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A spectrophotometric study of erbium (III) speciation in chloride solutions at elevated temperatures

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Abstract

The speciation of erbium in chloride-bearing solutions was investigated spectrophotometrically at temperatures of 100 to 250 °C and a pressure of 100 bars. The hydrated ion, Er^{3+}, is predominant at ambient temperature, but chloride complexes are dominant at elevated temperature. Formation constants were calculated for the following reactions:

$$Er^{3+} + Cl^{-} = ErCl^{2+} \qquad (\beta_1)$$

$$Er^{3+} + 2\cdot Cl^{-} = ErCl_2^{+} \qquad (\beta_2)$$

The values obtained for the first formation constant (β_1) were 0.88 ± 0.11, 1.59 ± 0.12, 2.34 ± 0.11, and 3.09 ± 0.14 at 100, 150, 200 and 250 °C, respectively. Values of the second formation constant could only be determined at 200 and 250 °C, and were 2.95 ± 0.34 and 4.12 ± 0.12, respectively.

The values for the first formation constant (β_1), are identical within experimental error to the values predicted by Haas et al. [Haas, J. R., Shock, E. L., and Sassani, D. C. (1995). Rare Earth Elements in hydrothermal systems: estimates of standard partial molal thermodynamic properties of aqueous complexes of the Rare Earth Elements at high pressures and temperatures. Geochim. Cosmochim. Acta, 59, 4329–50.], whereas the values for the second formation constant (β_2) agree relatively well with those predicted by Haas et al. (1995) and determined experimentally by Gammons et al. [Gammons, C.H., Wood, S.A., and Li, Y. (2002). Complexation of the Rare Earth Elements with aqueous chloride at 200 °C and 300 °C and saturated water vapor pressure. Special Publication — The Geochemical Society, (Water–Rock Interactions, Ore Deposits, and Environmental Geochemistry), 191–207.].

Keywords: Rare Earth Elements; Erbium; Chloride; Aqueous solution; Speciation; Formation constants; Elevated temperatures

1. Introduction

Although numerous studies have shown that hydrothermal processes are important in mobilizing and concentrating the Rare Earth Elements (REE) (e.g., Smith and Henderson, 2000; Williams-Jones et al., 2000), experimental studies of REE speciation at elevated temperatures have been largely restricted to only one element of the group, i.e., Nd (Gammons et al., 1996; Stepanchikova and Kolonin, 1999; Migdisov and Williams-Jones, 2002; Migdisov et al., 2006) and, consequently, the behaviour of other REE in hydrothermal fluids is known mainly from theoretical predictions such as those of Wood (1990) and

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Haas et al. (1995). The only experimental study reporting formation constants for REE other than Nd was that of Gammons et al. (2002), who investigated the stability of a large set of REE in Cl-bearing solutions. However, due to the limitation of the method employed in the study (solubility) it was not possible for Gammons et al. (2002) to evaluate the first formation constant ($REE^{3+}+Cl^{-}=REECl^{2+}$), and they were only able to reliably determine values of the stepwise formation constant ($REECl^{2+}+Cl^{-}=REECl_2^{+}$) for 200 °C.

In previous studies we have reported results of investigations of the speciation of Nd in chloride- and sulfate-bearing aqueous solutions using UV-visible spectroscopy and a high-temperature flow-through spectroscopic cell (Migdisov and Williams-Jones, 2002; Migdisov et al., 2006). This paper extends our study of the REE to erbium and, by using exactly the same method employed in our other studies, permits reliable comparison of the speciation of Er with that of Nd. Here we report the results of an experimental investigation of the speciation of Er in chloride-bearing solutions at temperatures of 26 to 250 °C.

2. Method

The study was conducted using a high temperature, flow-through, ultraviolet (UV)-visible spectroscopic cell at temperatures of 26, 100, 150, 200 and 250 °C and a pressure of 100 bars. Temperature was controlled by an Omega CN-2001 regulator to within ±0.5 °C of a pre-determined value. Pressure was controlled using a solution delivery system, consisting of a HP 1050-Ti HPLC pump, PEEK and Ti capillaries, and a PEEK back pressure regulator. The cell was constructed from grade 4 titanium alloy and spectra were recorded in situ through sapphire windows, which were sealed in the cell using Graflex® (polymerized graphite) o-rings. Experimental solutions were therefore only in contact with chemically inert materials. The path length (0.97 cm) was determined by a calibration procedure involving measurements of the absorbance of a solution of Er ($1.3 \cdot 10^{-1}$ mol dm^{-3}) at 26 °C in a standard 1-cm quartz cuvette and in the experimental flow-through cell. The optical path length changes with temperature were calculated from the coefficients of thermal expansion for titanium and sapphire.

Absorption spectra were collected for 26 solutions, having total Er concentrations ranging from $3.9 \cdot 10^{-2}$ to $1.3 \cdot 10^{-1}$ mol dm^{-3} (concentrations reported here and below are for solutions at 26 °C), and total chloride concentrations from $3.5 \cdot 10^{-2}$ to 1.91 mol dm^{-3}. The solutions were prepared by dissolving REacton®-grade erbium(III) oxide (Alfa Aesar, 99.99%) in Nanopure® deionized water acidified by Optima-grade perchloric acid (Fisher Scientific) to a final pH of 1.56 to prevent hydrolysis of erbium (Wood et al., 2002). Chloride was introduced by adding appropriate quantities of NaCl (Fisher Scientific, A.C.S.). In order to determine the molar absorbance of Er^{3+}, absorption spectra were also collected for eight chloride-free solutions having total concentrations of Er^{3+} ranging from $3.9 \cdot 10^{-2}$ to $1.3 \cdot 10^{-1}$ mol dm^{-3}. The Er concentrations were verified by analysing the experimental solutions using neutron activation (Ecole Polytechnique, Montreal, Canada).

Spectrophotometric measurements were made at 0.5-nm intervals over the range 300 to 700 nm using a Cary 100 double-beam spectrophotometer. To correct the spectra for background absorption, the cell was filled with Nanopure deionized water, and its absorbance was recorded before each spectrum was collected. An estimate of the error of the measured absorbance values (which were reproducible to a tolerance that varied from 0.01 to 0.02) was obtained by repeated measurements of the spectrum of a solution having a total Er concentration of $1.3 \cdot 10^{-1}$ mol dm^{-3}.

3. Results

A spectroscopic study of REE^{3+} solutions at 25 °C by Choppin et al. (1966) demonstrated that the perchloric ion does not form spectroscopically detectable complexes with REE at concentrations below 6 mol dm^{-3}. Given that the perchloric ion is transparent over the range of wavelengths investigated, we attributed the spectra collected for chloride-free ClO_4-based solutions entirely to the absorbance of hydrated Er^{3+} ions. The Er^{3+} spectra collected at 26 °C were found to be indistinguishable from those presented by Carnall (1979). The molar absorbances of hydrated Er^{3+} were calculated from the concentration of Er^{3+} in chloride-free solutions using the Beer–Lambert law:

$$A = \varepsilon_{Er^{3+}} \cdot M_{Er^{3+}} \cdot l \qquad (1)$$

where A is the absorbance, ε is the molar absorbance for Er^{3+}, l is the pathlength, and M is the molar concentration of Er^{3+} in mol/dm^3. As was the case for Nd^{3+} (Stepanchikova and Kolonin, 1999; Migdisov and Williams-Jones, 2002), absorbances decrease with increasing temperature (Fig. 1).

The spectra collected for Cl-bearing solutions at 26 °C are identical to those recorded for solutions free of chloride ions. However, at higher temperatures, increasing the concentration of chloride ions resulted in a shift

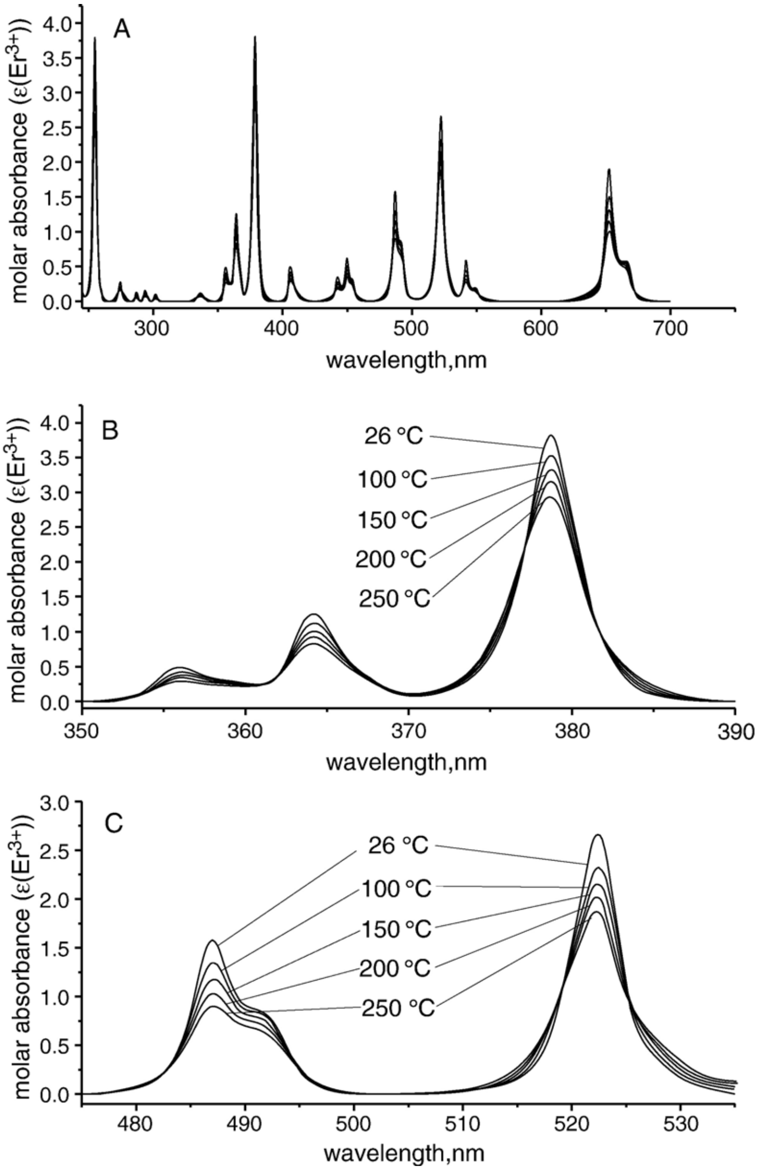

Fig. 1. A) Molar absorbance of Er^{3+}, measured at temperatures of 26, 100, 150, 200 and 250 °C; B) and C) enlargements of selected parts of the spectra.

of the recorded spectra. This spectral shift is illustrated in Fig. 2A and B for selected regions of spectra at 150 and 250 °C representing solutions having the same concentration of erbium and variable concentrations of chloride ions. The spectra shown in the figure were corrected for solvent and window absorbance. Both peak intensity and wavelength varied with temperature, however, the changes were non-systematic (Fig. 3). For example, the intensity of the 378 nm peak decreases to a minimum at ~ 100 °C and then increases, whereas the 522 nm peak has a minimum intensity at ~ 150 °C and a maximum at ~ 200 °C. Moreover, the distribution of minima and maxima in peak intensity varied from one solution to another depending on the metal/ligand ratio. We therefore conclude that these changes reflect variations in the stability of Er(III) chloride complexes.

4. Data treatment

The number of absorbing species was determined for each temperature investigated by calculating the ranks of an absorbance matrix corrected for solvent and window absorbance. Assuming a conventional linear model with respect to chemical composition, each of the

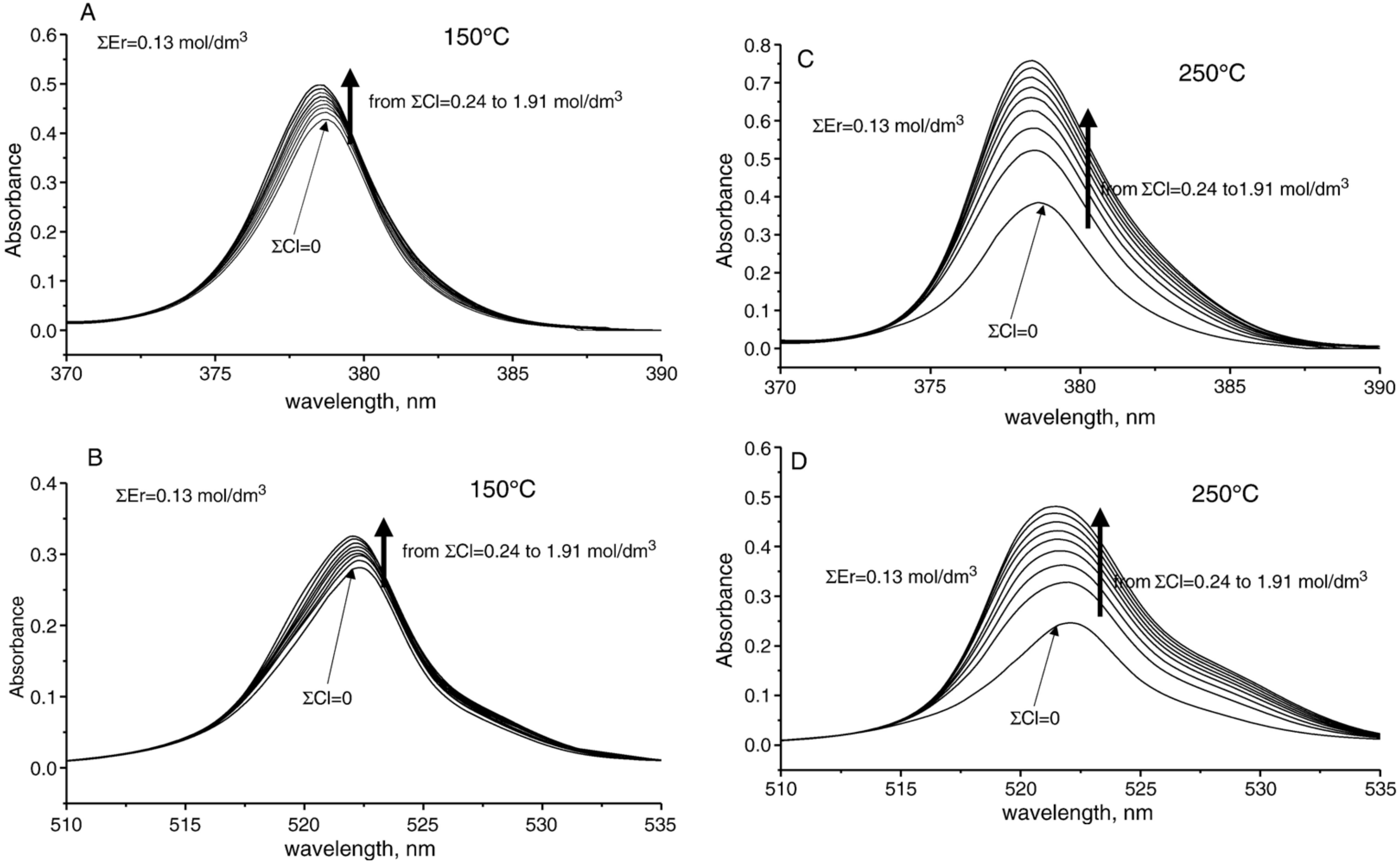

Fig. 2. Selected parts of spectra for solutions with the same Er concentrations but variable concentrations of chloride ion. A, B) 250 °C; C, D) 150 °C.

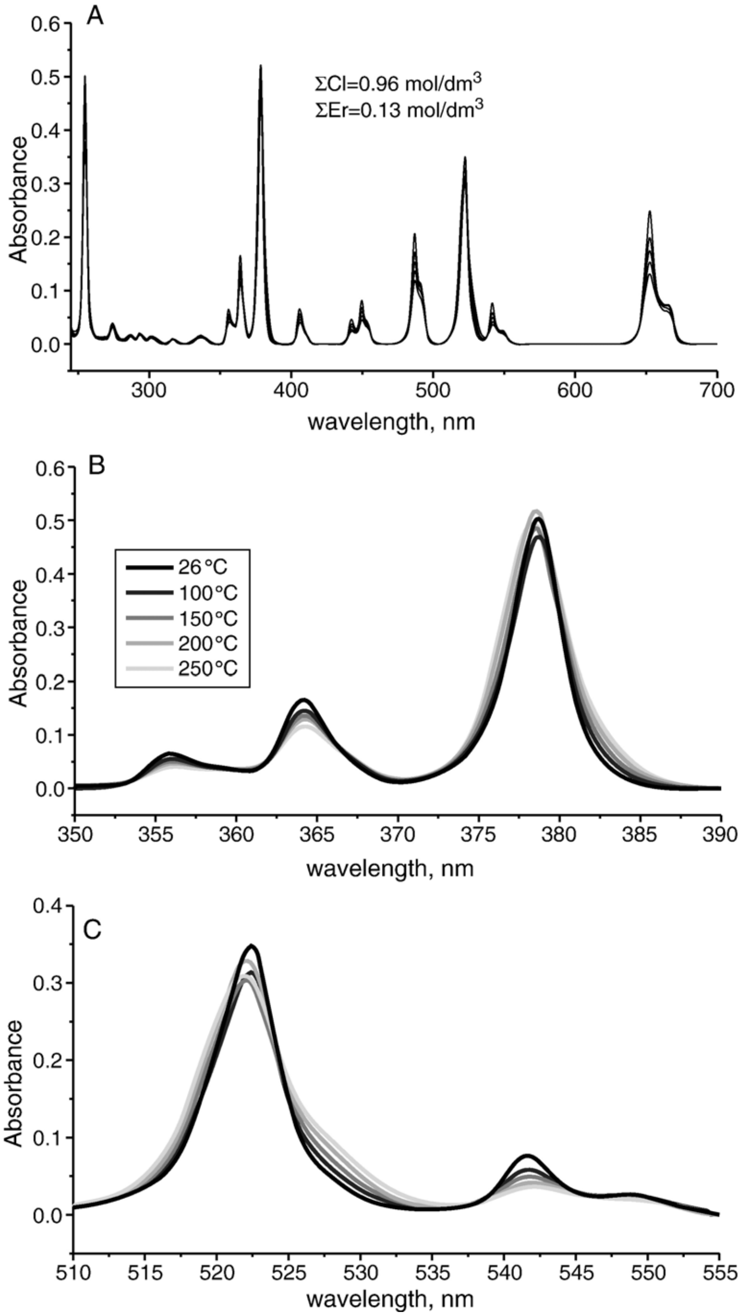

Fig. 3. A) Spectra collected at 26, 100, 150, 200 and 250 °C for a solution containing a total chloride concentration of 0.96 mol/dm^3 and a total erbium concentration of 0.13 mol/dm^3. B, C) Enlargements of selected parts of the spectra shown in A).

experimental measurements at any given wavelength is defined by:

$$\frac{A}{l} = \sum_i \varepsilon_i \cdot M_i \qquad (2)$$

where A is absorbance, ε_i is the molar absorbance of the corresponding species, l is the pathlength, and M_i is the molar concentration of the corresponding species. If no two species have the same molar extinction coefficient, the maximum number of linearly independent columns (which is the number of absorbing species) can be found by determining the rank of the absorbance matrix (for more details see Suleimenov and Seward, 2000; Migdisov and Williams-Jones, 2002; Boily and Seward,

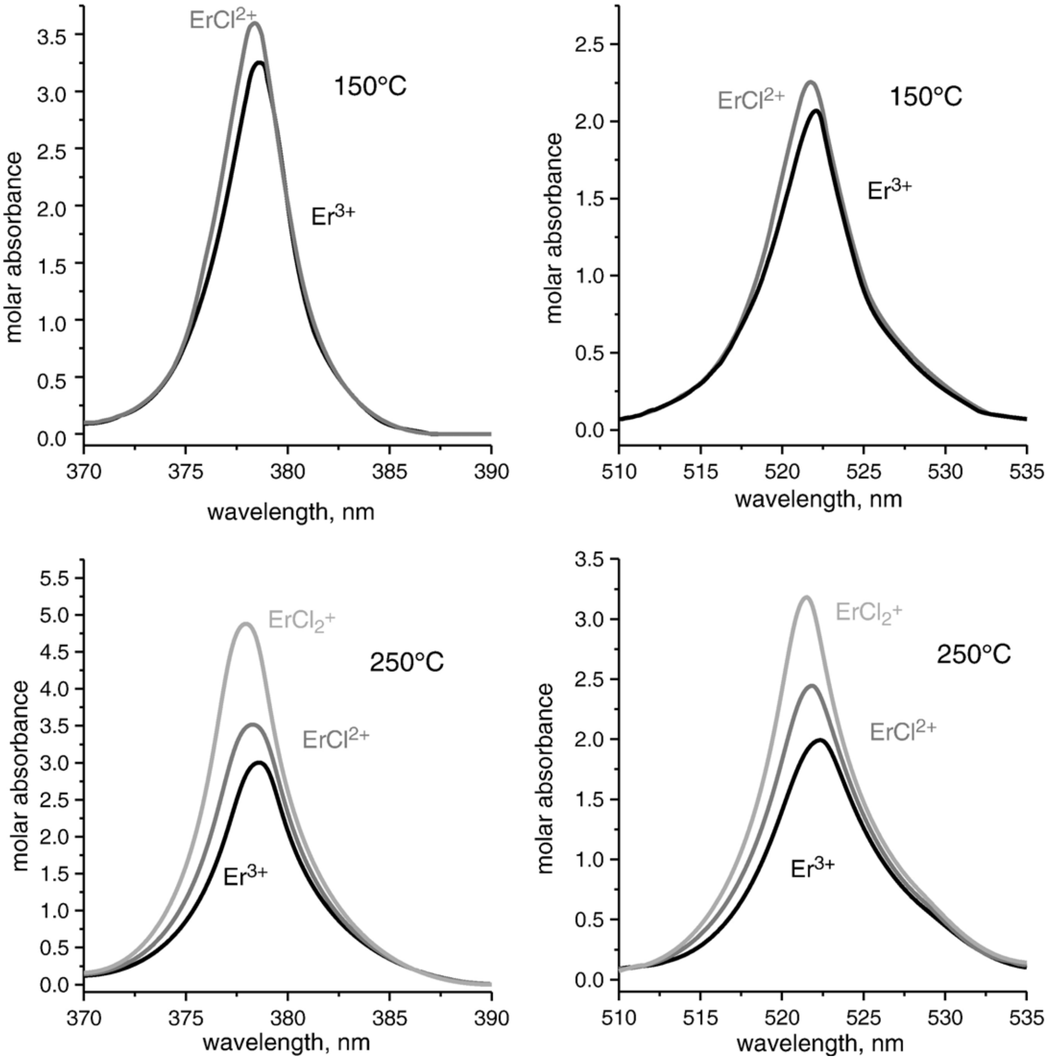

Fig. 4. De-convolution of spectra. Molar absorbances for Er^{3+}, $ErCl^{2+}$ and $ErCl_2^+$ were obtained experimentally (Er^{3+}) and calculated using the optimization procedure described in the text ($ErCl^{2+}$ and $ErCl_2^+$).

2005; Migdisov et al., 2006). The latter was calculated using MATLAB® software, which employs a method, based on the singular value decomposition (Dongarra et al., 1979; ($[L,\mathbf{S},V]=\mathbf{S}VD\ (A)$), where **S** is a diagonal matrix characterizing uncertainties associated with a particular rank). As the experimentally determined uncertainties in the absorption values varied from 0.010 to 0.020, the results of the rank calculations for these tolerance intervals were taken as the total number of absorbing species. The absorbance matrix was reduced in order to restrict it to the wavelength ranges for which peaks were detected, excluding areas for which the maximum absorbance recorded during the runs was below 0.01. The resulting ranks of the matrix for the interval of 350–700 nm are 2 for 100 and 150 °C, and 3 for higher temperatures. Considering that the only REE species described in the literature for Cl-bearing solutions are REE^{3+}, $REECl^{2+}$ and $REECl_2^+$ (e.g., Wood, 1990), and given that complexes involving hydroxide are unlikely to be important under highly acidic conditions, we concluded that the species absorbing in the experimental solutions were Er^{3+} and $ErCl^{2+}$ at 100 and 150 °C, and Er^{3+}, $ErCl^{2+}$ and $ErCl_2^+$ at 200 and 250 °C. Given that $REECl_3$ and $REECl_4^-$ are predicted to be of very minor importance (Haas et al., 1995) and have never been identified experimentally, we ignored these species in our treatment. We also chose to ignore the polynuclear species Er_mCl_n, as we consider their formation extremely unlikely given the weak complexation of REE with Cl^- (e.g., Gammons et al., 1996,

Table 1
Values of the formation constants for $ErCl^{2+}$ and $ErCl_2^+$ (for reactions (3) and (4), respectively) obtained in this study

T °C	log β_1	log β_2
25	–	–
100	0.88±0.11	–
150	1.59±0.12	–
200	2.34±0.11	2.95±0.34
250	3.09±0.14	4.12±0.12

2002) and low concentrations of Er in the solutions. Finally, although all the solutions contained Na^+, ClO_4^- and Cl^-, these species could be ignored as they are transparent in the spectral region investigated.

Equilibrium constants were calculated for the following complexation reactions:

$$Er^{3+} + Cl^- = ErCl^{2+}$$

$$\log\beta_1 = \log a_{ErCl^{2+}} - \log a_{Cl^-} - \log a_{Er^{3+}}$$

and

$$Er^{3+} + 2\cdot Cl^- = ErCl_2^+$$

$$\log\beta_2 = \log a_{ErCl_2^+} - 2\cdot\log a_{Cl^-} - \log a_{Er^{3+}}$$

As in earlier studies (e.g., Migdisov and Williams-Jones, 2002; Suleimenov and Seward, 2000; Migdisov et al., 2006), the calculations involving the Beer–Lambert law employed molarity units, which were corrected to molality units during the calculation of formation constants.

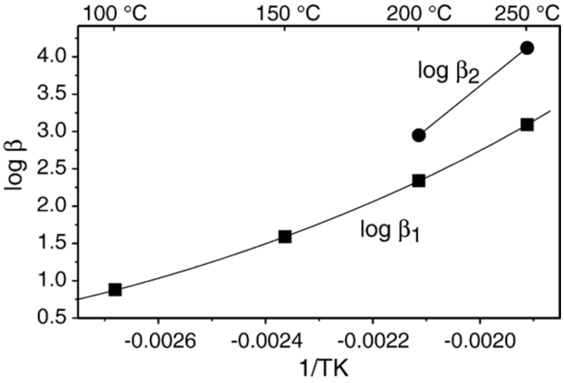

Fig. 5. Values of the optimized formation constants obtained in this study. log β_1 and log β_2 correspond to reactions (3) and (4), respectively.

One of the major goals of this study was to obtain a set of data which would be consistent with those published previously. The activity model employed in this study and parameters used were therefore identical to that employed by Gammons et al. (1996, 2002), and Migdisov and Williams-Jones (2002) to describe speciation of Nd in Cl-bearing solutions. Individual ion activity coefficients were calculated using the extended Debye–Hückel equation (Helgeson, 1969):

$$\log\gamma_i = \frac{A\cdot[z_i]^2\cdot\sqrt{I}}{1+B\cdot a\cdot\sqrt{I}} + b_\gamma\cdot I \qquad (5)$$

where I is the ionic strength, z is the charge, a is the distance of closest approach, A and B are the Debye–Hückel coefficients and b_γ is the extended parameter for a NaCl-based electrolyte (Helgeson et al., 1981). Following Gammons et al. (1996) and Gammons et al. (2002), values for a for H^+ and Cl^- were taken from Kielland (1937), that for Er^{3+} was set at 9 Å, and those for $ErCl^{2+}$ and $ErCl_2^+$ were set at 4.5 Å.

The formation constants were evaluated iteratively from initial guesses via successive minimization of the function U, where U was defined as follows (Suleimenov and Seward, 2000; Migdisov et al., 2006):

$$U = \sqrt{\sum_{i=1}^{I}\left[\sum_{k=1}^{K}\left(\frac{A_{ik}^{\mathrm{obs}}-A_{ik}^{\mathrm{calc}}}{A_{ik}^{\mathrm{obs}}}\right)^2\right]} \qquad (6)$$

and i is the wavelength, I is the total number of wavelengths at which measurements were made, and K is the number of solutions. The variable A_{ik}^{calc} is the calculated absorbance, and is a function of the concentrations of the absorbing species and their molar absorbances, whereas A_{ik}^{obs} is the experimentally determined absorbance.

The calculations involved several cycles of iteration, which minimized U (Eq. (6)) with respect to the formation constants. Each of the iterations involved calculation of the concentrations of species for each of the experimental solutions starting with initial guesses of the formation constants. As in Migdissov and Williams-Jones (2002) our data treatment accounted for both NaCl and HCl ion pairing (Tagirov et al., 1997; Sverjensky et al., 1997). The concentrations of Er species were in turn used to de-convolute the absorbance matrix and to produce optimized values of molar absorbances for each of the experimental wavelengths. The algorithm used in these calculations is described in detail in Migdisov et al. (2006) and employs the approaches developed by Hug and Sulzberger (1994) and Boily and Seward (2005). Fig. 4 shows results of the de-convolution of selected peaks at 150 and 250 °C. The values of the optimized formation constants are listed in Table 1 and are illustrated in Fig. 5.

The distribution of the overall error for the treatment of the spectra was modeled to estimate the errors

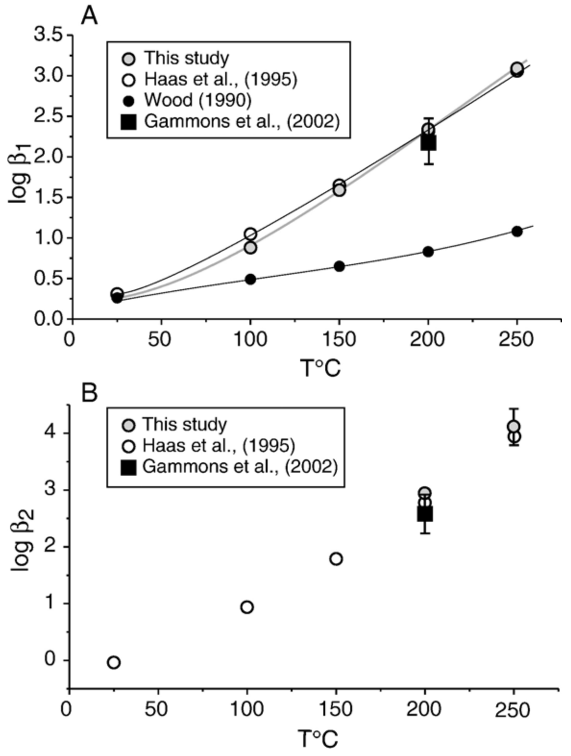

Fig. 6. A comparison of the values of log β_1 and log β_2 obtained in this study with those estimated theoretically by Wood (1990) and Haas et al. (1995), and determined experimentally at 200 °C by Gammons et al. (2002). Where error bars are not shown for the experimentally determined formation constants they are narrower than the corresponding symbol.

associated with the derivation of the formation constants using the relationship:

$$\mathit{Overall\ Error} = 100\cdot\sqrt{\frac{\sum_{i=1}^{I}\left[\sum_{k=1}^{K}\left(A_{ik}^{\mathrm{obs}}-A_{ik}^{\mathrm{calc}}\right)^{2}\right]}{\sum_{i=1}^{I}\left[\sum_{k=1}^{K}A_{ik}^{\mathrm{obs}^{2}}\right]}} \qquad (7)$$

where I is the total number of wavelengths at which measurements were made and K is the number of solutions. The values of the overall error were compared with the accuracy of the spectral measurements, which was calculated from the values of the tolerance (see Speciation model):

$$\mathit{Accuracy} = 100\cdot\sqrt{\frac{\sum_{i=1}^{I}\left[\sum_{k=1}^{K}\mathrm{tol}^{2}\right]}{\sum_{i=1}^{I}\left[\sum_{k=1}^{K}A_{ik}^{\mathrm{obs}}2\right]}} \qquad (8)$$

where tol is the minimum tolerance required for the given speciation model. The range of formation constant values for which the overall error was lower than the accuracy of measurement gives the uncertainties listed in Table 1. More detailed descriptions of the method are given in Migdisov and Williams-Jones (2002) and Migdisov et al. (2005). The uncertainties obtained vary from ±0.11 to ±0.14 log units with the exception of that for β_2 at 200 °C, which was determined to an error of ±0.34 log units. The latter indicates that, at 200 °C, concentrations of ErCl_2^+ in experimental solutions are low and that the shifts in the spectra caused by the presence of ErCl_2^+ are of the same order of magnitude as the accuracy of the spectral recording.

5. Discussion

Although there is an extensive literature reporting basic physico-chemical properties for erbium chloride such as apparent molar volume, viscosity, and heat of dilution (e.g., Spedding et al., 1966), the only study devoted to the speciation of erbium in chloride-bearing aqueous solutions is that of Mironov et al. (1982), which reported data for 25 °C. Fortunately, the aqueous speciation of the rest of the REE group at ambient temperature has been better addressed by experimentalists (e.g., Peppard et al., 1962; Choppin and Unrein, 1963) permitting researchers to interpolate data for Er at this temperature (Wood, 1990; Haas et al., 1995). In contrast, there are no published experimental data for elevated temperatures, except one experimental determination of log K_s reported by Gammons et al. (2002) for 200 °C. We have therefore also compared the data obtained in this study with those predicted by Haas et al. (1995) and Wood (1990), and with data available for Nd species (Gammons et al., 1996; Migdisov and Williams-Jones, 2002).

In Fig. 6a and Table 2, we compare the values of log β_1 obtained in this study to those predicted theoretically by Wood (1990) and Haas et al. (1995) and a value for 200 °C estimated by Gammons et al. (2002). The values obtained in this study are in good agreement with predictions of Haas et al. (1995) and are close to the value of Gammons et al. (2002). By contrast, the values

Table 2
A comparison of the values of log β_1 obtained in this study with those recommended by others authors

T °C	This study	Haas et al., 1995	Wood, 1990	Gammons et al., 2002
25		0.31	0.26	
100	0.88	1.05	0.49	
150	1.59	1.65	0.65	
200	2.34	2.31	0.83	2.17
250	3.09	3.06	1.08	

Table 3
A comparison of the values of $\log \beta_2$ obtained in this study with those recommended by Haas et al. (1995) and Gammons et al. (2002)

T °C	This study	Haas et al., 1995	Gammons et al., 2002
25		−0.04	
100		0.94	
150		1.79	
200	2.95	2.77	2.57
250	4.12	3.94	

predicted by Wood (1990) diverge sharply from our data with increasing temperature, and at 250 °C are ~ 2 log units lower than those estimated in our study. Our values for $\log \beta_2$ (Fig. 6b, Table 3) agree reasonably well with both the theoretical estimates of Haas et al. (1995) and the value calculated by Gammons et al. (2002) at 200 °C. It should be noted, that the only parameter precisely determined by Gammons et al. (2002) was the stepwise formation constant at 200 °C. Their value for $\log \beta_1$ was estimated from theoretical reasons, and had a much higher associated error, which resulted in a similarly large error for $\log \beta_2$. The results of our experiments are therefore more accurately compared with those of Gammons et al. (2002) using stepwise formation constants ($\log K_s = \log \beta_2 - \log \beta_1$). The value of $\log K_s$ obtained in our study is 0.61 versus 0.4 in Gammons et al. (2002), which considering the relatively large uncertainty associated with determination of $\log \beta_2$ (±0.34) makes the two values indistinguishable within experimental error.

The data predict that $ErCl_2^+$ plays an important role in erbium solubility at temperatures above 100 °C and, for a wide range of Cl concentrations, predominates over $ErCl^{2+}$ at temperatures above 150 °C. Compared to the values of $\log \beta_1$ obtained for neodymium chloride species by Migdisov and Williams-Jones (2002) those obtained for erbium chloride are 0.2 to 0.4 log units higher for all temperatures, except 250 °C (Tables 4 and 5; Fig. 7). The same trend is predicted by the data of Haas et al. (1995), except that the difference ranges up to 0.6 log units. However, whereas our data for $\log \beta_2$ show that $NdCl_2^+$ is more stable than $ErCl_2^+$ at elevated temperatures (consistent with the observation of Gammons et al. (2002), that chloride complexation weakens across the lanthanide series), the data of Haas et al. (1995) predict the opposite. In order to evaluate the significance of these findings for REE mobility, we calculated the solubility of Nd-monazite ($NdPO_4$) and Er-monazite ($ErPO_4$) at 200 and 250 °C in acidic solutions ($pH = 2$) with variable chloride ion activity. Data on the solubility product of Nd-monazite were taken from Poitrasson et al. (2004) and, as there are no thermodynamic data available for Er-monazite, its solubility product was assumed to be the same as that of Nd-monazite. Results of the calculations are shown in Fig. 8, from which it can be seen that our speciation data and those of Haas et al. (1995) predict very similar solubilities for Er-monazite. However, our data predict appreciably higher solubility for Nd-monazite than do those of Haas et al. (1995). Moreover, at 250 °C we predict a higher solubility for Nd-monazite than for Er-monazite, which is the reverse of that predicted by the data of Haas et al. (1995). It thus seems likely that Nd is more mobile at elevated temperature than Er, although it should be cautioned that in the particular case of monazite-controlled REE solubility, this conclusion could be reversed if it were to be shown that the solubility product of Er-monazite is lower than that of Nd-monazite.

Table 4
A comparison of the values of $\log \beta_1$ for Er- and Nd-chloride complexes in aqueous solutions from this study and Migdisov and Williams-Jones (2002) with those of Haas et al. (1995)

T °C	$\log \beta_1$ for Er, this study	$\log \beta_1$ for Nd, Migdisov and Williams-Jones, 2002	$\log \beta_1$ for Er, Haas et al. (1995)	$\log \beta_1$ for Nd, Haas et al. (1995)
100	0.88	0.58	1.05	0.92
150	1.59	1.22	1.65	1.36
200	2.34	2.25	2.31	1.86
250	3.09	3.4	3.06	2.45

To summarize, the data obtained in this study confirm the conclusion of previous experimental (Gammons et al., 1996, 2002; Migdisov and Williams-Jones, 2002) and theoretical studies (Wood, 1990; Haas et al., 1995) that the REE form relatively weak complexes with chloride ions. However, although the stability of chloride complexes is probably about four orders of magnitude weaker than that of REE complexes with F^- (Migdisov and Williams-Jones, in preparation) which are widely believed to be the principal agents of hydrothermal REE transport, the concentration of

Table 5
A comparison of the values of $\log \beta_2$ for Er- and Nd-chloride complexes in aqueous solutions from this study and Migdisov and Williams-Jones (2002) with those of Haas et al. (1995)

T °C	$\log \beta_2$ for Er, this study	$\log \beta_2$ for Nd, Migdisov and Williams-Jones, 2002	$\log \beta_2$ for Er, Haas et al. (1995)	$\log \beta_2$ for Nd, Haas et al. (1995)
200	2.95	3.15	2.77	2.28
250	4.12	4.64	3.94	3.2

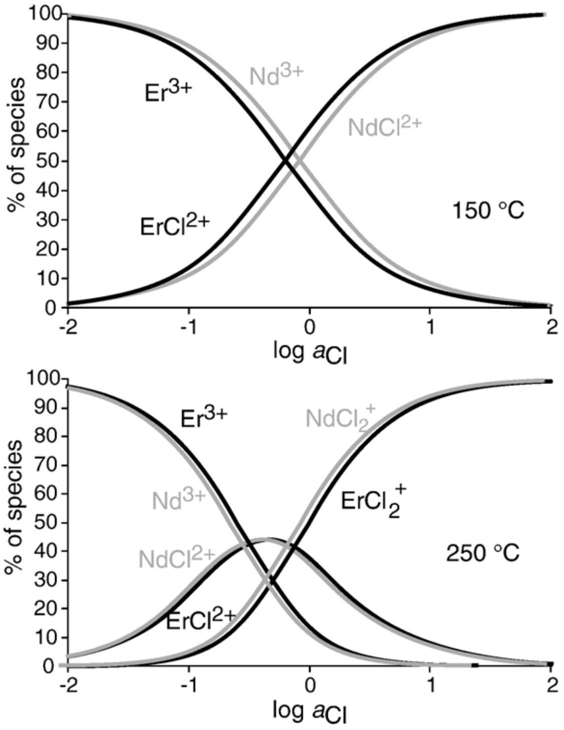

Fig. 7. Proportions of the different Er and Nd species as a function of chloride activity at 150 and 250 °C.

chlorine in REE-bearing hydrothermal solutions is commonly on the order of tens of wt.%, whereas that of fluorine is on the order of hundreds of ppm (e.g., Chiodini et al., 1991; Banks et al., 1994; Williams-Jones et al., 2000). Thus, it is possible that chloride complexation may be of far greater importance in REE transport than previously considered and in some cases may be as important for the genesis of hydrothermal REE deposits as REE-fluoride complexation.

6. Conclusions

The experimental data obtained in this study show that chloride-bearing aqueous solutions of erbium contain at least three Er species: Er^{3+}, ErCl^{2+} and ErCl$_2^+$. At 25 °C and low chloride concentrations, Er^{3+} is the dominant form of erbium in aqueous solutions. However, with increasing temperature the speciation changes, ErCl^{2+} and ErCl$_2^+$ becoming dominant for a wide range of Cl concentrations. The values of the first formation constant (β_1) are in near perfect agreement with those predicted by Haas et al. (1995), and those for the second formation constant (β_2) also agree reasonably well with their predictions. However, in contrast to Haas et al. (1995), our data suggest that at elevated temperatures Nd may be more soluble in Cl-rich aqueous solutions, than Er, i.e., that the LREE may be more readily mobilized by hydrothermal solutions than the HREE.

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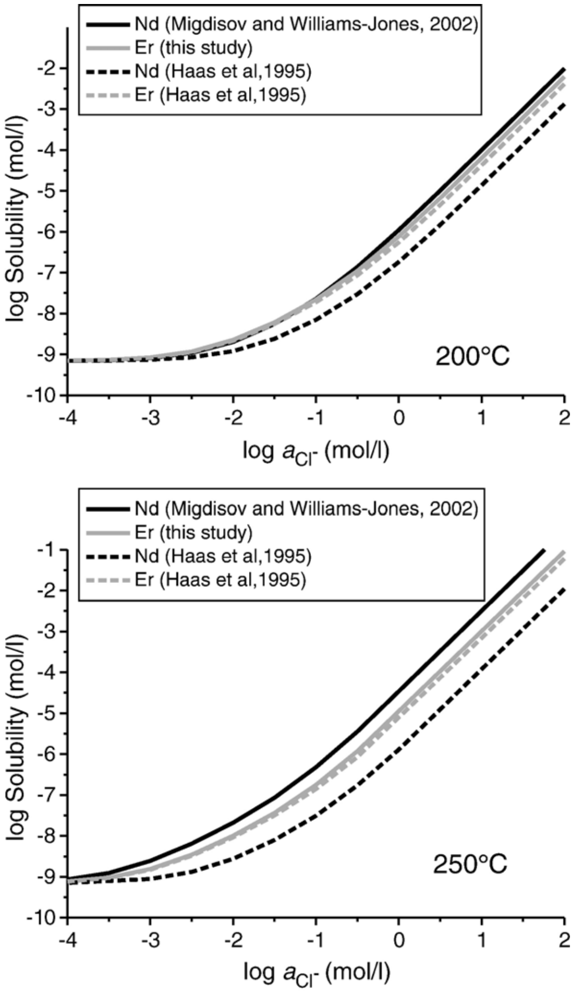

Fig. 8. The solubility of Er- and Nd-monazite at 200 and 250 °C in Cl-bearing solutions calculated using the experimental data obtained in this study and the data from Migdisov and Williams-Jones (2002). Results of the calculations are compared with predictions made using the values recommended by Haas et al. (1995). Data for the solubility products of Nd-monazite were taken from Poitrasson et al. (2004). The solubility products for Er-monazite were assumed to be the same as those for Nd-monazite.

References

Banks, D.A., Yardley, B.W.D., Campbell, A.R., Jarvis, K.E., 1994. REE composition of an aqueous magmatic fluid: a fluid inclusion study from the Capitan Pluton, New Mexico, U.S.A. Chem. Geol. 113, 259–272.

Boily, Jean-Francois, Seward, Terry M., 2005. Palladium(II) chloride complexation: spectrophotometric investigation in aqueous solutions from 5 to 125 °C and theoretical insight into Pd–Cl and Pd–OH_2 interactions. Geochim. Cosmochim. Acta. 69 (15), 3773–3789.

Carnall, W.T., 1979. The absorption and fluorescence spectra of rare earth ions in solution. Handb. Phys. Chem. Rare Earths 3, 171–208.

Chiodini, G., Cioni, R., Guidi, M., Marini, L., 1991. Chemical geothermometry and geobarometry in hydrothermal aqueous solutions: a theoretical investigation based on a mineral–solution equilibrium model. Geochim. Cosmochim. Acta 55 (10), 2709–2727.

Choppin, G.R., Unrein, P.J., 1963. Halide complexes of the lanthanide elements. J. Inorg. Nucl. Chem. 25, 387–393.

Choppin, G.R., Kelly, D.A., Ward, E.E., 1966. Effect of changes in the ionic medium on the stability constant of $Eu(NO_3)^{2+}$. AEC Access. Nos., (ORO-1797-2). 21 pp.

Dongarra, J.J., Bunch, J.R., Moler, C.B., Stewart, G.W., 1979. LINPACK Users' Guide. SIAM, Philadelphia.

Gammons, C.H., Wood, S.A., Williams-Jones, A.E., 1996. The aqueous geochemistry of the rare earth elements and yttrium: VI. Stability of neodymium chloride complexes from 25 to 300 °C. Geochim. Cosmochim. Acta 60, 4615–4630.

Gammons, C.H., Wood, S.A., Li, Y., 2002. Complexation of the rare earth elements with aqueous chloride at 200 °C and 300 °C and saturated water vapor pressure. Special Publication — The Geochemical Society, (Water–Rock Interactions Ore Deposits, and Environmental Geochemistry), pp. 191–207.

Haas, J.R., Shock, E.L., Sassani, D.C., 1995. Rare earth elements in hydrothermal systems: estimates of standard partial molal thermodynamic properties of aqueous complexes of the rare earth elements at high pressures and temperatures. Geochim. Cosmochim. Acta 59, 4329–4350.

Helgeson, H.C., 1969. Thermodynamics of hydrothermal systems at elevated temperatures and pressures. Am. J. Sci. 267, 729–804.

Helgeson, H.C., Kirkham, D.H., Flowers, G.C., 1981. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600 °C and 5 kb. Am. J. Sci. 281, 1249–1516.

Hug, S.J., Sulzberger, B., 1994. In situ Fourier transform infrared spectroscopic evidence for the formation of several different surface complexes of oxalate on TiO_2 in the aqueous phase. Langmuir 10, 3587–3597.

Kielland, J., 1937. Individual activity coefficients of ions in aqueous solutions. J. Am. Chem. Soc. 59, 1675–1678.

Migdisov, Art.A., Williams-Jones, A.E., 2002. A spectrophotometric study of neodymium (III) complexation in chloride solutions. Geochim. Cosmochim. Acta 66, 4311–4323.

Migdisov, Art.A, Williams-Jones, A.E., in preparation. An experimental study of solubility and speciation of neodymium (III) fluoride in HF-bearing solutions at temperatures up to 250 °C.

Migdisov, Art.A., Reukov, V.V., Williams-Jones, A.E., 2006. A spectrophotometric study of neodymium (III) complexation in sulfate solutions at elevated temperatures. Geochim. Cosmochim. Acta. 70 (4), 983–992.

Mironov, V.E., Avramenko, N.I., Koperin, A.A., Blokhin, V.V., Eike, M.Yu., Isayev, I.D., 1982. Thermodynamics of the formation reaction of the monochloride complexes of the rare earth metals in aqueous solutions. Koord. Khim. 8, 636–638.

Peppard, D.F., Mason, G.W., Hucher, I., 1962. Stability constants of certain lanthanide(III) and actinide(III) chloride and nitrate complexes. J. Inorg. Nucl. Chem. 24, 881–888.

Poitrasson, F., Oelkers, E., Schott, J., Montel, J.-M., 2004. Experimental determination of synthetic $NdPO_4$ monazite end-member solubility in water from 21 °C to 300 °C: implications for rare earth element mobility in crustal fluids. Geochim. Cosmochim. Acta 68, 2207–2221.

Smith, M.P., Henderson, P., 2000. Preliminary fluid inclusion constraints on fluid evolution in the Bayan Obo Fe–REE–Nb deposit, Inner Mongolia, China. Econ. Geol. 95, 1371–1388.

Spedding, F.H., Pikal, M.J., Ayers, B.O., 1966. Apparent molal volumes of some aqueous rare earth chloride and nitrate solutions at 25 °C. J. Phys. Chem. 70, 2440–2449.

Stepanchikova, S.A., Kolonin, G.R., 1999. Spectrophotometric study of complexation of neodymium in chloride solutions at temperatures up to 250 °C. Zh. Neorg. Khim. 44, 1744–1751.

Sverjensky, D.A., Shock, E.L., Helgeson, H.C., 1997. Prediction of the thermodynamic properties of aqueous metal complexes to 1000 °C and 5 kb. Geochim. Cosmochim. Acta 61, 1359–1412.

Suleimenov, O.M., Seward, T.M., 2000. Spectrophotometric measurements of metal complex formation at high temperatures: the stability of Mn(II) chloride species. Chem. Geol. 167, 177–192.

Tagirov, B., Zotov, A.V., Akinfiev, N.N., 1997. Experimental study of dissociation of HCl from 350 to 500 °C and from 500 to 2500 bars, thermodynamic properties of HCl°(aq). Geochim. Cosmochim. Acta 61, 4267–4280.

Williams-Jones, A.E., Samson, I.M., Olivo, G.R., 2000. The genesis of hydrothermal fluorite-REE deposits in the Gallinas Mountains, New Mexico. Econ. Geol. 95, 327–341.

Wood, S.A., 1990. The aqueous geochemistry of the rare-earth elements and yttrium. Theoretical predictions of speciation in hydrothermal solutions to 350 °C at saturation water vapor pressure. Chem. Geol. 88, 99–125.

Wood, S.A., Palmer, D.A., Wesolowski, D.J., Benezeth, P., 2002. The aqueous geochemistry of the rare earth elements and yttrium. Part XI. The solubility of $Nd(OH)_3$ and hydrolysis of Nd^{3+} from 30 to 290 °C at saturated water vapor pressure with in-situ pH measurement. Special Publication — The Geochemical Society, (Water–Rock Interactions Ore Deposits, and Environmental Geochemistry), pp. 229–256.