the Al experiment and 0.88 in the Ga experiment, and large changes in log \( \log K_S \) were observed. A plot of log \( \log K_S \) vs. pH for the Al experiment indicated that the influence of pH on log \( \log K_S \) was well described by the equation:

\[
\log K_S(A) = \log K_S(B) + Q \times (pH_A - pH_B).
\]

where \( Q \) is a constant. For comparison with the Fe(III) and In experiments, observations of log \( \log K_S(B) \) and pH\( B \) from the Al and Ga experiments were used to predict log \( \log K_S(A) \) values corresponding to pH\( A = 6.10 \). This was done with the Microsoft® Excel routine Solver by changing \( Q \) to minimize the following sum of squares:

\[
\sum (\log K_S(B) + Q \times (6.10 - pH_B) - \log K_S(A))^2,
\]

where \( \log K_S \) indicates an average and the summation is over all patterns and all elements (YREEs). For Ga, the pattern at low pH (5.47) was discordant and therefore excluded. Best agreements were obtained with \( Q = 1.66 \) for Al and \( Q = 2.79 \) for Ga (Figure 2.3). Figure 2.3B shows a range in log \( \log K_Ga \) on the order of 0.2. Table 2.1 provides averaged log \( \log K_S \) results for the data shown in Figures 2.2A,B and 2.3.

The nearly constant magnitudes of log \( \log K_Fe \) and log \( \log K_In \), as well as log \( \log K_{Al} \) corrected to constant pH, suggest that transformation from amorphous to more crystalline solids was a very slow process. Larger variations in log \( \log K_{Ga} \) could be indicative of significant changes in the crystallinity or hydration state of the Ga(OH)\(_3\). However, since the log \( \log K_{Ga} \) variations shown in Figure 2.3B are small with no consistent trend through time (uppermost to lowest log \( \log K_{Ga} \) results were obtained at 90 minutes, 44 hours, 15 minutes, 5 hours, and 24 hours), it is possible that the observed variability is caused by a variety of factors.
Figure 2.3. log \( iK_S \) results normalized to pH 6.10. (A) 1 mM Al(OH)\(_3\). (B) 1 mM Ga(OH)\(_3\). See text for details.
Table 2.1. Average log $\beta_S$ results for iron, aluminum, gallium, and indium (Figures 2.2A, 2.3A, 2.3B, and 2.2B, respectively). Results for Fe(III) and In did not vary significantly over the small range of experimental pH and were averaged. Results for Al and Ga showed a linear dependence on pH and were averaged after normalizing each measurement to pH 6.1 (see text). Uncertainties in pH and log $\beta_S$ values represent one standard deviation of the mean.

<table>
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<tr>
<th>$[\text{M}^{3+}]$</th>
<th>pH 6.12 ± 0.04</th>
<th>pH 6.10</th>
<th>pH 6.10</th>
<th>pH 6.08 ± 0.04</th>
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<td></td>
<td>log $\beta_{\text{Fe}}$</td>
<td>log $\beta_{\text{Al}}$</td>
<td>log $\beta_{\text{Ga}}$</td>
<td>log $\beta_{\text{In}}$</td>
</tr>
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<td>Y</td>
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</tr>
<tr>
<td>La</td>
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<tr>
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</tr>
<tr>
<td>Pr</td>
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<tr>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>3.32 ± 0.07</td>
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2.4.2. Linear Free-energy Relationships

In previous work, the sorptive characteristics of surfaces that coordinate with trace metals via O-donor groups have been assessed and modeled in terms of the characteristics of trace metal hydrolysis behavior (Huang and Stumm, 1973; Balistrieri et al., 1981; Schindler and Stumm, 1987). Applying this approach, sorption constants for a variety of trace metals have been estimated using equation (2.6) (Dzombak and Morel, 1990; Erel and Morgan, 1991) or simplified versions of equation (2.6) wherein $b = 0$ (Erel and Stolper, 1993). Equation (2.6) indicates that log $\beta_S$ patterns should resemble log $\beta_1$ patterns that are stretched or compressed with the factor “$a$”. The ability of
equation (2.6) to estimate YREE sorptive characteristics can be directly evaluated using the log $iK_S$ results in Table 2.1 and YREE hydroxide stability constants of Klungness and Byrne (2000). The log $\log_{OH}\beta_1$ data shown in Figure 2.4 were selected for this analysis, because they are based on very coherent results obtained with both spectrophotometric and potentiometric techniques. Problems with older values in the literature were discussed by Klungness and Byrne (2000). The regressions of log $iK_S$ (Table 2.1) vs. log $\log_{OH}\beta_1$ (Figure 2.4), shown in Figure 2.5, reveal that the YREE sorptive behaviors of Al, Ga, and In hydroxide precipitates are very well modeled in terms of YREE hydrolysis behavior. The log $iK_Fe$ data, however, are poorly described in terms of YREE hydrolysis. Thus, the comparative affinities of YREEs toward at least one abundant, naturally occurring substrate is poorly predicted using the linear free-energy approach of equation (2.6).

![Figure 2.4. Stability constants for YREE complexes with hydroxide (Klungness and Byrne, 2000) and fluoride (Luo and Byrne, 2000), for the conditions of our experiments ($T = 25^\circ C; I = 0.014 M$). Horizontal dotted lines were drawn through Y to emphasize its position with respect to the REE.](image-url)
The results in Figure 2.5 suggest that relationships between YREE solution chemistries and surface chemistries can vary significantly in complexity. An appropriate model for YREE sorption on Fe(III) hydroxides must include factors that are not tightly coupled to YREE hydrolysis. As we will demonstrate in Section 2.4.3, some aspects of the log $K_S$ behavior shown in Figure 2.2 more closely resemble fluoride stability constant data (Schijf and Byrne, 1999; Luo and Byrne, 2000), than the hydrolysis data (Figure 2.4). This is particularly true for heavy rare earth element (HREE) sorption on In and Fe(III) hydroxides.

![Figure 2.5. Linear free-energy relationships between the log $K_S$ results from this work and log $\text{OH}^\beta_1$ data from Klungness and Byrne (2000). (A) 100 $\mu$M Fe(OH)$_3$. (B) 1 mM In(OH)$_3$. (C) 1 mM Al(OH)$_3$. (D) 1 mM Ga(OH)$_3$. Dotted lines represent 95% confidence intervals.](image-url)
2.4.3. Inter-element Patterns in YREE Solution Complexation and Surface Complexation

Patterns of YREE solution complexation data can be qualitatively described in terms of at least two components. One component is the overall intensity of complexation. Ligands such as hydroxide exhibit large complexation constants (log \( \beta_{1\text{Gd}} \) ~ 6) and, consequently, there is often a similarly large change in stability constants for such ligands across the YREE series (\( \Delta_{\text{OH}} \beta_{1} \sim 1.5 \)). Another example is NTA (log \( \beta_{1\text{Gd}} \) ~ 13), with a range of stability constants between La and Lu that spans more than two orders of magnitude (Li and Byrne, 1997). A second component of YREE equilibrium constant behavior is embodied in the complex inter-element sequence of YREE fluoride stability constants in solution (Schijf and Byrne, 1999; Luo and Byrne, 2000). This sequence, easily visible in Figure 2.4 (lower pattern), is less discernable for YREE hydroxide stability constants (Figure 2.4, upper pattern). YREE fluoride stability constants are relatively small (log \( \beta_{1\text{Gd}} \) ~ 3) and increase relatively little across the YREE series (\( \Delta_{f} \beta_{1} \sim 0.6 \)) hence the inflections are more prominent.

The surface complexation constant patterns seen in Figures 2.2 and 2.3 can be compared and contrasted with patterns of solution complexation constants. As is the case for complexation constants (log \( i\beta_{n} \) appropriate to a variety of solution ligands (L_i)), the relative magnitudes of log \( iK_{S} \) data between La and Lu vary substantially for different types of surfaces. The difference between log \( iK_{S} \) values for La and Lu (\( \Delta \text{log } iK_{S} \)) is as small as 0.8 for Fe(III) hydroxide precipitates and as large as 1.7 in the case of Al hydroxide precipitates. In contrast to the general correspondence between log \( i\beta_{n} \) and \( \Delta \text{log } i\beta_{n} \) observed for solution complexation, \( \Delta \text{log } iK_{S} \) is not tightly coupled to the overall magnitudes of the log \( iK_{S} \) data for each solid substrate. In the case of Fe(III), log \( iK_{Fe\text{Gd}} \) ~ 4.0 and \( \Delta \text{log } iK_{Fe} \sim 0.8 \), while for Al, log \( iK_{Al\text{Gd}} \) ~ 2.7 and \( \Delta \text{log } iK_{Al} \sim 1.7 \). Also, in contrast to the general case for solution complexation, the sequence of inflections in log \( iK_{S} \) data is clearly discernable not only when \( \Delta \text{log } iK_{S} \) is small (Figure 2.2A) but also, in some cases (Figure 2.2B), when \( \Delta \text{log } iK_{S} \) is comparatively large (\( \Delta \text{log } iK_{In} \sim 1.5 \)). It appears that some generalities appropriate to comparative YREE solution complexation behavior are not applicable to comparative observations of log \( iK_{S} \).
The linear free-energy relationships shown in Figure 2.5 demonstrate that, in some cases, YREE surface chemistries are tightly correlated with YREE hydrolysis behavior. As a means of highlighting certain similarities in the characteristics of log $iK_S$ data (Figures 2.2A,B and 2.3) and log $f\beta_1$ characteristics (Figure 2.4), Figure 2.6 shows $iK_S/f\beta_1$ ratios plotted against YREE identity (atomic number). The relatively smooth plots of log ($iK_S/f\beta_1$) vs. YREE atomic number in Figure 2.6 lack the “patterns-of-four” or “tetrad” effects (Monecke et al., 2002, and references therein) that are seen in Figures 2.2–2.4. They are absent in Figure 2.6 because tetrad effects are present to a similar extent in the surface complexation term, log $iK_S$, and the solution complexation term, log $f\beta_1$. A measure of the smoothness of the patterns in Figures 2.2, 2.3, and 2.6 can be obtained by calculating the anomalies of the last three “triads” (Eu–Gd–Tb, Dy–Ho–Er,

Figure 2.6. Ratio of $iK_S$ (this work) and $f\beta_1$ (Luo and Byrne, 2000), shown as log ($iK_S/f\beta_1$). (A) 100 $\mu$M Fe(OH)$_3$. (B) 1 mM In(OH)$_3$. (C) 1 mM Al(OH)$_3$. (D) 1 mM Ga(OH)$_3$. 

35
and Tm–Yb–Lu), where the anomaly of the triad Eu–Gd–Tb is defined as 
\[ \log \left[ 2 \times \frac{iKS(Gd)}{iKS(Eu) + iKS(Tb)} \right] \] and so forth. A “smoothness index” can then be determined by summing the squares of these three anomalies for each pattern, with a smaller index signifying a smoother pattern. Smoothness indices for the \( i_{KS} \) patterns in Figures 2.2A,B and 2.3 decrease in the order In \( \gg \) Fe \( \approx \) Al \( \approx \) Ga. Smoothness indices for the \( f\beta_1 \)-normalized patterns in Figure 2.6 are 3-8 times smaller than the indices calculated for Figures 2.2A,B and 2.3. This demonstrates that \( i_{KS} \) patterns for all four solid substrates share features of the \( f\beta_1 \) pattern (for elements heavier than Sm), but more so for In and Fe(III) than for Al and Ga.

By combining equations (2.3) and (2.5) it can be shown that the ratio \( \log \left( \frac{i_{KS}}{f\beta_1} \right) \) is equal, within a constant, to \( \log \left( \frac{[MS_i]}{[MF^{2+}]} \right) \). In other words, the patterns in Figure 2.6 are identical to the \( i_{KS} \) patterns that would be observed if MF\(^{2+} \) were the dominant YREE solution species. Since free YREE ions are rarely the dominant species in natural waters, this analysis implies that the extent to which tetrad effects are observable in the aqueous environment can be diminished, or even entirely obscured, when dissolved YREE concentrations are controlled by opposing sorption/complexation equilibria. It is likely that the inflections that are easily visible in Figures 2.2 and 2.3 are obscured in the aqueous environment when dissolved YREE concentrations are controlled by competitive solution and surface complexation.

2.4.4. Oceanic log \( i_{KS} \) Patterns

YREE concentrations in seawater have evolved at least in large part through opposing equilibria in which particle surfaces coordinate M\(^{3+} \) ions (surface complexation) and solution ligands (e.g., CO\(_3^{2-} \)) strongly associate with M\(^{3+} \) ions (solution complexation). Equations (2.1) through (2.5) prescribe the use of observed shale-normalized YREE concentrations and characterizations of YREE solution chemistry to model the average YREE surface complexation characteristics (i.e., log \( i_{KS} \) characteristics) of marine particles. Byrne and Sholkovitz (1996) modeled the surface chemistries of marine particulate matter using solution complexation data that involved direct measurements of
carbonate complexation for five elements (Ce, Eu, Gd, Tb, Yb) and linear free-energy relationships to model the remaining elements. It is currently possible to obtain calculations of YREE solution complexation using directly measured carbonate, hydroxide, sulfate, chloride, and fluoride association constants for all YREEs (Liu and Byrne, 1998; Schijf and Byrne, 1999, 2004; Klungness and Byrne, 2000; Luo and Byrne, 2000, 2001, 2004). Figure 2.7C shows calculated log \( iK_S \) results that were obtained using (i) the shale-normalized YREE distributions obtained by Zhang and Nozaki (1996) (Figure 2.7A) and (ii) the above-referenced solution complexation constants for all YREEs (Figure 2.7B). Very similar results are obtained using published seawater YREE patterns for different oceanic regions.

The log \( iK_S \) results displayed in Figure 2.7C show a strong resemblance to the distribution coefficient data obtained for Fe(III) (Figure 2.2A). This is very clearly demonstrated in Figure 2.8 where the seawater patterns for the three depths are individually compared with the log \( iK_{Fe} \) pattern of Figure 2.2A. A constant, calculated with the same sum-of-squares optimization technique described above (equation (2.8)), was added to each seawater pattern to maximize the degree of overlap. The agreement is most striking for the deepest sample (Figure 2.8C). These results indicate that the YREE sorption characteristics of natural marine particles (corrected for solution complexation) are remarkably similar to those of Fe(III) hydroxides. It can also be seen that the correspondence between Figures 2.7C and 2.2A is better, in some respects, than the relationship between Figure 2.7C and the data of Bau (1999) (Figure 2.1B). The log \( iK_{Fe} \) data reported by Bau (1999) for the middle rare earth elements (MREEs i.e., Sm and Eu) are larger than distribution coefficients obtained for the HREEs. In contrast, in Figures 2.1A, 2.2A, and 2.7C, the log \( iK_S \) data for the MREEs are quite similar to the log \( iK_S \) data for Yb and Lu. This is discussed further in Sections 2.4.5 and 2.4.7.
Figure 2.7. (A) Directly measured YREE concentrations in seawater at three depths (Zhang and Nozaki, 1996), normalized to Post-Archean Australian Shale (PAAS) (McLennan, 1989). (B) The calculated solution complexation term from equation (2.2) at pH 7.6, 7.9, and 8.2 with a bicarbonate concentration of $2 \times 10^{-3}$ M. (C) Predicted log $i K_S$ values, calculated by subtracting each of the curves in Figure 2.7A from the curve for pH 7.9 in Figure 2.7B.
Figure 2.8. Comparison between the log \( i_{Fe} \) values from this work and log \( i_{KS} \) values for the three seawater samples from Figure 2.7C. A different constant was added to each of the seawater patterns. These constants were optimized to attain maximum overlap for each pair of patterns (see text).
Figure 2.9. Comparison between the log $i_{K_{Fe}}$ values from this work at pH 6.12, Bau (1999) at pH 5.97 (A), and Ohta and Kawabe (2000, 2001) at pH 6.01 (B). A different constant was added to the results of Bau (1999) and to those of Ohta and Kawabe (2000, 2001). These constants were optimized to attain maximum overlap for each pair of patterns (see text).

2.4.5. Comparative log $i_{K_{Fe}}$ Data Obtained for Freshly Precipitated Fe(III) Hydroxides

Figure 2.9 shows direct comparisons between the log $i_{K_{Fe}}$ results obtained in this work (Table 2.1), and the results of Bau (1999) and Ohta and Kawabe (2000, 2001). The log $i_{K_{Fe}}$ results shown in Figure 2.9 were collected between pH 5.9 and 6.1. The results obtained in the present work are in particularly good agreement with the data of Ohta and Kawabe (2000, 2001). While noting that the results for all three studies have been brought into agreement with the same optimization technique used for the comparisons in
Figure 2.8, it is seen that our results for the MREEs are closer to those of Ohta and Kawabe (2000, 2001) than to the results of Bau (1999).

In addition to the contrasting log $K_{Fe}$ characteristics shown in Figure 2.9, it should be noted that the log $K_{Fe}$ pattern obtained by Bau (1999) is substantially pH dependent. At pH values below about 4.5, the log $K_{Fe}$ patterns observed by Bau (1999) were relatively flat and positive Ce anomalies were observed. The appearance of Ce anomalies is in itself quite counterintuitive. It is well established that abiotic Ce oxidation occurs primarily in the presence of Mn oxide surfaces and Ce anomalies are generally not observed for YREE sorption onto ferric oxyhydroxides (Koeppenkastrop and De Carlo, 1992; De Carlo et al., 1998; Ohta and Kawabe, 2001). Moreover, de Baar et al. (1988) and De Carlo et al. (1998) have both argued that abiotic Ce oxidation should be strongly suppressed at low pH. Ohta and Kawabe (2000, 2001) observed no changes in their patterns of log $K_{Fe}$ data over a pH range between approximately 5.6 and 6.6. The very small Ce anomalies in their patterns show no systematic behavior as a function of pH and may be due to a minor analytical artifact.

2.4.6. Comparative log $K_S$ Behavior of Yttrium and the Rare Earth Elements

The position of Y among the REEs is an important aspect of the data summarized in Table 2.1. The value of $K_{Fe}$ for Y falls between La and Ce (Figure 2.2A). In the remaining experiments, Y is positioned between Pr and Nd (Figure 2.3B, Ga), between Nd and Sm (Figure 2.2B, In), and near Eu (Figure 2.3A, Al). This itinerant behavior of Y among the REEs has been ascribed to the enhanced covalency of REEs relative to Y (Siekierski, 1981), and may involve delocalization of electrons in lanthanide 4f orbitals (Borkowski and Siekierski, 1992).

In ionic interactions, Y behaves as a heavy REE. For example, in the case of complexation by fluoride, whose interactions are exceptionally ionic (Martell and Hancock, 1996), Y acts as a super-heavy REE with a $f\beta_1$ formation constant exceeding that of any REE (Figure 2.4). In interactions with more covalent ligands, the complexation constants of REEs are covalently enhanced relative to Y, and Y acts as a comparatively light REE. As such, the results in Figures 2.2 and 2.3 indicate that YREE
interactions with Fe(III) hydroxides are comparatively covalent and interactions with Al hydroxides are comparatively ionic.

Shale-normalized Y concentrations in seawater are higher than those of any REE (Figure 2.7A). This behavior would be predicted if interactions of YREEs with marine particles are relatively covalent (weaker Y sorption, Figure 2.7C) and solution complexation is comparatively ionic (stronger Y complexation, Figure 2.7B). Inspection of Figures 2.2A and 2.7C indicates that Fe(III) hydroxides exhibit affinities for both Y and the REEs that closely resemble the modeled scavenging behaviors of natural particulate matter in the oceans.

2.4.7. Critical Issues in YREE Surface Complexation Behavior

Given that ferric oxyhydroxides are demonstrably important natural substrates for YREE scavenging in some, if not most, aqueous environments (Sholkovitz, 1976; Sholkovitz and Elderfield, 1988; Schijf et al., 1994; Johannesson and Lyons, 1995; Johannesson and Zhou, 1999; De Carlo et al., 2000), it is important that log $iK_S$ values are accurately characterized for such phases. In this regard, it has been noted above that there is significant disagreement in the log $iK_S$ characterizations of Bau (1999), on the one hand, and the results of Ohta and Kawabe (2000, 2001) and the present work, on the other. More importantly, however, the work of Bau (1999) indicated that the log $iK_{Fe}$ pattern obtained for YREE sorption on ferric oxyhydroxides is substantially pH dependent. This result is in contrast with the observations of Ohta and Kawabe (2000, 2001) where such variations were not discernable over a pH range between approximately 5.6 and 6.6. This issue deserves careful investigation. If log $iK_S$ patterns, such as those in Table 2.1, are invariant over a wide range of pH, then log $iK_S$ data might be regarded in much the same manner as conditional solution complexation constants. Like solution complexation constants, the log $iK_S$ data in Table 2.1 are expected to vary with temperature, pressure and ionic strength. However, in the same manner that YREE formation constant patterns are largely unaffected by medium composition (e.g., ionic strength), log $iK_S$ patterns of YREEs might also exhibit medium-composition invariance. In this case the absolute magnitudes of YREE associations with surfaces would, of
course, be dependent on solution pH and composition, but relative YREE affinities for particle surfaces (the shape of the log $iK_S$ patterns) would be independent of solution chemistry. The existence of such a simplifying characteristic would be quite important to models of YREE environmental chemistry.
3. Sorption of Yttrium and Rare Earth Elements by Amorphous Ferric Hydroxide: Influence of pH and Ionic Strength


3.1 Abstract

The sorption of yttrium and the rare earth elements (YREEs) by amorphous ferric hydroxide at low ionic strength (0.01 M \( \leq I \leq 0.09 \) M) was investigated over a wide range of pH (3.9 \( \leq \) pH \( \leq \) 7.1). YREE distribution coefficients, defined as 

\[
iK_{Fe} = \frac{[MS_i]_T}{M_T[Fe^{3+}]_S},
\]

where [MS\(_i\)]\(_T\) is the concentration of YREE sorbed by the precipitate, \(M_T\) is the total YREE concentration in solution, and \([Fe^{3+}]_S\) is the concentration of precipitated iron, are weakly dependent on ionic strength but strongly dependent on pH. For each YREE, the pH dependence of \(\log iK_{Fe}\) is highly linear over the investigated pH range. The slopes of \(\log iK_{Fe}\) versus pH regressions range between 1.43 \(\pm\) 0.04 for La and 1.55 \(\pm\) 0.03 for Lu. Distribution coefficients are well described by an equation of the form 

\[
iK_{Fe} = \frac{s\beta_1[H^+]^{-1} + s\beta_2[H^+]^{-2}}{sK_1[H^+] + 1},
\]

where \(s\beta_n\) are stability constants for YREE sorption by surface hydroxyl groups and \(sK_1\) is a ferric hydroxide surface protonation constant. Best-fit estimates of \(s\beta_n\) for each YREE were obtained with \(\log sK_1 = 4.76\). Distribution coefficient predictions, using this two-site surface complexation model, accurately describe the \(\log iK_{Fe}\) patterns obtained in the present study, as well as distribution coefficient patterns obtained in previous studies at near-neutral pH. Modeled \(\log iK_{Fe}\) results were used to predict YREE sorption patterns appropriate to the open ocean by accounting for YREE solution complexation with the major inorganic YREE ligands in seawater. The predicted \(\log iK'_{Fe}\) pattern for seawater, while distinctly
different from $\log \chi_{K_F}$ observations in synthetic solutions at low ionic strength, is in good agreement with results for natural seawater obtained by others.

3.2 Introduction

Distributions of yttrium and the rare earth elements (YREEs) in natural waters have been intensively investigated for more than 40 years (Goldberg et al., 1963; Høgdahl et al., 1968; Kolesov et al., 1975). The absolute and relative concentrations of the 15 stable YREEs have been determined in a variety of open ocean environments (e.g., de Baar et al., 1985a; German et al., 1995; Zhang and Nozaki, 1996; Nozaki and Alibo, 2003); estuaries (e.g., Sholkovitz and Elderfield, 1988; Sholkovitz et al., 1992; Sholkovitz, 1993, 1995); rivers (e.g., Goldstein and Jacobsen, 1988; Sholkovitz, 1993; Zhang et al., 1998; Nozaki et al., 2000); lakes (e.g., Johannesson and Lyons, 1994; Johannesson et al., 1994; De Carlo and Green, 2002); ground waters (e.g., Smedley, 1991; Johannesson et al., 1996, 1997; Duncan and Shaw, 2003); hydrothermal fluids (e.g., Klinkhammer et al., 1983, 1994; Michard, 1989; Bau and Dulski, 1999); and pore waters (e.g., Elderfield and Sholkovitz, 1987; Sholkovitz et al., 1989; Haley et al., 2004). It is generally recognized that YREE distributions in natural waters are largely controlled by the interplay of YREE surface and solution chemistries. Quantitative investigations of YREE interactions with particle surfaces were preceded by decades of work describing the complexation of hydrated trivalent YREE cations with a variety of common inorganic anions, including carbonate, hydroxide, sulfate, fluoride, and chloride (see for instance Wood, 1990; Byrne and Sholkovitz, 1996, for references). As a result, YREE interactions with major solution ligands are much better characterized than YREE interactions with particle surfaces. In order to enable descriptions, and accurate predictions, of YREE behavior in terms of key environmental variables, such as pH and ionic strength, it is essential that YREE surface chemistry is modeled as quantitatively as YREE solution complexation. Toward this goal, investigations are increasingly being undertaken to examine the equilibrium distribution of YREEs between solutions and relevant mineral surfaces (Byrne and Kim, 1990; De Carlo et al., 1998; Bau, 1999; Ohta and Kawabe, 2000, 2001; Quinn et al., 2004).
In modeling studies, Lee and Byrne (1993) and Byrne and Sholkovitz (1996) combined a quantitative model of seawater YREE speciation with measurements of seawater YREE concentrations to estimate the comparative, average affinities of YREEs for particle surfaces in the ocean. The resultant sorption pattern, expressed in terms of free ion concentrations (Byrne and Sholkovitz, 1996), could not be compared with any directly measured distribution coefficients at the time: while an early investigation of YREE interactions with mineral surfaces (Koeppenkastrerop and De Carlo, 1992) had examined YREE distributions between Fe and Mn oxides and seawater, these authors presented their results only in graphical form. The groundbreaking work of Koeppenkastrerop and De Carlo (1992) showed that, for REE sorption by Fe and Mn oxides, light rare earth elements (LREEs) are preferentially removed from seawater compared to heavy rare earth elements (HREEs). As their seawater experiments were performed at a single pH (viz., pH = 7.8), the influence of pH on YREE sorption by the minerals in seawater was not revealed. However, more recent investigations in synthetic solutions (De Carlo et al., 1998), demonstrated the profound effect of pH on the extent of REE sorption by ferric hydroxides. Marmier and Fromage (1999) showed that, at low loading, the influence of pH on La sorption by hematite could be modeled satisfactorily with a non-coulombic surface complexation model (SCM). The experiments of Bau (1999) extended the work of De Carlo et al. (1998) to include Y, and although his sorption data, in contrast to Marmier and Fromage (1999), were not used to derive a SCM, it was shown that not only the absolute magnitudes, but also the relative magnitudes of YREE sorption (i.e., the distribution coefficient pattern) vary with pH. Quinn et al. (2004) noted, for the first time, that the distribution coefficient patterns obtained at near-neutral pH by Bau (1999), and subsequently by Ohta and Kawabe (2000, 2001), closely resemble the modeled distribution coefficient patterns of Byrne and Sholkovitz (1996), which are appropriate to marine particles. Quinn et al. (2004) also showed that the distribution coefficient pattern for YREE sorption by amorphous ferric hydroxide is quite distinct from patterns observed for YREE sorption by other trivalent amorphous hydroxides (aluminum, gallium, and indium).
Whereas the most frequently utilized substrate for investigation of YREE sorption appears to be amorphous ferric hydroxide, to date use of this substrate has included only a few investigations (De Carlo et al., 1998; Bau, 1999; Ohta and Kawabe, 2000, 2001; Quinn et al., 2004). In these studies, YREE sorption by amorphous ferric hydroxide was measured over a range of pH (3.5 – 9.0) but the magnitudes of estimated distribution coefficients for individual YREEs, at constant pH, differ by as much as a factor of 400. Distribution coefficients have been obtained at ionic strengths close to or equal to that of seawater (De Carlo et al., 1998; Ohta and Kawabe, 2000, 2001) and at very low ionic strengths (De Carlo et al., 1998; Bau, 1999; Quinn et al., 2004). Although the pH dependence of YREE sorption by amorphous ferric hydroxide was modeled quantitatively by Ohta and Kawabe (2000, 2001), their data were obtained at high substrate loading (i.e., high $\Sigma$ [YREE]/[Fe$^{3+}$]$_T$ ratios) within a small pH range (approximately one unit). In the present work, we have produced a quantitative model of YREE sorption at low substrate loadings (similar to those used by Bau, 1999), based on data obtained over an ionic strength range of 0.01 – 0.09 M and a relatively wide pH range of 3.9 – 7.1. We use this model to assess the nature and the importance of YREE sorption by amorphous ferric hydroxides in the open ocean.

3.3 Materials and Methods

3.3.1. Materials and Preparation of the Experimental Solutions

A class-100 clean air laboratory or laminar flow bench was utilized for all chemical manipulations. Teflon and polypropylene laboratory materials and polycarbonate filter membranes were cleaned by soaking in HCl or HNO$_3$ for at least one week, followed by several thorough rinses with trace metal-clean water (Milli-Q water) from a Millipore (Bedford, MA) purification system. Solution pH, on the free hydrogen-ion concentration scale, was measured using a Ross-type combination pH electrode (No. 810200) connected to a Corning 130 pH meter in the absolute millivolt mode. Nernstian behavior of the electrode was verified periodically by titrating a 0.3 M NaCl solution with concentrated HCl. The electrode was calibrated daily during each experiment using an HCl standard solution.
Ammonium nitrate (99.999%), ammonium chloride (99.998%), and certified 1.000 M hydrochloric acid were purchased from Sigma-Aldrich (St. Louis, MO). TraceMetal Grade nitric acid, TraceMetal Grade ammonium hydroxide, and ferric chloride solution (40 ± 3% w/v in HCl) were purchased from Fisher Scientific (Pittsburgh, PA). A YREE stock solution, containing 66.7 ppm of each YREE in 2% HNO₃, was prepared from single-element ICP standards (SPEX Certi Prep, Metuchen, NJ). All solutions were prepared with Milli-Q water.

At the start of each experiment, an experimental solution and a pH standard solution were prepared in Teflon wide-mouth bottles. The experimental solution consisted of 23.3 ppb of each YREE (total combined YREE concentration 2.36 µM) and 0.10 – 10 mM iron in 0.01 M HCl. The concentration of iron utilized depended on the desired experimental pH and was varied in order to obtain adequate YREE sorption. The pH standard solution consisted of 0.001 M HCl (pH 3.0) in 0.01 M NH₄NO₃. For all solutions containing ≤ 0.62 mM iron, the ionic strength was initially 0.011 ± 0.001 M. The experimental solution containing 10 mM iron had an ionic strength equal to 0.043 M. All solutions were equilibrated in a jacketed beaker, thermostated at T = (25.0 ± 0.1)°C, and continuously stirred with a Teflon-coated ‘floating’ stir bar. The experimental solution was bubbled throughout with ultra-pure N₂, which had been passed through an in-line trap (Supelco, Bellafonte, PA) that removed all traces of CO₂.

3.3.2. pH Dependence of YREE Sorption

Six experiments were performed to study the pH dependence of YREE sorption by amorphous ferric hydroxide precipitates. After the experimental solution had equilibrated for approximately 24 hours, a sample was taken at the initial solution conditions (pH 2; no YREE sorption) to determine total YREE concentrations, Mᵢ. The pH of the experimental solution was then increased by addition of 1 M NH₄OH from a Gilmont micro-dispenser, initiating precipitation of a yellow-brown ferric hydroxide colloid. Once the pH stabilized, samples were taken with a pipette. Experiments were performed either at constant pH (~5, 6, or 7) with several samples taken at fixed times within a 2-day
period, or over a range of pH (3.9 – 5.6, or 5.1 – 7.0) with one or more samples taken at each half-unit pH increment.

3.3.3. Ionic Strength Dependence of YREE Sorption

Two experiments were performed to study the ionic strength dependence of YREE sorption by amorphous ferric hydroxide. Both experiments covered the ionic strength range 0.01 – 0.09 M, in 0.02 M increments. An initial sample (pH 2, I = 0.01 M; no YREE sorption) was taken after a 24-hour equilibration period. The pH of the experimental solution was then increased to approximately 6.0 by addition of 1 M NH₄OH. After sampling at these conditions (pH 6, I = 0.01 M), the ionic strengths of both the experimental solution and the pH standard were increased by addition of 5 M NH₄Cl. At each new ionic strength, the pH of the experimental solution was readjusted to 6.0 with 1 M NH₄OH. Several samples were taken after each pH readjustment. In the first experiment, four samples were taken at each ionic strength: one at 5 minutes, one at 4 hours, and two at either 90 minutes, 24 hours, or 48 hours. In the second experiment, two samples were taken at each ionic strength: one at 15 minutes and one at 60 minutes.

3.3.4. Sampling and Analysis

Two sampling techniques were used concurrently. One sample aliquot was filtered using a polypropylene syringe with a Nuclepore filter membrane (polycarbonate, 0.10 µm pore size) mounted in a polypropylene filter holder. The syringe and membrane were first rinsed with 5 mL of solution and then another 5 mL were collected in a polypropylene centrifuge tube. A second sample aliquot was centrifuged using a Centra-4B centrifuge (International Equipment Company, Needham Heights, MA) for one hour at about 4,000 rpm. A combination of these two techniques was used in the experiment with 10 mM iron, because the copious precipitate was difficult to filter directly: after centrifuging 5 mL of sample, 3.5 mL of the resulting supernatant was filtered (using ~1 mL as a rinse). Because filtration provided better separation of particles from solutions containing the lowest concentration of iron (0.10 mM), centrifugation was not used in every experiment.
The filtered samples and the supernatant of the centrifuged samples were diluted 5-fold with 1% HNO₃, and a small amount of internal standard solution containing equal amounts of In, Cs, and Re was added. The resulting mixtures were analyzed for YREEs with an Agilent Technologies 4500 Series 200 inductively-coupled plasma mass spectrometer (ICP-MS) following the procedure outlined in Quinn et al. (2004). In brief, all standards and sample solutions were injected in triplicate. During instrument tuning, the formation of oxide and double-charged ions was minimized with a 10 ppb Ce solution. MO⁺ and M²⁺ peaks were always less than 1% and 3% of the corresponding M⁺ peak, respectively, and correction for this effect proved unnecessary. YREE concentrations were calculated from linear regressions of four standards (0.5, 1, 2, and 5 ppb). Ion counts were corrected for minor instrument drift by normalizing ⁸⁹Y to ¹¹⁵In, ¹³⁹La–¹⁶¹Dy to ¹³³Cs, and ¹⁶³Dy–¹⁷⁵Lu to ¹⁸⁷Re. To check the validity of the drift correction, a comparison was made of the Dy concentrations calculated from ¹⁶¹Dy and ¹⁶³Dy, which were usually identical within 2%. Whenever this difference was significantly larger than 2%, a mass-dependent correction was performed by interpolating between the internal standards, ¹³³Cs and ¹⁸⁷Re, using Excel.

Raw data from each experiment were corrected by a dilution factor, which was based on the amount of NH₄OH added to increase the pH. Distribution coefficients were calculated from these corrected data using the following equation:

$$K_{Fe} = \frac{[MS_i]_T}{[M^{3+}]_T[S_i]} = \frac{[MS_i]_T}{M_T[Fe^{3+}]_S}, \quad (3.1)$$

where brackets denote the concentration of each indicated species. Over the range of experimental conditions employed in this work, the concentration of free YREE was set equal to the total dissolved YREE concentration ([M⁴⁺] = Mₜ). The concentration of sorptive solid substrate was set equal to the concentration of precipitated iron ([Sᵢ] = [Fe³⁺]ₛ), which was assumed to be equal to the initial dissolved Fe concentration. The concentration of sorbed YREE, [MSᵢ]ₜ, was calculated as the difference between the YREE concentration of the initial sample at pH 2 and the YREE concentration of the filtrate at each subsequent time after a pH or ionic strength adjustment.
3.4 Data Analysis

3.4.1. Modeling of pH and Ionic Strength Effects

Observed distribution coefficient data were initially modeled using an empirical equation wherein log $iK_{Fe}$ was presumed to have simple linear dependences on pH and ionic strength (I):

$$\log iK_{Fe} = Q_{pH} \times pH + Q_{I} \times I + \log iK_{Fe}(pH 0, I = 0).$$  \hspace{1cm} (3.2)

The slopes ($Q_{pH}$ and $Q_{I}$) and intercept ($\log iK_{Fe}(pH 0, I = 0)$) in equation (3.2) were determined by least squares analysis of the data given in Appendices B and C. $Q_{pH}$ and $\log iK_{Fe}(pH 0, I = 0)$ were determined from fits of $\log iK_{Fe}$ versus pH at constant ionic strength ($I \approx 0.011 \text{ M}$, Tables B.1–B.5; and $I = 0.043 \text{ M}$, Table B.6) using equation (3.2) written as:

$$Q_{I} = \log iK_{Fe}(pH 6.13, I = 0) - Q_{I} \times I - Q_{pH} \times pH + \log iK_{Fe}(pH 0, I = 0).$$  \hspace{1cm} (3.3a)

$Q_{I}$ was determined from log $iK_{Fe}$ versus ionic strength datasets at pH $\approx 6.13$ (Tables C.1 and C.2) using equation (3.2) written as:

$$Q_{pH} = \log iK_{Fe}(pH 6.13, I = 0) - Q_{I} \times I - Q_{pH} \times pH + \log iK_{Fe}(pH 0, I = 0).$$  \hspace{1cm} (3.3b)

After initially setting $Q_{I} = 0$ in equation (3.3a), iterations of equations (3.3a) and (3.3b) were performed until $Q_{pH}$ and $Q_{I}$ converged to constant values. Examination of equation (3.2) shows that $\log iK_{Fe}$ at $I = 0 \text{ M}$ and pH $6.13$ is larger than $\log iK_{Fe}$ at $I = 0 \text{ M}$ and pH $0$ by the additive term $Q_{pH} \times 6.13$ (i.e., $\log iK_{Fe}(pH 6.13, I = 0) = \log iK_{Fe}(pH 0, I = 0) + Q_{pH} \times 6.13$).

3.4.2. Surface Complexation Model

The surface complexation model (SCM) of Schindler and Stumm (1987) describes metal sorption onto hydroxide precipitates in terms of proton exchange with either one or two surface hydroxyl groups. The sorption reactions are written in the form:

$$S - \text{Fe(OH)}_{3} + M^{3+} \rightleftharpoons S - \text{FeO(OH)}_{2}M^{2+} + H^{+},$$  \hspace{1cm} (3.4)

$$S - \text{Fe(OH)}_{3} + M^{3+} \rightleftharpoons S - \text{FeO}_{2}(OH)M^{+} + 2H^{+},$$  \hspace{1cm} (3.5)

and
S – Fe$_2$(OH)$_6$ + M$^{3+}$ ⇌ S – Fe$_2$O$_2$(OH)$_4$M$^+$ + 2H$^+$, \hspace{1cm} (3.6)

where S– represents the bulk solid and M$^{3+}$ is a YREE ion. The total concentration of sorbed YREE can then be written as:

\[ [\text{MS}]_T = [S – \text{FeO(OH)}_2M^{2+}] + [S – \text{FeO}_2(\text{OH})M^+] + [S – \text{Fe}_2\text{O}_2(\text{OH})_4M^+] \]. \hspace{1cm} (3.7)

Since there is no means of differentiating reactions (3.5) and (3.6) in our experiments, the last term in equation (3.7) can be omitted. Surface complexation constants, $\beta_n$, for reactions (3.4) and (3.5) can be written in the form:

\[ s\beta_n = \frac{[S – \text{FeO}_n(\text{OH})_{3-n}M^{3-n}][H^+]^n}{M_T[S – \text{Fe(OH)}_3]}, \hspace{1cm} (3.8) \]

and then substituted into the first two terms of equation (3.7) to give:

\[ [\text{MS}]_T = M_T[S – \text{Fe(OH)}_3](s\beta_1[H^+]^{-1} + s\beta_2[H^+]^{-2}). \hspace{1cm} (3.9) \]

Equations (3.1) and (3.9) then yield an expression for $K_{Fe}$ in terms of surface complexation constants:

\[ K_{Fe} = (s\beta_1[H^+]^{-1} + s\beta_2[H^+]^{-2})[S – \text{Fe(OH)}_3]/[\text{Fe}^{3+}]_s. \hspace{1cm} (3.10) \]

The total concentration of iron in each experiment is equal to the sum of the dissolved and precipitated iron:

\[ [\text{Fe}^{3+}]_T = [\text{Fe}^{3+}]_D + [\text{Fe}^{3+}]_S, \hspace{1cm} (3.11) \]

where

\[ [\text{Fe}^{3+}]_D = [\text{Fe}^{3+}] + [\text{FeOH}^{2+}] + [\text{Fe(OH)}^+] + [\text{Fe(OH)}^0] \hspace{1cm} (3.12) \]

and

\[ [\text{Fe}^{3+}]_S = [S – \text{Fe(OH)}^0] + [S – \text{Fe(OH)}^+] + [S – \text{Fe(OH)}^2]. \hspace{1cm} (3.13) \]

Based on our experimental conditions ([Fe$^{3+}$]$_T$ ≥ 0.10 mM and pH ≥ 4.0), the concentration of dissolved iron is quite small compared to that of the precipitated iron, which supports the assumption that [Fe$^{3+}$]$_T$ = [Fe$^{3+}$]$_S$. Equation (3.13) partitions precipitated iron hydroxide among three types of charged surface sites. At lower pH values, the first term dominates so the surface is positively charged. Surface protonation at low pH is described by the following reaction:

\[ S – \text{Fe(OH)}^0 + H^+ \Leftrightarrow S – \text{Fe(OH)}^+ + H_2O, \hspace{1cm} (3.14) \]
with a stability constant defined by:

$$sK_1 = \frac{[S-Fe(OH)^{+}_3]}{[S-Fe(OH)^0][H^+]}. \quad (3.15)$$

At higher pH values, the third term in equation (3.13) dominates so the surface is negatively charged. The surface deprotonation reaction at high pH is written as:

$$S-Fe(OH)^{0}_3 + H_2O \rightleftharpoons S-Fe(OH)^{+}_4 + H^+, \quad (3.16)$$

with a stability constant defined by:

$$sK_2 = \frac{[S-Fe(OH)^{+}_4][H^+]}{[S-Fe(OH)^0]]}. \quad (3.17)$$

Combining equations (3.13), (3.15), and (3.17), gives:

$$[Fe^{3+}]_s = [S-Fe(OH)^{0}]_{s}(sK_1[H^+] + 1 + sK_2[H^+]^{-1}). \quad (3.18)$$

Since the pH was always less than 7.2 in our experiments and the pristine point-of-zero-charge is approximately 8.0 for amorphous ferric hydroxide (Dzombak and Morel, 1990, and references therein), it was assumed that $sK_2[H^+]^{-1} \ll 1$, hence the last term in equation (3.18) could be omitted. Using equations (3.10) and (3.18), the expression for $iK_Fe$ (equation (3.1)) is then written as:

$$iK_Fe = \frac{[MS]_I}{M_I[Fe^{3+}]_s} = \frac{s\beta_1[H^+]^{-1} + s\beta_2[H^+]^2}{sK_1[H^+] + 1}. \quad (3.19)$$

In contrast to equation (3.2), which is an empirical model, the SCM embodied in equation (3.19) provides a description of distribution coefficient results in terms of specific chemical equilibria. Since equation (3.19) expresses log $iK_Fe$ solely as a function of pH, log $iK_Fe$ data from experiments at constant ionic strength (I ~ 0.011 M, Tables B.1–B.5; I = 0.043 M, Table B.6) were used to determine the parameters in equation (3.19). In order to remove small variations in log $iK_Fe$ attributable to the ~0.032 M ionic strength difference in the datasets of Tables B.1–B.5 and Table B.6 ($\Delta \log iK_Fe \leq 0.03$), the QI results in Table 3.1, applied to the data in Tables B.1–B.6, were used to generate $iK_Fe$ data appropriate to I = 0.025 M, the average ionic strength of these datasets. SigmaPlot (Version 8.02) was then used to solve equation (3.19) for $s\beta_1$, $s\beta_2$, and $sK_1$ through minimization of the following residual sum of squares (RSS) function:
where the summation was performed over all pH values. Values of $sK_1$ for each YREE were obtained from equation (3.20), but since $sK_1$ is a property of the iron hydroxide, a single value needed to be determined for all YREEs. The average $sK_1$ value was therefore optimized by finding the minimum RSS over all pH values and all YREEs when $sK_1[H^+]$ was kept constant in equation (3.20). Best-fit estimates for $s\beta_1$ and $s\beta_2$ were obtained for each individual YREE from equation (3.20) using this optimized $sK_1$.

### 3.5 Results and Discussion

#### 3.5.1. Empirical Model of the log $iK_{Fe}$ Dependence on pH and Ionic Strength

Based on the data compiled in Tables B.1–B.6, which were obtained over a range of pH, and the data compiled in Tables C.1 and C.2, which were obtained over a range of ionic strength, distribution coefficients (log $iK_{Fe}$) were observed to exhibit a strong dependence on pH and a much weaker dependence on ionic strength. Four representative regressions for the final iteration of the pH data and the ionic strength data (i.e., using equations (3.3a) and (3.3b)) are shown in Figures 3.1 and 3.2. Based on these regressions for each YREE, the three coefficients of equation (3.2) ($Q_{pH}$, $Q_I$, and log $iK_{Fe}(pH=0, I=0)$) are summarized in Table 3.1 and are depicted graphically in Figure 3.3.

To examine the goodness-of-fit for the model, the ratios of predicted distribution coefficients (equation (3.2)) to measured distribution coefficients were plotted against pH. This is shown in Figure 3.4 for four representative REEs. The generally random scatter around the horizontal line (log $iK_{Fe}(pred)/log iK_{Fe}(meas) = 1$) indicates that equation (3.2) satisfactorily models the data.

In Figure 3.3, it can be seen that there are substantial uncertainties associated with each of the coefficients of equation (3.2). These coefficient uncertainties are consistent with uncertainties in measured log $iK_{Fe}$ patterns over time, which are on the order of 0.1 – 0.3 units. Figure 3.5 shows log $iK_{Fe}$ observations from two representative experiments. The log $iK_{Fe}$ patterns obtained in the experiment at pH = 7.06 ± 0.05 are highly consistent
**Figure 3.1.** Final regressions of log $i_{K_{Fe}}$ (Tables B.1–B.6; normalized to I = 0 M) versus pH for La, Sm, Dy, and Lu. Dashed lines represent 95% confidence intervals.
Figure 3.2. Final regressions of log \( K_{Fe} \) (Tables C.1 and C.2; normalized to pH 6.13) versus ionic strength (I) for La, Sm, Dy, and Lu. Dashed lines represent 95% confidence intervals.
Table 3.1. Results for the coefficients of equation (3.2) (see text for details). Uncertainties represent one standard error.

<table>
<thead>
<tr>
<th>[M^{3+}]</th>
<th>Q_{\text{pH}}</th>
<th>Q_{I}</th>
<th>\log K_{Fe}(\text{pH 0, } I = 0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>1.534 ± 0.05</td>
<td>0.64 ± 0.5</td>
<td>-5.60 ± 0.3</td>
</tr>
<tr>
<td>La</td>
<td>1.426 ± 0.04</td>
<td>0.43 ± 0.3</td>
<td>-5.15 ± 0.2</td>
</tr>
<tr>
<td>Ce</td>
<td>1.450 ± 0.04</td>
<td>0.73 ± 0.3</td>
<td>-4.85 ± 0.2</td>
</tr>
<tr>
<td>Pr</td>
<td>1.506 ± 0.03</td>
<td>0.90 ± 0.4</td>
<td>-4.90 ± 0.2</td>
</tr>
<tr>
<td>Nd</td>
<td>1.500 ± 0.04</td>
<td>0.98 ± 0.4</td>
<td>-4.92 ± 0.2</td>
</tr>
<tr>
<td>Pm</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sm</td>
<td>1.540 ± 0.03</td>
<td>0.67 ± 0.3</td>
<td>-4.94 ± 0.2</td>
</tr>
<tr>
<td>Eu</td>
<td>1.542 ± 0.03</td>
<td>0.51 ± 0.3</td>
<td>-5.00 ± 0.2</td>
</tr>
<tr>
<td>Gd</td>
<td>1.522 ± 0.03</td>
<td>0.44 ± 0.3</td>
<td>-5.07 ± 0.2</td>
</tr>
<tr>
<td>Tb</td>
<td>1.568 ± 0.03</td>
<td>0.20 ± 0.3</td>
<td>-5.29 ± 0.2</td>
</tr>
<tr>
<td>Dy</td>
<td>1.584 ± 0.03</td>
<td>0.43 ± 0.3</td>
<td>-5.41 ± 0.2</td>
</tr>
<tr>
<td>Ho</td>
<td>1.570 ± 0.03</td>
<td>0.57 ± 0.3</td>
<td>-5.39 ± 0.2</td>
</tr>
<tr>
<td>Er</td>
<td>1.571 ± 0.03</td>
<td>0.68 ± 0.3</td>
<td>-5.37 ± 0.2</td>
</tr>
<tr>
<td>Tm</td>
<td>1.572 ± 0.03</td>
<td>0.76 ± 0.3</td>
<td>-5.29 ± 0.1</td>
</tr>
<tr>
<td>Yb</td>
<td>1.581 ± 0.03</td>
<td>0.84 ± 0.3</td>
<td>-5.25 ± 0.1</td>
</tr>
<tr>
<td>Lu</td>
<td>1.551 ± 0.03</td>
<td>0.90 ± 0.3</td>
<td>-5.11 ± 0.1</td>
</tr>
</tbody>
</table>
Figure 3.3. Coefficients of equation (3.2). Upper panel ($Q_{pH}$) is the slope of the linear regression with respect to pH. Middle panel ($Q_I$) is the slope of the linear regression with respect to ionic strength. Lower panel ($\log_{10} K_{Fe}(pH 0, I = 0)$) is the intercept of the linear regression. Error bars represent one standard error.
Figure 3.4. $\log K_{Fe}(pred)/\log K_{Fe}(meas)$ versus pH for La, Sm, Dy, and Lu, where $\log K_{Fe}(pred)$ are distribution coefficients predicted from equation (3.2) using the coefficients listed in Table 3.1, and $\log K_{Fe}(meas)$ are experimentally observed distribution coefficients (Tables B.1–B.6).
over periods of time from 90 minutes up to 48 hours (Figure 3.5A). The same consistency over time (from 5 minutes up to 46 hours) is seen in the log $\log K_{Fe}$ patterns obtained at $I = 0.0503$ M (Figure 3.5B). These observations indicate that the uncertainties shown in Figure 3.3 are strongly correlated across the YREE series. Hence the absolute values of log $\log K_{Fe}$, but not the relative values (patterns), are affected by these uncertainties. This ensures that, despite large standard errors, the coefficients of equation (3.2) ($Q_{pH}$, $Q_{i}$, and
log \( \log i_{K_{Fe}}(pH 0, I = 0) \), summarized in Table 3.1, accurately represent measured \( \log i_{K_{Fe}} \) patterns as a function of pH and ionic strength.

The large uncertainty associated with \( Q_I \) also results from the weak dependence of YREE sorption on ionic strength, as indicated by the small (< 0.25) correlation coefficients in Figure 3.2. This lack of an ionic strength effect for sorption by ferric hydroxides, both amorphous and crystalline, has been observed in previous experiments with other cations, including copper, lead, and cadmium (Swallow et al., 1980; Hayes and Leckie, 1987). Swallow et al. (1980) suggested that the lack of an ionic strength effect indicates there is no net change in charge during the sorption reaction and therefore coulombic interactions do not play a role in the process. Using a generalized two-layer model with the best available estimates for zinc surface complexation constants, Dzombak and Morel (1990) indicated that ionic strength has a minimal influence on zinc sorption by amorphous ferric hydroxide. Dzombak and Morel (1990) explained the absence of an ionic strength effect in terms of the Gouy-Chapman and Debye-Hückel theories, stating that variations in ionic strength produce similar changes in the free energies of species at the surface and in the bulk solution, whereupon the standard free energy change of the sorption reaction remains nearly constant.

### 3.5.2. Surface Complexation Model Results

Using Sm as an example, Figure 3.6 compares surface complexation model results obtained by (i) setting \( sK_1[H^+] \) in equation (3.19) equal to zero (Figure 3.6A) and (ii) determining the \( \log sK_1 \) value which minimized the RSS in equation (3.20) (Figure 3.6B). The ratios of predicted distribution coefficients (equation (3.19)) to measured distribution coefficients (\( \log i_{K_{Fe}(pred)}/\log i_{K_{Fe}(meas)} \)) exhibit systematic, pH-dependent variations when \( sK_1[H^+] \) is set equal to zero (Figure 3.6A). In contrast, no such systematic deviations between predicted and measured \( \log i_{K_{Fe}} \) values (Figure 3.6B) are observed when using the \( \log sK_1 \) value that minimized the RSS in equation (3.20) (i.e., \( \log sK_1 = 4.76 \)). Comparisons of \( \log i_{K_{Fe}} \) predictions and experimental observations, exemplified by the results shown for Sm in Figures 3.6A and 3.6B, clearly demonstrate the importance of variations in the \([S–Fe(OH)_{2+}\)/[S–Fe(OH)_{3}] \) ratio (equation (3.15)) at low pH.
Figure 3.6. $\log iK_{Fe}(pred)/\log iK_{Fe}(meas)$ versus pH for Sm. (A) $\log iK_{Fe}(pred)$ are distribution coefficients predicted from equation (3.19) with the assumption that $sK_1[H^+] \ll 1$. (B) $\log iK_{Fe}(pred)$ are distribution coefficients predicted from equation (3.19) using $\log sK_1 = 4.76$ and the surface complexation constants ($s\beta_n$) listed in Table 3.2. For both panels, $\log iK_{Fe}(meas)$ are distribution coefficients from experiments at constant ionic strength (Tables B.1–B.6), normalized to $I = 0.025$ M.
The final best-fit results for the amorphous ferric hydroxide YREE surface complexation constants ($\beta_1$ and $\beta_2$) are summarized in the first two columns of Table 3.2 and are depicted graphically in Figure 3.7. It can be seen that the patterns for the two surface complexation constants are fairly similar except for (i) the location of Y relative to the REEs and (ii) the sequence of inflections seen in the middle-to-heavy REEs, which is more pronounced for log $\beta_2$. At low pH, $\beta_1[H^+] > \beta_2[H^+]$ in equation (3.19) so reaction (3.4) represents the dominant sorption reaction. At high pH, the dominant sorption reaction is reaction (3.5), which is represented by the $\beta_2$ term in equation (3.19) (Figure 3.7B). The pH at which $[S–FeO_2(OH)\text{M}^+] = [S–FeO(OH)_2\text{M}^{2+}]$ is equal to the ratio $\beta_2/\beta_1$. This ratio is listed in the third column of Table 3.2 for each YREE and has an average value of 6.30.

The distribution coefficients (log $K_{Fe}$) used to determine $\beta_1$, $\beta_2$, and $K_1$ were expressed in terms of total (MT) rather than free ([M$^{3+}$]) YREE concentrations. For most

Table 3.2. YREE surface complexation constants ($\beta_n$) determined with equation (3.19) and the data in Tables B.1–B.6. Best fits of $K_{Fe}$ versus [H$^+$] were obtained with log $K_1 = 4.76$ (see text for details). Uncertainties represent one standard error.

<table>
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<th>[M$^{3+}$]</th>
<th>log $\beta_1$</th>
<th>log $\beta_2$</th>
<th>-log ($\beta_2/\beta_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
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<td>-8.93 ± 0.07</td>
<td>5.97</td>
</tr>
<tr>
<td>La</td>
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<td>-9.49 ± 0.11</td>
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</tr>
<tr>
<td>Ce</td>
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<td>6.62</td>
</tr>
<tr>
<td>Pr</td>
<td>-2.25 ± 0.03</td>
<td>-8.73 ± 0.08</td>
<td>6.48</td>
</tr>
<tr>
<td>Nd</td>
<td>-2.16 ± 0.03</td>
<td>-8.66 ± 0.09</td>
<td>6.49</td>
</tr>
<tr>
<td>Pm</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sm</td>
<td>-2.05 ± 0.03</td>
<td>-8.40 ± 0.07</td>
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<tr>
<td>Eu</td>
<td>-2.10 ± 0.03</td>
<td>-8.42 ± 0.07</td>
<td>6.32</td>
</tr>
<tr>
<td>Gd</td>
<td>-2.27 ± 0.03</td>
<td>-8.67 ± 0.08</td>
<td>6.40</td>
</tr>
<tr>
<td>Tb</td>
<td>-2.28 ± 0.03</td>
<td>-8.49 ± 0.06</td>
<td>6.21</td>
</tr>
<tr>
<td>Dy</td>
<td>-2.31 ± 0.03</td>
<td>-8.46 ± 0.06</td>
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</tr>
<tr>
<td>Ho</td>
<td>-2.36 ± 0.03</td>
<td>-8.55 ± 0.06</td>
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</tr>
<tr>
<td>Er</td>
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<tr>
<td>Yb</td>
<td>-2.16 ± 0.03</td>
<td>-8.27 ± 0.05</td>
<td>6.11</td>
</tr>
<tr>
<td>Lu</td>
<td>-2.15 ± 0.03</td>
<td>-8.34 ± 0.06</td>
<td>6.19</td>
</tr>
</tbody>
</table>
Figure 3.7. Surface stability constants (equation (3.19)) for YREE sorption by amorphous ferric hydroxide. Error bars represent one standard error.

of our solution conditions (pH ≤ 6.5), this approximation is acceptable because M³⁺ is weakly hydrolyzed ([M³⁺]/M₇ ≥ 0.87). At pH 7, the proportions of LREE hydroxides are small (e.g., [LaOH²⁺]/[La³⁺] ≤ 0.01) but the formation of HREE hydroxides is sufficiently large (e.g., [YbOH²⁺]/[Yb³⁺] ≤ 0.4) that it is necessary to assess the possible impact of YREE hydrolysis on our results. As such, distribution coefficient behavior was also modeled using free YREE concentrations. M₇/[M³⁺] ratios were calculated using the hydrolysis constants (β⁺) of Klungness and Byrne (2000). Distribution coefficients (iKFe) expressed in terms of M₇ and [M³⁺] are related as follows:
\[ iK_{Fe}([M^{3+}]) = iK_{Fe}(M_T) \times (1 + \beta_1^i[H^+]^{-1}) \]  

(3.21)

Using distribution coefficients expressed in terms of free YREE concentrations, the equilibrium constants in equation (3.19) \( (s\beta_1, s\beta_2, \text{ and } sK_1) \) were recalculated using methods identical to those described above. Residual sum of squares (RSS) results were then compared for the model expressed in terms of \( M_T \) and the model expressed in terms of \([M^{3+}]\). For each YREE, the RSS was slightly larger \(< 5\% \) for LREEs and \(< 20\% \) for HREEs) using \( \log iK_{Fe} \) results expressed in terms of \([M^{3+}]\). The lack of improvement when \( \log iK_{Fe} \) was modeled in terms of free YREE concentrations rather than total concentrations may be caused by the rather small extent of YREE hydrolysis under the conditions used in this work. Since the magnitude of \( \log(1 + \beta_1^i[H^+]^{-1}) \) in equation (3.21) was less than 0.15 for Yb at pH 7, and much smaller for most other elements, the extent of YREE hydrolysis appears to have been too small, relative to experimental uncertainties in \( \log iK_{Fe} \) determinations, to distinguish YREE hydrolysis effects from experimental uncertainties in \( \log iK_{Fe} \). This issue will be addressed in future investigations of the effect of solution complexation on YREE sorption.

3.5.3. Comparative log \( iK_{Fe} \) Predictions using SCM Results

The log \( iK_{Fe} \) patterns obtained in this work are compared, in Figure 3.8, with the log \( iK_{Fe} \) results obtained by Bau (1999), Ohta and Kawabe (2000, 2001), and De Carlo et al. (1998). Figure 3.8A compares the log \( iK_{Fe} \) predictions of equation (3.19) with the observed result of Bau (1999) at pH 5.97, Figure 3.8B compares equation (3.19) predictions with the result of Ohta and Kawabe (2000, 2001) at pH 6.59, and Figure 3.8C compares the predictions of equation (3.19) with the result of De Carlo et al. (1998) at pH 6.25 and \( I = 0.1 \text{ m} \). In order to emphasize similarities/differences in log \( iK_{Fe} \) patterns, rather than absolute log \( iK_{Fe} \) magnitudes, the predicted patterns in Figure 3.8 were vertically adjusted with scaling constants (see also Quinn et al., 2004). The comparisons shown in Figure 3.8 demonstrate that equation (3.19), along with the regression data given in Table 3.2, accurately predicts the shape of patterns obtained at near-neutral pH by Bau (1999), Ohta and Kawabe (2000, 2001), and De Carlo et al. (1998). Overall, there
Figure 3.8. Comparison between measured distribution coefficients and log $K_{Fe}$ values predicted from equation (3.19). (A) Result from Bau (1999) at pH 5.97. (B) Result from Ohta and Kawabe (2000, 2001) at pH 6.59. (C) Result from De Carlo et al. (1998) at pH 6.25 and $I = 0.1$ m. The overlap of each pair of patterns was separately maximized by addition of a scaling constant, determined by RSS analysis, to the predicted pattern only (see Quinn et al., 2004).
is slightly better agreement between the predictions of equation (3.19) and the results of Ohta and Kawabe (2000, 2001) than is observed for comparisons with the results of Bau (1999) or the results of De Carlo et al. (1998). This is somewhat surprising because the degree of substrate loading (\(\Sigma[YREE]/[Fe^{3+}]_T\)) was much larger in the experiments of Ohta and Kawabe (2000, 2001) (0.4) than in the experiments of Bau (1999) (0.004), De Carlo et al. (1998) (0.06), or the present work (0.0002 – 0.02). Since the present study was not intended to examine the effect of loading, additional studies are needed to assess the influence of substrate loading on YREE log \(iK_{Fe}\) behavior.

Although there is good general agreement between log \(iK_{Fe}\) patterns obtained at pH > 5.0 (i.e., Figure 3.8), the log \(iK_{Fe}\) results of Bau (1999) at low pH differ substantially from the log \(iK_{Fe}\) patterns obtained in the present study. Figure 3.9 compares, for example, the log \(iK_{Fe}\) pattern obtained by Bau (1999) at pH 3.91 with the average log \(iK_{Fe}\) pattern obtained in the present work at pH = 3.96 ± 0.10 (Table B.6). The log \(iK_{Fe}\) pattern obtained by Bau (1999) is very flat relative to log \(iK_{Fe}\) patterns observed in the present study. The cause of the observed differences in the log \(iK_{Fe}\) patterns at low pH (Figure 3.9) is unknown. Further investigations of YREE sorption onto amorphous ferric hydroxide at low pH are needed to resolve these differences.

In addition to comparing distribution coefficient patterns obtained at specific pH values (Figures 3.8 and 3.9), it is informative to compare log \(iK_{Fe}\) versus pH relationships. In the present work, log \(iK_{Fe}\) is linearly dependent on pH (Figure 3.1) over the entire investigated pH range (3.9 – 7.1). This linearity is also seen in the results of Ohta and Kawabe (2000, 2001) between pH 5.8 and 6.6 (Figure 3.10), and in the log \(iK_{Fe}\) results of De Carlo et al. (1998) between pH 4.0 and 7.0 (Figure 3.11). The results of De Carlo et al. (1998) show non-linearity only at higher pH (> 7.0, not shown), where a correction for hydrolysis (equation (3.21)) is required. Although the log \(iK_{Fe}\) versus pH slope obtained by De Carlo et al. (1998) is somewhat smaller than those obtained in Ohta and Kawabe (2000, 2001) and the present work, the results of Bau (1999) exhibit characteristics that differ both qualitatively and quantitatively from the log \(iK_{Fe}\) versus pH results obtained by others (Figures 3.10 and 3.11). The data of Bau (1999) can be divided
Figure 3.9. Comparison between the average $\log K_{Fe}$ result at pH = 3.96 ± 0.10 from the present work (Table B.6) and the $\log K_{Fe}$ result at pH 3.91 from Bau (1999). The values obtained in the present work are shown on the left axis while the values obtained by Bau (1999) are shown on the right axis.
Figure 3.10. Regressions of log \( K_{Fe} \) versus pH for La, Sm, Dy, and Lu. (●) Results from the present work (Tables B.1–B.6; normalized to \( I = 0 \) M). (○) Results from Ohta and Kawabe (2000, 2001) on the mole fraction scale were corrected by a multiplicative factor \(((\text{Fe}^{3+}) + \Sigma \text{REE})/\text{Fe}^{3+}\)) to make them consistent with \( K_{Fe} \) as defined by equation (3.1). The slopes (\( Q_{pH} \pm 1 \) standard error) are listed next to each regression line.
Figure 3.11. Regressions of log $iK_{Fe}$ versus pH for La, Sm, Dy, and Lu. (△) Results from Bau (1999) were normalized to his average iron concentration. (●) Results from the present work (Tables B.1–B.6; normalized to $I = 0$ M). (○) Results from De Carlo et al. (1998) at $I = 0.1$ m on the percent sorbed scale were converted to distribution coefficients as defined by equation (3.1), which included normalization to their iron concentration in moles of amorphous ferric hydroxide per kilogram of solution. The slopes ($Q_{pH} \pm 1$ standard error) are listed next to each regression line.

into two separate linear regressions (pH $\sim 3.6 – 5.0$ and pH $\sim 5.3 – 6.2$). The log $iK_{Fe}$ versus pH slope in the upper pH region is two to four times larger than the slope obtained by De Carlo et al. (1998) and, near pH 6.0, the $iK_{Fe}$ values of Bau (1999) are 2 to 3 orders of magnitude larger than the values reported by De Carlo et al. (1998), Ohta and Kawabe (2000, 2001), and the present work.
It should be noted here that the present work (Tables B.1–B.6) was performed at low ionic strength \( (I \leq 0.043 \text{ M}) \), whereas the study of Ohta and Kawabe (2000, 2001) was performed at \( I = 0.5 \text{ M} \). The good agreement between the results in the present work and the results in the work of Ohta and Kawabe (2000, 2001) supports the conclusion that ionic strength does not have a strong effect on YREE sorption by amorphous ferric hydroxide. The distribution coefficients for Eu and Tb of De Carlo et al. (1998), after correcting for nitrate complexation using the stability constants of Choppin and Strazik (1965), also showed a weak dependence on ionic strength over the range 0.1 – 0.7 \( m \) (similar to that seen in Figure 3.2). In contrast, the \( \log \, iK_{Fe}(\text{Eu, Tb}) \) results of De Carlo et al. (1998) at zero ionic strength were larger than their \( I = 0.1 \text{ m} \log \, iK_{Fe}(\text{Eu, Tb}) \) values by \( \leq 0.6 \text{ log units} \) over the pH range 4.0 – 7.0. While the origin of this difference is uncertain, the range of \( \log \, iK_{Fe} \) values observed by De Carlo et al. (1998) between 0.0 and 0.7 \( m \) ionic strength may simply be attributable to the typical experimental errors encountered in \( \log \, iK_{Fe} \) determinations.

3.5.4. \( \log \, iK_{Fe} \) Predictions for Seawater

Distribution coefficients \( (iK_{Fe}) \) predicted from equation (3.19) at high pH (> 7.5) can be converted to results expressed in terms of total YREE concentration in seawater \( (iK'_{Fe}) \) using the following equation:

\[
iK'_{Fe} = (iK_{Fe}) \left(1 + \sum_{i,n} i\beta_n [L_i]^n\right)^{-1} = \frac{[MS_i]_r}{M_{sw}[Fe^{3+}]_s}, \tag{3.22}
\]

where \( i\beta_n \) are stability constants for formation of YREE solution complexes:

\[
i\beta_n = \frac{[M(L_i)_n]}{[M^{3+}][L_i]^n}, \tag{3.23}
\]

and \( M_{sw} \) represents the total concentration of each YREE in seawater:

\[
M_{sw} = [M^{3+}] + [MCO_3^+] + [M(CO_3)_2^-] + [MOH^{2+}] + [MSO_4^2-] + \cdots . \tag{3.24}
\]

Stability constants used in equation (3.22) include those for YREE complexation by chloride (Luo and Byrne, 2001), fluoride (Luo and Byrne, 2000), sulfate (Schijf and Byrne, 2004), hydroxide (Klungness and Byrne, 2000), and carbonate and bicarbonate (Luo and Byrne, 2004).
Figure 3.12A shows predicted (equation (3.19) and Table 3.2) distribution coefficients (log \( iK_{Fe} \)) expressed in terms of free YREE concentrations at several pHs relevant to seawater. Figure 3.12B shows the Figure 3.12A log \( iK_{Fe} \) results transformed to log \( iK'_{Fe} \) values using equation (3.22). The results shown in Figure 3.12B indicate that amorphous ferric hydroxide preferentially removes (scavenges) LREEs from seawater. Comparison of Figures 3.12A and 3.12B shows that log \( iK_{Fe} \) patterns vary little with pH while log \( iK'_{Fe} \) patterns are strongly pH dependent. This is largely due to the strong pH dependence of carbonate complexation. Figure 3.12B also shows that the pH dependence of log \( iK'_{Fe} \) is much larger for the LREEs than for the HREEs. Between pH 7.6 and 8.2, log \( iK'_{Fe} \) for La increases by 0.6 units while log \( iK'_{Fe} \) for Lu increases by only 0.2 units.

Koeppenkastrop and De Carlo (1992) directly measured REE sorption by amorphous goethite in seawater. Figure 3.12C compares the log \( iK'_{Fe} \) pattern predicted in the present work at pH 7.8 (equations (3.19) and (3.22)) with the pattern obtained by Koeppenkastrop and De Carlo (1992) at pH 7.8. In order to compare log \( iK'_{Fe} \) results on the same concentration scale, the partition coefficients obtained by Koeppenkastrop and De Carlo (1992) were calculated in terms of moles of amorphous ferric hydroxide per kilogram of seawater. The patterns shown in Figure 3.12C are quite similar, especially for the HREEs. The log \( iK'_{Fe} \) results of Koeppenkastrop and De Carlo (1992) are approximately 0.6 units smaller than the results predicted from equations (3.19) and (3.22). This difference is generally similar to observed experimental errors in log \( iK_{Fe} \) observations (e.g., Figure 3.1). On the other hand, it might also be expected that the absolute magnitude of log \( iK'_{Fe} \) observations in seawater could be diminished by competitive sorption of major cations (e.g., Mg\(^{2+}\)).
Figure 3.12. (A) Distribution coefficients ($\log iK_{Fe}$) expressed in terms of free YREE concentrations ([M$^{3+}$]) using equation (3.19) and the surface complexation constants ($s\beta_n$) listed in Table 3.2. (B) Distribution coefficients ($iF elog K'_{Fe}$) expressed in terms of total YREE concentrations in seawater ($M_{sw}$) using equations (3.19) and (3.22) and assuming $[HCO_3^-]_T \approx 2 \times 10^{-3}$ M. (C) Comparison between the predicted $\log iK'_{Fe}$ pattern for seawater at pH 7.8 (equations (3.19) and (3.22)) and the measured $\log iK'_{Fe}$ pattern at pH 7.8 from Koeppenkastrop and De Carlo (1992). (Continued on next page).
(Figure 3.12 caption – continued). The results of De Carlo et al. (1998) (not shown) are consistent with the results of Koeppenkastrop and De Carlo (1992), but exhibit a somewhat reduced precision, perhaps due to experimental differences such as a two-fold decrease (De Carlo et al., 1998) in the experiment’s total YREE concentration.

Distribution coefficients expressed in terms of total YREE concentrations in seawater (equation (3.22)) can be used to calculate the fraction of each YREE that would be removed from the water column, on a millennial scale, by settling amorphous ferric hydroxide. Column 2 in Table 3.3 lists $\log K'_{Fe}$ values at pH 7.9. Equation (3.22) written in the form:

$$K'_{Fe} \times M_{sw} = \frac{[MS_i]_T}{[Fe^{3+}]_S},$$

provides YREE/iron molar ratios ([MS$_i$]$_T$/[Fe$^{3+}$]$_S$) for YREEs sorbed onto amorphous ferric hydroxide, presuming that YREEs maintain their average steady state concentrations ($M_{sw}$) in the water column. Using the $M_{sw}$ concentrations obtained by Zhang and Nozaki (1996) for each YREE at a depth of 2469 m (column 3), [MS$_i$]$_T$/[Fe$^{3+}$]$_S$ values (column 4) were calculated via equation (3.25). The authigenic flux of iron ($[Fe^{3+}]_{flux}$) to the ocean floor is estimated to range from 14 to 50 $\mu$mol cm$^{-2}$ kyr$^{-1}$ (Krishnaswami, 1976; Thomson et al., 1984). Columns 5 and 6 show the predicted number of moles of each YREE that would be associated with authigenic iron fluxes equal to 14 and 50 $\mu$mol cm$^{-2}$ kyr$^{-1}$, respectively ($([MS_i]_T/[Fe^{3+}]_S) \times [Fe^{3+}]_{flux}$). These YREE fluxes can be compared with authigenic REE fluxes estimated by Thomson et al. (1984), where authigenic is defined as non-terrigenous and therefore may include phases other than amorphous ferric hydroxide. The authigenic fluxes calculated by Thomson et al. (1984) are 10 to 50 times larger, except for Ce, which is 3 orders of magnitude larger, than the rates of YREE removal by authigenic iron estimated in the present work.

The number of moles of each YREE associated with the flux of authigenic iron (i.e., columns 5 and 6) can also be compared to the total inventory ($\Sigma M_{sw}$) of each YREE in
Table 3.3. Estimated removal rates for YREEs via authigenic iron. Log, $K_{Fe}^{'}$ (column 2) are distribution coefficients expressed in terms of total YREE concentrations in seawater ($M_{sw}$) at pH 7.9 (equations (3.19) and (3.22)). The $M_{sw}$ values in column 3 are directly measured seawater concentrations for each YREE at 2469 m (Zhang and Nozaki, 1996). The $[MS_i]/[Fe^{3+}]_s$ values in column 4 are YREE/iron molar ratios for each YREE sorbed by amorphous ferric hydroxide. The $[MS_i]_T$ values in columns 5 and 6 are the number of moles of each YREE that accumulate in 1 cm$^2$ of ocean floor per millennium of amorphous ferric hydroxide sorption and deposition. The $[MS_i]_T/\Sigma M_{sw}$ values in columns 7 and 8 are the ratios (percentages) of the number of moles of each YREE removed per millennium of amorphous ferric hydroxide sorption to the total inventory of each YREE in the water column. (a) Authigenic flux of iron equal to 14 µmol cm$^{-2}$ kyr$^{-1}$ (Krishnaswami, 1976). (b) Authigenic flux of iron equal to 50 µmol cm$^{-2}$ kyr$^{-1}$ (Thomson et al., 1984).

<table>
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<tr>
<th>[M$^{3+}$]</th>
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<th>$M_{sw}$</th>
<th>$[MS_i]_T/[Fe^{3+}]_s$</th>
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<td>pmol cm$^2$ kyr$^{-1}$</td>
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<td>b</td>
</tr>
<tr>
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<td>228.9</td>
<td>30.69</td>
<td>429.6</td>
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<td>1.24</td>
<td>0.18</td>
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the 4-km column of water overlying a square centimeter of the ocean floor \( (\Sigma M_{sw} = M_{sw} \times 400 \text{ L}) \). The number of moles of each YREE removed per millennium of sorption by amorphous ferric hydroxide relative to the total inventory of each YREE in the water column \([\text{[M]}_{1T}/\Sigma M_{sw}\]) is summarized in columns 7 and 8. This calculation shows that the number of moles of each YREE in the water column is between 15 and 200 times greater than the number of moles of each YREE delivered to the sea floor per millennium by settling amorphous ferric hydroxide. Despite the range in flux values, the small fractions (%) shown in columns 7 and 8 suggest that sorption by amorphous ferric hydroxide and subsequent removal to the ocean floor is not a significant sink for YREEs in the open ocean. The sorptive removal of YREEs by amorphous ferric hydroxides in estuaries, where extensive iron colloid formation is generated by mixing of freshwater and seawater (Sholkovitz, 1976, 1992; Sholkovitz and Elderfield, 1988) should greatly dominate sorptive removal by amorphous ferric hydroxides in the open ocean.

3.6 Conclusions

This investigation of YREE sorption by amorphous ferric hydroxide, in conjunction with the works of De Carlo et al. (1998) and Ohta and Kawabe (2000, 2001), indicates that \( \log iK_{Fe} \) is linearly dependent on pH over a wide range of conditions. Plots of \( \log iK_{Fe} \) versus pH in the present work have slopes that range between 1.43 ± 0.04 for La and 1.55 ± 0.03 for Lu. These results, obtained at low ionic strengths \( (0.011 \text{ M} \leq I \leq 0.043 \text{ M}) \), are in good agreement with the results obtained by Ohta and Kawabe (2000, 2001) at \( I = 0.5 \text{ M} \). In view of the very similar stability constants of trivalent YREEs and Cu\(^{2+}\) (Smith and Martell, 1976, 1989) it is interesting to note that the absolute magnitudes of \( \log iK_{Fe}(\text{Cu}^{2+}) \) obtained by Swallow et al. (1980) for \( \text{pH} > 5.5 \) is very similar to the \( \log iK_{Fe}(\text{YREE}) \) results in the present study, and the slope of \( \log iK_{Fe}(\text{Cu}^{2+}) \) versus pH \( (\Delta \log iK_{Fe}/\Delta \text{pH} = 1.5) \) is very similar to the slopes obtained for YREEs in the present work.

Over an ionic strength range where the activity coefficients of dissolved ions exhibit strong variations \( (0.0 \text{ M} \leq I \leq 0.1 \text{ M}) \), the results of this study indicate that YREE sorption constants \( (\log iK_{Fe}) \) are nearly constant. This is consistent with previous
observations (Swallow et al., 1980; Hayes and Leckie, 1987; Dzombak and Morel, 1990) of very weak dependencies of metal sorption coefficients on ionic strength.

The log $\log K_{Fe}$ results of this study can be used to predict the sorption behavior of YREEs in seawater. Predicted YREE sorption behavior for seawater is generally similar to the REE sorption results observed by Koeppenkastrop and De Carlo (1992) in seawater at pH 7.8. Although the removal of YREEs from seawater via sorption onto amorphous ferric hydroxide does not appear to be significant in the open ocean, it should be expected that oceanic YREE patterns are strongly influenced by the YREE sorption onto amorphous ferric hydroxides that occurs in estuaries.
4. Sorption of Yttrium and Rare Earth Elements by Amorphous Ferric Hydroxide:

Influence of Solution Complexation with Carbonate

The following chapter has been peer-reviewed and will be published essentially in this form:

4.1 Abstract

The influence of solution complexation on the sorption of yttrium and the rare earth elements (YREEs) by amorphous ferric hydroxide was investigated at 25°C over a range of pH (4.0 – 7.1) and carbonate concentrations (0 M ≤ [CO$_3^{2-}$]$_T$ ≤ 150 µM). Distribution coefficients, defined as $K^T_{Fe} = [MS_i]/(M_T[S_i])$, where [MS$_i$]$_T$ is the total concentration of sorbed YREE, $M_T$ is the total YREE concentration in solution, and [S$_i$] is the concentration of amorphous ferric hydroxide, initially increased in magnitude with increasing carbonate concentration, and then decreased. The initial increase of $K^T_{Fe}$ is due to sorption of YREE carbonate complexes ([MCO$_3$]$^+$), in addition to sorption of free YREE ions (M$^{3+}$). The subsequent decrease of $K^T_{Fe}$, which is more extensive for the heavy REEs, is due to the increasing intensity of YREE solution complexation by carbonate ions. The competition for YREEs between solution complexation and surface complexation was modeled via the equation:

$$K^T_{Fe} = \frac{s\beta_1[H^+]^{-1} + s\beta_2[H^+]^{-2} + CO_3\beta_1HCO_3^-HCO_3^-H^+]^{-2}}{(sK_1[H^+] + 1) x (1 + HCO_3\beta_1HCO_3^-H^+)^{-1} + CO_3\beta_2HCO_3^-HCO_3^-H^+)^{-2}}$$

where $s\beta_1$ and $s\beta_2$ are equilibrium constants for free YREE surface species, $CO_3\beta_1$ is the equilibrium constant for the YREE-carbonate surface species, $sK_1$ is the surface protonation constant for amorphous ferric hydroxide, and $HCO_3\beta_1$, $CO_3\beta_1$, and $CO_3\beta_2$ are
YREE solution complexation constants expressed in terms of bicarbonate concentrations. The equation, which includes (i) a single new constant \((CO_3^2\beta_1)\) for each YREE, (ii) previously published sorption coefficients \((S\beta_1\) and \(S\beta_2\)) determined in the absence of carbonate, and (iii) previously published solution complexation constants, precisely predicts both the absolute magnitude of \(iK_{Fe}^T\) and the pattern of \(iK_{Fe}^T\) values over our range of experimental conditions. Experimentally observed \(iK_{Fe}^T\) values, spanning more than five orders of magnitude, are accurately described by our surface/solution complexation model. The \(\log CO_3S\beta_1\) values determined for each YREE in this work are: Y(-1.30±0.04), La(-0.39±0.02), Ce(-0.21±0.02), Pr(-0.22±0.02), Nd(-0.20±0.02), Sm(-0.20±0.02), Eu(-0.26±0.02), Gd(-0.38±0.02), Tb(-0.40±0.02), Dy(-0.51±0.02), Ho(-0.57±0.02), Er(-0.59±0.02), Tm(-0.56±0.02), Yb(-0.62±0.02), and Lu(-0.59±0.02).

4.2 Introduction

It is generally recognized that distributions of yttrium and the rare earth elements (YREEs) in the ocean are controlled by competition between solution complexation and surface complexation. Since YREE solution chemistry has been relatively well characterized (see for instance Wood, 1990; Byrne and Sholkovitz, 1996), recent studies of YREE fractionation processes have focused on YREE surface chemistry. Early investigations of REE sorption in seawater utilized radiotracers and a variety of substrates, both organic (Bingler et al., 1989; Byrne and Kim, 1990; Stanley and Byrne, 1990) and inorganic (Byrne and Kim, 1990; Koeppenkastrop et al., 1991). These studies showed that for most substrates, light REEs (LREEs) are preferentially removed from seawater compared to heavy REEs (HREEs). Silica phases, which displayed a greater affinity for HREEs (Byrne and Kim, 1990), were an exception to this generality. The major limitation of these early YREE sorption investigations was the omission of many REEs whose radionuclides were too short-lived or not commercially available. Toward a more comprehensive view of YREE sorption in seawater, Koeppenkastrop and De Carlo (1992) examined sorption of all REEs, except Pm and Sm, onto amorphous ferric hydroxide and crystalline FeOOH. Despite more extensive sorption by the amorphous
phase, the crystalline phase produced stronger fractionation and a residual seawater pattern that resembled shale-normalized REE patterns in the ocean (Koeppenkastrop and De Carlo, 1992).

As noted by Koeppenkastrop and De Carlo (1992), interpretation of experiments performed in seawater is complicated by the presence of strong solution complexation. As such, it was recognized that experiments should be undertaken in simple synthetic media in the absence of strongly complexing ligands. Starting with the work of De Carlo et al. (1998), (Y)REE sorption onto amorphous ferric hydroxide in simple synthetic solutions (without complexing ligands) has been investigated over a range of pH (4.0 – 9.0) and ionic strength (0 – 0.7 M) (Bau, 1999; Kawabe et al., 1999b; Ohta and Kawabe, 2001; Quinn et al., 2004, 2006a). In general these experiments showed that, in the absence of solution complexation, sorption does not preferentially remove LREEs from solution. Quinn et al. (2004) showed that the YREE pattern obtained in experiments at near-neutral pH closely resembles the sorption pattern of natural marine particles that is predicted (Byrne and Sholkovitz, 1996) using shale-normalized oceanic YREE concentrations and a quantitative model of YREE solution complexation in seawater.

It has been well established that YREE sorption is strongly influenced by pH. In addition to an increase in the absolute magnitude of YREE sorption with increasing pH, Bau (1999) showed that there is a pH dependence in the pattern of YREE fractionation. Based on experimental results from Eu and La sorption onto hematite, Rabung et al. (1998a) and Marmier and Fromage (1999) used a surface complexation model to describe sorption intensity as a function of pH. Extending the work of Rabung et al. (1998a) and Marmier and Fromage (1999) to include the entire YREE series, Quinn et al. (2006a) modeled YREE distribution coefficient results (3.9 ≤ pH ≤ 7.1) in terms of free ion \( (M^{3+}) \) sorption with a two-site surface complexation model.

Relatively few studies have compared YREE sorption in the absence and presence of solution complexation. Fairhurst et al. (1995) and Rabung et al. (1998b) showed that Eu\(^{3+}\) sorption onto hematite was suppressed at pH > 5.0 in the presence of humic acid and fulvic acid. At lower pH values, Eu\(^{3+}\) sorption was enhanced to varying degrees, depending on the concentration of humic acid (Fairhurst et al., 1995). Davranche et al.
(2004) studied sorption of the entire REE series onto iron oxyhydroxide. A flat YREE sorption pattern was observed in the presence of humic acid, compared to an HREE-enriched pattern in the absence of solution complexation (Davranche et al., 2004). YREE sorption in these studies was interpreted in terms of complexation with humate, with the latter being both dissolved in solution and sorbed onto hematite (Fairhurst et al., 1995; Rabung et al., 1998b; Davranche et al., 2004).

Despite the fact that YREE solution complexation in the open ocean appears to be dominated by carbonate ions (Byrne and Sholkovitz, 1996), its direct role in YREE sorption is poorly understood. Koeppenkastrop and De Carlo (1993) observed that carbonate complexation slowed the rate of uptake of Eu by manganese and iron oxides. Based on their observations of sorption kinetics, Koeppenkastrop and De Carlo (1993) proposed that dissolved REEs dissociate from carbonate ligands before being sorbed as free ions onto a solid. Kawabe et al. (1999a) and Ohta and Kawabe (2000) investigated YREE sorption onto amorphous ferric hydroxide in the presence of carbonate over a narrow pH range (7.6 – 8.7) at an ionic strength of ~0.5 M. Their results showed that HREE sorption was strongly suppressed in the presence of strong carbonate complexation. Despite the fact that YREE solution chemistry is relatively well understood compared to YREE surface chemistry, Ohta and Kawabe (2000) used their distribution coefficient results along with a theoretical model of surface complexation to derive YREE-carbonate solution complexation constants. As discussed by Luo and Byrne (2004), the results obtained by Ohta and Kawabe (2000) are approximately an order of magnitude larger than previous results obtained using a variety of procedures: solubility (e.g., Ferri et al., 1983), solvent exchange (e.g., Liu and Byrne, 1998), and potentiometry (e.g., Luo and Byrne, 2004).

In the present study, we have examined the effect of carbonate solution complexation on YREE sorption by amorphous ferric hydroxide at low ionic strength (I < 0.1 M) over a relatively wide range of pH (4.0 – 7.1). Distribution coefficient results are quantitatively examined using the surface complexation model of Quinn et al. (2006a) and the carbonate complexation constants of Luo and Byrne (2004). Experimental results are
used to extend the model of Quinn et al. (2006a) to include sorption of YREE solution complexes (i.e., $\text{MCO}_3^-$) in addition to sorption of free YREE ions ($\text{M}^{3+}$).

### 4.3 Theory

Measurements of YREE solution concentrations in the presence of freshly precipitated amorphous ferric hydroxide and dissolved carbonate ($0 \text{ M} \leq \left[\text{CO}_3^{2-}\right]_r \leq 150 \ \mu\text{M}$) were used to calculate distribution coefficients ($K_{\text{Fe}}^T$) in the following form:

$$K_{\text{Fe}}^T = \frac{[\text{MS}]_T}{M_T[S]}.$$  \hspace{1cm} (4.1)

where $[\text{MS}]_T$ is the total molar concentration of a sorbed YREE, $M_T$ is the total molar concentration of a dissolved YREE, and $[S]$ is the total molar concentration of precipitated amorphous ferric hydroxide. The total concentration of a sorbed YREE can be written as the sum of three or more terms. As one example, in solutions containing carbonate, $[\text{MS}]_T$ can be written as:

$$[\text{MS}]_T = [\text{S–FeO(OH)}_2\text{M}^{2+}] + [\text{S–FeO}_2(\text{OH})\text{M}^+] + [\text{S–FeO(OH)}_2\text{MCO}_3^0].$$  \hspace{1cm} (4.2)

The first two terms on the right-hand side of equation (4.2) follow from the work of Quinn et al. (2006a) in carbonate-free solutions. The final term in equation (4.2) is one of a number of potentially important surface-bound YREE species. Equilibrium constants for the formation of $\text{S–FeO(OH)}_2\text{M}^{2+}$, $\text{S–FeO}_2(\text{OH})\text{M}^+$, and $\text{S–FeO(OH)}_2\text{MCO}_3^0$ can be written, respectively, as:

$$s\beta_1 = \frac{[\text{S–FeO(OH)}_2\text{M}^{2+}][\text{H}^+]}{[\text{M}^{3+}][\text{S–Fe(OH)}_3]},$$  \hspace{1cm} (4.3)

$$s\beta_2 = \frac{[\text{S–FeO}_2(\text{OH})\text{M}^+]^2[\text{H}^+]}{[\text{M}^{3+}][\text{S–Fe(OH)}_3]},$$  \hspace{1cm} (4.4)

and

$$\text{co}_3^\beta_1 = \frac{[\text{S–FeO(OH)}_2\text{MCO}_3^0][\text{H}^+]}{[\text{MCO}_3^0][\text{S–Fe(OH)}_3]},$$  \hspace{1cm} (4.5)

where brackets denote concentrations of the indicated species and $\text{S–Fe(OH)}_3$ represents uncharged amorphous ferric hydroxide surface sites (as distinguished from $\text{S–Fe(OH)}_2^+$).
and S – Fe(OH)$_4$). Under the conditions of our experiments, S – Fe(OH)$_4$ is unimportant (Quinn et al., 2006a) and the concentration of S–Fe(OH)$_3$ in equations (4.3), (4.4), and (4.5) can be expressed in terms of [S$_i$] (equation (4.1)) via the equation:

$$[S – Fe(OH)_3] = [S_i]sK_1[H^+]^{-1},$$  \hspace{1cm} (4.6)

where $sK_1$ is the surface protonation constant for amorphous ferric hydroxide:

$$sK_1 = \frac{[S – Fe(OH)_2^+]}{[S – Fe(OH)_3][H^+]}.$$  \hspace{1cm} (4.7)

The value of $sK_1$ used in this study (i.e., log $sK_1 = 4.76$) was taken from the work of Quinn et al. (2006a).

For carbonate-free solutions (i.e., [S – FeO(OH)$_2$MCO$_3$] = 0 M), equations (4.1–4.4), (4.6), and (4.7) were used by Quinn et al. (2006a) to model YREE sorption in the absence of significant solution complexation. In the presence of YREE carbonate complexation, additional sorbed species must be considered in equation (4.2) including the putative species S – FeO(OH)$_2$MCO$_3$ (equation (4.5)). Additionally, the sorption model of Quinn et al. (2006a) must be extended to include the relationship between total dissolved YREE concentrations ($M_T$) and free YREE concentrations ($[M^{3+}]$) as follows:

$$M_T = [M^{3+}] \times (1 + \text{HCO}_3^β_1[\text{HCO}_3^-] + \text{HCO}_3^β_1[\text{HCO}_3^-]_T[H^+]^{-1} + \text{CO}_2^β_2[\text{CO}_3^-]_T[H^+]^{-2}),$$  \hspace{1cm} (4.8)

where the YREE solution complexation constants ($\text{HCO}_3^β_1$, $\text{CO}_2^β_1$, and $\text{CO}_2^β_2$) are expressed in terms of bicarbonate concentrations (Luo and Byrne, 2004):

$$\text{HCO}_3^β_1 = \frac{[\text{MHCO}_3^{2+}]}{[M^{3+}][\text{HCO}_3^-]_T},$$  \hspace{1cm} (4.9)

$$\text{CO}_2^β_1 = \frac{[\text{MCO}_3^-][H^+]}{[M^{3+}][\text{HCO}_3^-]_T},$$  \hspace{1cm} (4.10)

and

$$\text{CO}_2^β_2 = \frac{[\text{M(CO}_3^-]^2[H^+]^2}{[M^{3+}][\text{HCO}_3^-]_T},$$  \hspace{1cm} (4.11)

and $[\text{HCO}_3^-]_T$ is the sum concentration of free bicarbonate ions ($\text{HCO}_3^-$) and ion pairs ($\text{NaHCO}_3^0$). A term for the formation of MOH$^{2+}$ is not included in equation (4.8) since
Quinn et al. (2006a) showed that, even in the absence of carbonate complexation, the influence of hydrolysis on the behavior of $\kappa^T_{\text{Fe}}$ at pH $\leq 7.0$ is insignificant.

Equations (4.1) through (4.11) can be combined to produce an equilibrium model for YREE sorption by amorphous ferric hydroxide in the presence of carbonate:

$$
\kappa^T_{\text{Fe}} = \frac{s\beta_1[H^+]^{-1} + s\beta_2[H^+]^{-2} + \frac{C_{\text{CO}_3}}{s\beta_1} \times \frac{H}{H} \beta_1[HCO_3^-][H^+]^{-2}}{K[H^+] + 1}(1 + HCO_3\beta_1[HCO_3^-][H^+]^{-1} + H CO_3\beta_2[HCO_3^-][H^+]^{-2})
$$

(4.12)

Empirical $\kappa^T_{\text{Fe}}$ data, as defined by equation (4.1), were fit using equation (4.12) with the residual sum of squares (RSS) function as follows:

$$
\text{RSS} = \sum \left(1 - \left[\frac{s\beta_1[H^+]^{-1} + s\beta_2[H^+]^{-2} + \frac{C_{\text{CO}_3}}{s\beta_1} \times \frac{H}{H} \beta_1[HCO_3^-][H^+]^{-2}}{K[H^+] + 1}\right]\times\left(\frac{|M^+|}{M_T}\right)\times(\kappa^T_{\text{Fe}})^{-1}\right)^2.
$$

(4.13)

Defined in this manner, the RSS provides equal weight to each experimental $\kappa^T_{\text{Fe}}$ result as distribution coefficients range over more than five orders of magnitude.

The carbonate complexation constants in equation (4.12) were taken from the results of Luo and Byrne (2004):

$$
\log_{HCO_3}\beta_1 = \log_{HCO_3}\beta_0^0 - 3.066 \times 10^0 (1 + 1.269 \times 10^5) + 0.297 \times 1,
$$

(4.14)

$$
\log_{CO_3}\beta_1 = \log_{CO_3}\beta_0^0 - 4.088 \times 10^5 (1 + 3.033 \times 10^5) + 0.042 \times 1,
$$

(4.15)

and

$$
\log_{CO_3}\beta_2 = \log_{CO_3}\beta_0^0 - 4.088 \times 10^5 (1 + 3.033 \times 10^5) + 0.042 \times 1,
$$

(4.16)

where the values of $\log_{HCO_3}\beta_1$, $\log_{CO_3}\beta_1$, and $\log_{CO_3}\beta_2$ for each YREE can be found in Table 5 of Luo and Byrne (2004). Bicarbonate concentrations were calculated from the equation:

$$
[HCO_3^-][H^+] = K_gK'_1P_{CO_2}[H^+],
$$

(4.17)

where the product $K_gK'_1$ describes the equilibrium.
\[ \text{CO}_2(g) + \text{H}_2\text{O} \Leftrightarrow \text{HCO}_3^- + \text{H}^+. \]  

(4.18)

The CO\textsubscript{2} partial pressure (P\textsubscript{CO\textsubscript{2}}) in equation (4.17) is expressed in terms of the total atmospheric pressure (P\textsubscript{T}), the partial pressure of H\textsubscript{2}O at 25°C (P\textsubscript{H\textsubscript{2}O}), and the mole fraction of CO\textsubscript{2}/N\textsubscript{2} gas mixtures (X\textsubscript{CO\textsubscript{2}}) using the following equation:

\[ P_{\text{CO}_2} = X_{\text{CO}_2} (P_T - P_{\text{H}_2\text{O}}) = 0.969X_{\text{CO}_2} \text{ atm}. \]  

(4.19)

K\textsubscript{0}K\textsubscript{1}' data appropriate to equation (4.18) were taken from the results of Luo and Byrne (2004):

\[ \log K_0K_1' = -7.829 + 1.022 \times 10^{0.5} \times (1 + 1.390 \times 10^{0.5}) - 0.191 \times 1. \]  

(4.20)

For the purpose of creating graphs, carbonate concentrations were calculated using the following equation:

\[ [\text{CO}_3^{2-}]_T = K_0K_1'K_2'P_{\text{CO}_2}[\text{H}^+]^{-2}, \]  

(4.21)

where \([\text{CO}_3^{2-}]_T\) is the sum concentration of free carbonate ions (CO\textsubscript{3}\textsuperscript{2−}) and ion pairs (NaCO\textsubscript{3}), and K\textsubscript{2}' is the equilibrium constant for the dissociation of bicarbonate:

\[ \text{HCO}_3^- \Leftrightarrow \text{CO}_3^{2-} + \text{H}^+. \]  

(4.22)

K\textsubscript{2}' was calculated from the results of Luo and Byrne (2004):

\[ \log K_2' = -10.331 + 2.044 \times 10^{0.5} \times (1 + 1.060 \times 10^{0.5}) - 0.184 \times 1. \]  

(4.23)

Equations (4.14) through (4.23) explicitly show the substantial ionic strength dependences for equilibria in the solution phase. In contrast, a wide variety of previous work has shown that the affinities of sorptive solid substrates for dissolved cations do not vary with ionic strength (Swallow et al., 1980; Hayes and Leckie, 1987; Dzombak and Morel, 1990; Quinn et al., 2006a). The data of Quinn et al. (2006a) showed that the influence of ionic strength on s\beta_1 and s\beta_2 (equations (4.3) and (4.4)) was very weak. Based on these observations appropriate to the YREEs, and a variety of observations obtained using other cations (Swallow et al., 1980; Hayes and Leckie, 1987), it was assumed in this work that not only s\beta_1 and s\beta_2 but also \textsuperscript{CO}_3\beta_1 (equation (4.5)) was invariant over the range of ionic strength utilized in this investigation (0.01 M \leq I \leq
0.1 M). It should be noted in this case that the product $\frac{c^\text{CO}_2}{s^\text{H}} \times \frac{c^\text{H}}{c^\text{CO}_2}$ has an ionic strength dependence identical to that of $\frac{c^\text{H}}{c^\text{CO}_2}$ (equation (4.15)).

### 4.4 Materials and Methods

Three types of experiment were undertaken to investigate the influence of carbonate solution complexation on YREE sorption by amorphous ferric hydroxide. In one type of experiment, sorption was examined as a function of time at constant pH and constant $P_{\text{CO}_2}$. In the other types of experiment, either solution pH was increased at constant $P_{\text{CO}_2}$ or the $P_{\text{CO}_2}$ was increased at constant pH.

All solutions were prepared with trace metal-clean water (Milli-Q water) from a Millipore (Bedford, MA) purification system. Ammonium nitrate (99.999%) and certified 1.000 M hydrochloric acid were purchased from Sigma-Aldrich (St. Louis, MO). TraceMetal Grade nitric acid, TraceMetal Grade ammonium hydroxide, and ferric chloride solution (40% w/v in HCl) were purchased from Fisher Scientific (Pittsburgh, PA). Sodium bicarbonate (Baker Analyzed) was purchased from J.T. Baker Inc. (Phillipsburg, NJ). A YREE stock solution, containing 66.7 ppm of each YREE in 2% HNO$_3$, was prepared from single-element ICP standards (SPEX CertiPrep, Metuchen, NJ). Ultra-pure N$_2$ and various certified CO$_2$/N$_2$ gas mixtures (30%, 3%, 1%, 0.5%, 0.3%, 0.1%, and 0.01% CO$_2$) were obtained from Airgas South Inc. (Clearwater, FL).

All chemical manipulations were performed in a class-100 clean air laboratory or laminar flow bench. Teflon and polypropylene laboratory materials and polycarbonate filter membranes were cleaned by soaking in HCl or HNO$_3$ for at least a week, followed by several thorough rinses with Milli-Q water. Solution pH, on the free hydrogen ion scale, was monitored using a Ross-type combination pH electrode (No. 810200) connected to a Corning 130 pH meter in the absolute millivolt mode. Nernstian behavior of the electrode was verified periodically by titrating a 0.3 M NaCl solution with concentrated HCl.

At the beginning of each experiment, a pH standard solution and an experimental solution, both with an ionic strength (I) equal to 0.011 M, were prepared in Teflon wide-
mouth bottles. The pH standard solution was composed of 1 mM HCl (pH 3.0) in 0.01 M NH₄NO₃. The experimental solution was composed of 107.8 µM ferric iron and 23.3 ppb of each YREE ([YREE]ₜ = 2.36 µM) in 0.01 M HCl. Both solutions were placed in jacketed beakers thermostated at T = (25.0 ± 0.1)°C and were equilibrated for approximately 24 hours. Throughout each experiment, solutions were continuously stirred with a Teflon-coated ‘floating’ stir bar and the experimental solution was continuously bubbled with a gas mixture, except during titrant additions. Ultra-pure N₂ gas was first passed through an in-line trap (Supelco, Bellafonte, PA) that removed all traces of CO₂. After bubbling for one hour at pH 2.0, starting with ultra-pure N₂ for experiments conducted over a range of P_CO₂, and with either 3% or 30% CO₂ for experiments at constant P_CO₂, an initial solution sample was taken to determine the total dissolved YREE concentration, Mₜ. Solution pH was then increased by addition of 0.7 M NaHCO₃ with a Gilmont micro-dispenser, resulting in rapid formation of a yellow-brown Fe(OH)₃ colloid.

One experiment was performed at constant P_CO₂ (30%) and constant pH (5.4), and samples were taken at 15 minutes, 90 minutes, 5 hours, 24 hours, 46 hours, and 48 hours. Two experiments were performed at constant P_CO₂ and increasing pH: one at 3% CO₂ and the other at 30% CO₂. Samples were taken at fixed pH increments between 4.0 and 6.6 after the solution had been equilibrated with the gas mixture for one hour. Four experiments were performed at increasing P_CO₂ and constant pH: two at pH ~ 6.6 and two at pH ~ 7.1. After taking the initial sample (pH 2.0), the pH was raised by addition of 1 M NH₄OH using a Gilmont micro-dispenser. While bubbling with ultra-pure N₂, four samples were taken: one at 15 minutes, one at 90 minutes, one at 5 hours, and one at ~ 22 hours. Subsequently, CO₂/N₂ gas mixtures were used to progressively increase P_CO₂ between 0.01% and 30% CO₂ (two experiments) and between 0.3% and 30% CO₂ (two experiments). After each P_CO₂ increase, solutions were equilibrated for approximately one hour. The pH was then readjusted by addition of 1 M NaHCO₃. At each P_CO₂, samples were taken at 15 minutes, 90 minutes, and either ~ 22 hours or between 45 and
70 hours. Occasionally, a fourth sample was taken at 47 or 66 hours. Because increases in the carbonate concentration caused increases in the ionic strength of the experimental solutions, the ionic strengths of pH standard solutions were matched using 1 M NH₄NO₃.

The sampling method was similar to that described in Quinn et al. (2006a). To summarize, during most experiments two samples were collected, one filtered and one centrifuged. During a few experiments, only filtered samples were taken because better phase separation was achieved with filtration. Each filtered sample consisted of two 5-mL aliquots of solution. The first was used to rinse the polypropylene syringe and the Nuclepore filter membrane (polycarbonate, 0.10 µm pore size). The second was collected in a polypropylene centrifuge tube. The centrifuged sample consisted of one 5-mL aliquot of solution, which was centrifuged for one hour using a Centra-4B centrifuge (International Equipment Company, Needham Heights, MA) at about 2200 × g.

The filtered samples and the supernatant of the centrifuged samples were diluted 5-fold with 1% HNO₃ except where concentrations were below the lowest calibration standard (0.5 ppb), in which case no dilution was performed. A small amount of internal standard solution containing equal concentrations of In, Cs, and Re was added to each sample. The resulting mixtures were analyzed for YREEs with an Agilent Technologies 4500 Series 200 inductively-coupled plasma mass spectrometer (ICP-MS) following the procedure outlined in Quinn et al. (2004). In brief, all standards and sample solutions were injected in triplicate. During instrument tuning, the formation of oxide and double-charged ions was minimized with a 10 ppb Ce solution. MO⁺ and M²⁺ peaks were always less than 1% and 3% of the corresponding M⁺ peak, respectively, and correction for this effect proved unnecessary. YREE concentrations were calculated from linear regressions of four standards (0.5, 1, 2, and 5 ppb). Ion counts were corrected for minor instrument drift by normalizing ⁸⁹Y to ¹¹⁵In, ¹³⁹La–¹⁶¹Dy to ¹³³Cs, and ¹⁶³Dy–¹⁷⁵Lu to ¹⁸⁷Re. To check the validity of the drift correction, a comparison was made of the Dy concentrations calculated from ¹⁶¹Dy and ¹⁶³Dy, which were usually identical within 2%.

For each experiment, raw ICP-MS data were corrected for dilution based on the volume of NH₄OH and/or NaHCO₃ titrants added to adjust the pH. Corrected data were then used to calculate distribution coefficients (KᵢFₑ) defined by equation (4.1). The
concentration of sorbed YREE, \([\text{MS}_i]_T\), was calculated as the difference between the YREE concentration in the initial sample (pH 2.0) and the YREE concentrations in subsequent samples after a pH or \(P_{CO_2}\) adjustment. Based on the solubility behavior of Fe\(^{3+}\) (Liu and Millero, 1999), the concentration of precipitated iron at pH > 4.0 was assumed to be equal to the initial dissolved iron concentration (~100 µM).

Quinn et al. (2006a) noted that YREE equilibrium between experimental solutions and freshly precipitated Fe(OH)\(_3\) is reached in about 15 minutes. In the present work, variations in \(\log_{i}K^T_{Fe}\) for equilibration times \(\geq 15\) minutes are smaller than the uncertainty in experimental \(\log_{i}K^T_{Fe}\) values. Therefore all data in Appendix D, which lists 111 \(\log_{i}K^T_{Fe}\) observations for each rare earth element, were used in our data analysis, except for two observations identified in Table D.3. These were obtained under conditions (pH 3.98 and pH 4.49) that produced very weak sorption, and therefore poorly constrained \(\log_{i}K^T_{Fe}\) data. This problem was expected, a priori, from the work of Quinn et al. (2006a), in which well defined \(\log_{i}K^T_{Fe}\) results at low pH (~4.0) were obtained by conducting experiments using 10 mM concentrations of precipitated amorphous ferric hydroxide. Utilization of the data in Tables B.1–B.6 along with the data shown in Appendix D resulted in regressions via equations (4.12) and (4.13) that incorporated as many as 166 \(\log_{i}K^T_{Fe}\) observations for each REE.

### 4.5 Results and Discussion

#### 4.5.1. Model Results Considering Sorption of Only Free YREEs

Since carbonate-free samples were included in the present experiments, \(s\beta_1\) and \(s\beta_2\) values were recalculated using new non-carbonate \(i\)\(K^T_{Fe}\) data (Tables D.4–D.7) plus the previous non-carbonate \(i\)\(K^T_{Fe}\) data in Tables B.1–B.6. The \(s\beta_1\) and \(s\beta_2\) results calculated using equations (4.12) and (4.13) with \([HCO_3^-]_T = 0\) M are listed in Table 4.1. Comparison of these results with the \(s\beta_1\) and \(s\beta_2\) results of Quinn et al. (2006a)
Table 4.1. YREE surface complexation constants ($s\beta_1$ and $s\beta_2$) determined using equations (4.12) and (4.13) with $[\text{HCO}_3^-]_T = 0$ M, log $sK_1 = 4.76$ (Quinn et al., 2006a), and the experimental distribution coefficient results from carbonate-free solutions in the present work (Tables B.1–B.6 and D.4–D.7). Uncertainties represent one standard error.

<table>
<thead>
<tr>
<th>[M$^{3+}$]</th>
<th>log $s\beta_1$</th>
<th>log $s\beta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>-2.98 ± 0.06</td>
<td>-8.86 ± 0.05</td>
</tr>
<tr>
<td>La</td>
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<tr>
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<tr>
<td>Eu</td>
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</tr>
<tr>
<td>Gd</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>Lu</td>
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<td>-8.26 ± 0.05</td>
</tr>
</tbody>
</table>

demonstrates agreement within approximately 1%, well within the listed uncertainties for both constants.

Distribution coefficient results from experiments containing carbonate were initially modeled by assuming that only free YREE ions sorb onto amorphous ferric hydroxide. In this case, the $^{CO_3}s\beta_1$ term in equation (4.12) is zero. Figure 4.1A shows log $K_{Fe}^T$ patterns at pH 7.06 predicted using equation (4.12) with the $s\beta_1$ and $s\beta_2$ results listed in Table 4.1 and $^{CO_3}s\beta_1 = 0$. Predicted log $K_{Fe}^T$ values decrease monotonically with increasing $[\text{CO}_3^{2-}]_T$, and the decrease in log $K_{Fe}^T$ for heavy REEs is approximately four orders of magnitude.
Figure 4.1: \( \log_i K_{Fe}^T \) results at pH 7.06 and various carbonate concentrations, \([CO_3^{2-}]_T\), listed in the legend. (A) \( \log_i K_{Fe}^T(\text{pred}) \) are distribution coefficients predicted from equation (4.12) using the \( S\beta_1 \) and \( S\beta_2 \) results listed in Table 4.1 and \( ^{CO}S\beta_1 = 0 \). (B) \( \log_i K_{Fe}^T(\text{meas}) \) are directly measured distribution coefficients from an experiment performed at constant pH (7.06) and increasing \( P_{CO_2} \) (Table D.6). Each pattern represents an average over time for a single carbonate concentration. For clarity, the \( \log_i K_{Fe}^T \) pattern at \([CO_3^{2-}]_T = 0.88 \mu M \) (\( P_{CO_2} = 0.5\% \)) is not shown.
Figure 4.1B shows experimental $\log_i K^T_{Fe}$ results obtained at pH 7.06 for the same carbonate concentrations depicted in Figure 4.1A. In sharp contrast to the predicted behavior shown in Figure 4.1A, measured $\log_i K^T_{Fe}$ values at low carbonate concentrations are larger than those at $[CO_3^{2-}]_T = 0$ M. Furthermore, the range of $\log_i K^T_{Fe}$ values shown in Figure 4.1B is orders of magnitude smaller than the predictions shown in Figure 4.1A. Predicted and observed $\log_i K^T_{Fe}$ values are directly and quantitatively compared in Figure 4.2. In the absence of carbonate (open circles), $\log_i K^T_{Fe}$ values are well described using equation (4.12). In the presence of carbonate (closed circles), $\log_i K^T_{Fe}$ observations are uniformly larger than equation (4.12) $\log_i K^T_{Fe}$ predictions obtained assuming $CO_3^{2-} \beta_1 = 0$. Figure 4.2 clearly shows that YREE sorption data in the presence of carbonate cannot be appropriately modeled solely in terms of the sorption of free ions, $M^{3+}$.

4.5.2. Model Results Including Sorption of a YREE Carbonate Complex

Non-linear least squares regressions (equations (4.12) and (4.13)) of the combined (carbonate plus non-carbonate) $\log_i K^T_{Fe}$ data obtained in this work (Tables B.1–B.6 and D.1–D.7) produced well-constrained estimates for $CO_3^{2-} \beta_1$ as well as $s \beta_1$ and $s \beta_2$ (Table 4.2). Figures 4.3A, 4.3B, and 4.3C provide graphical representations of the $s \beta_1$, $s \beta_2$, and $CO_3^{2-} \beta_1$ data given in Table 4.2 (open circles). Also shown in Figures 4.3A and 4.3B are the $s \beta_1$ and $s \beta_2$ data given in Table 4.1 (closed circles). The $CO_3^{2-} \beta_1$ results in Figure 4.3C (closed circles) were obtained in fits (equations (4.12) and (4.13)) of data at $[CO_3^{2-}]_T > 0$ M using the $s \beta_1$ and $s \beta_2$ values from Table 4.1. It is seen in Figures 4.3A and 4.3B that $\log s \beta_1$ and $\log s \beta_2$ results obtained in both two-parameter fits ($s \beta_1$ and $s \beta_2$ in Table 4.1) and three-parameter fits ($s \beta_1$, $s \beta_2$, and $CO_3^{2-} \beta_1$ in Table 4.2) are in very good agreement. Figure 4.3C shows that $\log CO_3^{2-} \beta_1$ results from three-parameter fits ($s \beta_1$, $s \beta_2$, and $CO_3^{2-} \beta_1$ in
Figure 4.2: $\log_i K_{Fe}^T$(meas) versus $\log_i K_{Fe}^T$(pred) for La, Sm, Dy, and Lu. $\log_i K_{Fe}^T$(meas) are directly measured distribution coefficients from the present work (Tables B.1–B.6 and D.1–D.7). Observed $\log_i K_{Fe}^T$ values represent YREE sorption corresponding to 5.0% – 99.9% of the total YREE concentration. $\log_i K_{Fe}^T$(pred) are distribution coefficients predicted from equation (4.12) using the $s\beta_1$ and $s\beta_2$ results listed in Table 4.1 and $^{CO}_s\beta_1 = 0$. Open circles represent carbonate-free samples and closed circles represent samples containing carbonate. Diagonal lines represent perfect agreement between predicted and measured values ($\log_i K_{Fe}^T$(pred) = $\log_i K_{Fe}^T$(meas)).
Table 4.2. YREE surface complexation constants ($\log s\beta_1$, $s\beta_2$, and $\log ^{CO}_s\beta_1$) determined with equations (4.12) and (4.13), $\log sK_1 = 4.76$ (Quinn et al., 2006a), and the experimental distribution coefficient results from the present work (Tables B.1–B.6 and D.1–D.7). Uncertainties represent one standard error.

<table>
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<th>$\log s\beta_2$</th>
<th>$\log ^{CO}_s\beta_1$</th>
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<td>Pm</td>
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<td>-</td>
</tr>
<tr>
<td>Sm</td>
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<tr>
<td>Eu</td>
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<tr>
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<tr>
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<tr>
<td>Tm</td>
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</tr>
<tr>
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<td>Lu</td>
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Figure 4.3: Surface stability constants (equation (4.12)) for YREE sorption by amorphous ferric hydroxide. Open circles in panels A, B, and C represent the $s_1$, $s_2$, and $C_{CO_3}^\beta$ results (Table 4.2) obtained in three-parameter fits using equations (4.12) and (4.13). Open circles in panel D represent the product $C_{CO_3}^\beta \times C_{H^\beta}$ obtained by multiplying the $C_{CO_3}^\beta$ results from the present work and the $C_{H^\beta}$ results from Luo and Byrne (2004). Closed circles in panels A and B represent the $s_1$ and $s_2$ results (Table 4.1) obtained in two-parameter fits using equations (4.12) and (4.13) with $[HCO_3^-]_r = 0$ M. Closed circles in panel C represent the $C_{CO_3}^\beta$ results obtained in single-parameter fits using equations (4.12) and (4.13). See text for details. Error bars on the open circles represent standard errors. For $C_{CO_3}^\beta$, standard errors are within the size of the symbol. For $C_{CO_3}^\beta \times C_{H^\beta}$, error bars were determined by statistically combining the standard errors from both stability constants.
Table 4.2) and from single-parameter fits ($s\beta_1$ and $s\beta_2$ taken from Table 4.1) are indistinguishable. The pattern in Figure 4.3D, which represents the product $\frac{c^{\text{CO}_3}\beta_1 \times c^{\text{H}}\beta_1}{c^{\text{CO}_3}\beta_1}$ used in equation (4.12), was obtained by multiplying the formation constant for the surface species $S-\text{FeO(OH)}_2\text{MCO}_3^0$ ($c^{\text{CO}_3}\beta_1$; Table 4.2) and the formation constant for the solution species $\text{MCO}_3^+$ at zero ionic strength ($c^{\text{H}}\beta_1$; taken from Luo and Byrne, 2004). It should be noted that the pattern for $\frac{c^{\text{CO}_3}\beta_1 \times c^{\text{H}}\beta_1}{c^{\text{CO}_3}\beta_1}$ will not change as a function of ionic strength but the absolute magnitude has an ionic strength dependence identical to that of $c^{\text{H}}\beta_1$ (equation (4.15)).

As a visual demonstration of the goodness-of-fit for the model, Figure 4.4 compares observed $\log_{10} K_{\text{Fe}}^T$ data in the absence (open circles) and presence (closed circles) of carbonate with $\log_{10} K_{\text{Fe}}^T$ data predicted using equation (4.12) and the parameters given in Table 4.2. The four REE shown in Figure 4.4 are representative of the entire YREE series, which all display excellent fits with slopes close to one and intercepts close to zero. It can be seen that YREE sorption by amorphous ferric hydroxide in the presence of carbonate is well described by accounting for solution complexation ($\text{MHCO}_3^{2+}$, $\text{MCO}_3^+$, and $\text{M(CO}_3)_2^-$ formation), and the formation of three surface-bound YREE species ($S-\text{FeO(OH)}_2\text{M}^{2+}$, $S-\text{FeO}_2(\text{OH})\text{M}^+$, and $S-\text{FeO(OH)}_2\text{MCO}_3^0$).

In addition to predicted versus observed $\log_{10} K_{\text{Fe}}^T$ comparisons for individual YREEs, it is also informative to examine predicted versus observed patterns for the entire YREE series. In Figure 4.5, directly measured $\log_{10} K_{\text{Fe}}^T$ patterns are compared with $\log_{10} K_{\text{Fe}}^T$ patterns predicted from equation (4.12) using the $s\beta_1$, $s\beta_2$, and $c^{\text{CO}_3}\beta_1$ results listed in Table 4.2. The $\log_{10} K_{\text{Fe}}^T$ patterns shown in Figure 4.5 were selected from Appendix D to represent the progression of shapes observed over the range of carbonate concentrations used here. It can be seen that these shapes are generally well predicted using equation (4.12) and the data given in Table 4.2. Although positive and negative deviations between
Figure 4.4: Regressions of $\log_i K^T_{Fe}(\text{meas})$ versus $\log_i K^T_{Fe}(\text{pred})$ for La, Sm, Dy, and Lu. $\log_i K^T_{Fe}(\text{meas})$ are directly measured distribution coefficients from the present work (Tables B.1–B.6 and D.1–D.7). $\log_i K^T_{Fe}(\text{pred})$ are distribution coefficients predicted from equation (4.12) using the $s\beta_1$, $s\beta_2$, and $^{CO}_s\beta_1$ results listed in Table 4.2. Open circles represent carbonate-free samples and closed circles represent samples containing carbonate. Dashed lines represent 95% confidence intervals.
predicted and measured values are seen in Figure 4.5, no systematic differences were observed for the log $K_{Fe}^T$ patterns obtained in this investigation.

Other than the species $S - {FeO(OH)}_2 {MCO}_3$ , two additional terms ($S - {FeO(OH)}_2 {MHCO}_3$ and $S - {FeO}_2 (OH){MCO}_3$ ) were considered in the equation (4.2) summation for [MS$_i$]$_T$. The surface complexation constants for these two species can be written as:

$$HCO_3 S\beta_1 = \frac{[S - {FeO(OH)}_2 {MHCO}_3][H^+] }{[MHCO_3^2+][S - {Fe(OH)}_2]} , \quad (4.24)$$
and
\[ \beta_2^{\text{CO}_2} = \frac{[S - \text{FeO}_2\text{(OH)}M \text{CO}_3^0][H^+]^2}{[\text{MCO}_3^+][S - \text{Fe(OH)}_3]} \]  
(4.25)

Replacement of the term for \( S - \text{FeO(OH)}_2 \text{MCO}_3^0 \) formation (equation (4.5)) in equation (4.12) with terms for either \( S - \text{FeO(OH)}_2 \text{MHCO}_3^+ \) or \( S - \text{FeO}_2(\text{OH})\text{MCO}_3^- \) formation (equations (4.24) and (4.25)) produced residual sum of squares (RSS) results much inferior to those obtained using equation (4.13). Furthermore, inclusion of terms for \( S - \text{FeO(OH)}_2 \text{MHCO}_3^+ \) and \( S - \text{FeO}_2(\text{OH})\text{MCO}_3^- \) in addition to the term for \( S - \text{FeO(OH)}_2 \text{MCO}_3^0 \) led to insubstantial improvements relative to fits with only three surface terms (\( s\beta_1, s\beta_2, \) and \( \beta_2^{\text{CO}_2} \)). Equation (4.12) provides a robust description of the data obtained in this investigation.

Additional sorption terms may be required at higher pH and higher carbonate concentrations than were investigated in the present work. Tang and Johannesson (2005) reported \( M(\text{CO}_3)_2^- \) sorption on Carrizo sand for \( \text{pH} > 7.3 \). Under the conditions of our experiments (\( \text{pH} \leq 7.15 \)), sorption of \( M(\text{CO}_3)_2^- \) was not required to describe partitioning of YREEs between the aqueous phase and amorphous ferric hydroxide.

4.5.3 Examination of the Competing Influences of Surface and Solution Complexation on \( K_{\text{Fe}}^T \)

The distribution coefficients predicted from equation (4.12) can be separated into contributions from solution species (\( \text{MHCO}_3^+, \text{MCO}_3^+, \) and \( M(\text{CO}_3)_2^- \)) and surface species (\( S - \text{FeO(OH)}_2M^{2+}, S - \text{FeO}_2(\text{OH})M^+, \) and \( S - \text{FeO(OH)}_2 \text{MCO}_3^0 \)). This is shown by rearranging equation (4.1) as follows:
\[ \log K_{\text{Fe}}^T = \log \frac{[\text{MS}_1^T]}{[\text{M}^{3+}][S_1]} - \log \frac{M_{\text{Fe}}}{[\text{M}^{3+}]} \]  
(4.26)

The first term on the right-hand side of equation (4.26) describes the affinity of amorphous ferric hydroxide for free dissolved YREE ions (\( M^{3+} \)). Using equations (4.2–4.6) and (4.10), this term is written as:
\[
\frac{[\text{MS}_i]_{T}}{[\text{M}^{3+}][S_i]} = \frac{s\beta_1[H^+]^{-1} + s\beta_2[H^+]^{-2} + \frac{\text{CO}_3\beta_1}{s\beta_1} \times \frac{\text{CO}_2\beta_1}{s\beta_1} [\text{HCO}_3^{-}]_T [H^+]^{-2}}{sK_i [H^+] + 1}.
\] (4.27)

The second term in equation (4.26) is the complexation intensity of YREEs in solution (i.e., equation (4.8)). This term is a measure of the relative proportions of YREEs that remain in solution as free ions. The competitive influences of surface versus solution complexation on observed \(\log K_{Fe}^T\) patterns (Figure 4.5) are shown in Figures 4.6 and 4.7, respectively.

The patterns shown in Figure 4.6, which are calculated with equation (4.27), are relatively constant over a wide range of conditions. The uniformity of these patterns is due to the fact that the terms \(s\beta_1, s\beta_2,\) and \(\frac{\text{CO}_3\beta_1}{s\beta_1} \times \frac{\text{CO}_2\beta_1}{s\beta_1}\) in equation (4.27) have very

**Figure 4.6:** Patterns of the surface complexation term (\(\log ([\text{MS}_i]_T [\text{M}^{3+}]^{-1} [S_i]^{-1})\)) in equation (4.26) calculated with equation (4.27).
Figure 4.7: Patterns of the solution complexation term \( \log \left( \frac{M_T}{[M^{3+}]} \right) \) in equation (4.26) calculated with equation (4.8). The symbols for each pattern correspond to the same symbols in Figure 4.6. Horizontal dotted lines were drawn through \( Y \) to emphasize the relative slopes of the patterns, except for the pattern at \([CO_3^{2-}]_T = 9.64 \text{ nM}\), which is relatively flat. For clarity, the vertical axis is extended below zero although all of the solution complexation values are positive.

Similar patterns (Figures 4.3A, 4.3B, and 4.3D) across the YREE series. In contrast, the patterns of the solution complexation term \( \left( \frac{M_T}{[M^{3+}]} \right) \) shown in Figure 4.7 exhibit large changes over the same range of conditions.

Equation (4.26) indicates that the predicted \( \log \, K^T_{Fe} \) patterns in Figure 4.5 can be obtained by subtracting the solution complexation curves in Figure 4.7 from the corresponding surface complexation curves in Figure 4.6. Since the solution complexation term labeled \( A \) in Figure 4.7 is very close to zero and displays a relatively flat pattern, the conjugate \( \log \, K^T_{Fe} \) pattern at \([CO_3^{2-}]_T = 9.64 \text{ nM}\) (Figure 4.5A) closely resembles the pattern for the surface complexation term in Figure 4.6A. The \( \log \, K^T_{Fe} \) values in Figure 4.5B are 0.5 to 0.6 units larger than the \( \log \, K^T_{Fe} \) values shown in Figure
4.5A. This is caused by a nearly one unit increase in the magnitude of the surface complexation term (Figure 4.6B) and a much smaller increase in the solution complexation intensity (Figure 4.7B). Compared to the pattern in Figure 4.5A, the log \( K_{Fe}^T \) pattern at \([CO_3^{2-}]_r = 103 \) nM (Figure 4.5B) shows a small decrease in the HREEs (e.g., Lu) relative to the middle REEs (e.g., Sm). This is caused by larger increases in HREE solution complexation intensity than is the case for LREEs. The log \( K_{Fe}^T \) pattern at \([CO_3^{2-}]_r = 974 \) nM (Figure 4.5C) displays a gradual decrease along the YREE series from Sm to Lu compared to the patterns in Figures 4.5A and 4.5B. This is due to the rapidly increasing significance in solution complexation for HREEs (Figure 4.7C). The log \( K_{Fe}^T \) pattern at \([CO_3^{2-}]_r = 5,770 \) nM (Figure 4.5D) exhibits a pronounced decrease across the YREE series from Sm to Lu due to the sharp increase in the solution complexation term (Figure 4.7D). Although the magnitudes of log \( K_{Fe}^T \) values increase for all YREEs between Figures 4.5A and 4.5D, changes are smallest for the HREEs due to the stronger increase in intensity of HREE solution complexation. These results show that the somewhat complex log \( K_{Fe}^T \) behavior shown in Figure 4.1B has a relatively simple explanation in terms of competitive solution and surface complexation.

### 4.6 Summary

The present work describes the influence of carbonate complexation on YREE sorption by amorphous ferric hydroxide. In the absence of carbonate, YREE sorption is well explained by complexation of free trivalent YREEs (M\(^{3+}\)) at two surface sites (Quinn et al., 2006a). When carbonate is added to the system, YREE sorption behavior is well described by adding only one new term to the surface complexation model that is appropriate in the absence of solution complexation. The new term accounts for sorption of YREE carbonate complexes (MCO\(_3^−\)) by amorphous ferric hydroxide. The YREE sorption model developed in this work (equation (4.12)), which incorporates the influences of both surface and solution complexation, quantitatively predicts (i) the increase in log \( K_{Fe}^T \) that is caused by an increase in pH, (ii) the increase in log \( K_{Fe}^T \) that
occurs at low carbonate concentrations due to sorption of $\text{MCO}_3^-$ in addition to $M^{3+}$, and (iii) the decrease in $\log_{10} K_{\text{Fe}}^{\text{T}}$ that occurs at high carbonate concentrations, especially for HREEs, due to increasing solution complexation.
5. Sorption of Yttrium and Rare Earth Elements by Amorphous Ferric Hydroxide: Influence of Temperature

5.1 Introduction

In previous work (Quinn et al., 2006a,b), YREE sorption by amorphous ferric hydroxide was shown to be strongly dependent on pH and carbonate concentration ([CO$_3^{2-}$]$_T$), but weakly dependent on ionic strength (I). Using the surface complexation model developed by Quinn et al. (2006a,b), YREE sorption can now be described over a wide range of solution conditions found in natural waters (3.9 ≤ pH ≤ 7.1; 0 M ≤ [CO$_3^{2-}$]$_T$ ≤ 150 µM; 0.01 M ≤ I ≤ 0.09 M). In addition to variations in pH, ionic strength, and carbonate concentration, however, natural waters exhibit a range in temperature (-2°C ≤ T ≤ 400°C) that may also affect YREE sorption behavior.

As an example, in mountain streams it has been observed that diel (24-hour) fluctuations in temperature and pH produce changes in concentrations of trace metals, including iron, aluminum, zinc, and the REEs (e.g., Gammons et al., 2005a,b, and references therein). At a stream station with neutral pH, Gammons et al. (2005b) found that dissolved REE concentrations increased at night and particulate REE concentrations increased during the day. Since the diel pH variation was very small (0.06 units) compared to the diel temperature change (11.7°C), these observations were attributed to temperature-dependent sorption of REEs by hydrous ferric and aluminum oxides. Using the linear relationship between dissolved REE concentrations and reciprocal temperature, Gammons et al. (2005b) estimated sorption enthalpies for each REE, which ranged from 57 to 120 kJ/mol (13.6 to 28.7 kcal/mol). Because stream particles are composed of several different phases, the enthalpies determined by Gammons et al. (2005b) should be considered conditional.
Only a few studies have examined REE sorption by pure solids over a range of temperatures (Miller et al., 1982; Koeppenkastrop, 1992; Ridley et al., 2005; Takahashi et al., 2005; Tertre et al., 2005). Despite the variety of substrates used, including montmorillonite (Miller et al., 1982; Tertre et al., 2005), amorphous FeOOH (Koeppenkastrop, 1992), bacteria (Takahashi et al., 2005), and rutile (Ridley et al., 2005), all of these studies showed that REE sorption increased with increasing temperature. Using either the van ’t Hoff equation or a modified form of the Clausius-Clapeyron equation, REE sorption enthalpies were determined to be positive and relatively small (≤ 45 kJ/mol or 11 kcal/mol) compared to other reaction enthalpies such as cation hydration, indicating a relatively weak temperature dependence for REE sorption (Koeppenkastrop, 1992; Ridley et al., 2005; Tertre et al., 2005). Koeppenkastrop (1992) and Ridley et al. (2005) suggested that the endothermic sorption reaction for REEs is driven by a large entropy increase. Enthalpy values were only reported for a few individual REEs, limiting interpretations of YREE behavior as a group.

To further improve descriptions of YREE behavior in natural waters, the current study investigates sorption of the entire YREE series by amorphous ferric hydroxide between 10 and 40°C. Observed temperature dependences are quantified in terms of sorption enthalpies that are incorporated in the surface complexation model originally developed by Quinn et al. (2006a).

5.2. Materials and Methods

YREE sorption by amorphous ferric hydroxide was investigated at 10 and 40°C over a range of pH (4.7 − 7.1) using procedures essentially identical to those employed by Quinn et al. (2006a) at 25°C. Two experiments were performed at each temperature. A brief description of the experimental procedure is provided below.

All chemical manipulations were performed in a class-100 clean air laboratory or laminar flow bench. Trace metal-clean water (Milli-Q water) from a Millipore purification system was used for all solution preparations. At the beginning of each experiment, a pH standard solution and an experimental solution, both with ionic strength I = 0.012 ± 0.002, were prepared in Teflon wide-mouth bottles. The pH standard solution
was composed of 1.0 mM HCl (pH 3.0) in 0.01 M NH₄NO₃. The experimental solution was composed of 23.3 ppb of each YREE ([YREE]₀ = 2.36 µM) and either 0.1 mM (experiments at 40°C) or 1.0 mM (experiments at 10°C) iron in 0.01 M HCl. The concentration of iron was increased for the experiments at 10°C in order to obtain adequate YREE sorption.

The experimental solution was bubbled with ultra-pure N₂ throughout each experiment. After equilibrating at the appropriate temperature for approximately two hours, an initial sample (pH 2.0) was taken to determine the total YREE concentration. The pH of the experimental solution was then increased by addition of 1 M NH₄OH using a Gilmont micro-dispenser. Two samples were taken at each half-unit pH increment: one at 15 minutes and one at either 60 minutes or 90 minutes. In contrast to previous experiments, only filtered samples were taken because filtration provided better phase separation than centrifugation.

The temperature of both solutions was measured after the two-hour equilibration period, and also at the end of each experiment. The pH standard solution differed by ±0.2° from the experimental solution, which was caused by differences in the physical configurations used for thermostating. The temperature changed approximately 0.5° during each experiment, which generally lasted < 15 hours. Solution pH on the free hydrogen-ion concentration scale was measured using a Ross-type combination pH electrode (No. 810200) connected to a Corning 130 pH meter in the absolute millivolt mode. Linearity and Nernstian behavior of the electrode was verified by titrating a 0.3 M NaCl solution with concentrated HCl at each temperature.

The filtered samples were diluted 5-fold with 1% HNO₃ except where concentrations were below the lowest calibration standard (0.5 ppb), in which case no dilution was performed. A small amount of internal standard solution containing equal concentrations of In, Cs, and Re was added to each sample. The resulting mixtures were analyzed for YREEs with an Agilent Technologies 4500 Series 200 inductively-coupled plasma mass spectrometer (ICP-MS) following the procedure outlined in Quinn et al. (2004). In brief, all standards and sample solutions were injected in triplicate. The instrument was tuned to minimize formation of oxide and double-charged ions using a 10 ppb Ce solution. MO⁺
and $M^{2+}$ peaks were always less than 1% and 3% of the corresponding $M^+$ peak, respectively, and correction for this effect proved unnecessary. YREE concentrations were calculated from linear regressions of four standards (0.5, 1, 2, and 5 ppb). Ion counts were corrected for minor instrument drift by normalizing $^{89}\text{Y}$ to $^{115}\text{In}$, $^{139}\text{La–161Dy}$ to $^{133}\text{Cs}$, and $^{163}\text{Dy–175Lu}$ to $^{187}\text{Re}$. To check the validity of the drift correction, a comparison was made of the Dy concentrations calculated from $^{161}\text{Dy}$ and $^{163}\text{Dy}$, which were usually identical within 2%.

Raw data from each experiment were corrected by a dilution factor, which was based on the amount of NH$_4$OH added to increase the pH. Distribution coefficients were calculated from these corrected data using the following equation:

$$K_{Fe} = \frac{[MS]_T}{[M^{3+}][S]} = \frac{[MS]_T}{M_T[Fe^{3+}]_S}, \quad (5.1)$$

where brackets denote the concentration of each indicated species. Over the range of experimental conditions employed in this work, the concentration of free YREE was set equal to the total dissolved YREE concentration ($[M^{3+}] = M_T$). The concentration of sorptive solid substrate was set equal to the concentration of precipitated iron ($[S] = [Fe^{3+}]_S$), which was assumed to be equal to the initial dissolved Fe concentration. The concentration of sorbed YREE, $[MS]_T$, was calculated as the difference between the YREE concentration of the initial sample at pH 2 and the YREE concentration of the filtrate at each subsequent time after a pH adjustment.

5.3 Results and Discussion

Distribution coefficient (log $K_{Fe}$) results from experiments performed over a range of temperatures (10 – 40°C) are shown in Figure 5.1. It can be seen that as the temperature increased, YREE sorption increased at both pH 5.6 (Figure 5.1A) and pH 7.1 (Figure 5.1B). The log $K_{Fe}$ data displayed in Figure 5.1 were selected from Appendices B and E to emphasize the shape of the YREE pattern at each temperature. Because the absolute increase in log $K_{Fe}$ was very similar across the series, YREE fractionation patterns remained relatively constant with increasing temperature between pH 5.6 and 7.1. This suggests that YREE fractionation is temperature independent, which was also observed.
by Tertre et al. (2005) in their study on YREE sorption by montmorillonite from 25 to 80°C. Figure 5.2 shows log $iK_{Fe}$ results versus pH for four representative REEs. Despite the scatter, especially at 25°C, the log $iK_{Fe}$ data in Figure 5.2 are clearly shifted to higher values with increasing temperature.

**Figure 5.1.** log $iK_{Fe}$ results obtained over a range of temperatures, indicated in the legend, at pH = 5.61 ± 0.05 (A) and pH = 7.06 ± 0.03 (B).
Figure 5.2. log ${iK_{Fe}}$ versus pH for La, Sm, Dy, and Lu at 10, 25, and 40°C. Closed triangles represent samples at 10°C, open circles represent samples at 25°C, and closed circles represent samples at 40°C.

To describe the pH dependence of YREE sorption at 25°C, Quinn et al. (2006a) proposed a surface complexation model (SCM) in the form:

$$ iK_{Fe} = \frac{s\beta_{1}[H^+]^{-1} + s\beta_{2}[H^+]^{-2}}{sK_{1}[H^+] + 1} $$

(5.2)

where $s\beta_n$ are stability constants for sorption of free YREE ions and $sK_1$ is the surface protonation constant for amorphous ferric hydroxide (log $sK_1 = 4.76$; Quinn et al., 2006a). In order to highlight the influence of temperature on $iK_{Fe}$, equation (5.2), with the $s\beta_n$ values at 25°C calculated by Quinn et al. (2006b), was used to predict distribution coefficients at 10 and 40°C. Figure 5.3 compares directly measured log $iK_{Fe}$ results at 10,
**Figure 5.3.** Regressions of log $iK_{Fe\text{ (meas)}}$ versus log $iK_{Fe\text{ (pred)}}$ for La, Sm, Dy, and Lu. log $iK_{Fe\text{ (meas)}}$ are directly measured distribution coefficients from the present work (Tables B.1–B.6, D.4–D.7, and E.1–E.4). log $iK_{Fe\text{ (pred)}}$ are distribution coefficients predicted from equation (5.2) using the $s_{\beta_1}$ and $s_{\beta_2}$ results listed in Table 4.1. Closed triangles represent samples at 10°C, open circles represent samples at 25°C, and closed circles represent samples at 40°C.
25, and 40°C with distribution coefficient values predicted using equation (5.2). Despite the fact that the regressions are fairly good \((r^2 = 0.95 \pm 0.01\) for all YREEs), data for 10°C consistently plot below the regression line while data for 40°C plot above the regression line, indicating the temperature effect on YREE sorption is not adequately modeled by equation (5.2).

The influence of temperature on the stability constants, \(s\beta_1\) and \(s\beta_2\), that are used to describe YREE sorption, can be characterized using the van ’t Hoff equation:

\[
\ln \frac{s\beta_n^{T_2}}{s\beta_n^{298.15}} = \frac{-\Delta H_n^0}{R} \left( \frac{1}{T_2} - \frac{1}{298.15} \right),
\]

(5.3)

where \(s\beta_n^{298.15}\) is a stability constant at 298.15 K, \(s\beta_n^{T_2}\) is a stability constant at some absolute temperature \((T_2)\), \(\Delta H_n^0\) is an enthalpy change, and \(R\) is the gas constant \((1.987 \text{ cal K}^{-1} \text{ mol}^{-1})\). Rearranging equation (5.3) and substituting into equation (5.2) for both \(s\beta_1\) and \(s\beta_2\) gives:

\[
K_{Fe} = \frac{s\beta_1^{298.15} \times 10^{p_n} \times [H^+]^{-1} + s\beta_2^{298.15} \times 10^{p_n} \times [H^+]^{-2}}{s K_i[H^+] + 1},
\]

(5.4)

where

\[
p_n = \frac{-\Delta H_1^0}{R \ln(10)} \left( \frac{1}{T_2} - \frac{1}{298.15} \right).
\]

(5.5)

SigmaPlot (Version 8.02) was used to solve equation (5.4) for \(s\beta_1^{298.15}\), \(s\beta_2^{298.15}\), \(\Delta H_1^0\), and \(\Delta H_2^0\) through minimization of the following residual sum of squares (RSS) function:

\[
RSS = \sum \left[ 1 - \left( \frac{s\beta_1^{298.15} \times 10^{p_n} \times [H^+]^{-1} + s\beta_2^{298.15} \times 10^{p_n} \times [H^+]^{-2}}{s K_i[H^+] + 1} \right) \times K_{Fe}^{-1} \right]^2,
\]

(5.6)

where the summation was performed over all pH values and all temperatures. The distribution coefficient \((iK_{Fe})\) data that were utilized for the determination of the parameters in equation (5.4) are listed in Tables B.1–B.6, D.4–D.7, and E.1–E.4 (note that the fit exclusively used data at \([\text{CO}_3^{2-}]_T = 0 \text{ M}\)).

YREE surface complexation constants \((s\beta_1^{298.15}\) and \(s\beta_2^{298.15}\)) and enthalpy values \((\Delta H_1^0\) and \(\Delta H_2^0\)) calculated using equations (5.4) and (5.6) are listed in Table 5.1. The
Table 5.1. YREE surface complexation constants ($s_1^{298.15}$ and $s_2^{298.15}$) and enthalpy values ($\Delta H^0_1$ and $\Delta H^0_2$; kcal/mol) determined with equations (5.4) and (5.6), log $sK_1 = 4.76$ (Quinn et al., 2006a), and the distribution coefficient data in Tables B.1–B.6, D.4–D.7, and E.1–E.4. Uncertainties represent one standard error.

<table>
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<tr>
<th>[M$^{3+}$]</th>
<th>$s_1^{298.15}$</th>
<th>$\Delta H^0_1$</th>
<th>$s_2^{298.15}$</th>
<th>$\Delta H^0_2$</th>
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<tr>
<td>Y</td>
<td>-2.95 ± 0.04</td>
<td>12.6 ± 2.5</td>
<td>-8.92 ± 0.04</td>
<td>9.9 ± 1.8</td>
</tr>
<tr>
<td>La</td>
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<td>-9.36 ± 0.06</td>
<td>7.7 ± 2.9</td>
</tr>
<tr>
<td>Ce</td>
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<td>12.7 ± 1.5</td>
<td>-8.85 ± 0.06</td>
<td>8.0 ± 2.9</td>
</tr>
<tr>
<td>Pr</td>
<td>-2.30 ± 0.03</td>
<td>12.5 ± 1.4</td>
<td>-8.62 ± 0.05</td>
<td>8.2 ± 2.3</td>
</tr>
<tr>
<td>Nd</td>
<td>-2.23 ± 0.03</td>
<td>12.1 ± 1.4</td>
<td>-8.55 ± 0.05</td>
<td>8.2 ± 2.4</td>
</tr>
<tr>
<td>Pm</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>-2.09 ± 0.03</td>
<td>11.8 ± 1.4</td>
<td>-8.32 ± 0.04</td>
<td>8.3 ± 2.1</td>
</tr>
<tr>
<td>Eu</td>
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<td>-8.35 ± 0.04</td>
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<td>9.8 ± 1.8</td>
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<td>Dy</td>
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<tr>
<td>Tm</td>
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<td>13.3 ± 1.4</td>
<td>-8.38 ± 0.04</td>
<td>11.8 ± 1.6</td>
</tr>
<tr>
<td>Yb</td>
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<td>13.4 ± 1.4</td>
<td>-8.26 ± 0.04</td>
<td>12.3 ± 1.5</td>
</tr>
<tr>
<td>Lu</td>
<td>-2.23 ± 0.03</td>
<td>13.1 ± 1.4</td>
<td>-8.32 ± 0.04</td>
<td>12.2 ± 1.6</td>
</tr>
</tbody>
</table>

$s_1^{298.15}$ and $s_2^{298.15}$ results obtained in the present study differ by approximately 2% from those determined by Quinn et al. (2006b), which is within the uncertainty of the estimates. In Figure 5.4, enthalpy values are plotted versus YREE atomic number. It can be seen that $\Delta H^0_1$ for all YREEs are identical within the experimental error (average $\Delta H^0_1 = 12.7$ kcal/mol). However, since the errors are strongly correlated across the YREE series, the observed pattern for $\Delta H^0_1$ is likely to represent significant YREE trends.

Enthalpy values determined with equations (5.4) and (5.6) can not be directly compared with previous REE thermodynamic results because either the model parameters (Ridley et al., 2005) or the solution chemical compositions (Koeppenkastrop, 1992) were distinctly different from those used in the current study. An indirect comparison may be
made with the results of Tertre et al. (2005) in their investigation of YREE sorption by montmorillonite between 25 and 80°C. By plotting distribution coefficients (log $K_d$) versus reciprocal temperature, Tertre et al. (2005) calculated an apparent enthalpy of 9.3 ± 2.4 kcal/mol for Eu sorption at pH 7.0. To make a similar assessment, distribution coefficients were predicted at pH 7.0 and 25, 40, and 80°C using equation (5.4) and the parameters listed in Table 5.1. Plots of predicted values versus reciprocal temperature (not shown), yielded an average enthalpy of 10.4 ± 1.2 kcal/mol for all YREEs.

Despite the lack of comparable YREE sorption enthalpies, the average $\Delta H_1^\circ$ value obtained in the present study is on the same order of magnitude as the enthalpy for the
first hydrolysis constant of iron (i.e., $\Delta H_1^* = 10.2 \pm 0.3$ kcal/mol; Byrne et al., 2000, and references therein), and also the average enthalpy for YREE hydrolysis (i.e., $\Delta H^0(M) = 11.3$ kcal/mol for all YREEs; Klungness and Byrne, 2000). The coherence of these values suggests that the enthalpies involved in YREE sorption are related to the enthalpy of dissociation of $H_2O$ in the first coordination sphere of cations such as $Fe^{3+}$ (Baes and Mesmer, 1981).

To demonstrate the goodness-of-fit for the temperature-dependent SCM, distribution coefficients were predicted at 10, 25, and 40°C using equation (5.4) and the parameters listed in Table 5.1. Figure 5.5 compares these predictions with directly measured $\log K_{Fe}$ values for four representative REEs. The $r^2$ values ($0.98 \pm 0.01$ for all YREEs) for the regressions in Figure 5.5 are significantly better than those for the regressions in Figure 5.3. In addition, the data at 10 and 40°C are tightly grouped around the regression lines. These results indicate that the SCM was substantially improved by including terms ($\Delta H_1^0$ and $\Delta H_2^0$) for the temperature dependence of YREE sorption.

Based on the fact that sorption of free YREE ions ($M^{3+}$) is significantly dependent on temperature, it is expected that sorption of YREE solution complexes, such as $MCO_3^+$, may also be temperature dependent. In order to determine an enthalpy for $MCO_3^+$ sorption, experiments need to be performed over a range of temperatures in the presence of carbonate. Additionally, the temperature dependence of YREE carbonate complexation must be known. Cantrell and Byrne (1987b) calculated enthalpies for carbonate and bicarbonate stability constants of Eu between 15 and 35°C. Their results indicated that YREE complexation by $CO_3^{2-}$ is weakly dependent on temperature relative to the influence of temperature on YREE sorption. Once enthalpy values for carbonate complexation and $MCO_3^+$ sorption are obtained for the entire YREE series, a SCM can be produced that will accurately describe YREE sorption over a wide range of solution conditions (i.e., pH, carbonate complexation, and temperature).
Figure 5.5. Regressions of log $i_{K_{Fe}}$(meas) versus log $i_{K_{Fe}}$(pred) for La, Sm, Dy, and Lu. log $i_{K_{Fe}}$(meas) are directly measured distribution coefficients from the present work (Tables B.1–B.6, D.4–D.7, and E.1–E.4). log $i_{K_{Fe}}$(pred) are distribution coefficients predicted from equation (5.4) using the $s\beta^{298.15}_1$, $s\beta^{298.15}_2$, $\Delta H^0_1$, and $\Delta H^0_2$ results listed in Table 5.1. Closed triangles represent samples at 10°C, open circles represent samples at 25°C, and closed circles represent samples at 40°C.
References


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Appendices
Appendix A: Data for Freshly Precipitated Hydroxides of Trivalent Cations (Al$^{3+}$, Ga$^{3+}$, and In$^{3+}$)

Table A.1. Distribution coefficient (log $K_{Al}$) results from the experiment performed at pH = 5.86 ± 0.18 with an aluminum concentration of 1.00 ± 0.05 mM.

<table>
<thead>
<tr>
<th>I (M)</th>
<th>0.016</th>
<th>0.016</th>
<th>0.016</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
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<td>5.81</td>
<td>5.70</td>
</tr>
<tr>
<td>time</td>
<td>15 min</td>
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Appendix A (Continued)

Table A.3. Distribution coefficient ($\log K_{in}$) results from the experiment performed at pH = 6.08 ± 0.04 with an indium concentration of 1.09 ± 0.05 mM.

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Appendix B: pH Dependent Data for Amorphous Ferric Hydroxide

Table B.1. Distribution coefficient ($\log K_{\text{Fe}}$) results from the experiment performed at pH = 5.15 ± 0.02 with an iron concentration of 0.613 ± 0.042 mM. The precision in $\log K_{\text{Fe}}$ was estimated to be $\leq 0.08$ by statistically combining the precision of the YREE analyses with the uncertainty in the concentration of the ferric chloride solution. For Y the $\log K_{\text{Fe}}$ precision is $\leq 0.2$.

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Appendix B (Continued)

Table B.2. Distribution coefficient (log $iK_{Fe}$) results from the experiment performed at pH = 6.12 ± 0.05 with an iron concentration of 0.108 ± 0.008 mM. The precision in log $iK_{Fe}$ was estimated to be $\leq 0.08$ by statistically combining the precision of the YREE analyses with the uncertainty in the concentration of the ferric chloride solution. For Y the log $iK_{Fe}$ precision is $\leq 0.2$.

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Appendix B (Continued)

Table B.3. Distribution coefficient ($\log K_{Fe}$) results from the experiment performed at pH = 7.06 ± 0.05 with an iron concentration of 0.108 ± 0.008 mM. The precision in $\log K_{Fe}$ was estimated to be ≤ 0.08 by statistically combining the precision of the YREE analyses with the uncertainty in the concentration of the ferric chloride solution. The sample at 15 minutes was excluded from all calculations because it was anomalously low, possibly due to a dilution error.

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Table B.4. Distribution coefficient (log $iK_{Fe}$) results from the experiment performed over the pH range 5.1 – 7.0 with an iron concentration of 0.108 ± 0.008 mM. The precision in log $iK_{Fe}$ was estimated to be ≤ 0.08 by statistically combining the precision of the YREE analyses with the uncertainty in the concentration of the ferric chloride solution.

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Appendix B (Continued)

Table B.5. Distribution coefficient ($\log iK_{Fe}$) results from the experiment performed over the pH range 5.1 – 7.0 with an iron concentration of 0.108 ± 0.008 mM. The precision in $\log iK_{Fe}$ was estimated to be $\leq 0.08$ by statistically combining the precision of the YREE analyses with the uncertainty in the concentration of the ferric chloride solution.

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Table B.6. Distribution coefficient (log $iK_{Fe}$) results from the experiment performed over the pH range 3.9 – 5.6 with an iron concentration of 10.0 ± 0.7 mM. The precision in log $iK_{Fe}$ was estimated to be ≤ 0.15 by statistically combining the precision of the YREE analyses with the uncertainty in the concentration of the ferric chloride solution. For Y the log $iK_{Fe}$ precision is ≤ 0.3. n.v. = no value because measured YREE concentrations were indistinguishable from YREE concentrations at t = 0 (i.e., [MS$_i$]$_T$ = 0 in equation (3.1)).

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Appendix C: Ionic Strength Dependent Data for Amorphous Ferric Hydroxide

Table C.1. Distribution coefficient (log \( iK_{Fe} \)) results from the experiment performed over the ionic strength range 0.01 – 0.09 M with an iron concentration of 0.108 \( \pm \) 0.008 mM. The precision in log \( iK_{Fe} \) was estimated to be \( \leq 0.08 \) by statistically combining the precision of the YREE analyses with the uncertainty in the concentration of the ferric chloride solution. The 5 minute sample at \( I = 0.03 \) M was excluded from all calculations because it was anomalously low, possibly due to a dilution error.

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Table C.2. Distribution coefficient ($\log \text{iK}_{\text{Fe}}$) results from the experiment performed over the ionic strength range 0.01 – 0.09 M with an iron concentration of 0.108 ± 0.008 mM. The precision in $\log \text{iK}_{\text{Fe}}$ was estimated to be ≤ 0.08 by statistically combining the precision of the YREE analyses with the uncertainty in the concentration of the ferric chloride solution.

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Appendix D: Data for Amorphous Ferric Hydroxide Covering a Range of Carbonate Concentrations ([CO$_3^{2-}$]$_T$)

Table D.1. Distribution coefficient (log $\lambda K^T_{Fe}$) results from the experiment performed at pH = 5.38 ± 0.02 and 30% CO$_2$.

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Appendix D (Continued)

Table D.2. Distribution coefficient ($\log_{i}K_{fe}^T$) results from the experiment performed over the pH range 4.6 – 6.6 at 3% CO$_2$. It should be noted that carbonate concentrations ([CO$_3^-$],T) are listed in nM units. n.v. = no value because measured YREE concentrations were indistinguishable from YREE concentrations at t = 0 (i.e., [MS]$_T$ = 0 in equation (4.1)).

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Appendix D (Continued)

Table D.3. Distribution coefficient (log $K^T_{Fe}$) results from the experiment performed over the pH range 4.0 – 6.6 at 30% CO₂. The samples at pH 3.98 and pH 4.49 for each YREE were excluded from any calculations due to weak sorption at low pH (see text for details). It should be noted that carbonate concentrations ([CO$_3^{2-}$]$_T$) are listed in nM units. n.v. = no value because measured YREE concentrations were indistinguishable from YREE concentrations at t = 0 (i.e., [MS$_i$]$_T$ = 0 in equation (4.1)).

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<th>Ce</th>
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## Table D.4

Distribution coefficient ($\log_\text{T}_{\text{Fe}^{\text{sol}}}$) results from the experiment performed over the $P_{\text{CO}_2}$ range 0% – 30% at pH = 6.52 ± 0.01.

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Appendix D (Continued)

Table D.4. (Continued)

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(μM)

| Y     | 5.11  | 5.16  | 5.20  | 5.21  | 5.24  | 5.28  | 5.27  | 5.28  | 5.34  | 5.37  |
| La    | 4.89  | 4.96  | 5.04  | 5.06  | 5.12  | 5.18  | 5.19  | 5.25  | 5.34  | 5.39  |
| Ce    | 5.41  | 5.46  | 5.52  | 5.54  | 5.60  | 5.65  | 5.64  | 5.70  | 5.76  | 5.81  |
| Pr    | 5.59  | 5.65  | 5.69  | 5.71  | 5.77  | 5.81  | 5.81  | 5.86  | 5.91  | 5.95  |
| Nd    | 5.67  | 5.72  | 5.76  | 5.79  | 5.84  | 5.86  | 5.87  | 5.91  | 5.96  | 6.00  |
| Pm    | -     | -     | -     | -     | -     | -     | -     | -     | -     | -     |
| Sm    | 5.82  | 5.88  | 5.90  | 5.93  | 5.96  | 5.99  | 5.99  | 6.02  | 6.05  | 6.10  |
| Eu    | 5.78  | 5.83  | 5.85  | 5.88  | 5.91  | 5.94  | 5.94  | 5.96  | 6.00  | 6.04  |
| Gd    | 5.58  | 5.63  | 5.66  | 5.69  | 5.73  | 5.77  | 5.76  | 5.79  | 5.84  | 5.87  |
| Tb    | 5.64  | 5.69  | 5.71  | 5.74  | 5.76  | 5.80  | 5.79  | 5.81  | 5.86  | 5.88  |
| Dy    | 5.64  | 5.68  | 5.70  | 5.72  | 5.74  | 5.78  | 5.76  | 5.77  | 5.82  | 5.84  |
| Ho    | 5.59  | 5.62  | 5.64  | 5.67  | 5.69  | 5.72  | 5.71  | 5.71  | 5.76  | 5.78  |
| Er    | 5.62  | 5.65  | 5.68  | 5.70  | 5.71  | 5.75  | 5.74  | 5.73  | 5.77  | 5.80  |
| Tm    | 5.71  | 5.75  | 5.76  | 5.79  | 5.79  | 5.82  | 5.81  | 5.80  | 5.84  | 5.86  |
| Yb    | 5.79  | 5.82  | 5.84  | 5.87  | 5.86  | 5.89  | 5.87  | 5.85  | 5.88  | 5.91  |
| Lu    | 5.75  | 5.79  | 5.80  | 5.84  | 5.83  | 5.86  | 5.85  | 5.82  | 5.86  | 5.88  |

(Continued on next page)
Appendix D (Continued)

**Table D.4.** (Continued)

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Table D.5. Distribution coefficient ($\log \left( K_{Fe}^{T} \right)$) results from the experiment performed over the $P_{CO_2}$ range 0% – 30% at pH = 6.68 ± 0.01.

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<td>70 hrs</td>
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<td>90 min</td>
<td>22 hrs</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.291</td>
<td>0.291</td>
<td>0.291</td>
<td>0.485</td>
<td>0.485</td>
<td>0.485</td>
</tr>
<tr>
<td>$[CO_3^{2-}]_r$ (µM)</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0884</td>
<td>0.0844</td>
<td>0.0925</td>
<td>0.148</td>
<td>0.141</td>
<td>0.148</td>
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| Y     | 4.69  | 4.76  | 4.83  | 4.81  | 5.55  | 5.61  | 5.68  | 5.72  | 5.70  | 5.71  |
| La    | 4.34  | 4.39  | 4.48  | 4.51  | 5.45  | 5.56  | 5.68  | 5.76  | 5.80  | 5.78  |
| Ce    | 4.79  | 4.89  | 4.99  | 5.03  | 5.95  | 6.06  | 6.09  | 6.18  | 6.20  | 6.19  |
| Pr    | 4.98  | 5.09  | 5.18  | 5.21  | 6.10  | 6.21  | 6.22  | 6.30  | 6.31  | 6.30  |
| Nd    | 5.04  | 5.16  | 5.26  | 5.28  | 6.23  | 6.37  | 6.29  | 6.39  | 6.37  | 6.38  |
| Pm    | -     | -     | -     | -     | -     | -     | -     | -     | -     | -     |
| Sm    | 5.26  | 5.38  | 5.48  | 5.47  | 6.42  | 6.56  | 6.41  | 6.47  | 6.48  | 6.46  |
| Eu    | 5.24  | 5.35  | 5.44  | 5.44  | 6.29  | 6.44  | 6.35  | 6.41  | 6.41  | 6.40  |
| Tb    | 5.14  | 5.26  | 5.35  | 5.33  | 6.11  | 6.20  | 6.20  | 6.24  | 6.23  | 6.23  |
| Dy    | 5.15  | 5.27  | 5.36  | 5.35  | 6.13  | 6.21  | 6.17  | 6.21  | 6.21  | 6.20  |
| Ho    | 5.10  | 5.21  | 5.30  | 5.29  | 6.05  | 6.13  | 6.10  | 6.14  | 6.12  | 6.12  |
| Er    | 5.13  | 5.25  | 5.33  | 5.32  | 6.10  | 6.18  | 6.12  | 6.16  | 6.13  | 6.13  |
| Tm    | 5.23  | 5.35  | 5.44  | 5.44  | 6.24  | 6.32  | 6.20  | 6.23  | 6.21  | 6.21  |
| Yb    | 5.33  | 5.47  | 5.56  | 5.56  | 6.22  | 6.31  | 6.23  | 6.25  | 6.23  | 6.23  |
| Lu    | 5.28  | 5.41  | 5.51  | 5.50  | 6.15  | 6.23  | 6.21  | 6.22  | 6.20  | 6.21  |
### Table D.5. (Continued)

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Appendix D (Continued)

Table D.6. Distribution coefficient ($\log_\text{IF} K^T_{fe}$) results from the experiment performed over the $P_{CO_2}$ range 0% – 30% at pH = 7.06 ± 0.01.

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Table D.6. (Continued)

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<td>15 min</td>
<td>90 min</td>
<td>20 hrs</td>
<td>15 min</td>
<td>90 min</td>
<td>20.5 hrs</td>
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<tr>
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<td>0.961</td>
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<tr>
<td>$[\text{CO}_3^{2-}]_T$ (µM)</td>
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<td>5.77</td>
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- Y: 6.07, 5.99, 6.08, 5.82, 5.90, 5.85, 4.69, 4.73, 4.71
- La: 6.52, 6.37, 6.56, 6.47, 6.46, 6.52, 6.58, 6.69, 6.75
- Ce: 7.04, 6.85, 7.06, 6.81, 6.88, 6.91, 6.44, 6.53, 6.57
- Pr: 6.91, 6.79, 6.93, 6.71, 6.79, 6.77, 6.55, 6.61, 6.60
- Nd: 7.02, 6.90, 7.06, 6.77, 6.85, 6.83, 6.51, 6.61, 6.56
- Pm: -
- Sm: 7.02, 6.92, 7.02, 6.73, 6.85, 6.77, 6.30, 6.39, 6.32
- Eu: 6.85, 6.77, 6.87, 6.61, 6.70, 6.65, 6.16, 6.24, 6.19
- Gd: 6.79, 6.68, 6.80, 6.54, 6.62, 6.56, 6.05, 6.13, 6.08
- Tb: 6.68, 6.60, 6.68, 6.41, 6.50, 6.44, 5.83, 5.91, 5.86
- Dy: 6.54, 6.47, 6.56, 6.26, 6.35, 6.29, 5.61, 5.68, 5.62
- Er: 6.39, 6.33, 6.40, 6.09, 6.18, 6.12, 5.33, 5.41, 5.33
- Tm: 6.43, 6.37, 6.43, 6.09, 6.20, 6.13, 5.27, 5.34, 5.28
- Yb: 6.45, 6.38, 6.45, 6.08, 6.18, 6.11, 5.21, 5.28, 5.22
- Lu: 6.43, 6.37, 6.43, 6.05, 6.16, 6.09, 5.16, 5.23, 5.16
Appendix D (Continued)

Table D.7. Distribution coefficient (log, $K_{T}^{T}$) results from the experiment performed over the $P_{CO_2}$ range 0% – 30% at pH = 7.10 ± 0.03. n.v. = no value because of an anomalous concentration reading.

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<tr>
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<tr>
<td>[CO$_3^{2-}$]$_T$ (µM)</td>
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Appendix E: Temperature Dependent Data for Amorphous Ferric Hydroxide

Table E.1. Distribution coefficient (log $iK_{Fe}$) results from the experiment performed at $T = 10.0^\circ C$ over the pH range 4.7 – 6.9 with an iron concentration of 1.08 ± 0.08 mM.

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Table E.3. Distribution coefficient \( \log(K_{Fe}) \) results from the experiment performed at \( T = 39.1^\circ C \) over the pH range 4.9 – 6.8 with an iron concentration of 0.108 ± 0.008 mM.

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Table E.4. Distribution coefficient (log $\log iK_{Fe}$) results from the experiment performed at $T = 39.3^\circ C$ over the pH range 5.3 – 7.1 with an iron concentration of $0.108 \pm 0.008$ mM.

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About the Author

Kelly Ann Quinn graduated Summa Cum Laude with a Bachelor of Science degree in Marine Biology and Chemistry from Fairleigh Dickinson University, NJ in 2000. After working at the Hershey Foods Analytical Department for six months, she entered the M.S. program at the University of South Florida in the College of Marine Science. Due to the quality and quantity of data collected, she switched to the Ph.D. program in the College of Marine Science in 2005.

While pursuing her Ph.D., Kelly was a research assistant, teaching assistant, and AAUS scientific diver. She also received the Von Rosensteil, Riggs, and Gulf Oceanographic Charitable Trust Endowed Fellowships from the College of Marine Science. The results obtained in her research were published in several peer-reviewed journals and presented at the Goldschmidt Geochemistry Conference.