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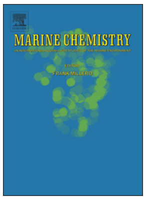

Europium silicate complexation at 25 °C and 0.7 molar ionic strength

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ABSTRACT

Previous determinations of rare earth element (REE) complexation by silicate have been confined to observations of $Eu(SiO(OH)_3)^{2+}$ formation. Critical assessment of these observations reveals order-of-magnitude ambiguities in the stability constants derived from a variety of experimental designs. A salient feature of prior $Eu(SiO(OH)_3)^{2+}$ stability constant assessments is that the largest silicate stability constants were obtained in the presence of substantial silica polymerization. In the present work, $Eu(SiO(OH)_3)^{2+}$ formation is described under conditions where polymerization should be negligible. Stability constants were obtained via observations of the following equilibrium: $Eu^{3+} + Si(OH)_4^0 \rightleftharpoons Eu(SiO(OH)_3)^{2+} + H^+$ with total silicon concentrations on the order of 0.5 mM or less. The formation constant for this equilibrium at 25 °C and 0.7 M ionic strength is

$$\log {}_{Si}^{*}\beta_1 = \frac{[Eu(OSi(OH)_3)^{2+}][H^+]}{[Eu^{3+}][Si(OH)_4^0]} = -3.27 \pm 0.18$$

This stability constant coupled with the first ionization constant of $Si(OH)_4^0$ yields $\log_{Si}\beta_1 = 6.18 \pm 0.18$ for the equilibrium $Eu^{3+} + OSi(OH)_3^- \rightleftharpoons Eu(SiO(OH)_3)^{2+}$. Both of these constants are more than an order of magnitude smaller than results obtained under conditions conducive to silica polymerization (i.e., total silica concentrations between 2 and 20 mM). These new stability constants indicate that $Eu(SiO(OH)_3)^{2+}$ is a significant fraction of the total dissolved europium in deep waters of the Atlantic and Pacific but a very minor species in surface waters. In contrast to predictions obtained via the recent speciation model of Akagi (2013), concentrations of REE–silicate complexes throughout the oceans are much smaller than those of REE–carbonate complexes.

1. Introduction

Very little experimental work has been devoted to determinations of rare earth element (REE) complexation by silicate ions ($OSi(OH)_3^-$). The review of Hummel (2014) indicates that studies of $REE(SiO(OH)_3)^{2+}$ formation have been limited to a single element (Eu^{3+}), using a single method (solvent extraction). The review notes that the three prior studies of $Eu(SiO(OH)_3)^{2+}$ formation (Jensen and Choppin, 1996; Pathak and Choppin, 2006; Thakur et al., 2007) came from a single laboratory but that the most recent study (Thakur et al., 2007) does not discuss the statistically significant differences between the earliest investigation (Jensen and Choppin, 1996) and the two later studies.

In an evaluation of the oceanic distributions of rare earth elements, Akagi (2013) used the formation constants of Thakur et al. (2007) — which exceed the formation constants of Jensen and Choppin (1996) by about a factor of five — to argue that REE complexation in seawater is dominated by $REE(SiO(OH)_3)^{2+}$ formation rather than the formation of REE carbonate species. In the absence of strong silicate complexation, carbonate complexation is expected to dominate the complexation of REEs in seawater (Cantrell and Byrne, 1987; Liu and Byrne, 1998; Luo and Byrne, 2004). In investigating ferric ion complexation by $OSi(OH)_3^-$, Patten and Byrne (2017) found that the $Eu(SiO(OH)_3)^{2+}$ formation constants obtained in the study of Jensen and Choppin (1996) were orders of magnitude larger than what would be expected from comparisons of Eu(III) and Fe(III) formation constant behavior. Furthermore, a reanalysis of the data of Jensen and Choppin (1996) indicated (Patten and Byrne, 2017) that the $Eu(SiO(OH)_3)^{2+}$ formation constant of Jensen and Choppin (1996) was overestimated by more than an order of magnitude. Patten and Byrne (2017) concluded that the formation constant results of Pathak and Choppin (2006) and Thakur et al. (2007) are larger than those of Jensen and Choppin (1996) principally due to complexation of europium by silicate polymers. On this basis, it is reasonable to assert that that no prior studies have provided a successful direct experimental evaluation of the equilibrium $REE^{3+} + OSi(OH)_3^- \rightleftharpoons REE(SiO(OH)_3)^{2+}$.

In the present work, we describe direct experimental observations of equilibrium constants for $Eu(SiO(OH)_3)^{2+}$ formation based on potentiometric analyses at 25 °C and 0.7 M ionic strength. Low silicate concentrations were used in these analyses in order to preclude significant complexation by silicate polymers. Our direct determinations of the $EuSiO(OH)_3^{2+}$ formation constant are consistent with the assessment

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of Patten and Byrne (2017) that the europium silicate formation constant estimates of Jensen and Choppin (1996), Pathak and Choppin (2006), and Thakur et al. (2007) are greatly in error.

2. Theory

The ionization behavior of orthosilicic acid,$Si(OH)_4^0$, has been extensively studied over a wide range of ionic strength (Sjöberg et al., 1983), and its first ionization is given as

$$Si(OH)_4^0 \rightleftharpoons H^+ + OSi(OH)_3^- \tag{1}$$

with the equilibrium constant for this reaction defined as

$$K_1 = \frac{[H^+][OSi(OH)_3^-]}{[Si(OH)_4^0]} \tag{2}$$

At 25 °C and an ionic strength of 0.70 M, the pK_1 of silicic acid has been determined to be 9.451 (Sjöberg et al., 1983). This result, obtained in NaCl solutions, is consistent with results obtained in $NaClO_4$ at 25 °C and similar ionic strengths (e.g., $pK_1 = 9.46$ in 0.5 M $NaClO_4$) (Baes and Mesmer, 1976). The second ionization of silicic acid is unimportant at the range of pH values in this experiment.

The complexation of europium(III) with the $OSi(OH)_3^-$ anion is given by the reaction

$$Eu^{3+} + OSi(OH)_3^- \rightleftharpoons Eu(OSi(OH)_3)^{2+} \tag{3}$$

where the formation constant, ${}_{Si}\beta_1$, is defined as

$${}_{Si}\beta_1 = \frac{[Eu(OSi(OH)_3)^{2+}]}{[Eu^{3+}][OSi(OH)_3^-]} \tag{4}$$

If Eqs. (1) and (3) are combined to produce an overall reaction between Eu^{3+} and $Si(OH)_4^0$, we obtain

$$Eu^{3+} + Si(OH)_4^0 \rightleftharpoons Eu(OSi(OH)_3)^{2+} + H^+ \tag{5}$$

with an equilibrium constant

$${}^*_{Si}\beta_1 = \frac{[Eu(OSi(OH)_3)^{2+}][H^+]}{[Eu^{3+}][Si(OH)_4^0]} \tag{6}$$

Therefore the europium–silicate formation constants in Eqs. (4) and (6) are related as follows:

$${}_{Si}\beta_1 = \frac{{}^*_{Si}\beta_1}{K_1} = \frac{[Eu(OSi(OH)_3)^{2+}]}{[Eu^{3+}][SiO(OH)_3^-]} \tag{7}$$

Because the value of the ionization constant, K_1, is already well established, the focus of this study was to design an experiment that would allow determination of ${}^*_{Si}\beta_1$ directly from the measured parameters of total europium, $(Eu)_T$, total silicon, $(Si)_T$, and the solution pH.

In a mixture of europium(III) with silicic acid/silicate at the equilibrium pH, the total europium concentration $(Eu)_T$ is given as

$$(Eu)_T = [Eu^{3+}] + [Eu(OH)^{2+}] + [Eu(OSi(OH)_3)^{2+}] \tag{8}$$

where $Eu(OH)^{2+}$ is the hydrolysis product for the reaction

$$Eu^{3+} + H_2O \rightleftharpoons Eu(OH)^{2+} + H^+ \tag{9}$$

with the hydrolysis constant ${}^*\beta_1$ defined as

$${}^*\beta_1 = \frac{[Eu(OH)^{2+}][H^+]}{[Eu^{3+}]} \tag{10}$$

Using Eq. (10), $[Eu(OH)^{2+}]$ is given as

$$[Eu(OH)^{2+}] = \frac{[Eu^{3+}]\,{}^*\beta_1}{[H^+]} \tag{11}$$

where ${}^*\beta_1$ at 25 °C and 0.7 M ionic strength was taken from the work of Klungness and Byrne (2000): ${}^*\beta_1 = 8.71 \times 10^{-9}$.

Silicon was added to each experiment as Na_2SiO_3, and the resulting solution was immediately acidified, in a single step acid addition, to a pH equal to the pK_1 of silicic acid (9.451). The amount of acid added in this single step addition is equal to $1.5(Si)_T$, whereupon silicon exists as an equimolar mixture of $Si(OH)_4^0$ and $OSi(OH)_3^-$. After adding europium to this solution, the total silicon in solution, $(Si)_T$, is given as

$$(Si)_T = [Si(OH)_4^0] + [Eu(OSi(OH)_3)^{2+}] + [OSi(OH)_3^-] \tag{12}$$

Under the conditions of this experiment, where the equilibrium pH is <7 and virtually all of the remaining $OSi(OH)_3^-$ is complexed by Eu^{3+}, the $[OSi(OH)_3^-]$ term in Eq. (12) is negligible and $(Si)_T$ can be written as

$$(Si)_T = [Si(OH)_4^0] + [Eu(OSi(OH)_3)^{2+}] \tag{13}$$

One additional characteristic of the solution is the total alkalinity, TA, which is the number of moles of hydrogen ion equivalent to the excess of proton acceptors over proton donors in 1 L of sample (DOE, 1994). Including all proton acceptors and donors in our experiments, TA is given as

$$\begin{aligned} TA = {} & 2[SiO_2(OH)_2^{2-}] + [OSi(OH)_3^-] + [Eu(OSi(OH)_3)^{2+}] \\ & + [Eu(OH)^{2+}] + [OH^-] - [H^+] \end{aligned} \tag{14}$$

At the equilibrium pH values observed in our experiments ($6 \le pH \le 7$), the solution concentrations of $[SiO_2(OH)_2^{2-}]$, $[OSi(OH)_3^-]$, $[OH^-]$, and $[H^+]$ are negligible. Under the original conditions of each experiment, the addition of sodium metasilicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$) to each solution resulted in a total alkalinity equal to the concentration of sodium added with the $Na_2SiO_3 \cdot 9H_2O$ (i.e., $TA = 2(Si)_T$). The subsequent addition of an amount of acid such that $(HCl)_{added} = 1.5(Si)_T$ results in the final TA of each solution (by difference): $TA = 2(Si)_T - 1.5(Si)_T = (Si)_T / 2$.

Therefore Eq. (14) reduces to

$$TA = [EuOH^{2+}] + [Eu(OSi(OH)_3)^{2+}] = \frac{(Si)_T}{2} \tag{15}$$

Combining Eqs. (8) and (15), the free (uncomplexed) concentration of europium is given as

$$[Eu^{3+}] = (Eu)_T - TA \tag{16}$$

By rearrangement of Eq. (15), the europium silicate concentration is given as

$$[Eu(OSi(OH)_3)^{2+}] = TA - [EuOH^{2+}] \tag{17}$$

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