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Sorption of yttrium and rare earth elements by amorphous ferric hydroxide: Influence of pH and ionic strength

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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 $_iK_{Fe} = [MS_i]_T/(M_T[Fe^{3+}]_S)$, 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 $_iK_{Fe} = (_S\beta_1[H^+]^{-1} + _S\beta_2[H^+]^{-2})/(_SK_1[H^+]+1)$, 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 $_iK_{Fe}$ observations in synthetic solutions at low ionic strength, is in good agreement with results for natural seawater obtained by others.
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1. 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 envir-

onments (e.g., de Baar et al., 1985; 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

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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 (Koeppenkastrop 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 Koeppenkastrop 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 an 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 to 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 $\sum[\text{YREE}]/[\text{Fe}^{3+}]_T$ 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.

2. Materials and methods

2.1. Materials and preparation of the experimental solutions

A class-100 clean air laboratory or laminar flow bench was utilized for all chemical manipulations.