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## Carbonate Complexation of Yttrium and the Rare Earth Elements in Natural Waters

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**Abstract**—Potentiometric measurements of Yttrium and Rare Earth Element (YREE) complexation by carbonate and bicarbonate indicate that the quality of carbonate complexation constants previously obtained via solvent exchange analyses are superior to characterizations obtained using solubility and adsorptive exchange analyses. The results of our analyses at 25°C are combined with the results of previous solvent exchange analyses to obtain YREE carbonate complexation constants over a wide range of ionic strength ( $0 \leq I \leq 3$  molal). YREE carbonate complexation constants are reported for the following equilibria,  $M^{3+} + n\text{HCO}_3^- \rightleftharpoons \text{M}(\text{CO}_3)_n^{3-2n} + n\text{H}^+$ , where  $n = 1$  or 2. Formation constants written in terms of  $\text{HCO}_3^-$  concentrations require only minor corrections for ion pairing relative to the corrections required for constants expressed in terms of  $\text{CO}_3^{2-}$  concentrations. Formation constants for the above complexation equilibria,  ${}_{\text{CO}_3}\beta_1^{\text{H}} = [\text{MCO}_3^+][\text{H}^+][\text{M}^{3+}]^{-1}[\text{HCO}_3^-]^{-1}$  and  ${}_{\text{CO}_3}\beta_2^{\text{H}} = [\text{M}(\text{CO}_3)_2^-][\text{H}^+]^2[\text{M}^{3+}]^{-1}[\text{HCO}_3^-]^{-2}$ , have very similar dependencies on ionic strength because the reaction  $\text{MCO}_3^+ + \text{HCO}_3^- \rightleftharpoons \text{M}(\text{CO}_3)_2^- + \text{H}^+$  is isocoulombic. Potentiometric analyses indicate that the dependence of  $\log {}_{\text{CO}_3}\beta_1^{\text{H}}$  and  $\log {}_{\text{CO}_3}\beta_2^{\text{H}}$  on ionic strength at 25°C is given as

$$\log {}_{\text{CO}_3}\beta_n^{\text{H}} = \log {}_{\text{CO}_3}\beta_n^{\text{H}0} - 4.088 I^{0.5} / (1 + 3.033 I^{0.5}) + 0.042 I \quad (\text{A})$$

where  ${}_{\text{CO}_3}\beta_n^{\text{H}0}$  denotes a formation constant at 25°C and zero ionic strength. Recommended values for  $\log {}_{\text{CO}_3}\beta_1^{\text{H}}$  and  $\log {}_{\text{CO}_3}\beta_2^{\text{H}}$ , expressed in the form (element,  $-\log {}_{\text{CO}_3}\beta_1^{\text{H}0}$ ,  $-\log {}_{\text{CO}_3}\beta_2^{\text{H}0}$ ), are as follows: (Y, 2.85, 8.03), (La, 3.60, 9.36), (Ce, 3.27, 8.90), (Pr, 3.10, 8.58), (Nd, 3.05, 8.49), (Sm, 2.87, 8.13), (Eu, 2.85, 8.03), (Gd, 2.94, 8.18), (Tb, 2.87, 7.88), (Dy, 2.77, 7.75), (Ho, 2.78, 7.66), (Er, 2.72, 7.54), (Tm, 2.65, 7.39), (Yb, 2.53, 7.36), (Lu, 2.58, 7.29). Copyright © 2004 Elsevier Ltd

## 1. INTRODUCTION

The environmental behavior of Yttrium and the Rare Earth Elements (YREEs) is strongly influenced by solution chemistry (Wood, 1990; Byrne and Sholkovitz, 1996). Due to the complexation of YREEs by a variety of ligands, only a small fraction of each YREE in circumneutral waters is typically in the form of free hydrated YREE ions ( $\text{M}^{3+}$ ). For alkaline waters with  $\text{CO}_2$  partial pressures ( $P_{\text{CO}_2}$ ) greater than or equal to the  $P_{\text{CO}_2}$  of the atmosphere, YREE complexation is generally dominated by the formation of carbonate complexes  $\text{MCO}_3^+$  and  $\text{M}(\text{CO}_3)_2^-$  (Byrne and Sholkovitz, 1996; Tang and Johannesson, 2003). As such, accurate models of YREE chemistry in natural waters are strongly dependent on experimentally determined YREE carbonate complexation constants.

The results of previous formation constant assessments appropriate to the equilibrium  $\text{M}^{3+} + \text{CO}_3^{2-} \rightleftharpoons \text{MCO}_3^+$  at 25°C and zero ionic strength are shown in Table 1. Comparisons of the data at the bottom of Table 1 (i.e., the data of Ohta and Kawabe, 2000) with the remaining data in the table demonstrates that YREE carbonate complexation constants,  ${}_{\text{CO}_3}\beta_1^{\text{H}} = [\text{MCO}_3^+][\text{M}^{3+}]^{-1}[\text{CO}_3^{2-}]^{-1}$ , at zero ionic strength, range over somewhat more than an order of magnitude. The smallest estimates for  ${}_{\text{CO}_3}\beta_1^{\text{H}}$  in Table 1, those of Millero (1992), are approximately thirty times smaller than the formation constants of Ohta and Kawabe (2000).

Only two previous studies have produced a comprehensive

set of YREE carbonate formation constants. Figure 1 compares the  $\log {}_{\text{CO}_3}\beta_n^{\text{H}}$  data of Liu and Byrne (1998) with the estimates of Ohta and Kawabe (2000). Although the stability constant patterns of Liu and Byrne (1998) and Ohta and Kawabe (2000) are quite similar, as noted previously (Table 1) they are offset by approximately one log-unit. As such, the comparisons shown in Table 1 and Figure 1 indicate that additional experimental data are needed to better constrain the absolute and comparative magnitudes of YREE carbonate complexation constants.

Four experimental procedures (solvent exchange analysis, solubility analysis, adsorptive exchange analysis and potentiometry) are widely applicable to the determination of YREE carbonate complexation constants. The most commonly used experimental method for examination of YREE equilibria is solvent exchange analysis. Previous solvent exchange analyses have involved the use of both radiochemical techniques (Lundqvist 1982; Cantrell and Byrne, 1987; Chatt and Rao, 1989; Rao and Chatt, 1991; Lee and Byrne, 1993) and Inductively Coupled Plasma-Mass Spectrometry (Liu and Byrne, 1998) to measure the partitioning of YREEs between solvent phases. Solvent exchange procedures are relatively simple, and the formation constant data obtained in a wide variety of investigations using solvent exchange analyses are coherent.

The use of solubility analysis for determination of YREE formation constants is inherently more complex than solvent exchange analyses. In addition to characterizations of YREE solution complexation, solubility analysis requires concomitant determinations of YREE solubility products. Solubility analysis generally requires lengthy equilibration times, and the precision of previous  ${}_{\text{CO}_3}\beta_1^{\text{H}}$  measurements obtained through solu-

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# In-Situ Measurements of Cu in an Estuarine Environment Using a Portable Spectrophotometric Analysis System

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Application of a portable in-situ spectrophotometric analysis system for the measurement of Cu in estuarine environments is described in this work. Our spectrophotometric elemental analysis system (SEAS) used for in-situ observations of Cu concentrations is capable of fully autonomous or user-controlled operations. The optical cells used in SEAS systems are flexible liquid core waveguides (LCWs) with optical path lengths as long as 5 m. The 1-m waveguide used in the present study provided a 3.0 nM detection limit and a 5.0% relative standard deviation for a 25 nM copper sample. Analysis times range between 1 and 5 min, allowing for acquisition of data on scales appropriate to the highly dynamic biogeochemical nature of copper in the coastal environment. Field deployments of SEAS-Cu in Tampa Bay, FL, showed low Cu concentrations near the mouth of the estuary (3–4 nM), with elevated concentrations (~25 nM) in anthropogenically impacted regions of the bay (e.g., marinas and areas adjacent wastewater treatment plants). Transect data between Tampa Bay and a deep water harborage exhibited copper concentrations ranging between 5 and 50 nM.

## Introduction

A new spectrophotometric elemental analysis system (SEAS) has been developed which is capable of fully autonomous in-situ chemical observations (1). In-situ analysis offers considerable advantages over laboratory and shipboard analyses by (i) reducing the potential for sample contamination, (ii) increasing sample throughput and observational endurance, (iii) providing adaptive sampling opportunities in dynamic chemical gradients, and (iv) lowering overall measurement costs (1). SEAS has been used for month-long autonomous pH measurements on a buoy in the North Pacific Ocean (2) and for in-situ nitrite measurements via hydrocasts to 200 m in the Gulf of Mexico (1). The analysis cell of the SEAS system is based on the same type-I liquid core waveguide (LCW) technology (3) used in long path length absorbance spectroscopy (LPAS) to enhance the detection limits of a wide variety of analytes. To date, LPAS has been used to measure  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , Fe,  $\text{CrO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{HS}^-$ , and Cu at nanomolar and subnanomolar levels (4–8).

In the present work, we describe the operation of SEAS during its first application as a monitoring tool for the input

and distribution of pollutants in coastal waters. Copper (Cu), considered one of the most widespread anthropogenic pollutants in natural waters (9), was the chosen analyte for this work. The input and distribution of copper in natural waters is of concern because this biogeochemically important element is essential in trace amounts but toxic to a wide variety of marine organisms at higher concentrations (10–16).

Copper concentrations in coastal waters typically range between 2 and 150 nM (17–19). Elevated copper concentrations are frequently associated with leaching from antifouling paints and pressure-treated docks pilings, effluents from septic tanks and municipal wastewater (11, 20), discharges from power and desalination plants (21), and runoff from various other land-based sources (22–23). Cu distributions are dependent upon local biogeochemical factors and can vary considerably in both time and space (11, 21, 24). For dynamic and influential trace analytes, such as copper, use of conventional laboratory instrumentation and traditional environmental sampling procedures is labor intensive and cost prohibitive. The analysis system described in this work combines the sensitivity and speed of LPAS copper analysis (8) with the autonomous, in-situ measurement capabilities of SEAS.

## Long Path Length Absorbance Spectroscopy of Copper.

Colorimetric procedures are generally simple, inexpensive, fast, and robust. A colorimetric method involving the reduction of copper followed by reaction with bathocuproine disulfonate (BDS) has been accepted as a standard procedure for analysis of aqueous copper (25). The sensitivity of the conventional Cu–BDS method is limited by optical path length (1–10 cm) and is typically considered inaccurate at concentrations below ~70 nM. By increasing optical path length, LPAS combined with conventional colorimetric procedures can improve the detection limits of a number of analytes by two or more orders of magnitude (4, 7, 26). The increased sensitivity of LPAS is achieved using long path length optical cells constructed from a flexible Teflon AF-2400 (Dupont) liquid core waveguide (LCW). The waveguide material (RI  $\approx$  1.29), surrounding a liquid core (RI  $\approx$  1.333), provides total internal reflection for light rays intersecting the water/Teflon interface at angles  $\geq 75.4^\circ$  as measured from the normal to the interface. For salinity 35 seawater (RI  $\approx$  1.340 at 20 °C) the critical angle of the seawater/Teflon interface differs only slightly from that observed using pure water. Long LCW optical path lengths (up to 10 m) have been used (27) for observations of subnanomolar iron concentrations in seawater. Recently, Callahan et al., (8) described an LPAS Cu–BDS method capable of subnanomolar detection limits for copper.

## Spectrophotometric Elemental Analysis System (SEAS).

SEAS is a compact, autonomous LPAS device for in-situ analysis. The main components of a two-pump SEAS system have been described by Steimle et al. and Kaltenbacher et al. (1, 2). For copper analyses, a three-pump SEAS system is required to eliminate occasional baseline alterations associated with small pH-dependent color variations in humic-rich environmental samples. A three-pump SEAS system was created by placing two SEAS units in tandem. One SEAS instrument serves as the master control for all electromechanical systems (spectrophotometer, light source, pump motors). Dual peristaltic pumps (custom) on the master SEAS unit deliver the sample (main pump) and colorimetric reagent (dye pump) to a light/fluid coupler. The coupler conveys fluids and light from a source lamp into one end of the LCW. A second light/fluid coupler, at the output end of the LCW,

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## Determination of ${}_{\text{SO}_4}\beta_1$ for yttrium and the rare earth elements at $I = 0.66\text{ m}$ and $t = 25^\circ\text{C}$ —Implications for YREE solution speciation in sulfate-rich waters

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**Abstract**—We present a complete set of stability constants ( ${}_{\text{SO}_4}\beta_1$ ) for the monosulfato-complexes of yttrium and the rare earth elements (YREE), except Pm, at  $I = 0.66\text{ m}$  and  $t = 25^\circ\text{C}$ , where  ${}_{\text{SO}_4}\beta_1 = [\text{MSO}_4^+] \times [\text{M}^{3+}]^{-1}[\text{SO}_4^{2-}]^{-1}$  ( $\text{M} \equiv \text{YREE}$  and brackets indicate free ion concentrations on the molal scale). Stability constants were determined by investigating the solubility of  $\text{BaSO}_4$  in concentrated aqueous solutions of  $\text{MCl}_3$ . This is the first complete set to be published in more than 30 years.

The resulting  ${}_{\text{SO}_4}\beta_1$  pattern is very similar in shape to one reported by de Carvalho and Choppin (1967a) ( $I = 2\text{ mol/L}$ ;  $t = 25^\circ\text{C}$ ) that has been largely ignored. Stability constants vary little between La and Sm, but display a weak maximum at Eu. Between Eu and Lu,  ${}_{\text{SO}_4}\beta_1$  decreases by 0.2 log units, substantially exceeding the  $\pm 0.02$  log unit average analytical precision. The stability constant for Y is approximately equal to that for Er. Our  ${}_{\text{SO}_4}\beta_1$  pattern is consequently distinctly different from the consensus pattern, based on a single data set from 1954, which is essentially flat, with a range of only 0.07 log units between the lowest and highest  ${}_{\text{SO}_4}\beta_1$  values within the lanthanide series (excluding Y).

Values of  ${}_{\text{SO}_4}\beta_1$  obtained in this work, in conjunction with the ion-pairing model of Millero and Schreiber (1982), allow prediction of  ${}_{\text{SO}_4}\beta_1$  between 0 and 1  $\text{m}$  ionic strength. These results are used to assess both the absolute and relative extent of YREE sulfate complexation in acidic, sulfate-rich waters. Copyright © 2004 Elsevier Ltd

### 1. INTRODUCTION

The environmental behavior of trace metals, involving properties like solubility, mobility, bio-availability, and toxicity, is a sensitive function of their speciation in solution. The solution speciation of yttrium and the rare earth elements (YREE) in natural waters is believed to be dominated by complexation with inorganic ligands (e.g., Turner et al., 1981; Byrne, 2002). In recent years, systematic investigation of YREE solution speciation has produced comprehensive sets of stability constants for YREE complexation with carbonate (Liu and Byrne, 1998; Luo and Byrne, 2004), fluoride (Schijf and Byrne, 1999; Luo and Byrne, 2000), hydroxide (Klungness and Byrne, 2000), oxalate (Schijf and Byrne, 2001), and weaker ligands that are of environmental importance, such as chloride (Luo and Byrne, 2001). These stability constants enable detailed modeling and prediction of YREE behavior in solution over a wide range of natural conditions.

Complexation of the YREE with sulfate has received relatively little attention in the geochemical literature. This is partly because the extent of YREE sulfate complexation is small in many environments and partly because the pattern of the stability constants of YREE monosulfato-complexes ( ${}_{\text{SO}_4}\beta_1$ ) is widely regarded as well known and rather featureless (e.g., Byrne and Sholkovitz, 1996). Under circumneutral and alkaline conditions, YREE speciation is normally dominated by carbonate complexation. Even in seawater, where  $\text{SO}_4^{2-}$  is the second most abundant anion after  $\text{Cl}^-$ , and in freshwaters, where lower pH often limits the free carbonate concentration, YREE sulfato-complexes are usually no more than minor species (Byrne et

al., 1988; Stanley and Byrne, 1990). Still, in certain environments, YREE sulfate complexation may become quite important. In systems where massive metal sulfide deposits, such as pyrite, are exposed to oxygenated waters, sulfate concentrations can reach values of 0.5 mol/L or more. Examples of such systems include acidic, sulfate-rich waters draining mine tailings (Miekeley et al., 1992), geothermal springs in Yellowstone National Park and Japan (Lewis et al., 1997, 1998; Bau et al., 1998), acidic to slightly alkaline, sulfate-rich groundwaters and brines (Johannesson et al., 1996; Gimeno Serrano et al., 2000; Johannesson and Hendry, 2000), and an acidic freshwater lake in the Canadian arctic (Johannesson and Lyons, 1995; Johannesson and Zhou, 1999). All are characterized by YREE patterns with unusual MREE enrichments that have defied satisfactory explanation. Speciation calculations suggest that, in the majority of these waters, free ions and monosulfato-complexes are the most important YREE species, with the latter sometimes dominating.

Sulfato-complexes of many metals have been extensively investigated and the YREE are no exception. Historical investigations of ion association in YREE sulfate solutions date back to the early 1900s (Noyes and Johnston, 1909; Neuman, 1933; Nathan et al., 1943; Moeller, 1946). Studies of YREE sulfate complexation are numerous and have employed a variety of techniques. A great deal of speculation has been particularly devoted to the inner-sphere versus outer-sphere character of YREE sulfato-complexes (Larsson, 1964; Manning, 1965; Ashurst and Hancock, 1977). Table 1 contains a compilation of published stability constants of YREE monosulfato-complexes. In some of these studies, stability constants were also obtained for YREE disulfato- and trisulfato-complexes. Table 2 contains stability constants at  $I = 0$  that were derived either from

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## Comparative Scavenging of Yttrium and the Rare Earth Elements in Seawater: Competitive Influences of Solution and Surface Chemistry

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**Abstract.** Distribution coefficients were obtained for yttrium and the rare earth elements (YREEs) in aqueous solutions containing freshly precipitated hydroxides of trivalent cations ( $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ , and  $\text{In}^{3+}$ ). Observed patterns of  $\log {}_iK_S$ , where  ${}_iK_S = [\text{MS}_i][\text{M}^{3+}]^{-1}[\text{S}_i]^{-1}$ ,  $[\text{MS}_i]$  is the concentration of a sorbed YREE,  $[\text{M}^{3+}]$  is the concentration of a free hydrated YREE ion, and  $[\text{S}_i]$  is the concentration of a sorptive solid substrate (Fe(III), Al, Ga, In) – exhibited similarities to patterns of YREE solution complexation constants with hydroxide ( ${}_{\text{OH}}\beta_1$ ) and fluoride ( ${}_{\text{F}}\beta_1$ ), but also distinct differences. The  $\log {}_iK_S$  pattern for YREE sorption on Al hydroxide precipitates is very similar to the pattern of YREE hydroxide stability constants ( $\log {}_{\text{OH}}\beta_1$ ) in solution. Linear free-energy relationships between  $\log {}_iK_S$  and  $\log {}_{\text{OH}}\beta_1$  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  $\log {}_iK_S$  and  $\log {}_{\text{F}}\beta_1$  was generally poor, patterns of  $\log ({}_iK_S/{}_{\text{F}}\beta_1)$  displayed substantially increased smoothness compared to patterns of  $\log {}_iK_S$ . This indicates that the conspicuous sequence of inflections along the YREE series in the patterns of  $\log {}_iK_S$  and  $\log {}_{\text{F}}\beta_1$  is very similar, particularly for In and Fe(III) hydroxide precipitates.

While the  $\log {}_iK_S$  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  $\log {}_iK_S$  patterns for Fe(III) hydroxide precipitates bear a striking resemblance to predicted  $\log {}_iK_S$  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.

**Key words:** yttrium, rare earth elements, ICP-MS, sorption, scavenging, iron hydroxide, seawater, linear free-energy relationships

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