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Stability constants for mono- and dioxalato-complexes of Y and the REE, potentially important species in groundwaters and surface freshwaters

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Abstract—We present the first measured set of stability constants for mono- and dioxalato-complexes of yttrium and all rare earths except Pm (Y+REE), ${}_{Ox}\beta_n = [MOx_n^{3-2n}]\,[M^{3+}]^{-1}\,[Ox^{2-}]^{-n}$(where [ ] ≡ concentrations, M ≡ Y+REE, and $Ox^{2-} \equiv C_2O_4^{2-}$). Aqueous solutions of Y+REE were titrated with oxalic acid in the presence of a cation-exchange resin, and Y+REE concentrations in the solution phase were measured by ICP-MS. This method allows investigation of all Y+REE simultaneously under identical conditions and is thus very sensitive to subtle inter-element variations in log ${}_{Ox}\beta_n$. Experiments were performed at a single ionic strength ($I = 0.05$ M), but at two values of pH. Patterns of log ${}_{Ox}\beta_1$ and log ${}_{Ox}\beta_2$, determined from our experiments, are similar in shape and reminiscent of those for carbonato-complexes. The average ratio of stepwise stability constants $K_2/K_1 = {}_{Ox}\beta_2/({}_{Ox}\beta_1)^2$ is 0.05 ± 0.02 for Y+REE excluding La and Ce.

Literature values of ${}_{Ox}\beta_1$(Eu) for 0.03 mol/L ≤ I ≤ 1 mol/L were used to derive the relation log ${}_{Ox}\beta_1$(Eu) = log ${}_{Ox}\beta_1^0$(Eu) − $6.132\sqrt{I}/(1 + 1.47\sqrt{I}) + 0.902I$, where log ${}_{Ox}\beta_1^0$(Eu) is the stability constant at infinite dilution. Applying this relation to all Y+REE, the following values of log ${}_{Ox}\beta_1^0$ (at zero ionic strength) were found: 6.66 (Y), 5.87 (La), 5.97 (Ce), 6.25 (Pr), 6.31 (Nd), 6.43 (Sm), 6.52 (Eu), 6.53 (Gd), 6.63 (Tb), 6.74 (Dy), 6.77 (Ho), 6.83 (Er), 6.89 (Tm), 6.95 (Yb), 6.96 (Lu). These values, which are based on direct measurements for each individual Y+REE, agree quite well with published extrapolations that are mostly based on linear free-energy relationships.

Total oxalate concentrations of 10^{-5}–10^{-3} M have been reported for soil solutions. Free oxalate ions persist at much lower pH than free carbonate ions and a simple speciation model demonstrates that oxalato-complexes can dominate Y+REE speciation in mildly acidic groundwaters of low-to-moderate alkalinity. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

Over the past decades yttrium and the rare earth elements (Y+REE) have become increasingly valued for their use as powerful geochemical tools in many branches of the earth sciences such as petrology and geochronology (Henderson, 1984), palaeoceanography and the aqueous biogeochemistry of trace metals (Elderfield, 1988). More recently, research has focused on their potential mobility in nuclear waste repositories. Some of the strictly trivalent lanthanides are considered chemical analogs of the actinides (Choppin, 1983), another major component of nuclear waste, whose toxicity, radioactivity, limited availability, and variety of oxidation states makes them difficult to study (Choppin and Wong, 1998). Consequently, numerous aspects of Y+REE geochemistry have been investigated extensively and particularly their solution chemistry is understood in greater detail than that of most other trace metals (Byrne and Kim, 1990).

Y+REE solution speciation in natural waters is dominated by complexation with the inorganic anions carbonate, hydroxide, chloride, sulfate, and fluoride. To accurately model Y+REE solution speciation under any condition occurring in nature, stability constants for complexes with these ligands must be known for each individual Y+REE as a function of ionic strength, pressure and temperature. Complete sets of stability constants for Y+REE have been compiled for most of the above ligands and many others, for freshwater as well as seawater (Turner et al., 1981; Byrne et al., 1988; Wood, 1990, 1993; Millero, 1992; Byrne and Sholkovitz, 1996). At a minimum, such compilations should comprise actual measurements for all Y+REE simultaneously in an inert standard medium (e.g., $NaClO_4$) and over a range of ionic strengths, so that accurate interpolations can be made to any ionic strength. However, a thorough inspection of the literature reveals that they are often based on data for only a few elements at a single ionic strength, while the remaining stability constants were estimated from linear free-energy relationships (LFERs) (Lee and Byrne, 1992) or general trends (Cantrell and Byrne, 1987). Our group has endeavoured to refine models of Y+REE behaviour by employing new analytical techniques to measure stability constants for complexes of all Y+REE with environmentally important ligands under a variety of conditions (Liu and Byrne, 1998; Schijf and Byrne, 1999; Klungness and Byrne, 2000; Luo and Byrne, 2000).

Y+REE oxalate complexation and especially the solubility of Y+REE oxalates has been studied in great detail since the 1950s, because of the common use of oxalate precipitation to purify and produce high-grade preparations of Y+REE and, historically, as a means to determine their concentrations. Because of the limited solubility of Y+REE oxalates, these studies could only be pursued at very low concentrations, requiring the use of radioisotopes. Therefore, reports of stability constants have generally included only those elements providing

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affordable radioisotopes with appropriate half-lives and, moreover, different investigators have performed their experiments in different media.

Very little seems to be known about the biogeochemistry of oxalate other than that it is a thermal degradation product of complex organic matter and a metabolic product of certain plants. It has been found at μmol/L concentrations in surface waters and at mmol/L and higher concentrations in soil solutions and oil field brines (see references in Gammons and Wood, 2000). Stability constants of REE oxalato-complexes are high, approaching those of the carbonato-complexes. Oxalic acid dissociates more readily than carbonic acid, hence free oxalate ions persist at concentrations higher than those of free carbonate ions in low pH and low-to-intermediate alkalinity waters. In those environments, oxalate complexation could quite possibly exert a strong influence on Y+REE speciation, as well as on that of other metals such as Pb and U. Wood (1993) presented stability constants for mono- and dioxalato-complexes of all REE at infinite dilution, which were based on measurements for Ce, Eu, and Yb at $I = 0.68$ m by Cantrell and Byrne (1987) and on LFERs for the other REE. Only recently, Gammons and Wood (2000) pointed out that no single study had yet produced a complete set of stability constants for REE oxalato-complexes even at 25°C and 1 bar and that such a study was long overdue.

We present the first complete sets of stability constants for mono- and dioxalato-complexes of all Y+REE except Pm. By measuring stability constants for all Y+REE simultaneously under identical conditions insight is gained into their comparative behaviour. Combining our measurements with selected literature data allows us to predict values of the stability constants at ionic strengths between 0 and 1 mol/L.

2. MATERIAL AND METHODS

All chemical manipulations were performed inside a class 100 clean air laboratory or laminar flow bench, using triple subboiling quartz-distilled (3Q) reagents and acid-cleaned Teflon materials, unless otherwise indicated.

2.1. Titrations

Oxalic acid (ethanedioic acid, $H_2Ox \equiv H_2C_2O_4$) is a dicarboxylic acid. The equilibrium constant for the reaction $H^+ + HOx^- \rightleftharpoons H_2Ox$ is low ($\log K_{a1} \cong 1$), but the equilibrium constant for the reaction $H^+ + Ox^{2-} \rightleftharpoons HOx^-$ is much higher ($\log K_{a2} \cong 4$). Experiments were thus performed at two different pH (1.6 and 1.3), so that any effect of the bioxalate anion on Y+REE speciation could be accounted for. To enable a direct comparison of the results from both experiments, the ionic strength of the pH 1.6 solutions was matched to that of the pH 1.3 solutions ($I = 0.05$ mol/L) by addition of ammonium nitrate (NH_4NO_3), which fully dissociates in the ICP-MS, causing no appreciable matrix effect.

An H_2Ox solution of approximately 0.5 mol/L was prepared by dissolution of 22.51 g of H_2Ox (anhydrous, 99+%; Aldrich, Milwaukee, WI) in 0.500 L of Milli-Q water. This solution was titrated in triplicate with a certified 1 N NaOH standard (Fisher Scientific, Pittsburgh, PA) and its concentration established as 0.4862 ± 0.0003 mol/L. For the experiments at pH 1.6, 1.5 mL of 3Q 15.82 N HNO_3 and 3.5 mL of a mixed Y+REE solution were pipetted into a 1 L wide-mouth bottle, 2.001 ± 0.001 g of NH_4NO_3 (99.999%; Aldrich) was added, and the total volume was adjusted to 1.000 L with Milli-Q water. For the experiments at pH 1.3, 3 mL of HNO_3 was used and no NH_4NO_3 was added. The mixed Y+REE solution, containing 66.67 ppm each of all Y+REE (except Pm), was made up from 1000 ppm single-element solutions in 2% HNO_3 (SPEX, Metuchen, NJ). The initial concentration after dilution was 233.3 ppb for each element. Next, 0.200 ± 0.005 g and 0.100 ± 0.005 g of clean, dry cation-exchange resin was weighed into the wide-mouth bottles for the experiments at pH 1.6 and pH 1.3, respectively. The bottles were then placed in jacketed beakers thermostated at 25.0 ± 0.1°C. The solutions were gently stirred with 'floating' Teflon-coated stir bars to prevent grinding of the resin beads.

After at least 48 h, stirring was discontinued and a 20 mL sample was taken with a polypropylene syringe and filtered through a 13 mm cellulose acetate membrane cartridge filter (0.2 μm pore size). These filters were not cleaned since exposure to strong acid was found to alter their pore size. A new syringe and cartridge were used for each sample. The first 5 mL of filtrate were discarded and the rest was stored in a 15 mL polypropylene centrifuge tube with screw cap until analysis. As soon as the samples were taken, a known amount of the H_2Ox solution was carefully pipetted into the wide-mouth bottles and stirring was resumed. This procedure was repeated every 24 h. Two experiments were performed at pH 1.6 with total H_2Ox additions of 0, 0.5, 1, 2, 3, 4, 5, and 6 mL and 0, 1, 2, 4, 6, 8, 10, and 12 mL, and two experiments at pH 1.3 with total H_2Ox additions of 0, 1, 2, 3, 4, 5, and 6 mL, and 0, 1, 2, 4, 6, 8, 10, and 12 mL.

A period of 24 h after each H_2Ox addition was sufficient to re-establish equilibrium between the solution and the resin i.e., longer periods caused no significant change in the Y+REE solution concentrations. At initial equilibrium (no H_2Ox), Y+REE concentrations had decreased from 233.3 ppb to less than 0.7 ppb so that >99.7% of each element had been adsorbed onto the resin. This fraction never fell below 89% for any Y+REE during any of the experiments.

2.2. Choice and Preparation of the Cation-Exchange Resin

The experiments were performed with Bio-Rad AG 50W-X8 cation-exchange resin (50–100 mesh, hydrogen form). The resin was cleaned and dried as described previously (Schijf and Byrne, 1999). The clean, dry resin was transferred to a 120 mL polypropylene sample jar for storage. Since the resin has about twice the relative selectivity for NH_4^+ ions that it has for H^+ ions (Bio-Rad Laboratories, 1998/99), the experiments at pH 1.6 were performed with 200 mg and the experiments at pH 1.3 (no NH_4^+) with 100 mg dry resin, to have approximately the same initial amount of Y+REE adsorbed onto the resin in each case. The wet capacity of the resin is given as 2.1 meq/g (Bio-Rad Laboratories, 1998/99). From this it can be estimated that initially, in the experiments at pH 1.3, Y+REE occupy at most 30% of the available sites (15% in the experiments at pH 1.6). Note that the degree of loading, which is dictated by analytical constraints, while relatively high, does not change by more than about 4% during any of the experiments. It was shown that our results are not affected by this small variation, or by small variations in the solution composition (see Section 2.5.).

2.3. Inductively-Coupled Plasma Mass Spectrometry

After each experiment the filtered sample solutions were analysed for Y+REE with an Agilent Technologies (formerly HP) 4500 Series 200 ICP-MS. Each solution, after appropriate dilution with 1% HNO_3, was pipetted into a polypropylene autosampler tube and thoroughly mixed with a small amount of an internal standard solution containing equal concentrations of In, Cs, and Re. Solutions were introduced into the ICP-MS with a Babington-type PEEK nebuliser and a double-pass (Scott-type) quartz spraychamber, Peltier-cooled to 1°C. During instrument tuning, the formation of oxide and double-charged ions was minimised with a 10 ppb Ce solution. MO^+ and M^{2+} peaks were always less than 1 and 2% of the corresponding M^+ peak, respectively, and correction for this effect proved unnecessary.

Y+REE concentrations were calculated from linear regressions of four standard solutions (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, Milli-Q water was aspirated for 10 s followed by a 1% HNO_3 wash solution for 50 s after each autosampler position, to thoroughly clean the outside of the autosampler probe and the sample introduction system. All standard and sample solutions were injected in triplicate. Minor instrument drift was corrected for by normalising all isotopes to ^{187}Re. Samples from

the 'D^0 experiments' (see Section 2.5.), however, were corrected for drift by normalising ^{89}Y to ^{115}In, ^{139}La-^{161}Dy to ^{133}Cs, and ^{163}Dy-^{175}Lu to ^{187}Re. While the HP ChemStation software does not allow a mass-dependent correction by interpolation between internal standards, 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 should be identical. As evidenced by numerous replicates and analyses of various standard solutions, the average ($^{161}Dy+^{163}Dy$)/2, which is used as the final Dy concentration, and concentrations of neighbouring elements were always highly reproducible. Precision was generally better than 2%. Replicate analyses of sample solutions showed accuracy to be about 2% at the lowest concentrations. Blanks were below the instrument quantitation limit (0.002 ppb).

2.4. Theory and Data Processing

Under the conditions of our experiments, Y+REE are partitioned between the resin and the solution as follows:

$$[M]_T = [M]_{res} + [M]_{sol} \quad (1)$$

where $[M]_T$ is the total metal concentration and $[M]_{res}$ and $[M]_{sol}$ are concentrations on the resin and in solution, respectively. The dissolved metal fraction consists of free M^{3+} ions and M^{3+} ions complexed with HOx^- ions or Ox^{2-} ions. Based upon published ${}_{NO3}\beta_1$ data (Wood, 1990), the extent of complexation by NO_3^- ions is expected to be very small and approximately constant for all Y+REE. As such, complexation by NO_3^- ions was assumed to be negligible in our experiments. Since $[NO_3^-]$ was nearly constant, small corrections to ${}_{Ox}\beta_1$ and ${}_{Ox}\beta_2$ derived under this assumption can be readily calculated when better ${}_{NO3}\beta_1$ data, appropriate to our experimental conditions, become available.

The stability constants for the m^{th} bioxalato-complex are defined as:

$${}_{HOx}\beta_m = [M(HOx)_m^{3-m}]\,[M^{3+}]^{-1}[HOx^-]^{-m} \quad (2a)$$

and for the n^{th} oxalato-complex as:

$${}_{Ox}\beta_n = [MOx_n^{3-2n}]\,[M^{3+}]^{-1}[Ox^{2-}]^{-n} \quad (2b)$$

Satisfactory fits to the data were obtained by including only the first bioxalato-complex and mono- and dioxalato-complexes. Thus,

$$[M]_{sol} = [M^{3+}] + [MHOx^{2+}] + [MOx^+] + [M(Ox)_2^-]$$
$$= [M^{3+}](1+{}_{HOx}\beta_1[HOx^-] + {}_{Ox}\beta_1[Ox^{2-}] + {}_{Ox}\beta_2[Ox^{2-}]^2). \quad (3)$$

With distribution coefficients in the presence (D) and absence (D^0) of solution complexation given as:

$$D = \frac{[M]_{res}}{[M]_{sol}} \quad \text{and} \quad D^0 = \frac{[M]_{res}}{[M^{3+}]} \quad (4)$$

and combining (3) and (4)

$$\frac{D^0}{D} = 1 + {}_{HOx}\beta_1[HOx^-] + {}_{Ox}\beta_1[Ox^{2-}] + {}_{Ox}\beta_2[Ox^{2-}]^2. \quad (5)$$

Since it was impractical to measure REE concentrations on the resin directly, $[M]_{res}$ in Eqn. 4 was calculated from Eqn. 1. To minimise errors in case of an imperfect mass balance we ensured that $[M]_T >> [M]_{sol}$, so that variations in $[M]_{res}$ were small. The affinity of the resin for free M^{3+} ions, hence the value of D^0, is significantly dependent on the solution composition. Solution modeling showed that the solution composition varied slightly during each experiment, due to the addition of H_2Ox solution and the removal of sample. D^0 was therefore modeled as a function of $[H^+]$ and $[NH_4^+]$, after performing some ancillary experiments (see Section 2.5.). Throughout the text, any reference to D^0 should be understood to mean its modeled value.

Because of the limited solubility of Y+REE oxalates, precipitation was a concern. Bhat and Rao (1964) reported solubility products for pure REE oxalates in 0.1 mol/L EDTA solution ranging from $10^{-30.3}$ for Sm to $10^{-26.9}$ for La. Gammons and Wood (2000) reported a solubility product for Yb oxalate in 0.05 mol/L NaCl solution of $\leq 10^{-28}$. Barrett et al. (1964) reported precipitation of REE-ammonium oxalates of the form $REE(NH_4)Ox_2 \cdot yH_2O$ from low pH solutions upon addition of ammonia, whose solubility products may be similar to those for the REE-sodium oxalates $REE(Na)Ox_2 \cdot yH_2O$, which Grenthe et al. (1969) found to be of the order 10^{-16} at $I = 1$ mol/L. In our experiments the highest values of the corresponding ion activity products are estimated to be $[REE^{3+}]^2[Ox^{2-}]^3 \cong 10^{-36}$ and $[REE^{3+}][NH_4^+][Ox^{2-}]^2 \cong 10^{-20}$, accounting for complexation. This suggests that all solutions were sufficiently undersaturated with respect to these salts and indeed no evidence of precipitation was observed at any time.

2.5. Solution Modeling and Variation of D^0 with Solution Composition ('D^0 Experiments')

The solution composition appropriate to each H_2Ox addition was modeled for each of the four experiments. If we define the association constants of oxalic acid as:

$$K_{a1} = \frac{[H_2Ox^0]}{[H^+][HOx^-]} \quad \text{and} \quad K_{a2} = \frac{[HOx^-]}{[H^+][Ox^{2-}]} \quad (6)$$

it can be shown that

$$[HOx^-] = \frac{[H_2Ox]_T}{\{1+K_{a1}[H^+] + (K_{a2}[H^+])^{-1}\}} \quad (7a)$$

and

$$[Ox^{2-}] = \frac{[H_2Ox]_T}{\{1+K_{a2}[H^+] + K_{a2}K_{a1}[H^+]^2\}} \quad (7b)$$

The association constants K_{a1} and K_{a2} were estimated by fitting data of Kettler et al. (1991) to relations of the form $\log K_{an} = A_n + 0.511\Delta z^2\sqrt{I}/(1 + B_n\sqrt{I}) + C_nI$, by means of a non-linear regression technique, where A_n, B_n, and C_n (n = 1,2) are the free parameters and $\Delta z^2 = -2$ for K_{a1} and $\Delta z^2 = -4$ for K_{a2}. From these fits (regression coefficients $r^2 > 0.997$) it was estimated that $K_{a1} = 10^{1.09}$ and $K_{a2} = 10^{3.92}$ at T = 25°C and $I = 0.05$ mol/L. Data from Smith and Martell (1989), while deviating greatly for $I \geq 0.1$ mol/L, gave very similar results at T = 25°C and $I = 0.05$ mol/L ($K_{a1} = 10^{1.07}$ and $K_{a2} = 10^{3.92}$). Estimates based on extended and remodeled data presented by Kettler et al. (1998) are identical for K_{a2} but deviate significantly for K_{a1} ($10^{1.21}$). Use of the latter data increased $\log {}_{Ox}\beta_2$ by a few hundredths of a unit while leaving $\log {}_{Ox}\beta_1$ unchanged. However, since this leads to unrealistically high values of K_2/K_1, particularly for the lightest REE (La-Nd; see Section 3.2.), $K_{a1} = 10^{1.09}$ was used in our analyses.

The free oxalate and bioxalate concentrations and $[H^+]$ were calculated iteratively. The ionic strength was then calculated as:

$$I = \frac{1}{2}\{[H^+] + [NH_4^+] + [NO_3^-] + [HOx^-] + 4[Ox^{2-}]\}, \quad (8)$$

where $4[Ox^{2-}] < 8 \times 10^{-5}$ M (see Appendix) and the contribution of free M^{3+} ions and M^{3+} complexes is even smaller. Complexation of NH_4^+ with oxalate and bioxalate is negligible (Smith and Martell, 1989). Variations in $\log K_{a1}$ and $\log K_{a2}$ were always less than 0.01 and deemed negligible.

The modeling showed that in the experiments at pH 1.6 the pH had decreased by about 0.07, $[NH_4^+]$ had decreased by a little more than 1% and I had increased a little more than 7%, at the highest H_2Ox addition. For the experiments at pH 1.3 the pH had decreased by about 0.03 and I had increased a little more than 6%. These slight variations in solution composition, as well as a variation in the degree of resin loading of at most 4% (see Section 2.2.), had an insignificant effect on stability constant calculations. This was verified by successively removing data with the highest $[Ox^{2-}]$ (Fig. 1) and then refitting the remaining data. Three points, the equivalent of half the stated variations, were removed for each of two representative REE without causing a significant change in any of their stability constants. On the other hand, the variations in pH and I are large enough that a significant effect on the value of D^0 was anticipated. While minor, the variation of $[NH_4^+]$ in the experiment at pH 1.6 could also have a significant effect on the value of D^0, due to the cation-exchange resin's high relative specificity for

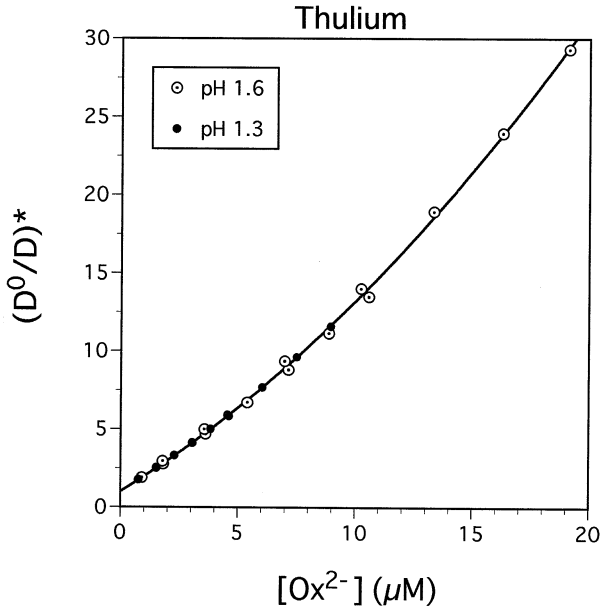

Fig. 1. Distribution data for Tm, shown as an example. Data were fitted with a relation of the form $D^0/D = 1 + {}_{HOx}\beta_1[HOx^-] + {}_{Ox}\beta_1[Ox^{2-}] + {}_{Ox}\beta_2[Ox^{2-}]^2$ and the bioxalate dependence was then removed by showing $(D^0/D)^* = D^0/D - {}_{HOx}\beta_1[HOx^-]$ as a function of $[Ox^{2-}]$. Data for pH 1.6 and pH 1.3 closely follow a single curve.

NH_4^+ ions (Bio-Rad Laboratories, 1998/99). It was therefore decided to perform some ancillary experiments to ascertain the dependence of D^0 on solution composition in the absence of oxalate.

Three experiments were performed in total. Solutions were prepared, sampled and analysed as described above. In the first experiment 0.100 g of cation-exchange resin was added to the solution, which contained no ammonium nitrate. The pH was then varied around 1.3 by increasing $[H^+]$ in five equal steps from 0.045 mol/L to 0.055 mol/L. In the other two experiments 0.200 g of cation-exchange resin was added to the solution. In the second experiment $[H^+]$ was fixed at 0.025 M and $[NH_4^+]$ was increased in five equal steps from 0.020 M to 0.030 M and in the third the roles of the two ions were reversed. This way, all parameters of interest were varied by amounts that exceed the ranges observed in the actual experiments. While the ionic strength could not be changed independently from $[H^+]$ and $[NH_4^+]$, the dependence of D^0 on I is implicitly represented by its dependence on $[H^+]$ and $[NH_4^+]$ and, in any case, this dependence is weak. For each of the 15 datapoints, D^0 was calculated from Eqn. 4 and $[H^+]$ and $[NH_4^+]$ were calculated taking into account changes in volume due to the addition of reagents and the removal of sample. Using a non-linear regression technique, data for each individual Y+REE were then fitted with relations of the form:

$$D^0 = a + b[H^+] + c[NH_4^+] + d[H^+]^2 + e[H^+][NH_4^+] + f[NH_4^+]^2, \quad (9)$$

where a–f are the free parameters. Note that since $I \propto ([H^+]+[NH_4^+])$, additional terms in I and I^2 are inherently incorporated within the general form of Eqn. 9. Using the best fit results for the parameters a–f, D^0 was calculated from Eqn. 9 for each datapoint for each individual Y+REE, based on the values of $[H^+]$ and $[NH_4^+]$ as determined from solution modeling. A correction factor was applied to the parameters a–f to assure that the calculated D^0 in the absence of oxalate equaled the D^0 actually measured at the beginning of each experiment. This correction factor is expected to be independent of REE atomic number, which was found to be true for Y and Sm-Lu. Correction factors for these elements were therefore averaged and used as the correction factor for all Y+REE.

Titration data (D^0/D and modeled $[Ox^{2-}]$ and $[HOx^-]$; see Appendix) were fitted to a relation as in Eqn. 5 by means of a non-linear regression technique (SAS Institute, 1996). Best fits were obtained by minimising the residual sum of squares

$$\sum_{i=1}^{n} \{(D^0/D)_i - (1+{}_{HOx}\beta_1[HOx^-]_i + {}_{Ox}\beta_1[Ox^{2-}]_i + {}_{Ox}\beta_2[Ox^{2-}]_i^2)\}^2 \quad (10)$$

with the SAS® procedure NLIN, using the Marquardt algorithm. The fit shown for Tm in Figure 1 is typical of those obtained for other elements and demonstrates that when minor complexation with bioxalate is accounted for, the pH dependence of the data is removed and all data fall on a single curve.

Table 1. Stability constants for bioxalato- and oxalato-complexes of Y+REE ± one standard error, determined at 25°C and 0.05 M ionic strength. $K_2/K_1 = {}_{Ox}\beta_2/({}_{Ox}\beta_1)^2$.

M^{3+}	${}_{HOx}\beta_1$	log ${}_{Ox}\beta_1$	log ${}_{Ox}\beta_2$	K_2/K_1
Y	121 ± 40	5.74 ± 0.01	10.09 ± 0.02	0.04
La	84 ± 31	4.94 ± 0.06	9.28 ± 0.10	0.25
Ce	267 ± 53	5.04 ± 0.08	9.67 ± 0.07	0.38
Pr	123 ± 35	5.32 ± 0.03	9.63 ± 0.05	0.10
Nd	144 ± 29	5.39 ± 0.02	9.64 ± 0.04	0.07
Pm	—	—	—	—
Sm	223 ± 47	5.51 ± 0.02	9.89 ± 0.04	0.08
Eu	161 ± 43	5.60 ± 0.02	9.90 ± 0.03	0.05
Gd	109 ± 45	5.60 ± 0.02	9.91 ± 0.03	0.05
Tb	193 ± 51	5.71 ± 0.02	10.08 ± 0.03	0.05
Dy	92 ± 45	5.82 ± 0.01	10.16 ± 0.02	0.03
Ho	149 ± 51	5.85 ± 0.01	10.23 ± 0.02	0.03
Er	124 ± 60	5.91 ± 0.01	10.32 ± 0.02	0.03
Tm	151 ± 92	5.97 ± 0.02	10.46 ± 0.02	0.03
Yb	258 ± 83	6.03 ± 0.01	10.57 ± 0.01	0.03
Lu	191 ± 79	6.04 ± 0.01	10.58 ± 0.01	0.03

3. RESULTS AND DISCUSSION

3.1. Stability Constants for the Bioxalato- and Mono- and Dioxalato-Complexes

Results for ${}_{HOx}\beta_1$, log ${}_{Ox}\beta_1$ and log ${}_{Ox}\beta_2$ are presented in Table 1 and in Figure 2. Errors in Table 1 are asymptotic standard errors calculated with SAS® (SAS Institute, 1996) and are generally on the order of 1% for both log ${}_{Ox}\beta_1$ and log ${}_{Ox}\beta_2$, but slightly larger for La and Ce. This is more clearly displayed in Figure 2 where 95% confidence intervals, which are about twice the standard errors, are shown as shading around the patterns.

The most conspicuous features of the patterns in Figure 2 are a steady increase across the REE series from La to Lu and small negative Gd anomalies. The stability constant for Y is almost equal to that for Tb in each case. For the heavy REE the patterns display very subtle behaviour, with slopes slightly decreasing around Tb-Dy, increasing around Ho-Er and then again decreasing at Yb. The ${}_{HOx}\beta_1$ are not plotted in Figure 2 since they show no discernable trend across the REE series. In fact, the values of ${}_{HOx}\beta_1$ in Table 1 are indistinguishable within their standard errors and are all compatible with an average value of 159 ± 55 mol/L^{-1}. Most studies of REE oxalate complexation have ignored the contribution of the bioxalate complex or assumed it to be negligible. One exception is Paramonova et al. (1963), who report a value of 32 ± 1 mol/L^{-1} for ${}_{HOx}\beta_1$(Eu) at $I = 0.5$ mol/L. Our result at $I = 0.05$

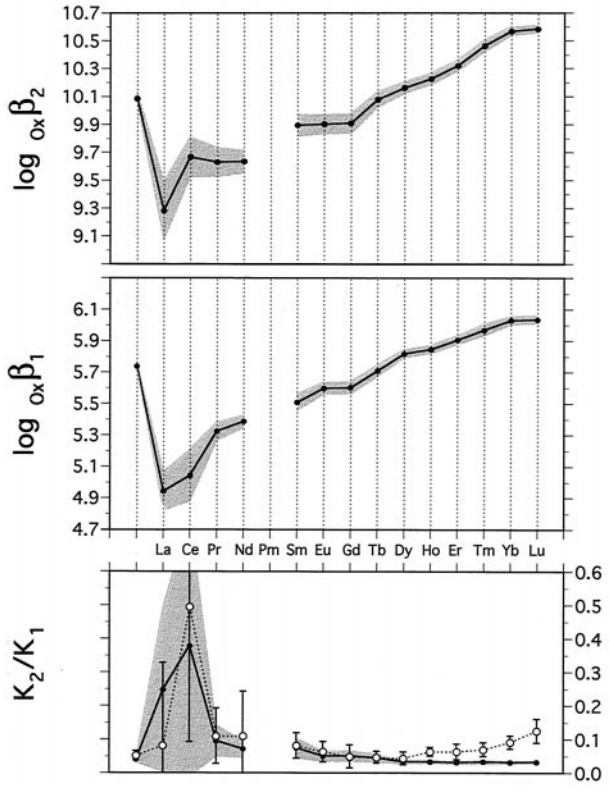

Fig. 2. Patterns of log $_{Ox}\beta_1$, log $_{Ox}\beta_2$ and $K_2/K_1 = {}_{Ox}\beta_2/({}_{Ox}\beta_1)^2$ for Y + REE at T = 25°C and I = 0.05 M. Shading represents 95% confidence intervals calculated with SAS® (SAS Institute, 1996), approximately equal to twice the standard errors given in Table 1. Note that K_2/K_1 for La and Ce are consistent with K_2/K_1 for the other Y + REE within these intervals. Also shown in the lower panel is the pattern of $K_2/K_1 = {}_F\beta_2/({}_F\beta_1)^2$ for Y + REE at T = 25°C and I = 0.025 M (Schijf and Byrne, 1999; open symbols, 95% confidence intervals represented by error bars).

mol/L is consistent with this value and also with values found by Liu and Byrne (1998) for $_{HCO3}\beta_1$ at I = 0.68 m (19 ± 8 mol/L^{-1}).

3.2. Interpretation of K_2/K_1

Also included in Table 1 and shown in Figure 2 are stepwise stability constant ratios, K_2/K_1, where

$$K_1 = [MOx^+][M^{3+}]^{-1}[Ox^{2-}]^{-1} = {}_{Ox}\beta_1 \qquad (11a)$$

and

$$K_2 = [MOx_2^-][MOx^+]^{-1}[Ox^{2-}]^{-1} = {}_{Ox}\beta_2/{}_{Ox}\beta_1. \qquad (11b)$$

We have argued previously (Schijf and Byrne, 1999) that inspection of the pattern of stepwise stability constant ratios, K_2/K_1, provides a measure of the validity of β_1 and β_2 data. This is because these ratios are very sensitive to errors in β_1 and β_2, which are strongly anticorrelated for each individual element. In view of electrostatic and statistical considerations the K_2/K_1 are generally expected to be smaller than unity (Cotton et al., 1999). Stepanov (1971) found K_2/K_1 = 0.024 ± 0.003 for oxalato-complexes of Y and six REE (including Pm) in acid solutions at I = 0.1 M while Cantrell and Byrne (1987) found K_2/K_1 = 0.09 ± 0.01 for oxalato-complexes of Ce, Eu, and Yb in $NaClO_4$ at I = 0.68 m. Here we find K_2/K_1 = 0.05 ± 0.02 for Y + REE excluding La and Ce, which have anomalous values of 0.23 and 0.36, respectively.

These results are reminiscent of what we previously reported for fluoro-complexes of Y + REE (Schijf and Byrne, 1999). In that case, we found K_2/K_1 = 0.07 ± 0.03 for Y+REE excluding Ce, for which the value was 0.49. While Ce oxidation was not expected under the conditions of those experiments, we tentatively ascribed the anomalous value to some aspect of its chemistry, which is unique within the REE series. However, the fact that an anomalous K_2/K_1 value is also observed for La oxalate complexation makes such an explanation less satisfactory. The K_2/K_1 in Schijf and Byrne (1999) were reported without errors. Here we have used SAS® (SAS Institute, 1996) to calculate 95% confidence intervals for each Y+REE as is shown for both oxalato-complexes and fluoro-complexes in Figure 2. Clearly, within these intervals the K_2/K_1 for La and Ce oxalato-complexes and for Ce fluoro-complexes are indistinguishable from the corresponding averages for the other Y+REE. The intervals are much larger for La and Ce in both cases and the fact that the value of K_2/K_1 for La fluoro-complexes was similar to that of the other REE appears fortuitous. These large intervals merely reflect the observation that La and Ce form much weaker complexes with oxalate anions which causes their D^0/D to depend much more weakly on $[Ox^{2-}]$. For example, the D^0/D of Lu increases by a factor of 36 in the presence of 19 μM free oxalate, while that of La increases by a factor of less than 4 (see Appendix). Thus, the low extent of formation of the first oxalato-complex for light REE does not constrain K_2/K_1 as well as is the case for heavy REE.

3.3. Ionic Strength Dependence of the Stability Constants

Y+REE oxalate complexation and the solubility of Y+REE oxalates has been described in many previous works (e.g., Crouthamel and Martin, 1950, 1951; Babko and Dubovenko, 1957; Feibush et al., 1958; Zaborenko et al., 1959; Yatsimirskii and Zhukov, 1962; Andreeva and Kolosov, 1962, 1963; Lyle and Naqvi, 1967; Aziz and Lyle, 1970; Gammons and Wood, 2000). Close inspection indicates that data quality is satisfactory overall, despite the many different media, ionic strengths and techniques used. The most comprehensive and high-quality data is available for Eu (Table 2), hence this element was chosen for ionic strength modeling. Values for log $_{Ox}\beta_1$(Eu) reported by Caceci and Choppin (1983), and for log $_{Ox}\beta_2$(Eu) reported by Manning (1966) deviate strongly from the trends suggested by all other data and were rejected. The value for log $_{Ox}\beta_2$(Eu) reported by Caceci and Choppin (1983) agreed well with the general trend but was rejected in view of the deviation of log $_{Ox}\beta_1$(Eu). Values of log $_{Ox}\beta_1$(Eu) and log $_{Ox}\beta_2$(Eu) reported by Sekine (1965) were increased by 0.1 as suggested by Grenthe et al. (1969), who pointed out that Sekine's curve of D^0/D for Eu does not approach unity at $[Ox^{2-}] = 0$. The selected data are shown in Figure 3. No data at infinite dilution were used, since these involve assumptions on how to extrapolate measurements at higher ionic strength and are thus model-dependent.

Table 2. Literature values of stability constants for mono- and dioxalato-complexes of europium, as well as for its trioxalato-complex, where reported.

I (M)	Medium	Method	log $_{Ox}\beta_1$(Eu)	log $_{Ox}\beta_2$(Eu)	log $_{Ox}\beta_3$(Eu)	ref.
0		Extrap	6.52			1
0		Extrap	6.72	11.22		2
0		Extrap	6.53	10.62		3
0.03	$NaClO_4$/NaCl	Liq/rad	5.77			1
0.04	$NaClO_4$/NaCl	Liq/rad	5.65			1
0.05	$NaClO_4$/NaCl	Liq/rad	5.46			1
0.05	$NH_4NO_3 + HNO_3$	Ion/MS	5.60	9.90		4
0.06	$NaClO_4$/NaCl	Liq/rad	5.31			1
0.1	H_2Ox	Mig/rad	5.36	9.04		5
0.5[a]	$NaNO_3$	Ion/rad	4.81	8.57	11.5	6
0.5	$NaClO_4$	Ion/rad	4.86	8.65		7
0.5	$NaClO_4$	Liq/rad	4.86	8.67		7
0.68	$NaClO_4$	Liq/rad	4.89	8.68	11.23	8
0.7[b]	NaCl	Liq/rad	4.63[d]	8.40[d]		9
0.95	$NaClO_4$	Liq/rad	4.88	7.64[d]		1
1	$NaClO_4$	Liq/rad	4.87[e]	8.82[e]	11.49[e]	10
1[c]	$NaClO_4$	Sol/rad	5.04	8.70	11.57	11

I = ionic strength. For details on extrapolations to infinite dilution ($I = 0$), see corresponding reference. Temperature: 25°C except [a] not specified, [b] 21°C, [c] 20°C. Methods: extrap = extrapolation; liq = solvent extraction; ion = ion-exchange resin; mig = electromigration; sol = solubility; rad = radioisotopes; MS = ICP-MS.

[d] Values rejected for use in Figure 3.

[e] Corrected as suggested by Grenthe et al. (1969).

References: 1. Manning (1966); 2. Wood (1993); 3. Liu et al. (1997); 4. This work; 5. Stepanov (1971); 6. Kereĭchuk and Paramonova (1963); 7. Lyle and Naqvi (1966); 8. Cantrell and Byrne (1987); 9. Caceci and Choppin (1983); 10. Sekine (1965); 11. Grenthe et al. (1969), who also reported log $_{Ox}\beta_4$(Eu) = 13.09.

It appears that data for log $_{Ox}\beta_1$(Eu) and log $_{Ox}\beta_2$(Eu) (including our data) are described quite well by relations of the form (Li and Byrne, 1997)

$$\log {}_{Ox}\beta_n(\mathrm{Eu}) = \log {}_{Ox}\beta_n^0(\mathrm{Eu}) + 0.511\Delta z^2\sqrt{I}/(1 + B_n\sqrt{I}) + C_nI \quad (12)$$

where log $_{Ox}\beta_n^0$(Eu) (the stability constants at infinite dilution), B_n, and C_n (n = 1,2) are the free parameters, $\Delta z^2 = -12$ for log $_{Ox}\beta_1$(Eu) and $\Delta z^2 = -16$ for log $_{Ox}\beta_2$(Eu). An additional term in $I\sqrt{I}$ (Li and Byrne, 1997) gave rise to a spurious maximum at high ionic strength and was omitted. Non-linear regressions of the data (Fig. 3) yield log $_{Ox}\beta_1^0$(Eu) = 6.52, B_1 = 1.47, and C_1 = 0.902 (r^2 = 0.96) for log $_{Ox}\beta_1$(Eu) and log $_{Ox}\beta_2^0$(Eu) = 11.09, B_2 = 1.05, and C_2 = 1.69 (r^2 = 0.90) for log $_{Ox}\beta_2$(Eu). The values of log $_{Ox}\beta_n^0$(Eu) are in excellent agreement with average extrapolations reported by others (Table 2): log $_{Ox}\beta_1^0$(Eu) = 6.59 ± 0.11 and log $_{Ox}\beta_2^0$(Eu) = 10.92 ± 0.42.

It has been argued on theoretical grounds (Kumok and Serebrennikov, 1965) and shown experimentally for REE complexation with NTA (Li and Byrne, 1997), with hydroxide (Klungness and Byrne, 2000), and with fluoride (Luo and Byrne, 2000), that the ionic strength dependence of stability constants is generally identical for all Y + REE. This means that Eqn. 12 must accurately describe the ionic strength dependence of not just Eu, but all Y+REE. Our data for log $_{Ox}\beta_1$(Eu) and log $_{Ox}\beta_2$(Eu) at $I = 0.05$ M are in good agreement with the best fits in Figure 3. Consequently, subtracting the measured values of log $_{Ox}\beta_n$ (Eu) at $I = 0.05$ M (Table 1) from the best fit values of log $_{Ox}\beta_n^0$(Eu), log $_{Ox}\beta_n^0$ and log $_{Ox}\beta_n$ are related for all Y+REE as follows:

$$\log {}_{Ox}\beta_1^0 = \log {}_{Ox}\beta_1 + 0.924 \quad (13a)$$

and

$$\log {}_{Ox}\beta_2^0 = \log {}_{Ox}\beta_2 + 1.187. \quad (13b)$$

The log $_{Ox}\beta_n^0$ results obtained using Eqn. 13a and 13b are given in Table 3 and shown in Figure 4.

In Figure 4, our patterns of log $_{Ox}\beta_n^0$ (Table 3) are compared with extrapolations by Wood (1993) and by Liu et al. (1997), based on LFERs, except those for Ce, Eu, and Yb (Wood, 1993) and for Y, Ce, Eu, Tb, Tm, and Yb (Liu et al., 1997), which are based on measured stability constants. Values of log $_{Ox}\beta_1^0$ are in excellent agreement with Liu et al. (1997) for Y-Tb. For Dy-Lu, values of Liu et al. (1997) are lower by a little more than 0.1 units. The extrapolations of Wood (1993), which do not include Y and show irregular behaviour for Ce, Dy, and Yb, match our predictions less well. The pattern of log $_{Ox}\beta_2^0$ is similar in shape to the extrapolations of Wood (1993), which again show irregular behaviour for Ce, as well as to the extrapolations of Liu et al. (1997). For Y-Nd our predictions exceed both extrapolations, while for Sm-Lu they fall in between the two, being closer to those of Wood (1993).

3.4. Potential Importance of Oxalato-Complexes to Y+REE Speciation in Groundwaters and Surface Freshwaters

In this final Section we will use a simple model to demonstrate the potential importance of oxalato-complexes to the

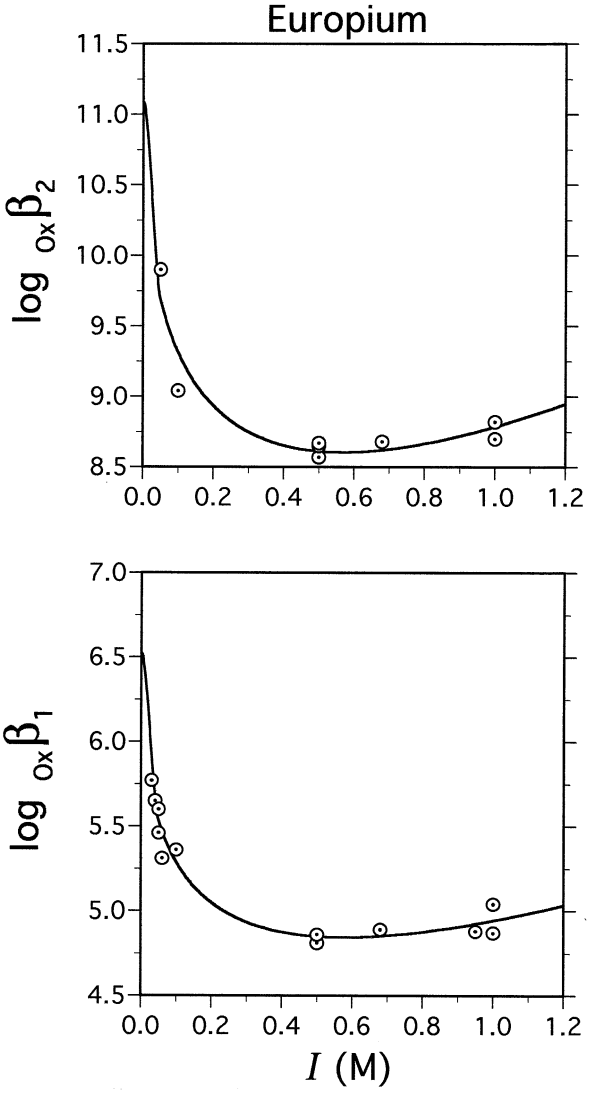

Fig. 3. Selected data (Table 2) for log $_{Ox}\beta_1$(Eu) and log $_{Ox}\beta_2$(Eu) as a function of ionic strength I, fitted with relations log $_{Ox}\beta_1$(Eu) = $6.52-6.132\sqrt{I}/(1 + 1.47\sqrt{I}) + 0.902I$ and log $_{Ox}\beta_2$(Eu) = $11.09-8.176\sqrt{I}/(1 + 1.05\sqrt{I}) + 1.69I$.

speciation of Y+REE in groundwaters and other freshwaters where elevated levels of free oxalate may occur. For our model we chose a hypothetical groundwater with $[Ox^{2-}]_T = 10^{-4}$ M and $[CO_3^{2-}]_T = 10^{-3}$ M. For convenience, the ionic strength was chosen to match that of our experiments. Both I and $[CO_3^{2-}]_T$ are well within the natural range reported for groundwaters (e.g., Johannesson and Hendry, 2000). The total oxalate concentration is near the middle of the range reported for soil solutions (10^{-5}–10^{-3} M; see references in Gammons and Wood, 2000). Note that $[CO_3^{2-}]_T$ is 10 times as high as $[Ox^{2-}]_T$ in our calculations. All free ligand concentrations were calculated as a function of pH. Only complexes with oxalate, bioxalate, carbonate, and bicarbonate were considered. The distributions shown in Figure 5 do not depend on total Y+REE concentrations within the range typical for groundwaters (10^{-12}–10^{-9} M; Johannesson and Hendry, 2000).

Concentrations of free oxalate, bioxalate, carbonate, and bicarbonate ions were calculated using the association constants $K_{a1,2}$ of oxalic acid (see Section 2.5.) and carbonic acid. $K_{a1,2}$ of carbonic acid were interpolated from the data of Patterson et al., (1982, 1984), using an ionic strength dependence similar to the one that was used to interpolate $K_{a1,2}$ of oxalic acid. The values at I = 0.05 M are $K_{a1} = 10^{6.24}$ and $K_{a2} = 10^{10.09}$. The contribution of each REE species was calculated from:

Table 3. Stability constants at infinite dilution, log $_{Ox}\beta_1^0$ and log $_{Ox}\beta_2^0$, for mono- and dioxalato complexes of Y+REE, respectively, obtained by applying the relations log $_{Ox}\beta_1^0$(M) = log $_{Ox}\beta_1$(M) + 0.924 and log $_{Ox}\beta_2^0$(M) = log $_{Ox}\beta_2$(M) + 1.187 to the stability constants at I = 0.05 M (Table 1).

M^{3+}	log $_{Ox}\beta_1^0$	log $_{Ox}\beta_2^0$
Y	6.66	11.27
La	5.87	10.47
Ce	5.97	10.86
Pr	6.25	10.82
Nd	6.31	10.82
Pm	—	—
Sm	6.43	11.08
Eu	6.52	11.09
Gd	6.53	11.10
Tb	6.63	11.27
Dy	6.74	11.35
Ho	6.77	11.41
Er	6.83	11.51
Tm	6.89	11.65
Yb	6.95	11.75
Lu	6.96	11.77

These relations were derived by fitting selected literature data for Eu (Table 2, Figure 3). It is assumed that the ionic strength dependence of the stability constants is identical for all Y + REE.

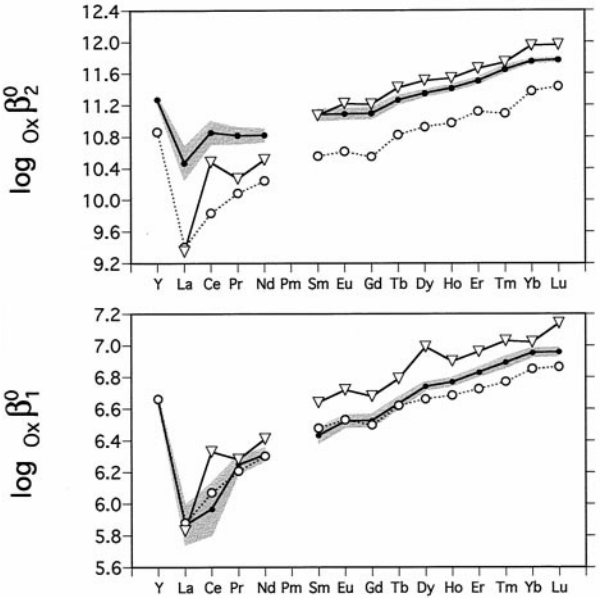

Fig. 4. Patterns of log $_{Ox}\beta_1^0$ and log $_{Ox}\beta_2^0$ (Table 3; ●), obtained by applying the translations log oxβ_1^0(M) = log $_{Ox}\beta_1$(M) + 0.924 and log $_{Ox}\beta_2^0$(M) = log $_{Ox}\beta_2$(M) + 1.187 to the patterns of log $_{Ox}\beta_1$ and log $_{Ox}\beta_2$ and the 95% confidence intervals (shading) depicted in Figure 2. Extrapolations by Wood (1993) (▽) and by Liu et al. (1997) (○) are shown for comparison.

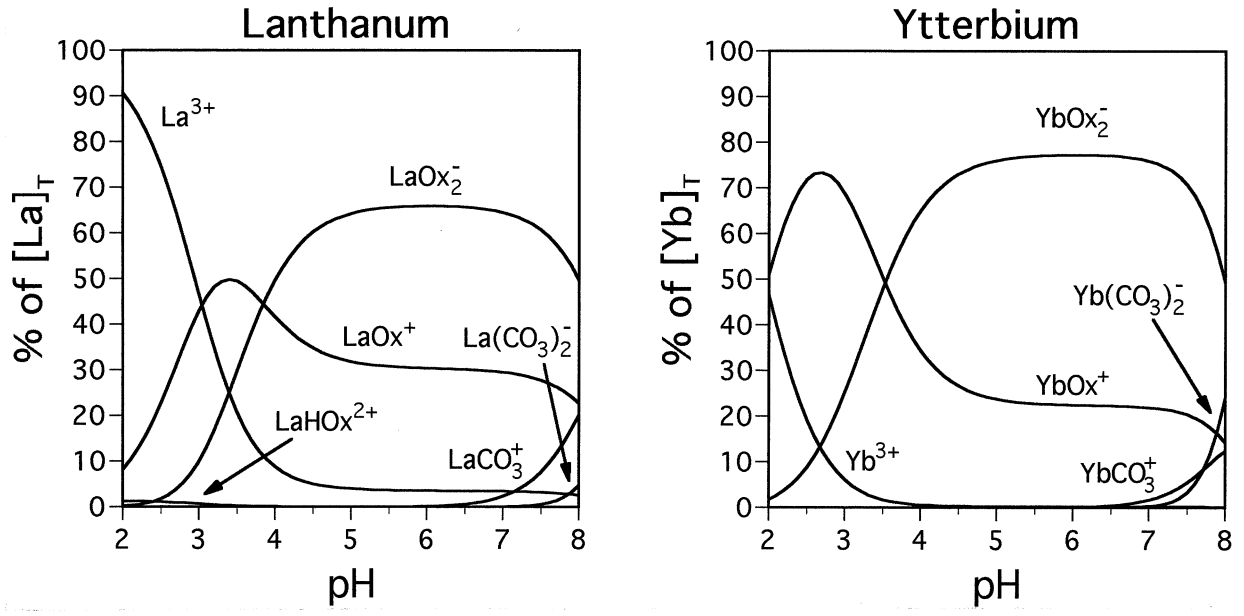

Fig. 5. Speciation of La and Yb in a model groundwater with $I = 0.05$ M, $[Ox^{2-}]_T = 10^{-4}$ M and $[CO_3^{2-}]_T = 10^{-3}$ M, as a function of pH. Only complexes with oxalate, bioxalate, carbonate, and bicarbonate were considered. Contributions of individual species are expressed as percentages of the total REE concentration ($[La]_T$ or $[Yb]_T$). Species contributing less than 1% are not shown.

$$[M]_T = [M^{3+}](1 + {}_{HOx}\beta_1[HOx^-] + {}_{Ox}\beta_1[Ox^{2-}] + {}_{Ox}\beta_2[Ox^{2-}]^2 + {}_{HCO3}\beta_1[HCO_3^-] + {}_{CO3}\beta_1[CO_3^{2-}] + {}_{CO3}\beta_2[CO_3^{2-}]^2). \quad (14)$$

Stability constants ${}_{Ox}\beta_{1,2}$ were taken from Table 1. The stability constant ${}_{HOx}\beta_1$ was set equal to the average (159 M^{-1}) for both La and Yb. Stability constants ${}_{CO3}\beta_{1,2}$ were derived from those at infinite dilution (Liu and Byrne, 1998) by applying the same ionic strength dependence as for ${}_{Ox}\beta_{1,2}$ (see Section 3.3.).

Figure 5 shows that the speciation of both La and Yb is dominated by oxalato-complexes at any pH between 3 and 8. Only at pH $>$ 7 do carbonato-complexes play a role, contributing 25 to 35% at pH 8, the monocarbonato-complex being more important for La and the dicarbonato-complex for Yb. Bicarbonato-complexes were insignificant in these calculations even with ${}_{HCO3}\beta_1$ as high as 100. At pH $<$ 4 the free M^{3+} ion becomes important. It dominates the speciation of La at pH $<$ 3 and continues to play a minor role ($<$10%) between pH 5 and 8. The mono-oxalato-complex dominates the speciation of Yb below pH 3.5 and that of La around pH 3.5. The dioxalato-complex dominates the speciation of both elements between pH 3.5 and 8. No other ligands were considered in this model. The only additional inorganic ligand that could be of some importance is PO_4^{3-}, yet Gammons and Wood (2000), modeling the speciation of a similar groundwater ($[Ox^{2-}]_T = 10^{-4}$ M; $[CO_3^{2-}]_T = 10^{-4}$ M; $[PO_4^{3-}]_T = 10^{-6}$ M), showed for Yb that monophosphato-complexes dominate only at pH $>$ 9.

It is clear that oxalate is a potentially important ligand for Y+REE in freshwaters at low pH, even at moderate alkalinity, because of the high stability of Y+REE oxalato-complexes and the persistence of the free oxalate ion under mildly acidic conditions. Taunton et al. (2000) have recently shown that bacteria and fungi may satisfy their need for phosphate in nutrient-poor soils by the solubilisation of REE-rich phosphate minerals such as apatite, possibly by excreting oxalate or other carboxylic acids. Far too little data are available to decide whether high oxalate levels are common in bulk groundwaters, but micro-environments created by these ubiquitous organisms at mineral surfaces could well have a considerable effect on REE solubility and mobility in soils. In view of this fact, we feel that measurements of oxalate concentrations (e.g., by ion chromatography) should become routine in any study of REE behaviour in groundwaters or surface freshwaters.

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Table A1. Measured D^0/D for modeled values of $[Ox^{2-}]$ and $[HOx^{-}]$ at two different pH. Each D^0/D is the average of two separate ICP-MS analyses of the same sample solution. D^0 was corrected for solution composition. Data from several experiments are arranged in order of increasing $[Ox]_T$.

$[Ox]_T$	$[Ox^{2-}]$	$[HOx-]$	D^0/D														
mM	μM	mM	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
pH 1.6																	
0.248	0.908	0.189	1.513	1.006	1.080	1.165	1.213	1.294	1.359	1.356	1.496	1.616	1.675	1.764	1.916	2.071	2.074
0.496	1.799	0.377	2.126	1.195	1.315	1.467	1.511	1.756	1.864	1.862	2.137	2.347	2.495	2.698	2.997	3.328	3.348
0.501	1.817	0.381	2.056	1.111	1.233	1.395	1.462	1.643	1.767	1.744	2.007	2.249	2.361	2.560	2.818	3.154	3.165
1.000	3.569	0.759	3.321	1.438	1.726	1.985	2.076	2.569	2.765	2.760	3.318	3.748	4.003	4.428	5.109	5.774	5.813
1.016	3.624	0.770	3.208	1.325	1.645	1.865	1.996	2.392	2.618	2.594	3.160	3.606	3.876	4.250	4.793	5.536	5.507
1.542	5.400	1.165	4.378	1.554	2.041	2.330	2.562	3.137	3.482	3.432	4.244	4.964	5.282	5.954	6.896	7.968	7.986
2.028	6.990	1.528	5.716	1.943	2.596	3.018	3.246	4.197	4.618	4.582	5.767	6.644	7.224	8.132	9.590	11.08	11.17
2.078	7.150	1.565	5.632	1.771	2.360	2.816	3.101	3.901	4.360	4.333	5.397	6.452	6.931	7.812	9.045	10.69	10.69
2.625	8.872	1.970	6.875	2.015	2.723	3.334	3.701	4.734	5.268	5.240	6.612	7.951	8.639	9.777	11.45	13.51	13.65
3.074	10.24	2.300	8.423	2.540	3.671	4.123	4.486	5.929	6.528	6.444	8.155	9.755	10.51	12.08	14.35	16.83	16.85
3.184	10.57	2.380	8.199	2.238	3.117	3.804	4.267	5.552	6.231	6.099	7.946	9.548	10.40	11.81	13.85	16.55	16.81
4.138	13.34	3.076	10.91	2.863	3.954	5.094	5.560	7.540	8.344	8.265	10.68	12.71	13.97	15.98	19.39	22.86	23.17
5.222	16.29	3.856	13.75	3.270	5.176	6.079	6.700	9.268	10.26	10.17	13.33	15.94	17.55	20.19	24.53	29.35	29.56
6.325	19.12	4.640	16.39	3.715	6.012	7.113	7.880	11.02	12.22	12.06	16.03	19.29	21.20	24.60	30.01	36.07	36.62
pH 1.3																	
0.496	0.761	0.309	1.461	1.074	1.157	1.205	1.237	1.308	1.374	1.361	1.454	1.562	1.593	1.701	1.809	1.948	1.977
0.496	0.761	0.309	1.460	1.046	1.126	1.157	1.189	1.311	1.340	1.333	1.463	1.536	1.606	1.673	1.798	1.962	1.954
1.001	1.525	0.623	1.934	1.166	1.322	1.412	1.477	1.649	1.750	1.709	1.934	2.131	2.207	2.398	2.608	2.930	2.920
1.001	1.525	0.623	1.936	1.136	1.268	1.365	1.425	1.636	1.695	1.670	1.945	2.094	2.221	2.357	2.634	2.898	2.913
1.515	2.292	0.941	2.419	1.264	1.509	1.630	1.715	1.998	2.122	2.056	2.404	2.697	2.840	3.111	3.457	3.920	3.927
2.028	3.047	1.258	2.951	1.349	1.641	1.797	1.925	2.336	2.461	2.424	2.966	3.260	3.541	3.838	4.332	4.977	4.966
2.040	3.063	1.264	2.925	1.396	1.704	1.837	1.983	2.361	2.532	2.440	2.897	3.266	3.451	3.849	4.305	4.923	4.955
2.575	3.837	1.593	3.469	1.525	1.963	2.104	2.300	2.729	2.949	2.822	3.416	3.944	4.131	4.656	5.254	6.072	6.009
3.074	4.549	1.898	4.039	1.603	2.035	2.283	2.481	3.091	3.301	3.228	4.013	4.524	4.900	5.397	6.204	7.219	7.225
3.120	4.614	1.926	4.015	1.659	2.181	2.329	2.564	3.094	3.366	3.214	3.941	4.557	4.828	5.475	6.128	7.179	7.138
4.138	6.033	2.545	5.027	1.802	2.356	2.722	2.969	3.768	4.089	3.954	5.043	5.663	6.235	6.887	8.066	9.437	9.399
5.222	7.500	3.198	6.257	2.072	3.050	3.241	3.560	4.629	4.943	4.880	6.154	7.081	7.772	8.589	10.10	11.98	11.93
6.325	8.951	3.857	7.272	2.249	3.461	3.704	4.044	5.338	5.758	5.628	7.253	8.326	9.132	10.30	12.18	14.44	14.39