



doi:10.1016/j.gca.2003.12.003

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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(Received July 23, 2003; accepted in revised form December 1, 2003)

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 BaSO_4 in concentrated aqueous solutions of 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 ± 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 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 SO_4^{2-} is the second most abundant anion after 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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Table 1. Stability constants of YREE monosulfato-complexes at $t = 25^\circ\text{C}$, unless stated otherwise. Data were collected in various media (column 2) and with different analytical techniques, as listed in the notes. Ionic strength units are given only when reported. Not included are sound propagation studies (Purdie and Vincent, 1967; Fay et al., 1969; Kor and Bhatti, 1969; Fay and Purdie, 1970; Farrow and Purdie, 1973b; Reidler and Silber, 1973; Qadeer, 1974), because the interpretation of the data is highly model-dependent. Also not included are data of Hardwick and Robertson (1951), who studied sulfate complexation of Ce(IV).

<i>I</i>	Medium	Y	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Notes
0.045 <i>m</i>	NaClO ₄								2.76									a
0.05	NaClO ₄								2.53									b
0.06	NaClO ₄								2.43									b
0.07	NaClO ₄								2.38									b
0.09	NaClO ₄								2.31									b
0.1	NaClO ₄								2.23									b
0.1 mol/L	NH ₄ Cl	2.43	2.48	2.47			2.48		2.49		2.48				2.41	2.39		c
0.1 mol/L	NaClO ₄			2.35														d
0.2 mol/L	NaClO ₄			1.88														e
0.25 mol/L	NaClO ₄			2.00														d
0.35 mol/L	NaClO ₄			1.67														e
0.5 <i>m</i>	NaClO ₄			1.80														f
0.5 mol/L	NaClO ₄			1.53														e
0.5 mol/L	NaClO ₄			1.75														g
0.5–0.6	NaClO ₄			1.95						1.90								h
0.5	NaClO ₄		1.77															i
0.5 mol/L	NaClO ₄			1.72														d
1	NaClO ₄		1.40															j
1 mol/L	NaClO ₄			1.63														k
1 mol/L	NaClO ₄			1.23														e
1 mol/L	NaClO ₄								1.57									l
1 mol/L	NaClO ₄		1.45						1.54								1.29	m
1 mol/L	NaClO ₄			1.76														n
1	NaClO ₄								1.71									o
1	NaCl			1.57					1.53		1.38							p
1 mol/L	NaClO ₄			1.51												1.26		d
1 mol/L	NaClO ₄		0.80															q
2 mol/L	NaClO ₄			1.02														e
2 mol/L	NaClO ₄	1.24	1.29	1.24/1.30	1.27	1.26	1.34	1.30	1.38	1.33	1.27	1.23	1.24	1.23	1.15	1.15	1.09	r
2	NaClO ₄										1.59							o
2 mol/L	NaClO ₄			1.25														d

Notes: (a) Hale and Spedding (1972a), UV-spectrophotometry. Stability constant expressed in terms of free ion concentrations. (b) Manning and Monk (1962), solvent extraction. Data corrected for YREE acetate complexation. (c) Stepanov (1973), electrophoresis, using Cm as an internal standard. Data extracted from graph. (d) Fedorov et al. (1983), IR-spectrophotometry. (e) Newton and Arcand (1953), UV-spectrophotometry. (f) Connick and Mayer (1951), cation-exchange. Average from Table IX, excluding lowest two sulfate concentrations. (g) Blatz (1962), cation-exchange. (h) Lyle and Naqvi (1967), cation-exchange and solvent extraction. (i) Aziz and Lyle (1970), solvent extraction. (j) Mattern (1951), UV/vis-spectrophotometry. (k) Fronæus (1952), cation-exchange, $t = 20^\circ\text{C}$. (l) Bansal et al. (1964), cation-exchange, $t = 26^\circ\text{C}$. Much lower value in 1 mol/L HClO₄ excluded. (m) Sekine (1964, 1965), solvent extraction. (n) Spiro et al. (1968), dilatometry. (o) Antipenko et al. (1973), relaxation spectroscopy. (p) Bilal and Koß (1980), solvent extraction. Data analysis suspect, because the authors claimed that a trisulfato-complex was formed, but found no evidence for a disulfato-complex. (q) Simpson and Matijević (1987), microcalorimetry. (r) de Carvalho and Choppin (1967a), Ag⁺-potentiometry. Second Ce value from solvent extraction.

measurements in dilute solutions, or from model-dependent extrapolations of measurements at higher ionic strengths. Additional publications that adopt these original data, directly or with slight modifications, are listed in the footnotes.

It should be emphasized that all but one of the stability constants in Table 1 are appropriate only to the medium in which they were measured. Most authors accounted for the presence of bisulfate, yet only rarely were corrections made for ion pairing of SO₄²⁻ with the major cation of the experimental medium (typically Na⁺). This tends to confound direct comparisons between results from different studies, even at the same ionic strength. Allowing for this complication, the level of disagreement about absolute as well as relative $\log_{10} \beta_1$ values is nevertheless surprising. Estimates of $\log_{10} \beta_1$ for Ce, for example, range from 1.23 to 1.76 at $I = 1$ mol/L (Table 1), a difference of 0.53 log units. That is significantly more than the difference between the largest and the smallest $\log_{10} \beta_1$ within the

lanthanide series (excluding Y), estimates of which range from 0.36 log units to as low as 0.07 log units (Table 2). A persistent problem is that data are commonly collected for a few or even just a single YREE. These types of studies fail to exploit the most powerful advantage that the YREE can provide: the unique insights gained from comparative complexation behavior across the entire lanthanide series (see earlier discussions in Schijf and Byrne, 1999, 2001). A thorough review of the literature reveals that only three complete sets of $\log_{10} \beta_1$ have ever been reported for the YREE (de Carvalho and Choppin, 1967a; Fay and Purdie, 1969; Izatt et al., 1969). These are shown in Figure 1.

The large number of $\log_{10} \beta_1$ compilations in both seawater and freshwater (e.g., Turner et al., 1981; Byrne et al., 1988; Brookins, 1989; Wood, 1990; Millero, 1992; Haas et al., 1995; Byrne and Sholkovitz, 1996) seems to imply that the wealth of data on YREE sulfate complexation has been critically evalu-

Table 2. Stability constants of YREE monosulfato-complexes at $I = 0$. These values are mostly based on measurements at low ionic strength, which required only short extrapolations.

Y	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Notes
	3.59															a
	3.55															b
	3.62															c
3.47	3.62	3.59	3.62	3.64		3.66		3.66			3.59	3.59		3.59		d
							3.72									e
			3.34			3.54	3.35									f
														3.56/3.59		g
	3.62															h
3.34	3.50	3.48	3.58	3.43		3.52	3.54	3.48	3.47	3.43	3.38	3.41	3.41	3.33	3.49	i
							3.68									j
							2.13									k
3.47	3.62	3.59	3.62	3.64		3.66	3.66*	3.66	3.64*	3.61*	3.59	3.59	3.59*	3.59	3.59*	l
	3.65	3.67	3.67	3.68		3.68	3.67	3.67			3.60	3.58		3.51	3.52	m
3.47	3.64	3.59	3.62	3.64		3.67	3.67	3.66	3.64	3.62	3.59	3.59	3.59	3.58	3.52	n
	3.21	3.29	3.27	3.26	3.34	3.28	3.37	3.25	3.20	3.15	3.16	3.15	3.07	3.06	3.01	o

Notes: (a) Davies (1930), recalculated from La Mer and Goldman (1929). (b) Davies (1945), value listed without reference. (c) Jenkins and Monk (1950), conductimetry. (d) Spedding and Jaffe (1954), conductimetry. (e) Laurie and Monk (1963), solubility. (f) Barnes (1964), Barnes and Monk (1964), UV-spectrophotometry. (g) Archer and Monk (1966a,b), H^+ -potentiometry. Second value from cation-exchange. (h) Fisher and Davis (1967), conductimetry. (i) Izatt et al. (1969), calorimetry. (j) Hale and Spedding (1972a,b), UV-spectrophotometry. (k) McDowell and Coleman (1972), solvent extraction. (l) Fay and Purdie (1969), data of Spedding and Jaffe (1954) supplemented with values determined by linear interpolation and extrapolation (marked with an asterisk). The resulting complete set was used by Powell (1974) to reanalyze the data of Izatt et al. (1969). Powell (1974) omitted values for Ce and Sm, because the data of Izatt et al. (1969) did not converge for those elements. The values of Powell (1974) were adopted by Wood (1990) with some minor deviations and a misprint for Dy, and also by Haas et al. (1995), who re-interpolated the omitted values for Ce and Sm, rather than reverting to the original data of Spedding and Jaffe (1954). (m) Farrow and Purdie (1973a), recalculated data of Spedding and Jaffe (1954). Eu value from Hale and Spedding (1972a). (n) Smith and Martell (1976), critical evaluation of the best available data in the literature. These values were adopted by Turner et al. (1981) with a misprint for Eu (probably due to confusion with Er). The values of Turner et al. (1981) (including the misprint) were subsequently adopted by Brookins (1989). The values of Smith and Martell (1976) were also adopted by Byrne et al. (1988) and Byrne and Sholkovitz (1996). (o) Millero (1992), extrapolation of (unpublished) high ionic strength data, obtained from G. R. Choppin through a private communication.

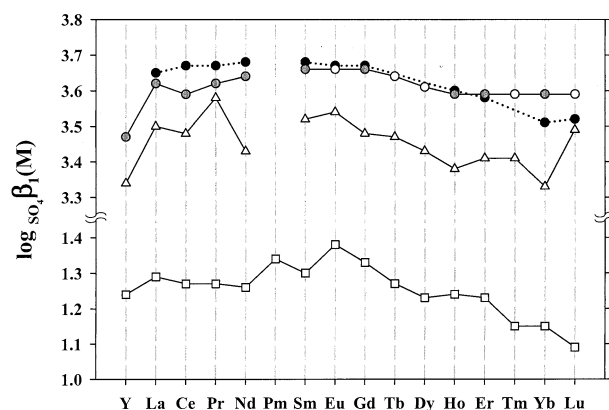


Fig. 1. Complete sets of $\log_{\text{SO}_4}\beta_1$ available in the literature (Tables 1 and 2). Conductivity data of Spedding and Jaffe (1954) (solid gray circles) were extended by Fay and Purdie (1969) (open circles) through interpolation and extrapolation and show a distinct lack of fractionation between Eu and Lu. This pattern was used by Powell (1974) and is widely quoted. The original data of Spedding and Jaffe (1954) were recalculated by Farrow and Purdie (1973a) (solid black circles). The pattern of Izatt et al. (1969) (open triangles) is based on calorimetric experiments. The pattern of de Carvalho and Choppin (1967a) (open squares) is based on potentiometric and solvent extraction experiments and has been largely ignored. The stability constants of de Carvalho and Choppin (1967a) are appropriate to 2 mol/L NaClO_4 (note the change of scale). The others apply to $I = 0$.

ated time and again. In reality, most of these “compilations” are ultimately derived from the pattern of Fay and Purdie (1969), who had extended conductivity data of Spedding and Jaffe (1954) to the entire lanthanide series by interpolation and extrapolation (Fig. 1). Powell (1974) considered the pattern of Fay and Purdie (1969) to be the best available at the time and, perhaps because of this opinion, many have treated his choice as a critical evaluation, which he clearly never intended it to be. The popularity of the $\log_{\text{SO}_4}\beta_1$ values of Powell (1974), which display a variation among the lanthanides (excluding Y) of only 0.07 log units, has engendered a consensus that the $\log_{\text{SO}_4}\beta_1$ pattern is “flat” and that sulfate complexation cannot contribute to the substantial YREE fractionation that is often observed in sulfate-rich waters.

The pattern of de Carvalho and Choppin (1967a) is relatively flat between La and Sm, and a maximum at Eu is followed by a very gradual decrease from Eu to Lu (Fig. 1). It is noteworthy that a recalculation of the data of Spedding and Jaffe (1954) by Farrow and Purdie (1973a), who incorporated new data and used revised values for the equivalent conductances of MSO_4^+ , led to a pattern somewhat similar to that of de Carvalho and Choppin (1967a). In addition, the pattern of Izatt et al. (1969), while showing considerable scatter among the LREE and a high value for Lu, more closely resembles the pattern of de Carvalho and Choppin (1967a) than that of Fay and Purdie (1969).

Due to a growing interest in YREE transport in groundwaters and contaminated surface waters, and the development of analytical techniques like ICP-MS, studies of YREE mobility and

fractionation in sulfate-rich waters are increasingly commonplace. Although interpretation of such investigations demands accurate data on the stability of YREE sulfato-complexes, the perceived abundance of stability constant compilations may have forestalled efforts to reconcile the conflicting $_{\text{SO}_4}\beta_1$ patterns shown in Figure 1. In this work we present the first determination of a complete set of $_{\text{SO}_4}\beta_1$ since the studies of de Carvalho and Choppin (1967a) and Izatt et al. (1969). Experimental constraints, specifically the need to minimize the sensitivity of the results to minor variations in ionic strength, plus our oceanographic focus, have compelled us to perform measurements at the ionic strength of seawater ($I = 0.7\text{ m}$). Our analyses involve observations of the solubility product of a sparingly soluble sulfate salt (BaSO_4) in concentrated solutions of single YREE chlorides. Our results demonstrate that the $_{\text{SO}_4}\beta_1$ pattern is not flat, but shows a fractionation between Eu and Lu of 0.20 log units. This has important implications for YREE behavior in acidic, sulfate-rich waters.

2. EXPERIMENTAL STRATEGY

Stability constants of YREE monosulfato-complexes ($_{\text{SO}_4}\beta_1$) were determined by comparing the solubility of BaSO_4 in 0.1167 mol/L YREE chloride sample solutions with that in a 0.70 mol/L ammonium chloride reference solution, all at pH 3.0 and $t = 25^\circ\text{C}$. In the following derivations, brackets [] indicate free (i.e., unpaired) ion concentrations, while total (i.e., free ion + all ion pairs) concentrations are indicated by the subscript T. Subscripts S and R represent sample and reference solutions, respectively, and M^{3+} represents the YREE ions. All concentrations, ionic strengths and equilibrium constants were converted to the molal scale.

The BaSO_4 solubility product is expressed in terms of free Ba and sulfate concentrations as

$$K_{\text{sp}}(\text{BaSO}_4) = [\text{Ba}^{2+}][\text{SO}_4^{2-}]. \quad (1)$$

Since solubility products expressed in terms of free ion concentrations depend only on ionic strength, the following equality applies when both sample solution and reference solution are in equilibrium with BaSO_4 , at the same ionic strength:

$$([\text{Ba}^{2+}][\text{SO}_4^{2-}]_S) = ([\text{Ba}^{2+}][\text{SO}_4^{2-}]_R). \quad (2)$$

Eqn. 2 can be equivalently written in terms of total Ba and sulfate concentrations, which are directly measurable:

$$\frac{([\text{Ba}^{2+}][\text{SO}_4^{2-}]_S)}{([\text{Ba}^{2+}][\text{SO}_4^{2-}]_R)} = \frac{([\text{Ba}^{2+}]_T[\text{SO}_4^{2-}]_T)_S}{([\text{Ba}^{2+}]_T[\text{SO}_4^{2-}]_T)_R} \quad (3)$$

Rearrangement of Eqn. 3 yields

$$\varphi = \frac{([\text{Ba}^{2+}]_T[\text{SO}_4^{2-}]_T)_S}{([\text{Ba}^{2+}]_T[\text{SO}_4^{2-}]_T)_R} = \frac{\left(\frac{[\text{Ba}^{2+}]_T}{[\text{Ba}^{2+}]_T}\right)_S \left(\frac{[\text{SO}_4^{2-}]_T}{[\text{SO}_4^{2-}]_T}\right)_R}{\left(\frac{[\text{Ba}^{2+}]_T}{[\text{Ba}^{2+}]_T}\right)_R \left(\frac{[\text{SO}_4^{2-}]_T}{[\text{SO}_4^{2-}]_T}\right)_S} \quad (4)$$

where φ is directly measurable as the ratio of the products $[\text{Ba}^{2+}]_T[\text{SO}_4^{2-}]_T$ in sample and reference solutions.

BaSO_4^0 ion pairs are comparable in stability to NH_4SO_4^- ion pairs (Smith and Martell, 1976) and much less stable than YREE monosulfato-complexes. Because ion pairing between Ba^{2+} and Cl^- is exceedingly weak (Smith and Martell, 1976) and sulfate concentrations in sample and reference solutions are low, it is assumed that $[\text{Ba}^{2+}] = [\text{Ba}^{2+}]_T$. Eqn. 4 can thus be simplified to

$$\varphi = \left(\frac{[\text{SO}_4^{2-}]_S}{[\text{SO}_4^{2-}]_T}\right)_R \left(\frac{[\text{SO}_4^{2-}]_T}{[\text{SO}_4^{2-}]_S}\right)_S^{-1}. \quad (5)$$

In the reference solution, SO_4^{2-} forms ion pairs with NH_4^+ and also forms bisulfate, so that

$$\left(\frac{[\text{SO}_4^{2-}]_T}{[\text{SO}_4^{2-}]_R}\right) = 1 + {}_{\text{SO}_4}\beta_1(\text{NH}_4) \cdot [\text{NH}_4^+] + K_a \cdot [\text{H}^+]_R \quad (6)$$

where ${}_{\text{SO}_4}\beta_1(\text{NH}_4)$ is the stability constant of the NH_4SO_4^- ion pair:

$${}_{\text{SO}_4}\beta_1(\text{NH}_4) = \frac{[\text{NH}_4\text{SO}_4^-]}{[\text{NH}_4^+][\text{SO}_4^{2-}]}, \quad (7)$$

K_a is the association constant of the bisulfate ion:

$$K_a = \frac{[\text{HSO}_4^-]}{[\text{H}^+][\text{SO}_4^{2-}]}, \quad (8)$$

and $[\text{H}^+] = 10^{-\text{pH}}$. In the sample solutions, SO_4^{2-} forms complexes with M^{3+} and also forms bisulfate, so that

$$\left(\frac{[\text{SO}_4^{2-}]_T}{[\text{SO}_4^{2-}]_S}\right) = 1 + {}_{\text{SO}_4}\beta_1(\text{M}) \cdot [\text{M}^{3+}] + K_a \cdot [\text{H}^+]_S \quad (9)$$

where ${}_{\text{SO}_4}\beta_1(\text{M})$ are the stability constants of YREE monosulfato-complexes:

$${}_{\text{SO}_4}\beta_1(\text{M}) = \frac{[\text{MSO}_4^+]}{[\text{M}^{3+}][\text{SO}_4^{2-}]}. \quad (10)$$

Experiments performed in the presence of 1 mmol/L excess SO_4^{2-} confirmed that there was no discernible contribution from YREE disulfato-complexes.

Combining Eqn. 5, 6, and 9, it follows that

$$\varphi = \frac{1 + {}_{\text{SO}_4}\beta_1(\text{M}) \cdot [\text{M}^{3+}] + K_a \cdot [\text{H}^+]_S}{1 + {}_{\text{SO}_4}\beta_1(\text{NH}_4) \cdot [\text{NH}_4^+] + K_a \cdot [\text{H}^+]_R}. \quad (11)$$

Rearranging, we obtain an expression that enables calculation of ${}_{\text{SO}_4}\beta_1(\text{M})$:

$${}_{\text{SO}_4}\beta_1(\text{M}) = \frac{\varphi \cdot (1 + {}_{\text{SO}_4}\beta_1(\text{NH}_4) \cdot [\text{NH}_4^+] + K_a \cdot [\text{H}^+]_R)}{[\text{M}^{3+}]} - \frac{(1 + K_a \cdot [\text{H}^+]_S)}{[\text{M}^{3+}]}. \quad (12)$$

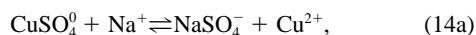
Ion pairing between M^{3+} and Cl^- is significant in the sample solutions, hence $[\text{M}^{3+}]$ in Eqn. 12 was calculated from the following two equations:

$$[\text{M}^{3+}]_T = [\text{M}^{3+}] \cdot (1 + {}_{\text{Cl}}\beta_1(\text{M}) \cdot [\text{Cl}^-]), \quad (13a)$$

$$[\text{Cl}^-]_{\text{T}} = [\text{Cl}^-] \cdot (1 + c_{\text{Cl}}\beta_1(\text{M}) \cdot [\text{M}^{3+}]). \quad (13\text{b})$$

Iterative calculations, using Eqn. 13a and 13b and the ionic strength dependence of $c_{\text{Cl}}\beta_1(\text{M})$ at $t = 25^\circ\text{C}$ (Luo and Byrne, 2001), indicated that $[\text{M}^{3+}] = (0.878 \pm 0.001) \cdot [\text{M}^{3+}]_{\text{T}}$ for all YREE. Ion pairing between M^{3+} and Cl^- lowered the free ionic strength of the sample solutions to $I = 0.66 \pm 0.01\text{ m}$. The highest sulfate concentrations in our experiments are $< 1\%$ of the highest YREE concentrations. Even if all SO_4^{2-} were complexed with M^{3+} , this would lower the free YREE concentration by $< 1\%$ and the free ionic strength by a negligible amount. Equations 2–4 and subsequent derivations dictate that BaSO_4 solubility products in sample and reference solutions must be compared at the same ionic strength. $K_{\text{sp}}(\text{BaSO}_4)$ in the reference solution ($I = 0.72\text{ m}$) must therefore be corrected to the ionic strength of the sample solutions ($I = 0.66\text{ m}$). Employing the ion-pairing model of Millero and Schreiber (1982), we determined that φ in Eqn. 4 and 12, obtained by comparing the solubility product of BaSO_4 in the sample solutions with that in a hypothetical $0.66 \pm 0.01\text{ m}$ NH_4Cl reference solution, would be larger than the actually measured φ by a factor of 1.109 ± 0.031 .

These corrections and the calculation of $s_{\text{O}_2}\beta_1(\text{M})$ from Eqn. 12 call for accurate estimates of the magnitudes of K_{a} and $s_{\text{O}_2}\beta_1(\text{NH}_4)$. The value $\log K_{\text{a}} = 1.49$ at $I = 0.7\text{ m}$ and $t = 25^\circ\text{C}$ was taken from Millero and Schreiber (1982). Given that $\log s_{\text{O}_2}\beta_1(\text{Na}) = 0.30 \pm 0.04$ at $I = 0.7\text{ m}$ and $t = 25^\circ\text{C}$ (Smith and Martell, 1989), it can be shown that the value of Millero and Schreiber (1982), which is appropriate to free ion concentrations, is in excellent agreement with the value of Dickson et al. (1990), appropriate to 0.7 m NaCl . K_{a} was assumed to vary little between $I = 0.66\text{ m}$ and $I = 0.72\text{ m}$ and any inaccuracies resulting from this assumption are minor since the $K_{\text{a}} \cdot [\text{H}^+]$ terms in Eqn. 12 are much smaller than unity ($K_{\text{a}} \cdot [\text{H}^+] \approx 0.03$). Due to the high ammonium concentration in the reference solution, the term $s_{\text{O}_2}\beta_1(\text{NH}_4) \cdot [\text{NH}_4^+]$ in Eqn. 12 may well be of similar magnitude as the term $1 + K_{\text{a}} \cdot [\text{H}^+]_{\text{R}}$. An accurate estimate of $s_{\text{O}_2}\beta_1(\text{NH}_4)$ is therefore of considerable importance. As the magnitude of $s_{\text{O}_2}\beta_1(\text{Na})$, unlike that of $s_{\text{O}_2}\beta_1(\text{NH}_4)$, is comparatively well known, we conducted experiments to determine their relative magnitudes. These experiments involved observations of the formation of CuSO_4^0 ion pairs in 0.7 mol/L NaClO_4 and 0.7 mol/L NH_4ClO_4 . It can be shown that the ratio of the equilibrium constants of the corresponding reactions:



expressed in terms of free ion concentrations, is equal to the ratio $s_{\text{O}_2}\beta_1(\text{Na})/s_{\text{O}_2}\beta_1(\text{NH}_4)$. If $[\text{Cu}^{2+}]_{\text{T}}$ and $[\text{SO}_4^{2-}]_{\text{T}}$ are the same in the two solutions and if $[\text{Na}^+]_{\text{T}} = [\text{NH}_4^+]_{\text{T}}$, the ratio of the equilibrium constants of reactions 14a and 14b depends only on the relative concentrations of CuSO_4^0 : if the CuSO_4^0 concentration in NaClO_4 is greater than in NH_4ClO_4 , it follows that $s_{\text{O}_2}\beta_1(\text{NH}_4) > s_{\text{O}_2}\beta_1(\text{Na})$ and vice versa. Such experiments could in principle be performed with any divalent metal that has a sufficiently stable monosulfato-complex, but Cu is especially suitable, because CuSO_4^0 absorbs strongly in the ultraviolet (UV). The absorbance at $\lambda = 280\text{ nm}$ (A_{280}) is dominated

by the CuSO_4^0 ion pair, with only minor contributions from other species (Byrne et al., 1983). When $[\text{Cu}^{2+}]_{\text{T}}$ was kept constant at 4.76 mmol/L and $[\text{SO}_4^{2-}]_{\text{T}}$ was varied between ~ 4 and $\sim 20\text{ mmol/L}$, A_{280} varied between 0.09 and 0.29 , yet its values in 0.7 mol/L NaClO_4 and in 0.7 mol/L NH_4ClO_4 agreed within 4% , on average. Therefore, in our calculations we assumed that $s_{\text{O}_2}\beta_1(\text{NH}_4) = s_{\text{O}_2}\beta_1(\text{Na})$, where the latter was derived from the ionic strength dependence of $s_{\text{O}_2}\beta_1(\text{Na})$ formulated by Pytkowicz and Kester (1969) and adopted by Millero and Schreiber (1982).

Experimental details are given in the Appendix. Preparation and equilibration of the sample and reference solutions is discussed in sections A.1 and A.2. Quantities required to calculate $s_{\text{O}_2}\beta_1(\text{M})$ from Eqn. 12 were measured with three analytical techniques: pH_{S} and pH_{R} by potentiometry (section A.3), $[\text{SO}_4^{2-}]_{\text{S}}$, $[\text{SO}_4^{2-}]_{\text{R}}$, and $[\text{NH}_4^+]_{\text{S}}$ by ion chromatography (section A.4), and $[\text{Ba}^{2+}]_{\text{S}}$, $[\text{Ba}^{2+}]_{\text{R}}$, and $[\text{M}^{3+}]_{\text{T}}$ by inductively-coupled plasma mass spectrometry (section A.5). Section A.6 describes the spectrophotometric experiments that supplied the relative magnitudes of $s_{\text{O}_2}\beta_1(\text{NH}_4)$ and $s_{\text{O}_2}\beta_1(\text{Na})$.

3. RESULTS AND DISCUSSION

3.1. Stability Constant Results, Estimated Dependence on Ionic Strength, and Comparisons With Previous Work

Stability constants of YREE monosulfato-complexes ($s_{\text{O}_2}\beta_1$) were calculated as described in section 2. Primary data are listed in the Appendix (Tables A1–A3) to permit prompt recalculation of $s_{\text{O}_2}\beta_1$, should more accurate values of $s_{\text{O}_2}\beta_1(\text{NH}_4)$, or other constants that were used in our calculations, become available in the future. Results are listed in Table 3 and shown graphically in Figure 2. Analytical precision, based on four experiments, two at low and two at high sulfate concentrations, is better than ± 0.03 log units. That is significantly less than the uncertainty of most literature values and certainly less than the variation of $s_{\text{O}_2}\beta_1$ throughout the lanthanide series. Between La and Eu, $\log s_{\text{O}_2}\beta_1$ varies within the range 1.93 to 1.97 , with a weak maximum at Eu. Between Eu and Lu, $\log s_{\text{O}_2}\beta_1$ decreases almost linearly with atomic number, from 1.97 to 1.77 . The stability constant for Y is lower than that for all but the heaviest REE.

All $s_{\text{O}_2}\beta_1$ values in Table 3 are expressed in terms of free ion concentrations. As such, they are directly comparable with the $s_{\text{O}_2}\beta_1$ values at $I = 0.7\text{ m}$ of Byrne and Sholkovitz (1996), also expressed in terms of free ion concentrations, which were extrapolated from the recommended values at $I = 0$ of Smith and Martell (1976). Our $s_{\text{O}_2}\beta_1$ values deviate from those of Byrne and Sholkovitz (1996) by ~ 0.05 log units, only slightly more than our analytical precision.

To make the results in Table 3 applicable to a wide range of natural conditions, it is necessary to evaluate the ionic strength dependence of $s_{\text{O}_2}\beta_1$. In the numerous studies of YREE sulfate complexation available in the literature, stability constants are almost never expressed in terms of free ion concentrations (Table 1). Ion pairing of SO_4^{2-} with the major cation (most frequently Na^+) of the experimental medium has generally been ignored, for lack of accurate $s_{\text{O}_2}\beta_1(\text{Na})$ values at appropriate ionic strengths. Experimental conditions are often re-

Table 3. Stability constants of YREE monosulfato-complexes at $I = 0.66\text{ m}$ and $t = 25^\circ\text{C}$, expressed in terms of free ion concentrations. Precision of $\log_{\text{SO}_4}\beta_1(\text{M})$ is given as one standard deviation (σ) based on four experiments, two at low and two at high sulfate concentrations. Stability constants in the last column were extrapolated to $I = 0$ as described in the text. Precision of $\log_{\text{SO}_4}\beta_1^0(\text{M})$ was approximated by statistically combining the precision of $\log_{\text{SO}_4}\beta_1(\text{M})$ with the estimated uncertainty of the extrapolation (Eqn. 16).

M^{3+}	No SO_4^{2-} added		1 mmol/L SO_4^{2-} added		$\log_{\text{SO}_4}\beta_1(\text{M})$	$\log_{\text{SO}_4}\beta_1^0(\text{M})$
	Experiment 1	Experiment 2	Experiment 3	Experiment 4	$I = 0.66\text{ m}$	$I = 0$
Y	1.88	1.83	1.81	1.83	1.83 ± 0.03	3.50 ± 0.03
La	1.95	1.93	1.93	1.95	1.94 ± 0.01	3.61 ± 0.02
Ce	1.93	1.93	1.94	1.94	1.94 ± 0.01	3.61 ± 0.01
Pr	1.96	1.95	1.93	1.95	1.95 ± 0.01	3.62 ± 0.02
Nd	1.94	1.95	1.93	1.90	1.93 ± 0.02	3.60 ± 0.02
Pm	—	—	—	—	—	—
Sm	1.99	1.95	1.94	1.95	1.96 ± 0.02	3.63 ± 0.02
Eu	1.99	1.96	1.96	1.95	1.97 ± 0.01	3.64 ± 0.02
Gd	1.96	1.93	1.94	1.92	1.94 ± 0.02	3.61 ± 0.02
Tb	1.92	1.92	1.92	1.91	1.92 ± 0.01	3.59 ± 0.01
Dy	1.93	1.90	1.90	1.88	1.90 ± 0.02	3.57 ± 0.03
Ho	1.90	1.86	1.86	1.86	1.87 ± 0.02	3.54 ± 0.02
Er	1.87	1.82	1.83	1.82	1.84 ± 0.02	3.51 ± 0.03
Tm	1.83	1.81	1.80	1.79	1.81 ± 0.02	3.48 ± 0.02
Yb	1.79	1.79	1.79	1.78	1.79 ± 0.01	3.46 ± 0.01
Lu	1.79	1.77	1.78	1.75	1.77 ± 0.02	3.44 ± 0.02

ported in insufficient detail to allow corrections to be made *ex post facto*. In this work, the ionic strength dependence of $_{\text{SO}_4}\beta_1$ was therefore assessed by using Eqn. 15 and the ion-pairing model of Millero and Schreiber (1982):

$$\log_{\text{SO}_4}\beta_1(\text{M}) = \log_{\text{SO}_4}\beta_1^0(\text{M}) + \log\left(\frac{\gamma_{\text{M}^{3+}}\gamma_{\text{SO}_4^{2-}}}{\gamma_{\text{MSO}_4^+}}\right), \quad (15)$$

where $_{\text{SO}_4}\beta_1^0(\text{M})$ represents the stability constant $_{\text{SO}_4}\beta_1(\text{M})$ at $I = 0$, and γ_i is the activity coefficient of species i . Ionic strength dependences of γ_i were obtained by using Eqn. 24 and 27 from Millero and Schreiber (1982) together with the Pitzer coefficients B_i^0 , B_i^1 , and C_i from their Table 9. Activity coefficients $\gamma_{\text{MSO}_4^+}$ were estimated from the Pitzer coefficients for a large monovalent cation, Cs^+ . Since Pitzer coefficients of the YREE do not vary greatly throughout the lanthanide series (Millero, 1992), the activity coefficient of Eu^{3+} was taken from

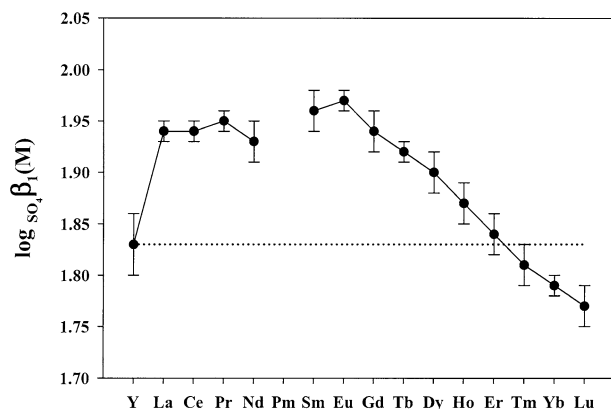


Fig. 2. Stability constants of YREE monosulfato-complexes at $I = 0.66\text{ m}$ and $t = 25^\circ\text{C}$, expressed in terms of free ion concentrations (Table 3). Error bars represent one standard deviation (σ), based on four experiments. Dotted horizontal line is drawn to show that the stability constant for Y is approximately equal to that for Er.

Millero and Schreiber (1982) to represent all YREE. Numerical values of the term $\log(\gamma_{\text{Eu}^{3+}}\gamma_{\text{SO}_4^{2-}}/\gamma_{\text{Cs}^+})$ were calculated for several ionic strengths between $I = 0.1$ and 0.8 m and the results were fitted to an extended Debye-Hückel equation:

$$\log_{\text{SO}_4}\beta_1(\text{M}) = \log_{\text{SO}_4}\beta_1^0(\text{M}) - 6.132 \frac{\sqrt{I}}{(1 + 2.283\sqrt{I})} + 0.1183 \cdot I. \quad (16)$$

Eqn. 16 can be used to generate $_{\text{SO}_4}\beta_1$ values, expressed in terms of free ion concentrations, for ionic strengths between 0 and 1 m . These values are applicable to natural waters of any composition, provided that the major ion speciation is known in sufficient detail to allow a reasonable estimate of the free sulfate concentration.

Values of $_{\text{SO}_4}\beta_1^0$, obtained for each YREE using our results at $I = 0.66\text{ m}$ and Eqn. 16, are given in the last column of Table 3. As regards their absolute magnitudes, these values show rather good agreement with the recommended $_{\text{SO}_4}\beta_1^0$ values of Smith and Martell (1976) (Fig. 3), as well as with short extrapolations of measurements in dilute solutions (Table 2 and Fig. 1). In contrast, the results of an extrapolation to $I = 0$ by Millero (1992) are nearly 0.5 log units lower than our $_{\text{SO}_4}\beta_1^0$ values (Fig. 3). The extrapolation of Millero (1992) is at least partly based on unpublished, high ionic strength data of G. R. Choppin that cannot be directly compared with published $_{\text{SO}_4}\beta_1$ values, because they were reproduced only in graphical form. These data are appropriate to sodium perchlorate solutions, hence extensive ion pairing between Na^+ and SO_4^{2-} had to be accounted for in the extrapolation. While the $_{\text{SO}_4}\beta_1^0$ values of Millero (1992) are lower than our $I = 0$ results and most of the $I = 0$ results in Table 2, our $_{\text{SO}_4}\beta_1$ pattern and that of Millero (1992) share certain features: little fractionation between La and Eu, a weak maximum at Eu, and an almost linear decrease between Eu and Lu. The only other extrapolation that is in poor agreement with our $I = 0$ results is that of Izatt et al. (1969) (Table 2 and Fig. 1). Powell (1974) has very carefully and

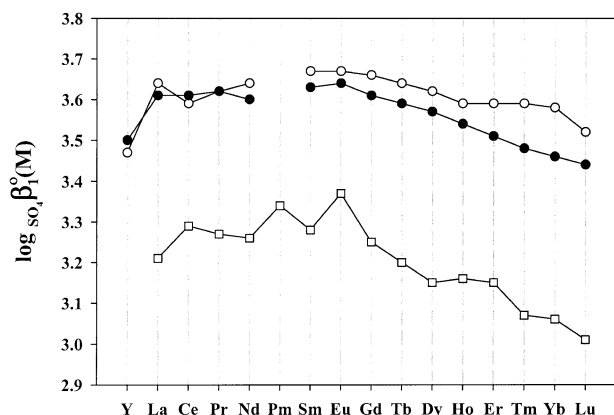


Fig. 3. Pattern of $\log_{\text{SO}_4}\beta_1^0$ (solid black circles), derived from our $\log_{\text{SO}_4}\beta_1$ values at $I = 0.66 m$ (Table 3) and the ionic strength dependence of $\log_{\text{SO}_4}\beta_1$, based on Eqn. 15 and the ion-pairing model of Millero and Schreiber (1982). Error bars were omitted for clarity. See text for details. Shown for comparison are patterns of Smith and Martell (1976) (open circles) and Millero (1992) (open squares), both at $I = 0$ (Table 2). The pattern of Millero (1992) was derived from an extrapolation of (unpublished) data of G. R. Choppin.

convincingly addressed some of the flaws in the data analysis of Izatt et al. (1969). Powell (1974) preferred the $\log_{\text{SO}_4}\beta_1^0$ values of Fay and Purdie (1969), which are in much better agreement with ours (Table 2).

3.2. YREE Sulfate Complexation in Natural Waters

YREE sulfato-complexes generally comprise a minor fraction of environmental YREE concentrations, because sulfate concentrations are low in most natural waters. SO_4^{2-} is also a weak YREE ligand in comparison with CO_3^{2-} , oxalate, OH^- , F^- , and humic acids. YREE sulfato-complexes can become dominant species when sulfate concentrations are high and free ion concentrations of competing ligands are very low. In systems where massive metal sulfide deposits are exposed to oxygenated waters, sulfate concentrations are often elevated to the 10 to 100 mmol/L range. Examples have been described at both low temperature (0.1–4.2°C, Johannesson and Lyons, 1995; Johannesson and Zhou, 1999) and high temperature (70–93°C, Lewis et al., 1997, 1998). These sulfate-rich waters typically have low ionic strength ($I \ll 0.1 \text{ mol/L}$), low pH (2–4), and very low alkalinity and DOC concentrations. Since the $\text{p}K_a$ of SO_4^{2-} at $I = 0$ approaches 2, which is well below the $\text{p}K_a$ values of CO_3^{2-} (6.4 and 10.3), carboxylic acid groups (4–5), F^- (3.2), and other competing ligands, YREE sulfate complexation is expected to be especially enhanced at low pH.

An assessment of the importance and general characteristics of YREE sulfate complexation in sulfate-rich waters can be obtained from Eqn. 16 and the $\log_{\text{SO}_4}\beta_1^0$ values in Table 3. To broaden the applicability of this assessment, it is useful to consider the influence of temperature on YREE sulfate complexation. Figure 4A shows two sets of formation enthalpies for all YREE at $t = 25^\circ\text{C}$, one at $I = 0$ (Smith and Martell, 1976), which is based on the very careful reanalysis by Powell (1974) of the original data of Izatt et al. (1969), and the other at $I = 2 \text{ mol/L}$ (de Carvalho and Choppin, 1967b). Formation enthalpies at $I = 2 \text{ mol/L}$ appear to be $\sim 1 \text{ kcal/mol}$ lower than

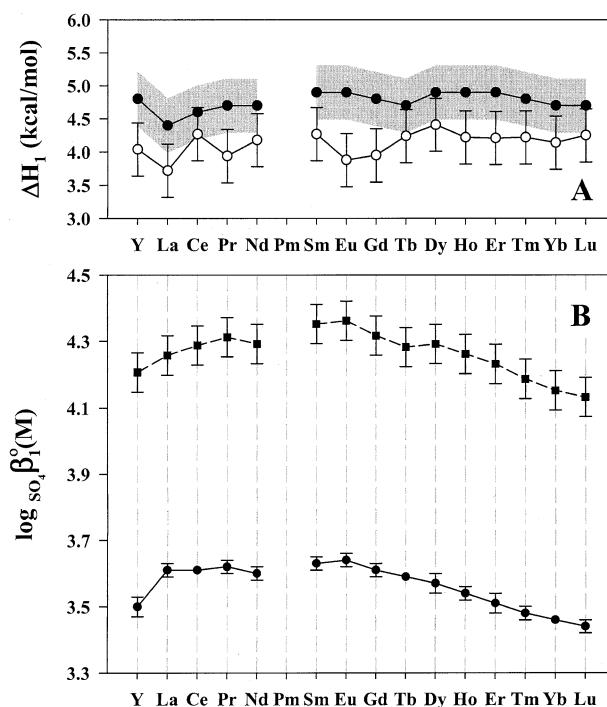


Fig. 4. (A) Formation enthalpies ($t = 25^\circ\text{C}$) of YREE monosulfato-complexes at $I = 0$ (Smith and Martell, 1976) (solid black circles) and at $I = 2 \text{ mol/L}$ (de Carvalho and Choppin, 1967b) (open circles). Analytical precision ($\pm 0.4 \text{ kcal/mol}$) is indicated with shading and error bars. (B) Patterns of $\log_{\text{SO}_4}\beta_1^0$ at $t = 25^\circ\text{C}$ (Table 3) (solid black circles, solid line) and extrapolated to $t = 100^\circ\text{C}$ using the formation enthalpies of Smith and Martell (1976) (solid black squares, dashed line). Some error bars are within the size of the symbols.

at $I = 0$ and show somewhat different behavior throughout the lanthanide series. In view of the large uncertainties of both data sets ($\pm 0.4 \text{ kcal/mol}$) these variations may not be significant. The importance of such details is demonstrated in Figure 4B, where our $\log_{\text{SO}_4}\beta_1^0$ values (Table 3) are extrapolated to $t = 100^\circ\text{C}$, using the formation enthalpies of Smith and Martell (1976) (Fig. 4A) and a simple Gibbs-Helmholtz equation:

$$\ln_{\text{SO}_4}\beta_1^0(T_2) - \ln_{\text{SO}_4}\beta_1^0(T_1) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (17)$$

with $R = 1.98726 \text{ (cal/mol)/K}$. Values of $\log_{\text{SO}_4}\beta_1^0$ at $t = 100^\circ\text{C}$ are about a factor of 6 higher than at $t = 25^\circ\text{C}$ and the $\log_{\text{SO}_4}\beta_1^0$ pattern at $t = 100^\circ\text{C}$ has a distinctly different shape, especially around Y-La-Ce and Tb-Dy-Ho. These differences are expected to be even more pronounced in hydrothermal waters, which can have temperatures as high as 300°C (Haas et al., 1995). It is interesting to note that increasing temperature promotes a $\log_{\text{SO}_4}\beta_1^0$ maximum near the middle of the lanthanide series.

To determine under exactly what conditions sulfato-complexes may be the dominant YREE species, we calculated the extent of YREE sulfate complexation in a pure sodium sulfate solution as a function of ionic strength ($0 \leq I \leq 0.1 m$) at $t = 25^\circ\text{C}$. Results are shown in Figure 5 for the YREE with the highest (Eu) and lowest (Lu) values of $\log_{\text{SO}_4}\beta_1$ (Table 3). The inset compares Eu results at $t = 25^\circ\text{C}$ with calculations at two

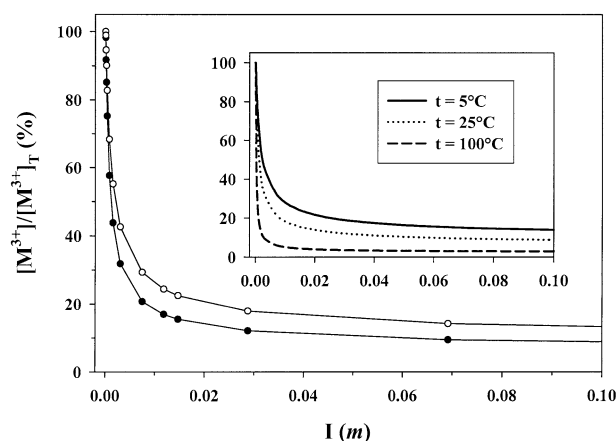


Fig. 5. Modeled ratios of free and total YREE concentrations, in pure sodium sulfate solutions at low ionic strength and pH 4.0, with trace amounts of YREE. Results are shown at $t = 25^\circ\text{C}$ for Eu (solid black circles) and Lu (open circles), which have the highest and lowest value of $s_{\text{O}_4}\beta_1$ within the lanthanide series, respectively (Table 3). Inset shows the effect of temperature for Eu. See text for details.

additional temperatures ($t = 5$ and 100°C). While YREE concentrations can reach 10 to 1000 nmol/L in sulfate-rich waters, the YREE may be considered a trace component of the solution. Major ion speciation was therefore determined separately by iterative calculations, taking into account the formation of bisulfate and of the NaSO_4^- ion pair. Upon convergence, the ionic strength and the free sulfate concentration were used to calculate the ratio of free and total YREE concentrations ($[\text{M}^{3+}]/[\text{M}^{3+}]_T$). The free hydrogen ion concentration was kept constant at 10^{-4} mol/L (pH 4.0), whereby the formation of bisulfate is negligible. Debye-Hückel limiting slopes, ranging from 0.4952 at $t = 5^\circ\text{C}$ to 0.6086 at $t = 100^\circ\text{C}$, were taken from Robinson and Stokes (1959). For the formation of bisulfate, we used the dissociation constants of Dickson et al. (1990), fitted to an extended Debye-Hückel equation, taking into account that these constants are appropriate to sodium chloride solutions. Smith and Martell (1989) list $\Delta H^\circ = +5.4$ kcal/mol for the formation of bisulfate. This value agrees well with data reported by Dickson et al. (1990). To obtain the ionic strength dependence of $s_{\text{O}_4}\beta_1(\text{Na})$, an accurate and precise value of $s_{\text{O}_4}\beta_1^0$ (Capewell et al., 1999) was extrapolated with the Davies equation (Millero and Schreiber, 1982). The formation enthalpy of the NaSO_4^- ion pair is not well known and the formation reaction has been variously reported as endothermic or exothermic. Since Smith and Martell (1989) list $\Delta H^\circ = +0.3 \pm 0.8$ kcal/mol, which is not significantly different from zero, it was assumed that formation of the NaSO_4^- ion pair does not depend on temperature. Consistent with Figure 4A, the formation enthalpy for Eu, $\Delta H^\circ = +4.9$ kcal/mol, was taken from Smith and Martell (1976). All temperature extrapolations of stability constants were performed in accordance with Eqn. 17.

Figure 5 shows that YREE monosulfato-complexes are the dominant species over much of the range 0 to 0.1 m , with the free ion dominating only at ionic strengths below ~ 0.001 m (at $t = 25^\circ\text{C}$). The ratio $[\text{M}^{3+}]/[\text{M}^{3+}]_T$ is a very steep function of ionic strength below 0.01 m and does not vary much with ionic

strength above 0.01 m . With increasing temperature, this behavior becomes more pronounced and YREE monosulfato-complexes dominate at progressively lower ionic strengths. The absolute degree of YREE sulfate complexation increases with temperature as well. For Eu at $I = 0.01$ m , it grows from $\sim 75\%$ at $t = 5^\circ\text{C}$ to $\sim 95\%$ at $t = 100^\circ\text{C}$.

Several authors have performed detailed modeling of YREE solution speciation in sulfate-rich waters, suggesting that YREE sulfato-complexes are indeed of far greater importance in these systems and are sometimes the dominant YREE species. Johannesson and Lyons (1995) calculated that dissolved YREE in Colour Lake are distributed about equally between the monosulfato-complex and the free ion. Lewis et al. (1998), who accounted for temperature in their speciation calculations, found that sulfato-complexes dominate YREE speciation in geothermal fluids from Yellowstone National Park. On the other hand, Johannesson and Hendry (2000) showed that carbonato-complexes dominate YREE speciation in sulfate-rich groundwaters of low ionic strength when the pH is 7.0 to 7.5. Johannesson and Lyons (1995) and Lewis et al. (1998) both noted that the monosulfato-complex and the free ion were the only YREE species present, except in waters with a low $\text{SO}_4^{2-}/\text{F}^-$ ratio, where a discernible fraction of the total YREE concentration consisted of fluoro-complexes. Gimeno Serrano et al. (2000) pointed out that the contribution of YREE fluoro-complexes may have been overestimated in these studies, since Al^{3+} , which can reach near-millimolar concentrations in these systems, interacts strongly with F^- , thereby lowering the free fluoride concentration.

It must be emphasized that our model solution was chosen to maximize YREE sulfate complexation by ensuring that the free sulfate concentration was always nearly equal to the total sulfate concentration, so that the free sulfate concentration is approximately equal to $I/3$. Figure 5 indicates that the ratio $[\text{M}^{3+}]/[\text{M}^{3+}]_T$ is a sensitive function of the free sulfate concentration, yet not necessarily that sulfate complexation dominates YREE solution speciation under all conditions at ionic strengths ≥ 0.01 m . In high ionic strength solutions the degree of YREE sulfate complexation is expected to be lower. This is exemplified by acidic, sulfate-rich groundwaters of high ionic strength ($I = 0.7\text{--}3.3$ mol/L), where sulfato-complexes constitute only 20 to 30% of total YREE concentrations, in the absence of competing ligands (Johannesson et al., 1996). Free sulfate concentrations in acidic, sulfate-rich waters could be lower than calculated for the sodium sulfate model solution, as a result of ion pairing with Mg^{2+} , Ca^{2+} , or divalent transition metals. The stability constants of SO_4^{2-} ion pairs with divalent metals are typically an order of magnitude higher than $s_{\text{O}_4}\beta_1(\text{Na})$ (Smith and Martell, 1976). YREE solution speciation in sulfate-rich waters thus reflects a chemical balance that depends on a large number of critical parameters. A meaningful description of such systems takes detailed knowledge, not only of fundamental characteristics such as ionic strength, pH, temperature, and alkalinity, but also of quantities that are measured less routinely, such as the concentrations of F, Al, Fe, and any divalent metals whose concentrations are substantially elevated. Figure 5 underscores the need for more accurate values of the stability constants and formation enthalpies of SO_4^{2-} ion pairs, particularly with Na^+ , over wide ranges of ionic strength and temperature.

Models of YREE speciation in acidic, sulfate-rich waters have predicted the dominance of YREE sulfato-complexes, yet none have succeeded in explaining the YREE abundance patterns with unusual MREE enrichments that are commonly observed in these environments. The shape of the $\text{SO}_4\beta_1$ pattern presented in this work agrees with that of Millero (1992), whereas our extrapolation to $I = 0$ supports the higher $\text{SO}_4\beta_1^0$ values of Fay and Purdie (1969) and others. Figure 4B shows relatively smooth $\text{SO}_4\beta_1$ behavior along the lanthanide series, which is expected in view of the great chemical similarity of neighboring YREE. Johannesson and Zhou (1999) have argued that MREE-enriched patterns are probably not caused by dominant YREE sulfate complexation, but instead reflect a source signature resulting from preferential dissolution of YREE-enriched ferric minerals in the low-pH waters of these systems. They found that acid leachates of sedimentary rocks from Colour Lake showed MREE-enriched patterns reminiscent of the lake water, but only if the rocks contained significant amounts of Fe-Mn oxyhydroxide cements. It is possible that these minerals acquire their YREE signatures by adsorption of YREE from the sulfate-rich waters or by secondary precipitation in the water column. Studies of YREE fractionation and distribution coefficients resulting from such adsorption/precipitation processes have been somewhat inconclusive (Bau et al., 1998; Gammons et al., 2003) and a final explanation will have to await additional data derived from controlled laboratory experiments. Interpretations of such experiments are likely to be improved by detailed calculations of YREE solution speciation that are based on the best available data.

Acknowledgments—We sincerely thank Yu-Ran Luo for the painstaking preparation of the YREE chloride solutions. Detailed comments from the associate editor and three anonymous reviewers were used in the revision of the original manuscript. This work was supported by a grant from the National Science Foundation (OCE-0136333).

Associate editor: D. J. Wesolowski

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- culated as six times the total YREE concentration and found to be $I_T = 0.71 \pm 0.02\text{ m}$, higher than the molar ionic strength by a factor of ~ 1.005 . Concentrations of all other ions in the sample solutions were converted to molal units by multiplying with the same factor.
- Ammonium chloride solution (0.70 mol/L, pH 3.0) was prepared by dissolving a weighed amount of NH_4Cl into a 500-mL polymethylpentene volumetric flask with addition of 500 μL of 1.000 mol/L HCl. This solution was stored in a Teflon FEP bottle and used in all four experiments. Densities of ammonium chloride solutions as a function of molality (Pearce and Pumphlin, 1937) were first fitted with a polynomial of the form suggested by Spedding et al. (1975) and then used to determine the molality of the solution as described for the YREE chloride solutions. Its ionic strength was found to be $I = 0.72 \pm 0.02\text{ m}$, a factor of 1.030 higher than the molar ionic strength. Concentrations of all other ions in the reference solution were converted to molal units by multiplying with the same factor.

A.2. Equilibration and Sampling

At the beginning of every experiment, 50.0 mL of each YREE chloride solution were transferred by pipette to a separate 60-mL Teflon FEP bottle. An additional 60-mL Teflon FEP bottle was filled with 50 mL of the ammonium chloride solution. To each bottle, $50 \pm 5\text{ mg}$ BaSO_4 was added. This represents a large excess, since the solubility of BaSO_4 at $I = 0.7\text{ mol/L}$ and $t = 25^\circ\text{C}$ is only $\sim 1\text{ mg}$ per 50 mL (Raju and Atkinson, 1988).

Next, the bottles were mounted in a rotating incubator oven (Barnstead-Thermoline, Melrose Park, IL) that gently rotated the solutions at 12 rpm and $t = 25.0 \pm 0.1^\circ\text{C}$ for several weeks. Whereas separate tests had indicated that equilibrium was reached after one week, equilibration periods of 2 to 4 weeks were typically used. During experiments 2 and 4, the incubator oven was incapable of maintaining a temperature of 25°C. In these two experiments, the bottles were first preequilibrated in the incubator oven at $t = 30^\circ\text{C}$ and then transferred to a water bath at $t = 25.0 \pm 0.1^\circ\text{C}$ for several weeks, with vigorous manual agitation once a day. Excellent agreement among all four experiments (Table 3) indicates that this altered treatment of the solutions did not affect the results.

At the end of the equilibration period, BaSO_4 was present at the bottom of each bottle as a finely dispersed precipitate. Suspended solids were allowed to settle for a few minutes. With a pipette, an aliquot was taken from each bottle in turn and transferred to a clean polypropylene syringe. Ten milliliters was filtered from the syringe through a Corning (Corning, NY) 13-mm cellulose acetate membrane cartridge filter (0.2- μm pore size), discarding the first 5 mL and collecting the rest in a polypropylene centrifuge tube. A new syringe and cartridge were used for each solution. The remaining 40 mL were retained for pH and sulfate measurements (sections A.3 and A.4).

A.3. Potentiometry

Solution pH was determined on the free hydrogen ion concentration scale, using an Orion (Beverly, MA) Ross-type combination pH electrode (No. 810200) connected to a Corning 130 pH meter in the absolute millivolt mode. The electrode was filled with 3 mol/L NaCl. After Nernstian response (59.16 mV/pH) had been verified by titrating a sodium chloride solution with concentrated HCl, solution pH was determined by comparison with a single standard (0.7 mol/L NaCl, pH = 3.00). Analyses were performed with $\sim 30\text{ mL}$ of unfiltered solution in a small Teflon PTFE beaker. Solutions and standard were gently agitated with a Teflon PTFE-coated magnetic stir bar and maintained at $t = 25.0 \pm 0.1^\circ\text{C}$ in a jacketed beaker. The electrode was rinsed with Milli-Q water after each measurement and the standard was reanalyzed after every three to four solutions.

An experimental pH of 3.0 was established with HCl to strongly suppress YREE hydrolysis, while at the same time minimizing the formation of bisulfate (section 2). In experiments 1 and 3, pH was checked after equilibration with BaSO_4 . It was generally within 0.2 units of the expected value, but occasionally higher pH (4–6) was found, mostly likely due to minor quantities of hydroxides in the YREE chlorides, which neutralized some of the added HCl. In experiments 2 and 4, pH was measured before equilibration with BaSO_4 and adjusted to pH 3.0 with additional HCl, if necessary. The measured pH was used in all calculations, but YREE hydrolysis was assumed to always be

APPENDIX: MATERIALS, METHODS, AND PRIMARY DATA

A.1. Preparation of Sample and Reference Solutions

All chemical manipulations were performed inside a class 100 clean air laboratory or laminar flow bench, using high purity salts and reagents, and acid-cleaned Teflon materials, unless stated otherwise. In this study, solubility products were obtained from four independent experiments. All salts used in the experiments were purchased from Sigma-Aldrich (St. Louis, MO), except sodium sulfate (Alfa Aesar, Ward Hill, MA). All salts were of the highest purity available (98–99.999%) and were used as received. YREE chlorides were hexahydrates or heptahydrates, except YCl_3 , LaCl_3 , and Ce(III)Cl_3 , which were anhydrous. The latter were shipped under argon and were used immediately after the ampoule was broken. Some YREE chlorides were strongly hygroscopic and had to be replaced regularly. Most non-YREE salts were anhydrous and were stored in a desiccator over silica gel drying agent. Certified 1.000 mol/L hydrochloric acid was purchased from Sigma-Aldrich (St. Louis, MO). Trace metal grade nitric acid was purchased from Fisher Scientific (Pittsburgh, PA). All solutions were made with water from a Millipore (Bedford, MA) purification system (Milli-Q water).

Fifteen YREE chloride solutions (0.1167 mol/L, pH 3) were prepared by dissolving a weighed amount of MCl_3 in a new, Milli-Q-rinsed 100-mL glass volumetric flask with addition of 100 μL of 1.000 mol/L HCl. Each solution was made in a separate flask and a fresh set of solutions was prepared for each experiment. In two of the four experiments, an excess of SO_4^{2-} was introduced by dissolving MCl_3 in 1 mmol/L $(\text{NH}_4)_2\text{SO}_4$, instead of Milli-Q water. After a set of solutions was prepared, 1-mL aliquots of each were combined and diluted in an acid-cleaned 100-mL glass volumetric flask. This mixed YREE solution was used to accurately determine actual YREE concentrations by ICP-MS (section A.5). Molar YREE concentrations were converted to molal units with polynomials that yield the density of YREE chloride solutions as a function of molality (Spedding et al., 1975). Using Eqn. 2.21 of Robinson and Stokes (1959) and the Solver function of Microsoft Excel, molality (and hence density) was varied until the corresponding molarity equalled the measured value, for each YREE. Since the YREE analyses (section A.5) were much more accurate and precise than the chloride analyses (section A.4), total ionic strength was cal-

Table A1. Composition of the sample solutions. Precision of the YREE concentrations is given as one standard deviation (σ) based on the indicated number of replicates (n). Precision of the chloride measurements is 3 to 5%. Calculations of $\text{SO}_4\beta_1$ were performed with the free ionic strength, which was derived by correcting the total ionic strength ($I_T = 6 \cdot [\text{M}^{3+}]_T$) for YREE chloride complexation (see text).

M^{3+}	Experiment 1 (no SO_4^{2-} added)			Experiment 2 (no SO_4^{2-} added)			Experiment 3 (1 mmol/L SO_4^{2-} added)			Experiment 4 (1 mmol/L SO_4^{2-} added)		
	$[\text{M}^{3+}]_T$ (m) ($n = 5$)	$[\text{Cl}^-]_T$ (m)	I (m)	$[\text{M}^{3+}]_T$ (m) ($n = 5$)	$[\text{Cl}^-]_T$ (m)	I (m)	$[\text{M}^{3+}]_T$ (m) ($n = 5$)	$[\text{Cl}^-]_T$ (m)	I (m)	$[\text{M}^{3+}]_T$ (m) ($n = 10$)	$[\text{Cl}^-]_T$ (m)	I (m)
Y	0.1173 ± 0.0007	0.355	0.66	0.1199 ± 0.0013	0.339	0.68	0.1229 ± 0.0009	0.347	0.69	0.1229 ± 0.0009	0.355	0.69
La	0.1194 ± 0.0005	0.347	0.67	0.1184 ± 0.0005	0.340	0.67	0.1187 ± 0.0004	0.336	0.67	0.1200 ± 0.0006	0.334	0.68
Ce	0.1201 ± 0.0004	0.365	0.68	0.1172 ± 0.0003	0.342	0.66	0.1104 ± 0.0002	0.321	0.62	0.1197 ± 0.0009	0.332	0.67
Pr	0.1138 ± 0.0005	0.333	0.64	0.1100 ± 0.0005	0.322	0.62	0.1120 ± 0.0003	0.322	0.63	0.1137 ± 0.0006	0.322	0.64
Nd	0.1213 ± 0.0005	0.350	0.68	0.1154 ± 0.0004	0.334	0.65	0.1191 ± 0.0002	0.343	0.67	0.1194 ± 0.0012	0.335	0.67
Sm	0.1185 ± 0.0008	0.351	0.67	0.1145 ± 0.0006	0.340	0.65	0.1180 ± 0.0003	0.334	0.66	0.1178 ± 0.0007	0.341	0.66
Eu	0.1188 ± 0.0006	0.356	0.67	0.1160 ± 0.0003	0.345	0.65	0.1175 ± 0.0004	0.340	0.66	0.1194 ± 0.0010	0.345	0.67
Gd	0.1202 ± 0.0010	0.364	0.68	0.1171 ± 0.0004	0.342	0.66	0.1183 ± 0.0005	0.344	0.67	0.1203 ± 0.0012	0.348	0.68
Tb	0.1176 ± 0.0008	0.349	0.66	0.1143 ± 0.0005	0.338	0.64	0.1167 ± 0.0003	0.341	0.66	0.1184 ± 0.0007	0.345	0.67
Dy	0.1198 ± 0.0008	0.358	0.67	0.1164 ± 0.0002	0.345	0.66	0.1180 ± 0.0005	0.344	0.66	0.1200 ± 0.0008	0.335	0.68
Ho	0.1160 ± 0.0003	0.353	0.65	0.1149 ± 0.0004	0.333	0.65	0.1164 ± 0.0004	0.336	0.66	0.1185 ± 0.0011	0.342	0.67
Er	0.1187 ± 0.0004	0.356	0.67	0.1141 ± 0.0003	0.331	0.64	0.1183 ± 0.0005	0.341	0.67	0.1206 ± 0.0004	0.337	0.68
Tm	0.1176 ± 0.0006	0.349	0.66	0.1142 ± 0.0004	0.340	0.64	0.1191 ± 0.0007	0.343	0.67	0.1195 ± 0.0005	0.343	0.67
Yb	0.1153 ± 0.0007	0.343	0.65	0.1169 ± 0.0006	0.348	0.66	0.1160 ± 0.0007	0.333	0.65	0.1211 ± 0.0005	0.350	0.68
Lu	0.1200 ± 0.0007	0.355	0.68	0.1173 ± 0.0005	0.344	0.66	0.1188 ± 0.0006	0.338	0.67	0.1209 ± 0.0007	0.354	0.68

negligible. Excellent agreement among all four experiments (Table 3) indicates that this assumption is valid and that the results were insensitive to the observed variations in the experimental pH.

A.4. Ion Chromatography

Anion concentrations were measured on a Dionex (Sunnyvale, CA) DX-500 ion chromatograph, using Dionex PeakNet software. The eluent, a mixture of 1.0 mmol/L NaHCO_3 and 3.5 mmol/L Na_2CO_3 in Milli-Q water, was made fresh and purged for 20 to 30 min with ultra-high purity He before each run. A preliminary test with six standards (containing 5, 10, 20, 30, 40, and 50 ppm each of Cl^- and SO_4^{2-}) revealed that the response of the IonPac AS14 column was somewhat non-linear for both Cl^- and SO_4^{2-} , yet that it was reproducible and could be well fitted with a quadratic curve through the origin. Calibration lines were constructed with the same type of fit, but using only three standards (5, 20, and 50 ppm). Each standard was analyzed several times during a run.

To bring chloride concentrations within range of the calibration line,

each solution was first diluted 1000-fold with Milli-Q water. Chloride concentrations were determined primarily to verify the correct stoichiometry of the YREE chlorides and to reveal the presence of impurities such as fluorides, nitrates, or hydroxides (the listed purity of the salts refers to metal content only). None of the chromatograms showed any detectable F^- or NO_3^- and the ratio of chloride and YREE concentrations was close to the expected stoichiometry. The chloride concentration of the reference solution was measured instead of its ammonium concentration, which could not be determined directly. Analyses of replicates within a run and between runs, and analysis of a certified reference material, indicated that precision and accuracy of the chloride analyses were 3 to 5%.

In sample solutions without added SO_4^{2-} , all SO_4^{2-} should derive from the dissolution of BaSO_4 , so it was initially assumed that the total sulfate concentration was equal to the total Ba concentration. However, since some of the YREE chlorides were found to contain minor but significant quantities of SO_4^{2-} , total sulfate concentrations had to be measured independently. Because of their very low sulfate concentra-

Table A2. Composition of the sample solutions. Precision of the Ba concentrations is given as one standard deviation (σ) based on the indicated number of replicates (n). Precision of the sulfate measurements is 5 to 7%.

M^{3+}	Experiment 1 (no SO_4^{2-} added)			Experiment 2 (no SO_4^{2-} added)			Experiment 3 (1 mmol/L SO_4^{2-} added)			Experiment 4 (1 mmol/L SO_4^{2-} added)		
	$[\text{Ba}^{2+}]_T$ (μM) ($n = 3$)	$[\text{SO}_4^{2-}]_T$ (μM)	pH	$[\text{Ba}^{2+}]_T$ (μM) ($n = 3$)	$[\text{SO}_4^{2-}]_T$ (μM)	pH	$[\text{Ba}^{2+}]_T$ (μM) ($n = 3$)	$[\text{SO}_4^{2-}]_T$ (μM)	pH	$[\text{Ba}^{2+}]_T$ (μM) ($n = 3$)	$[\text{SO}_4^{2-}]_T$ (μM)	pH
Y	127.8 ± 1.1	149.3	3.26	127.2 ± 1.0	138.7	2.89	17.33 ± 0.05	1009	2.97	17.25 ± 0.10	1044	2.99
La	145.1 ± 2.5	156.8	3.00	141.3 ± 2.7	152.2	2.90	21.69 ± 0.15	1002	3.03	22.08 ± 0.04	1040	3.26
Ce	151.0 ± 1.1	144.4	3.01	141.1 ± 1.3	152.6	3.08	20.39 ± 0.17	1021	3.01	21.50 ± 0.07	1029	3.06
Pr	144.9 ± 2.0	153.0	3.09	139.1 ± 1.3	152.4	2.77	20.78 ± 0.17	997.0	3.05	19.87 ± 0.07	1080	3.06
Nd	147.5 ± 1.2	152.6	3.02	139.9 ± 0.9	156.7	2.94	21.41 ± 0.08	1018	3.07	20.86 ± 0.08	983.0	3.06
Sm	149.2 ± 2.5	162.3	3.01	140.8 ± 2.5	154.3	2.86	22.02 ± 0.12	1001	3.00	21.70 ± 0.06	1030	3.07
Eu	148.5 ± 2.0	163.9	2.78	142.3 ± 2.1	158.8	3.00	22.68 ± 0.05	1014	3.02	21.87 ± 0.06	1044	3.11
Gd	147.4 ± 0.9	157.8	3.06	141.1 ± 1.2	151.1	3.00	21.73 ± 0.11	1019	3.09	20.84 ± 0.04	1028	2.98
Tb	139.3 ± 2.2	150.9	3.06	131.4 ± 0.4	157.5	2.93	20.29 ± 0.07	1024	3.14	20.42 ± 0.06	1016	3.15
Dy	141.6 ± 0.4	153.2	2.98	134.1 ± 0.9	149.8	2.94	19.80 ± 0.14	1011	3.04	19.34 ± 0.03	1010	2.95
Ho	125.5 ± 0.9	158.7	3.03	119.5 ± 0.7	153.4	2.89	17.60 ± 0.03	1047	3.05	17.71 ± 0.09	1062	3.02
Er	133.1 ± 0.4	143.9	2.97	122.6 ± 0.7	136.6	3.38	17.44 ± 0.29	1017	3.00	17.12 ± 0.04	1014	2.98
Tm	129.4 ± 2.1	134.5	5.59	120.6 ± 0.5	136.9	2.99	16.51 ± 0.05	1005	3.72	16.28 ± 0.05	1006	2.94
Yb	123.8 ± 1.0	128.1	6.14	108.0 ± 1.5	150.0	2.84	16.37 ± 0.12	979.7	6.03	15.49 ± 0.06	1055	2.81
Lu	123.2 ± 2.1	132.2	3.02	118.4 ± 1.2	131.4	2.70	15.59 ± 0.08	1017	3.13	15.10 ± 0.03	1008	3.09

Table A3. Composition of the reference solution. Precision is given as one standard deviation (σ) based on the indicated number of replicates (n). Since the ammonium concentration could not be determined directly, it was assumed that $[\text{NH}_4^+] = [\text{Cl}^-]$.

		n
$[\text{NH}_4^+]$ (m)	0.72	—
$[\text{Cl}^-]$ (m)	0.721 ± 0.016	8
I (m)	0.72	—
$[\text{Ba}^{2+}]_{\text{T}}$ (μm)	73.1 ± 1.8	15
$[\text{SO}_4^{2-}]_{\text{T}}$ (μm)	83.1 ± 5.4	12
pH	3.02 ± 0.04	5

tions, sample solutions from the experiments without added SO_4^{2-} were analyzed undiluted, whereas sample solutions from the experiments with excess SO_4^{2-} were diluted fourfold with Milli-Q water. Even after fourfold dilution, chloride concentrations were too high to allow direct analysis of SO_4^{2-} by ion chromatography. Before sulfate analysis, Cl^- was therefore removed with a Dionex OnGuard Ag cartridge. These cartridges are designed not to affect the concentrations of other anions and this was verified by testing with standards. A new syringe and cartridge were used for each solution. Cartridges were hydrated as specified by the manufacturer, yet they were preconditioned with a minimal amount of sample (2–3 mL), since the high chloride concentrations quickly exhausted their uptake-capacity. Breakthrough of Cl^- occurred occasionally, but due to the excellent separation of the chloride and sulfate peaks in the chromatogram (retention times 4 and >10 min, respectively) this rarely interfered with the sulfate analysis. In case of severe breakthrough, the sample was reanalyzed if sufficient solution was left. The relatively poor reproducibility of the sulfate analyses (5–7%) is probably the greatest source of uncertainty in the calculation of ${}_{\text{SO}_4}\beta_1$. The sulfate concentration of the reference solution, which had the least favorable $\text{SO}_4^{2-}/\text{Cl}^-$ ratio, was determined as many times as possible (Table A3) to minimize the standard deviation of that measurement.

A.5. Inductively-Coupled Plasma Mass Spectrometry (ICP-MS)

Solutions were analyzed for Ba and YREE on an Agilent Technologies 4500 Series 200 ICP-MS. Each solution was pipetted into a polypropylene autosampler tube and thoroughly mixed with a small quantity of an internal standard solution containing equal amounts of In, Cs, and Re. Solutions were introduced into the ICP-MS with a Babington-type PEEK nebulizer and a double-pass (Scott-type) quartz spraychamber, Peltier-cooled to $t = 2^\circ\text{C}$. During instrument tuning, the formation of oxide and double-charged ions was minimized with a 10-ppb Ce solution. MO^+ and M^{2+} peaks were always < 1% and < 2% 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% HNO_3 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% HNO_3 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 instru-

ment drift by normalizing ^{89}Y to ^{115}In , ^{139}La – ^{161}Dy to ^{133}Cs , and ^{163}Dy – ^{175}Lu to ^{187}Re . 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 ^{161}Dy and ^{163}Dy , which were usually equal to within 2%. To bring YREE concentrations within the range of the calibration line, the mixed YREE solution (section A.1) was diluted 1000-fold with 1% HNO_3 and then another 100-fold with 1% HNO_3 . YREE concentrations were determined by analysis of 5 to 10 replicates of this diluted solution. Reproducibility was better than 1%. Blanks were generally below the instrument quantitation limit (0.01 ppb). To determine the YREE content of BaSO_4 , which might affect its solubility in the reference solution, a saturated solution of BaSO_4 in Milli-Q water was analyzed. No YREE were found above the instrument quantitation limit.

Ba concentrations were calculated from linear regressions of four standards (2, 5, 10, and 25 ppb). ICP-MS runs were performed as described for the YREE. Since Ba concentrations were not a limiting factor, the less abundant ^{137}Ba isotope was used rather than the major ^{138}Ba isotope, to avoid isobaric interference from ^{138}La and ^{138}Ce . Instrument drift was corrected by normalizing to ^{133}Cs . To bring Ba concentrations within the range of the calibration line, the filtered solutions were diluted by factors of 1000 or 10,000 with 1% HNO_3 . Ba concentrations in the experiments with excess SO_4^{2-} were an order of magnitude lower and only a 1000-fold dilution was used. Each set of solutions was run several times at different dilutions and in different order. Three replicates were typically analyzed, with a reproducibility better than 2%. A procedural blank, measured in the ammonium chloride solution, was determined to be certainly < 1% of the lowest Ba concentration. Considering the very high YREE concentrations, even minute amounts of Ba in the YREE chlorides could have a significant effect on the equilibrium. While the presence of any Ba in the YREE chlorides would be accounted for in the measurement of the total Ba concentration, we wanted to make sure that the amount of Ba released by the YREE chlorides would not limit total sulfate concentrations to undetectable levels. One set of YREE chloride solutions was therefore analyzed for Ba after 100-fold dilution with 1% HNO_3 . The highest concentration found was ~100 ppb, which is no more than 5% of the lowest Ba concentration (in the experiments with excess SO_4^{2-}). This agrees with the highest Ba levels indicated on the Certificates of Analysis of the YREE chlorides (~1 ppm by weight, where reported).

A.6. Spectrophotometry

To quantitatively compare ${}_{\text{SO}_4}\beta_1(\text{NH}_4)$ with ${}_{\text{SO}_4}\beta_1(\text{Na})$, ion pairing of Cu^{2+} with SO_4^{2-} was examined in sodium perchlorate and ammonium perchlorate solutions under conditions identical to those in our solubility experiments ($I = 0.7\text{ mol/L}$, $\text{pH } 3$, $t = 25^\circ\text{C}$). In a thermostated 10-cm open-top quartz cell, 50 mL of 0.7 mol/L NaClO_4 or 0.7 mol/L NH_4ClO_4 were titrated with (0.100 mol/L $\text{CuSO}_4 + 0.7\text{ mol/L NaClO}_4$) and (0.100 mol/L $\text{CuSO}_4 + 0.7\text{ mol/L NH}_4\text{ClO}_4$), respectively. UV-absorbance spectra were examined with an HP 8453 diode-array spectrophotometer. In a second type of experiment the sulfate concentration was varied independent of the Cu concentration. This was accomplished by titrating (4.76 mmol/L $\text{CuSO}_4 + 0.7\text{ mol/L NaClO}_4$) or (4.76 mmol/L $\text{CuSO}_4 + 0.7\text{ mol/L NH}_4\text{ClO}_4$) with (0.100 mol/L $\text{Na}_2\text{SO}_4 + 4.76\text{ mmol/L CuSO}_4 + 0.7\text{ mol/L NaClO}_4$) and (0.100 mol/L $(\text{NH}_4)_2\text{SO}_4 + 4.76\text{ mmol/L CuSO}_4 + 0.7\text{ mol/L NH}_4\text{ClO}_4$), respectively. Cu and sulfate concentrations never exceeded 20 mmol/L in any of these experiments.