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Complexation of the rare earth elements with aqueous chloride at 200 °C and 300 °C and saturated water vapor pressure

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Abstract—The stabilities of aqueous chloride complexes of the rare earth elements (REE) at elevated temperature have been evaluated using the indirect solubility method. The solubility of silver chloride was measured at 200 °C and 300 °C, saturated vapor pressure, 0.1 or 1.0m NaCl + HCl, and 0 to 0.3m $LnCl_3$, where Ln stands for any trivalent lanthanide. The change in AgCl solubility in the presence of an incremental increase in $LnCl_3$ was used to quantify the extent of complexation between chloride ion and each REE cation. Combined with our previous results for neodymium (Gammons et al., 1996), we now have experimentally-derived estimates for the formation constants of Ln-chloride complexes at elevated temperature for all of the rare earth elements, with the exception of promethium and dysprosium.

This study shows that all of the rare earth elements have a similar affinity for aqueous chloride in high-temperature, acidic solutions. The average ligand number for REE-chloride complexes at 300 °C in 0.1 and 1.0m chloride solutions is 2.0±0.2, indicating that $LnCl_2^+$ is the dominant species under these conditions, in agreement with our previous results for neodymium. At 200 °C, 1.0m chloride, the average ligand number is 1.14±0.24, indicating that $LnCl^{2+}$ is dominant. Inter-element deviations in ligand number show no consistent variation across the periodic table at 300 °C, but show a weak trend towards decreased complexation with higher atomic number at 200 °C. The data at 200 °C were used to estimate log K for the reaction $Ln^{3+} + 2Cl^- \leftrightarrow LnCl_2^+$ (β_2). The average value for 11 elements was 2.73±0.47. This compares favorably with an estimate of log $\beta_2 = 2.52$ obtained by Gammons et al. (1996) from a more detailed study of neodymium. Attempts to calculate log β_1 were hindered by a lack of data over a sufficient range in chloride concentration.

Our experimental results are in close agreement with the theoretical estimates of Haas et al. (1995) at 200 °C; however, at 300 °C, our study indicates a wider predominance of the $LnCl_2^+$ species. Both our study and that of Haas et al. (1995) show small systematic variations in the stability of chloride complexes of the lanthanide elements across the periodic table. If chloride complexes are the dominant form of REE transport in hydrothermal systems, aqueous complexation by itself should not result in large REE fractionation trends.

1. INTRODUCTION

The hydrothermal geochemistry of the rare earth elements (REE) has relevance to a wide spectrum of geological disciplines, including igneous and metamorphic petrology, isotope geochemistry, economic geology, and environmental geochemistry. Much effort has been put forth in recent years to document the REE concentrations of naturally-occurring hydrothermal systems (see Michard et al., 1983; Michard and Albarède, 1986; Michard, 1989; Klinkhammer et al., 1994; Bau and Dulski, 1999; Douville et al., 1999; and references therein). Most of these studies have focused on deep-sea hydrothermal vents. In a compilation of existing data, Klinkhammer et al. (1994) showed that the REE concentrations of hydrothermal fluids near oceanic spreading centers are remarkably similar, with pronounced enrichments in LREE relative to chondrite compositions, and a very strong positive europium anomaly. Based on a limited database, Michard (1989) showed that continental geothermal waters are much more variable in terms of their REE content. Recent research (e.g., van Middlesworth and Wood, 1998; Shannon et al., 1999) is improving our understanding of REE in continental geothermal systems.

In order to fully understand the behavior of REE in hydrothermal systems, data are needed on the form and stability of aqueous REE complexes at elevated temperature. Using different approaches, Wood (1990) and Haas et al. (1995) derived theoretical estimates for the high-temperature stability constants of a large number of potentially important aqueous REE species. However, theoretical studies of this nature are prone to uncertainty due to the difficulty of extrapolating low-temperature data that are, in many cases, incomplete or of dubious accuracy. Gammons et al. (1996) used an experimental solubility method to derive stability constants for the chloride complexes of neodymium up to 300 °C. This study showed that the Nd-chloride complexes, although quite weak at ambient temperature, become much stronger as temperature increases. The stability constants at T > 200 °C were higher than originally predicted by Wood (1990), but were in closer agreement with the estimates of Haas et al. (1995). Based on these results, Gammons et al. (1996) suggested that chloride complexes could dominate the speciation of neodymium and other REE in high-temperature brines, such as sea-floor vents. A similar conclusion has recently been reached by Douville et al. (1999) and Bau and Dulski (1999).

The purpose of this paper is to expand on the experimental study of Gammons et al. (1996), to include all of the lanthanide elements. The same experimental approach and methods of interpretation are employed. The results are then used to identify inter-element variation in the stability of REE-chloride complexes at elevated temperature, and to predict systematic changes in the behavior of REE in chloride-rich hydrothermal fluids.

2. METHODOLOGY

The approach used in this study is identical to that of Gammons et al. (1996). Briefly, the effect of incremental addition of lanthanide chloride salt on the solubility of AgCl (the mineral chlorargyrite) is used to derive the stoichiometry of the dominant REE(III) chloride complexes. A number of previous experimental studies of hydrothermal complexation have used a similar technique, including Ruaya and Seward (1986), Williams-Jones and Seward (1989), Gammons (1995), and Gammons and Seward (1996).

2.1. Solution Preparation

A stock solution containing 0.9 molal NaCl and 0.1 molal HCl (1.0 molal total chloride) was prepared gravimetrically from analytical grade NaCl and a 1.0M HCl volumetric standard. A second set of stock solutions containing 1.0 molal $LnCl_3 \cdot xH_2O$ in a 0.9m NaCl + 0.1m HCl matrix was prepared for Ln = La, Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb. The lanthanide salts were purchased from Alfa Aesar, and had a quoted purity of > 99.9% in all cases. Neodymium was excluded from the list, as we have previously studied this element in detail (Gammons et al., 1996). Also, we did not attempt to investigate promethium, the radioactive lanthanide. With the exception of $DyCl_3 \cdot xH_2O$, all of the solids dissolved completely to yield solutions that were clear and of variable color. The holmium and erbium solutions were deep pink, the praseodymium solutions were deep green, samarium was pale yellow, and the remainder were colorless, or nearly so. Because the $DyCl_3$ solid did not dissolve completely, the concentration of this stock sample was reduced to 0.5 molal.

To confirm the stoichiometry of the lanthanide reagents, small aliquots of each salt were digested in dilute nitric acid and analyzed for their REE concentration by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and their chloride content by ion chromatography (IC). The results showed that all of the salts had the correct 1:3 REE:Cl stoichiometry, within the analytical precision (roughly 5%). Because of the hygroscopic nature of many of the salts (some were a watery crystal mush), the exact REE concentration of each nominal 1.0-molal stock solution was determined by ICP-AES after preparation of the solutions.

For each rare earth element, a set of 8 experimental solutions was prepared by mixing the 1.0m NaCl+HCl stock with the 1.0m lanthanide chloride stock to create solutions with final REE concentrations ranging from 0 to roughly 0.3 molal $LnCl_3$, all with a matrix of exactly 0.9m NaCl + 0.1m HCl. The acid was added to avoid potential complications associated with hydrolysis. A second set of experimental solutions containing variable amounts of REE in a 0.09m NaCl + 0.01m HCl matrix was prepared for the elements lanthanum, holmium, and lutetium by dilution of the corresponding 1.0m samples. Each solution was then used in separate solubility experiments at 300 °C and 200 °C, as discussed below. This procedure created a (15 x 8 x 2) data set, for a total of 240 individual samples. In addition, replicate samples were run for roughly 10% of the total matrix.

2.2. Indirect Solubility Experiments

For the solubility experiments, approximately 3 mL of each NaCl/HCl/$LnCl_3$ solution were transferred to a silica-glass tube (9mm O.D., 7mm I.D., 15cm length) which contained a pre-weighed pellet of AgCl and a narrow constriction at a point roughly 25-35% from one end (see Seward, 1976). The tubes were sealed under a slight vacuum, and were placed inside small stainless steel autoclaves containing 20 mL of distilled water. The autoclaves were then placed vertically inside an air-thermostated oven having a maximum temperature variation of ±1.0 °C at 300 °C. The experiments were equilibrated at 200 °C or 300 °C for a period of 1 to 2 weeks. This was considered ample time to achieve equilibrium, based on our previous experience and on the earlier study of Seward (1976). At the end of the experiment, the autoclaves were removed from the oven and immersed in water. Before quenching, the autoclaves were inverted and shaken, allowing the solutions to separate from the AgCl pellets (which remained trapped above the constrictions) during cooling. Within minutes of the quench, most of the dissolved silver had precipitated as fine-grained, feather-shaped AgCl crystals in the bottom of the tubes. This precipitate, like the AgCl pellets, was pure white in color.

After opening the tubes, the AgCl pellets were recovered, rinsed, dried, and weighed to ±0.1 mg to determine the high-temperature silver solubility by mass loss. An independent measure of the AgCl solubility was obtained by digesting the fresh precipitate in the bottom of each tube with concentrated NH_4OH solution. The tube walls and precipitate had to be carefully rinsed with water at least twice before this step to rid the solutions of aqueous lanthanide (otherwise, a fine-grained hydrolysis precipitate formed when the basic NH_4OH was added). These solutions were diluted with 1% NH_4OH prior to analysis for silver via flame atomic absorption spectroscopy (detection limit 0.1 mg/kg, precision ±2%), using matrix-matched standards. In most cases, the agreement between the mass loss and AAS results was better than ±5%. Because the AAS results were more precise (especially at 200 °C), they were deemed more reliable.

2.3. Data Interpretation

The methods used to interpret our solubility data are identical to those described in Gammons et al. (1996). The reader is referred to that paper for details that are not covered in the following summary.

Two methods were used to interpret our solubility results. The first was a forward modeling procedure in which the change in AgCl solubility due to addition of $LnCl_3(s)$ was calculated for a given set of initial conditions. Parallel calculations were made assuming integral values of the average ligand number of the Ln(III) chloride complexes (n = 0 to 4). By comparing these results with the measured solubilities, the average n values of the experimental solutions were obtained. In the second set of calculations, the measured solubility data were regressed to derive cumulative formation constants for the Ln(III) chloride complexes. The program employed at this step was a modification of the non-linear least squares algorithm HACK (Aldridge and Seward, 1976). The user first inputs a set of isothermal solubility data, along with a set of initial guesses for the $LnCl_n^{3-n}$ formation constants. For each data entry, a model AgCl solubility is calculated (S_{calc}), which is compared to the measured AgCl solubility (S_{meas}). On the basis of these results, new estimates of the Ln(III) formation constants are obtained, and the process is repeated until the sum of the squares of the residuals $[(S_{calc}-S_{meas})/S_{meas}]^2$ is minimized. Mass-balance relations for ΣH^+, ΣCl and ΣH_2O in each experiment were adjusted for dissolution of the solids.

To perform the modeling calculations, a complete aqueous speciation needed to be calculated for each solution. To be consistent with our previous study of neodymium, the same procedures were used. Individual ion activity coefficients for all charged species were calculated using the following version of the extended Debye-Hückel equation (Helgeson, 1969):

$$\log \gamma_n = -\frac{A|Z_n|^2 I^{1/2}}{1 + BaI^{1/2}} + bI \quad (1)$$

Values for *a* (distance of closest approach) for H^+ and Cl^- were taken from Kielland (1937); those for dissolved Ag species were taken from Seward (1976); those for all aqueous lanthanide species were set at 9 Ångstroms. Values for *b* (the deviation function) were taken from Table 26 of Helgeson et al. (1981), using NaCl as the model solute. Thermodynamic data for the Ag(I) chloride complexes were taken from Zotov et al. (1986a,b) and Levin (1991), and are similar to the results of the previous solubility study of Seward (1976). Data for NaCl and HCl ion-pairing were taken from Mesmer et al. (1988) and Frantz and Marshall (1984), respectively. Although considerable controversy remains as to the extent of HCl ion-pairing in hydrothermal solutions (cf. Pokrovskii, 1999), our results were not highly sensitive to uncertainty in this parameter due to the relatively low temperatures involved and the fact that NaCl was the dominant electrolyte. In addition, no attempt was made to adjust equilibrium constants for the slight deviation between the saturated vapor pressure of pure water vs. the $NaCl-HCl-LnCl_3$ solutions used in this study. Our most concentrated solutions were 1.9 molal in combined salts, which corresponds to roughly 10 wt% NaCl equivalent. Using tabulated data from Haas (1971), the saturated vapor pressure at 300 °C for pure water is 85.9 bars, vs. 80.0 bars for a 10 wt% NaCl solution. At 200 °C, the difference is 15.6 bars vs. 14.5 bars. Thus, we feel that any pressure effect in our study due to changes in salt concentration is negligible.

In previous studies employing the indirect solubility approach, effort has been made to perform experiments over as wide a range as possible in temperature and total chloride concentration. The data obtained were then regressed to determine the association constants for the aqueous metal chloride complexes as a function of temperature. A detailed study of this type has been performed for the neodymium(III) chloride system (Gammons et al., 1996). However, the number of experiments necessary to accomplish this task for all 12 of the remaining stable lanthanide elements was deemed prohibitive. Therefore, instead of repeating the entire range of experimental conditions for each element, we decided to select one initial experimental condi-

Table 1. Solubility data for 0.9m NaCl + 0.1m HCl matrix solutions.[1]

$LnCl_3$	AgCl solubility 200° C	AgCl solubility 300° C
lanthanum (La)		
0.0000	0.0179	0.115
0.0250	0.0198	0.116
0.0500	0.0184	0.123
0.1000	0.0197	
0.1500	0.0214	0.125
0.2000	0.0240	0.135
0.2500	0.0280	0.142
0.3000		0.147
cerium (Ce)		
0.0000	0.0191	0.114
0.0218	0.0198	0.117
0.0436	0.0208	0.121
0.0873	0.0215	0.131
0.1309	0.0241	0.133
0.1746		0.135
0.2182	0.0277	0.143
0.2618	0.0299	0.150
praseodymium (Pr)		
0.0000	0.0193	
0.0219	0.0228	0.121
0.0438	0.0197	0.119
0.0876	0.0235	0.122
0.1314	0.0251	0.125
0.1752	0.0276	0.131
0.2190	0.0292	0.139
0.2628	0.0314	0.137
samarium (Sm)		
0.0000	0.0193	0.102
0.0230	0.0183	0.100
0.0460	0.0188	0.110
0.0920	0.0213	0.114
0.1380	0.0196	0.125
0.1840	0.0267	0.138
0.2300	0.0295	0.140
0.2760	0.0296	0.143
europium (Eu)		
0.0000	0.0206	0.111
0.0225	0.0249	0.114
0.0450	0.0218	0.125
0.0900	0.0237	0.122
0.1350	0.0255	0.121
0.1800	0.0277	
0.2250	0.0296	0.133
0.2700	0.0317	0.139
gadolinium (Gd)		
0.0000	0.0164	0.100
0.0250	0.0178	0.114
0.0500	0.0194	0.108
0.1000	0.0189	0.112
0.1500	0.0239	0.120
0.2000	0.0279	0.131
0.2500	0.0269	0.134
0.3000	0.0313	0.144
terbium (Tb)		
0.0000	0.0212	0.105
0.0250	0.0221	0.111
0.0500	0.0221	0.104
0.1000	0.0268	0.116
0.1500	0.0255	0.135
0.2000	0.0273	0.134
0.2500	0.0296	0.143
0.3000	0.0321	0.148
holmium (Ho)		
0.0000	0.0183	0.106
0.0227		0.109
0.0454	0.0211	0.110
0.0907	0.0235	0.115
0.1361	0.0250	0.132
0.1814	0.0272	0.137
0.2268	0.0297	0.143
0.2721	0.0324	0.147
erbium (Er)		
0.0000	0.0199	0.117
0.0216	0.0214	0.119
0.0431	0.0208	0.121
0.0862	0.0240	0.126
0.1293	0.0253	
0.1724	0.0298	
0.2155	0.0297	
0.2586	0.0315	
thulium (Tm)		
0.0000	0.0193	0.125
0.0250	0.0207	0.132
0.0250	0.0203	
0.0500	0.0223	0.127
0.1000	0.0235	0.130
0.1500	0.0257	
0.2000	0.0306	0.145
0.2000	0.0282	
thulium (cont.)		
0.2500	0.0292	0.151
0.3000	0.0354	0.162
0.3000	0.0368	
ytterbium (Yb)		
0.0000	0.0193	0.112
0.0000	0.0193	0.112
0.0218	0.0205	0.114
0.0218	0.0204	
0.0435	0.0216	0.117
0.1740	0.0271	0.130
0.0870	0.0222	0.125
0.0870	0.0238	
0.1305	0.0248	0.124
0.1305	0.0253	
0.1740		0.128
0.1740		0.128
0.2175	0.0297	0.135
0.2610		0.141
0.2610		0.140
lutetium (Lu)		
0.0000	0.0212	0.115
0.0250	0.0207	0.119
0.0500	0.0243	0.130
0.1000	0.0274	0.127
0.1000	0.0274	0.127
0.1500	0.0315	0.137
0.2000	0.0319	0.142
0.2500	0.0322	0.148

[1] All concentrations are in molal (moles/kg H_2O).

tion (1.0 molal NaCl + HCl matrix), and perform a series of identical experiments for all of the REE. Additional experiments in a 0.1-molal NaCl + HCl matrix were performed for lanthanum (a light REE), holmium (a middle REE) and lutetium (a heavy REE). Two temperatures were selected for examination: 300 °C, where complexation is strong, and 200 °C, where interactions are weaker, but still measurable. The data so obtained provide an internally consistent comparison of the extent of interaction of each trivalent lanthanide with aqueous chloride.

3. RESULTS

The experimental data are summarized in Tables 1 and 2. The data have been arranged by element, with

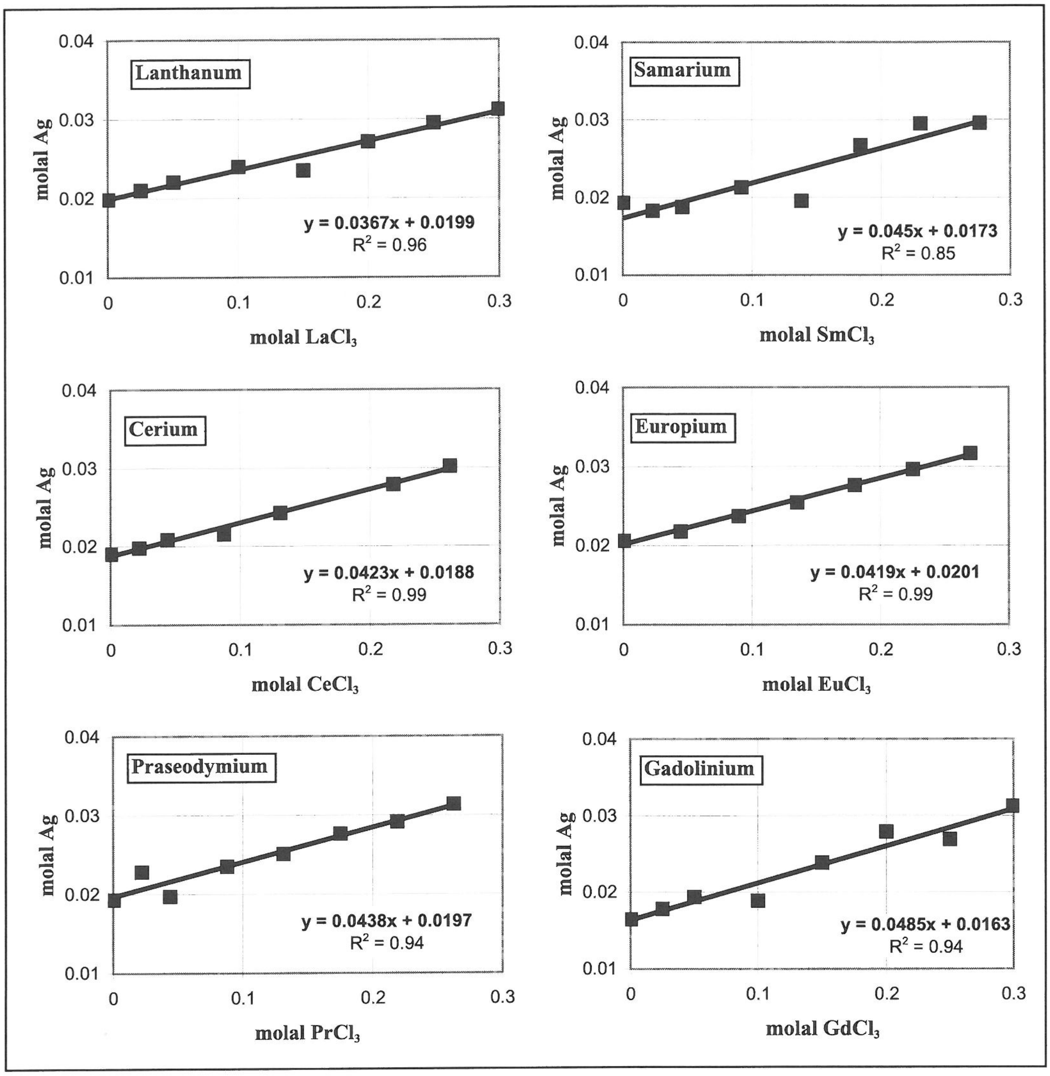

Fig. 1 The solubility of AgCl as a function of $LnCl_3$ concentration (Ln = La, Ce, Pr, Sm, Eu, Gd) at 200 °C, in 0.9m NaCl + 0.1m HCl matrix solutions.

the first column showing the total concentration of the 1:3 $LnCl_3$ salt, and the next two columns giving the measured AgCl solubility at 200 °C and 300 °C. Experiments using $DyCl_3$ gave results that were erroneous when compared to the other elements, and therefore data for dysprosium are not shown. This problem was traced to an error in preparation of the 0.5m $DyCl_3$ stock solution. Within a given series (i.e., same element, temperature, and NaCl/HCl concentration), all of the samples were run simultaneously in the same laboratory oven. The total initial chloride concentration of each sample (before interaction with AgCl) can be computed by the expression:

$$m\Sigma Cl_i = mNaCl_i + mHCl_i + 3mLnCl_{3,i} \qquad (2)$$

where $mLnCl_{3,i}$ is the $LnCl_3$ molality of the starting solutions. Lanthanide was added to the initial solutions as a chloride salt with a REE:Cl ratio of 1:3. This salt dissolves completely into the solutions by the general reaction:

$$LnCl_3(s) \rightarrow LnCl_n^{3-n} + (3-n)Cl^- \qquad (3)$$

where Ln stands for any trivalent rare earth element. The general reaction can be recast as follows, assuming integral values of n, the average ligand number, ranging from 0 to 4:

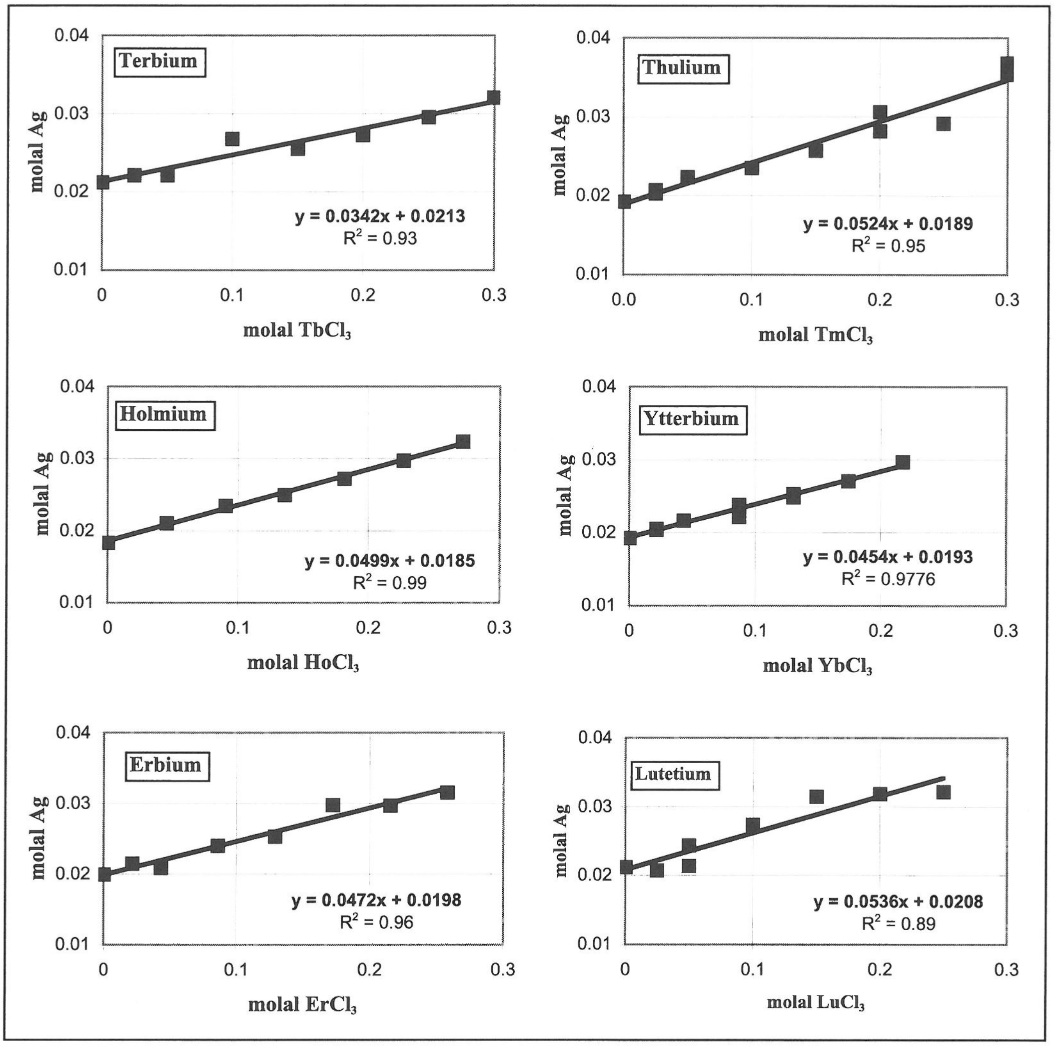

Fig. 2 The solubility of AgCl as a function of $LnCl_3$ concentration (Ln = Tb, Ho, Er, Tm, Yb, Lu) at 200 °C, in 0.9m NaCl + 0.1m HCl matrix solutions.

$$LnCl_3(s) \rightarrow Ln^{3+} + 3Cl^- \qquad (4)$$

$$LnCl_3(s) \rightarrow LnCl^{2+} + 2Cl^- \qquad (5)$$

$$LnCl_3(s) \rightarrow LnCl_2^+ + Cl^- \qquad (6)$$

$$LnCl_3(s) \rightarrow LnCl_3(aq) \qquad (7)$$

$$LnCl_3(s) \rightarrow LnCl_4^- - Cl^- \qquad (8)$$

Addition of lanthanide changes the total chloride mass balance to an extent that is proportional to the average ligand number of the dominant aqueous Ln species at the temperature of the experiment. Because the solubility of AgCl is sensitive to any such change in m_{Cl^-}, the data in Table 1 may be used to constrain the stoichiometry of the REE complexes.

3.1. Graphical Interpretation

Solubility data for each series of experiments are plotted vs. ΣLn molality in Figures 1 and 2 (1.0 molal NaCl/HCl at 200 °C), Figures 3 and 4 (1.0 molal NaCl/HCl at 300 °C), and Fig. 5 (0.1 molal NaCl/HCl at 200 °C and 300 °C). Linear regression was employed on each data set. The derived slope and intercept values are shown on each diagram, and are summarized in Table 3. All of the experiments at the

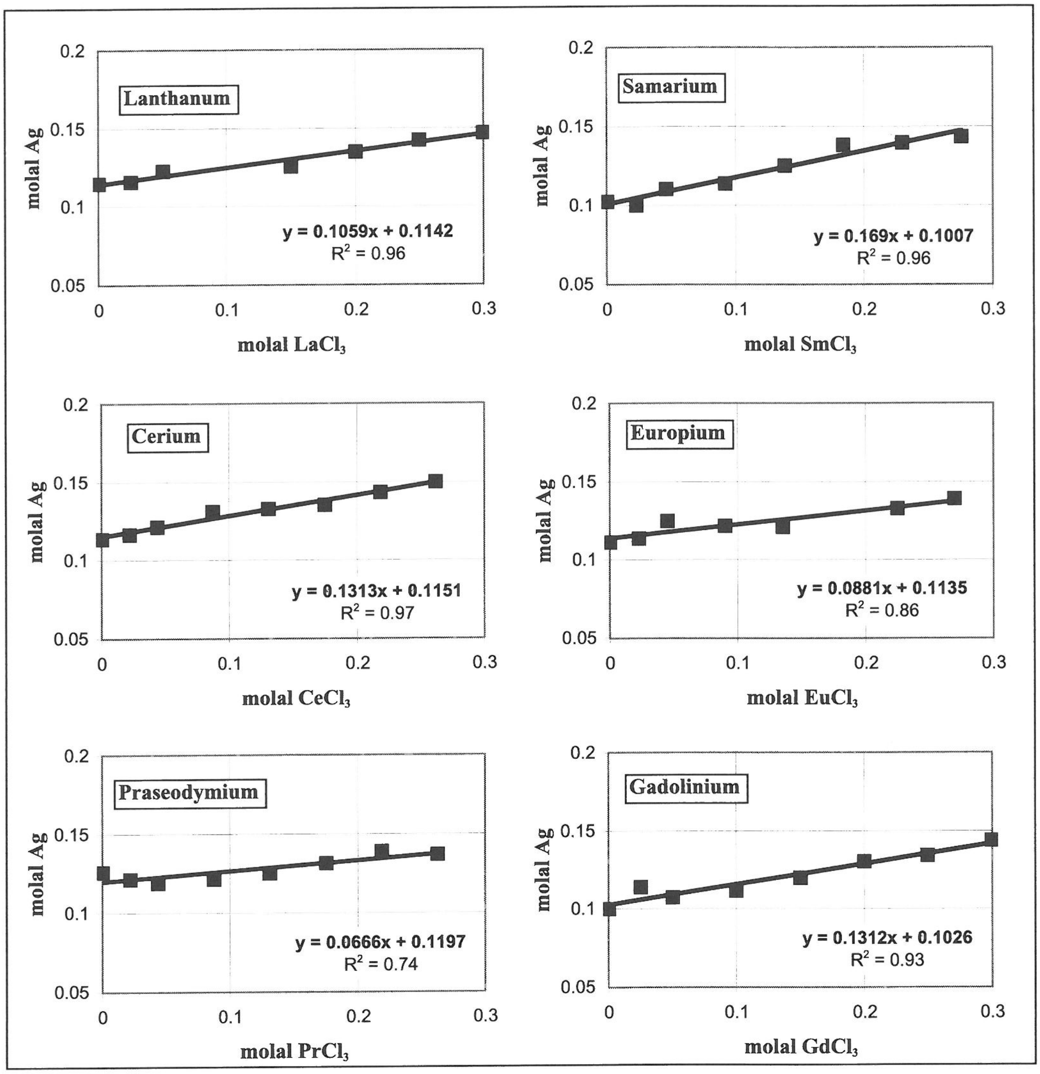

Fig. 3 The solubility of AgCl as a function of $LnCl_3$ concentration (Ln = La, Ce, Pr, Sm, Eu, Gd) at 300 °C, in 0.9m NaCl + 0.1m HCl matrix solutions.

same temperature and total chloride molality should theoretically give the same y-intercept, which is the Ag solubility value at $\Sigma Ln = 0$. Deviation in this case can be used to estimate the experimental error. At 200 °C, 1.0m ΣCl, the geometric mean intercept value was 0.0191±0.0014 molal Ag, with a relative standard deviation (1σ/mean) of 7.3%. At 300 °C, 1.0m ΣCl, the mean value was 0.112±0.0069 molal Ag, with a relative standard deviation of 6.2%. The corresponding relative standard deviations for experiments at 0.1 molal ΣCl were 4.1% and 3.3% at 200° and 300 °C, respectively. The smaller deviations at 0.1 molal are partly due to the smaller number of experiments run at this condition, but also to the fact that all of the 0.1-molal experiments were run simultaneously in the same oven, and therefore equilibrated at precisely the same temperature.

As a check on the accuracy of our experimental methods, our results for AgCl solubility at $\Sigma Ln = 0$ were compared with previous solubility studies of Seward (1976) and Zotov et al. (1986b). Seward (1976) obtained AgCl solubilities of 0.00196 and 0.0199 molal at 200 °C, 0.1m and 1.0m NaCl, respectively. These are both in excellent agreement with our mean intercept values of 0.0020 and 0.0190 molal, respectively. Seward (1976) did not perform

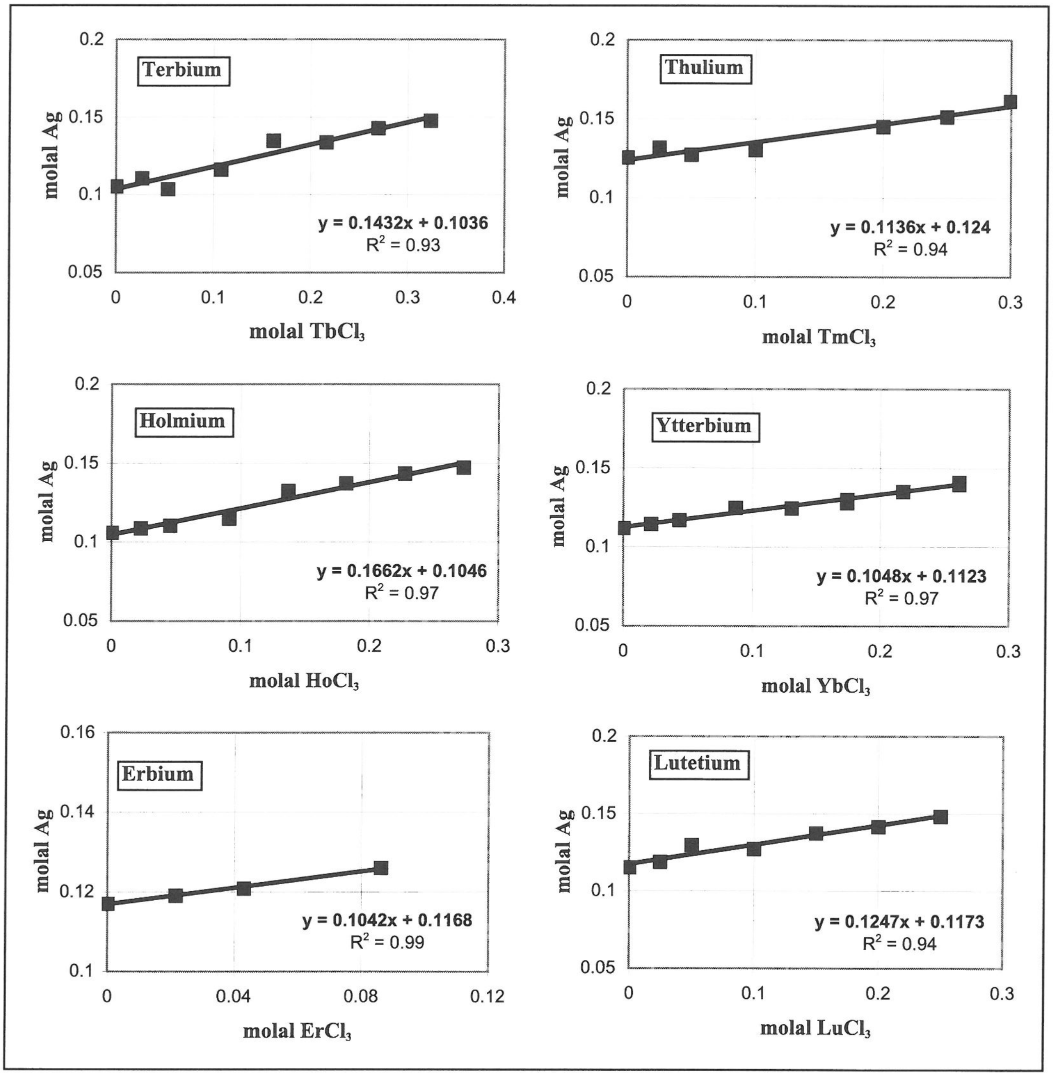

Fig. 4 The solubility of AgCl as a function of $LnCl_3$ concentration (Ln = Tb, Ho, Er, Tm, Yb, Lu) at 300 °C, in 0.9m NaCl + 0.1m HCl matrix solutions.

experiments at 300 °C, so a direct comparison cannot be made at this temperature. However, our results are in very close agreement with the data of Zotov et al. (1986), who obtained AgCl solubilities of 0.0166 and 0.080 molal at 300 °C and 0.1m and 1.0m NaCl, respectively.

The results of forward modeling calculations are summarized in Figures 6 through 9. Each diagram includes a group of curves emanating from the y-intercept ($\Sigma Ln = 0.0$). These represent hypothetical AgCl solubilities calculated by the forward modeling procedure assuming integral values of n (see Section 2.3). The curves have slopes that are positive (n = 0,1,2), zero (n = 3) or negative (n = 4). These contrasting effects are understood by examination of reactions (4) to (8). For example, dissolution of $LnCl_3$ as Ln^{3+} (n = 0) releases 3 moles of chloride ion for each mole of lanthanide salt added (reaction 4), resulting in a very sharp increase in AgCl solubility. In contrast, dissolution of $LnCl_3$ as $LnCl_4^-$ (n = 4) consumes free chloride (reaction 8), resulting in a proportional decrease in AgCl solubility.

The shaded regions in Figs. 6 to 9 show the total range in solubility for *all* of the REE-NaCl-HCl experiments. This information can be used to quickly assess what the dominant REE species are likely to be

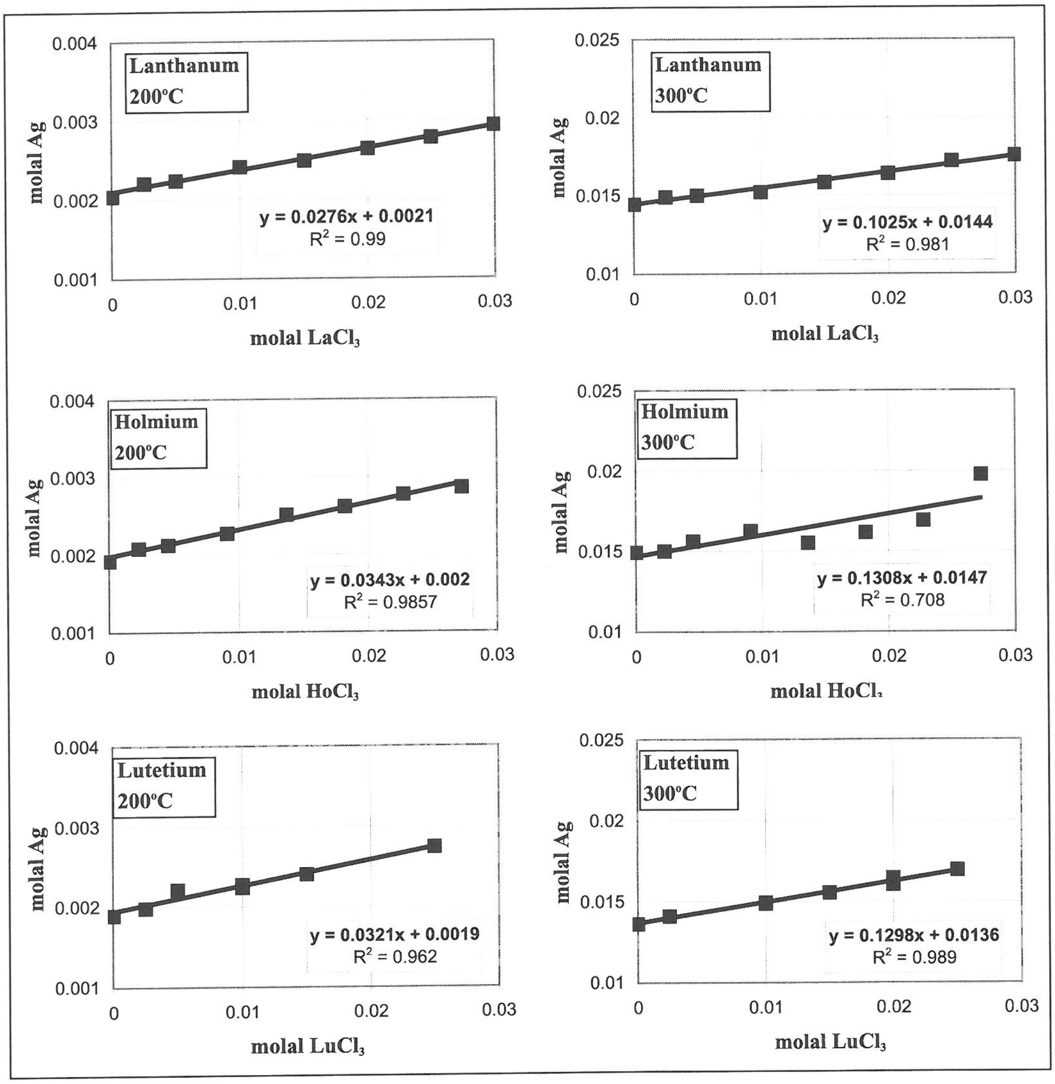

Fig. 5 The solubility of AgCl as a function of $LnCl_3$ concentration (Ln = La, Ho, Lu) in 0.09m NaCl + 0.01m HCl matrix solutions at both 200 °C and 300 °C.

at each temperature and chloride concentration. From Figures 6 and 7, it is evident that the ligand numbers for the REE at 200 °C and 0.1 to 1.0 molal NaCl/HCl matrix solutions tend to cluster around an average value slightly greater than one. This indicates that $LnCl^{2+}$, or the 1:1 species, is the dominant aqueous complex under these conditions, but that $LnCl_2^+$ is also present. In contrast, ligand numbers at 300 °C and 0.1 to 1.0 molal NaCl/HCl matrix (Figs. 8 and 9) are centered near a value of 2, suggesting that $LnCl_2^+$, the 1:2 species, is dominant.

The average ligand numbers (n) for each set of experimental data were quantified by comparing the experimental and forward modeling results using a simple spreadsheet. The derived n values are summarized in the final column of Table 3. At 200 °C, 1.0m ΣCl, the mean n value is 1.14 ± 0.24, with a relative standard deviation of 21%. At 300 °C, 1.0m ΣCl, the mean n value increases to 2.03 ± 0.21, with a relative standard deviation of 10%. Although fewer experiments were performed at 0.1 molal ΣCl, the results suggest that average ligand numbers are not appreciably different. This implies that, at each temperature, a single complex is dominant over a fairly large range in chloride concentration. At 200 °C, this complex must be the 1:1 species; at 300 °C, it is the 1:2 species.

Table 2. Solubility data for 0.09m NaCl + 0.01m HCl matrix solutions. [1]

$LnCl_3$	AgCl solubility		$LnCl_3$	AgCl solubility		$LnCl_3$	AgCl solubility	
	200° C	300° C		200° C	300° C		200° C	300° C
lanthanum (La)			**holmium (Ho)**			**lutetium (Lu)**		
0.0000	0.00204	0.0145	0.00000	0.00192	0.0150	0.0000	0.00189	0.0136
0.0025	0.00221	0.0149	0.00228	0.00208	0.0150	0.0025	0.00198	0.0141
0.0050	0.00224	0.0150	0.00455	0.00212	0.0156	0.0050	0.00221	
0.0100	0.00241	0.0152	0.00910	0.00227	0.0163	0.0100	0.00224	0.0149
0.0150	0.00249	0.0158	0.01365	0.00251	0.0155	0.0100	0.00228	0.0149
0.0200	0.00264	0.0164	0.01820	0.00261	0.0161	0.0150	0.00240	0.0156
0.0250	0.00278	0.0172	0.02275	0.00277	0.0169	0.0200		0.0164
						0.0200		0.0160

[1] All concentrations are in molal (moles/kg H_2O).

Table 3. Summary of graphical parameters derived from solubility data shown in Figures 1 to 5.

element	slope	intercept	lig.[1]	slope	intercept	lig.[1]
	200 °C, 0.9m NaCl + 0.1m HCl			**300 °C, 0.9m NaCl + 0.1m HCl**		
La	0.0324	0.0175	1.62	0.1059	0.1142	2.16
Ce	0.0423	0.0188	1.23	0.1313	0.1151	1.96
Pr	0.0438	0.0197	1.17	0.0837	0.1165	2.34
Sm	0.0450	0.0173	1.13	0.1690	0.1007	1.66
Eu	0.0419	0.0201	1.25	0.0881	0.1135	2.30
Gd	0.0485	0.0163	1.00	0.1312	0.1026	1.96
Tb	0.0342	0.0213	1.55	0.1432	0.1036	1.86
Ho	0.0499	0.0185	0.94	0.1662	0.1046	1.68
Er	0.0472	0.0198	1.04	0.1042	0.1168	2.17
Tm	0.0524	0.0189	0.85	0.1136	0.1240	2.10
Yb	0.0454	0.0193	1.11	0.1048	0.1123	2.17
Lu	0.0536	0.0208	0.81	0.1247	0.1173	2.01
mean	0.0447	0.0190	1.14	0.1220	0.1118	2.03
1σ	0.010	0.0014	0.24	0.026	0.0069	0.21
r.s.d.	14%	7.3%	21%	22%	6.2%	10%
	200 °C, 0.09m NaCl + 0.01m HCl			**300 °C, 0.09m NaCl + 0.01m HCl**		
La	0.0276	0.0021	1.40	0.1025	0.0144	2.20
Ho	0.0343	0.0020	1.01	0.1308	0.0147	2.00
Lu	0.0321	0.0019	1.14	0.1298	0.0136	2.00
mean	0.0313	0.002	1.18	0.121	0.0142	2.07
1σ	0.0028	8.2E-05	0.16	0.013	4.6E-04	0.09
r.s.d.	8.9%	4.1%	14%	10.8%	3.3%	4.6%

[1] Average ligand number of REE-Cl complexes, derived by graphical interpretation.

Trends in average ligand number across the periodic table are shown in Fig. 10. At 200 °C, 1.0m ΣCl, there is an apparent trend to lower n value with increase in atomic number. Assuming that this trend is real, this could account for some of the scatter (in terms of relative standard deviation) in the "averaged" n values at 200 °C. As discussed below, previous theoretical studies have predicted that REE-Cl complex stability should decrease with increase in atomic number, which is in agreement with the general trend we have obtained. However, at 300 °C, no consistent trend is seen between average ligand number and atomic number. There also appears to be no consistent "odd-even" or "tetrad" effects. This implies that all of the REE are behaving similarly at these conditions (300 °C, 1.0m ΣCl). Experimental uncertainty may be the main reason for the observed deviations.

3.2. *Equilibrium Constants*

Table 4 summarizes the results of least squares regression of equilibrium constants for the formation of

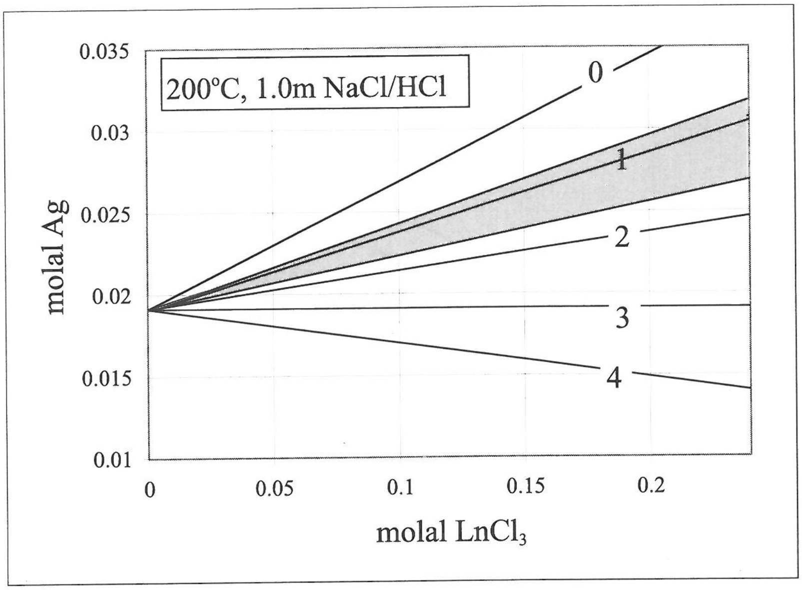

Fig. 6 Predicted vs. measured AgCl solubility, 200 °C, 1.0m NaCl/HCl. The lines labeled 0 to 4 correspond to predicted AgCl solubilities, assuming REE-chloride ligand numbers of 0 to 4. These lines were calculated using the forward modeling procedure (see text). The shaded sector shows the total range in slope and ligand number derived from solubility experiments for all of the rare earth elements investigated in this study.

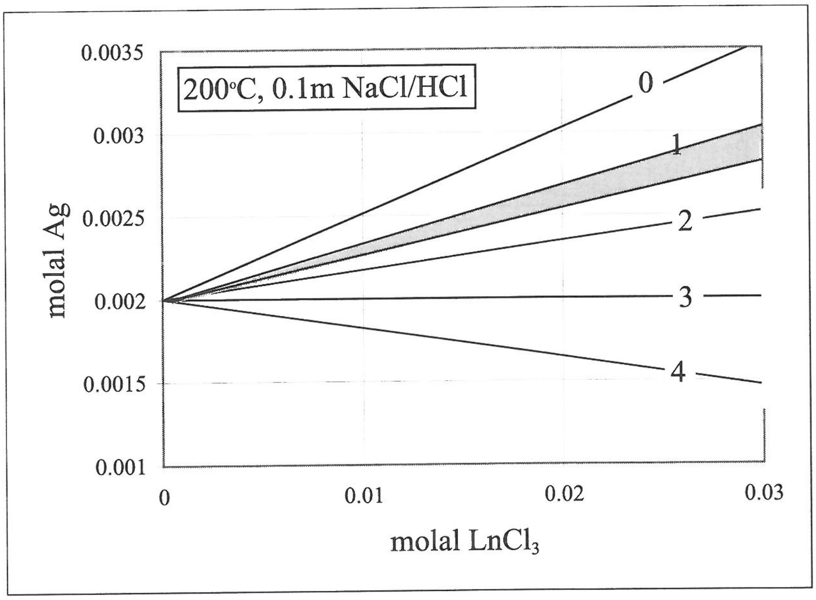

Fig. 7 Predicted vs. measured AgCl solubility, 200 °C, 0.1m NaCl/HCl (see caption to Fig. 4 for more details).

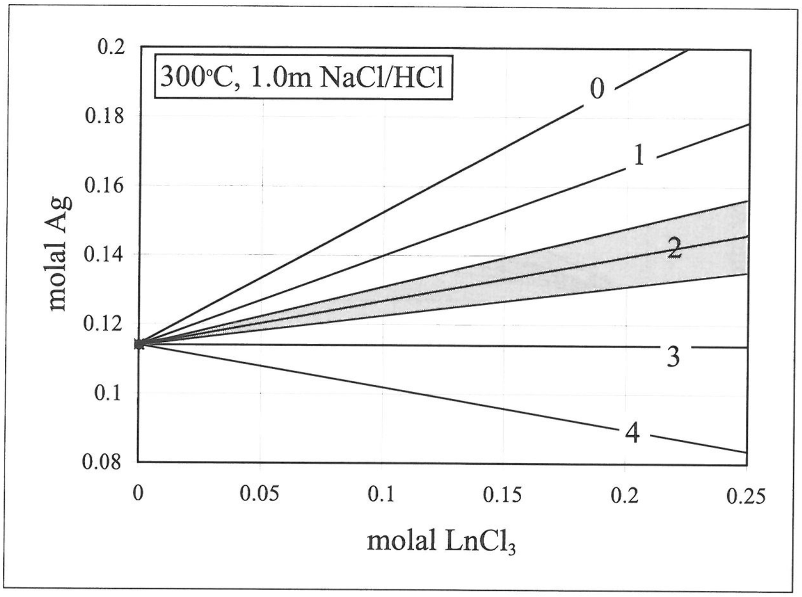

Fig. 8 Predicted vs. measured AgCl solubility, 300 °C, 1.0m NaCl/HCl (see caption to Fig. 4 for more details).

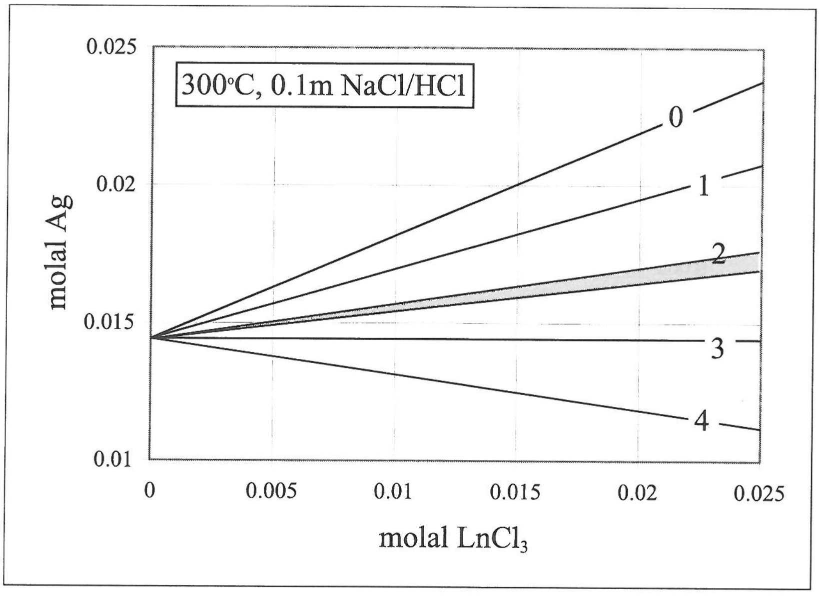

Fig. 9 Predicted vs. measured AgCl solubility, 300 °C, 0.1m NaCl/HCI (see caption to Fig. 4 for more details).

REE-chloride complexes at 200 °C (see section 2.3 for details). The headings β_1, β_2, and K_2 refer to the following reactions, respectively:

$$Ln^{3+} + Cl^- \leftrightarrow LnCl^{2+} \quad (9)$$

$$Ln^{3+} + 2Cl^- \leftrightarrow LnCl_2^+ \quad (10)$$

$$LnCl^{2+} + Cl^- \leftrightarrow LnCl_2^+ \quad (11)$$

For most of the elements of interest, it was not possi-

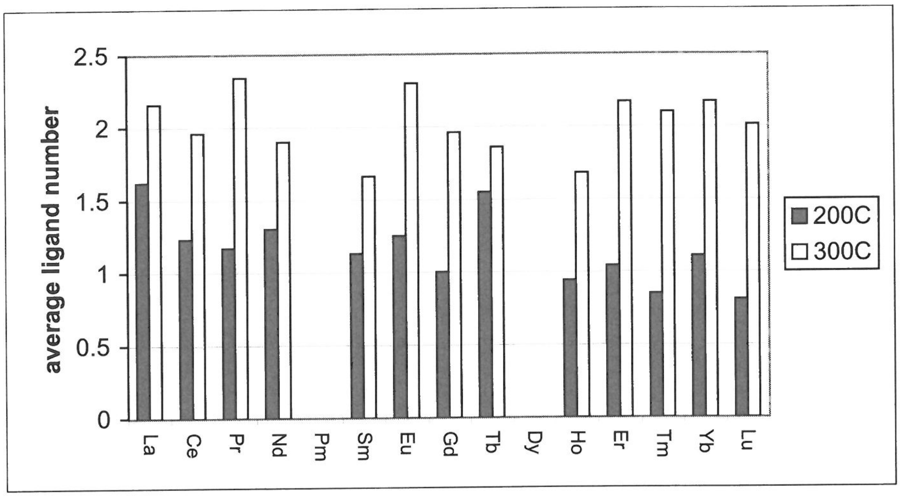

Fig. 10 Variation of experimentally determined chloride ligand numbers across the lanthanide series at 200 °C and 300 °C.

ble to refine β_1, the association constant for reaction (9). This is not surprising, considering the observation that derived ligand numbers were in most cases greater than 1, indicating a very minor contribution to the speciation of each lanthanide from the completely dissociated Ln^{3+} ion. An independent estimate of β_1 was obtained for gadolinium and thulium, but only by assuming $\beta_2 = 0$. Lutetium was the only element for which it was possible to refine *both* β_1 and β_2. Including our previous results for neodymium, the average of the 4 refined log β_1 estimates is 2.16±0.29 (1 standard deviation error). The limited data available preclude any attempt to identify trends in β_1 vs. atomic number. Additional indirect solubility experiments would be needed at lower chloride concentration (< 0.1 molal), but this was deemed beyond the scope of the present study.

Table 4. Cumulative and stepwise formation constants for REE-chloride complexes at 200 °C. [1]

element	**log β_1**	**log β_2**	**log K_2**
La	2.17 (fixed)	3.45	1.28
Ce	2.17 (fixed)	2.83	0.66
Pr	2.17 (fixed)	2.80	0.63
Nd	2.17 [2]	2.52 [2]	0.35
Sm	2.17 (fixed)	2.40	0.23
Eu	2.17 (fixed)	2.94	0.77
Gd	1.81	could not be refined	—
Tb	2.17 (fixed)	3.64	1.47
Ho	2.17 (fixed)	1.96	-0.21
Er	2.17 (fixed)	2.57	0.40
Tm	2.61	could not be refined	—
Yb	2.17 (fixed)	2.57	0.40
Lu	2.06	2.31	0.25
mean	2.16 [3]	2.73	0.57
1σ	0.29	0.47	0.46

[1] P = SWVP, I = 0.0; [2] from Gammons et al. (1996); [3] mean value calculated from refined estimates only.

Estimates of β_2 are given in the 3rd column of Table 4. For most of the elements of interest, it was impossible to derive a β_2 value unless the input file contained a fixed initial guess at β_1. For the latter, we chose the log β_1 value of 2.17 obtained for neodymium by Gammons et al. (1996), which is virtually identical to the average value of log β_1 reported above. The log β_2 values derived by least squares regression for 11 rare earth elements have a mean value of 2.73±0.47, which is in good agreement with our previous estimate of log β_2 = 2.52 for neodymium only (Gammons et al., 1996). Table 4 shows a weak trend to lower β_2 values with increase in atomic number. This is consistent with the previously mentioned trend to lower average ligand number across the periodic table.

The final column in Table 4 lists our estimates for the second stepwise formation constant, K_2, or reaction (11). These constants were found to be much less sensitive to our initial guess for log β_1. The reason for this is subtle, but can be explained as follows. If the average ligand number of a particular group of complexes over a range of chloride concentration is greater than 1 (as was the case in this study for most elements at 200 °C), a mixture of the $LnCl^{2+}$ and $LnCl_2^+$ species is most likely present. Equilibrium

Table 5. Comparison of log β_2 and log K_2 values at 200 °C obtained in this study vs. values from Haas et al. (1995).

REE	**log β_2**			**log K_2**		
	HSS [a]	**this study**	**deviation**	**HSS [a]**	**this study**	**deviation**
La	2.867	3.45	0.58	0.523	1.28	0.76
Ce	3.117	2.83	−0.29	0.597	0.66	0.06
Pr	2.839	2.80	−0.04	0.511	0.63	0.12
Nd	2.710	2.52 [b]	−0.19	0.43	0.35 [b]	−0.08
Sm	2.611	2.40	−0.21	0.348	0.23	−0.12
Eu	2.868	2.94	0.07	0.519	0.77	0.25
Gd	3.065			0.633		
Tb	2.863	3.64	0.78	0.561	1.47	0.91
Dy	3.034			0.669		
Ho	2.986	1.96	−1.03	0.633	−0.21	−0.84
Er	2.775	2.57	−0.21	0.463	0.40	−0.06
Tm	2.785			0.518		
Yb	2.589	2.57	−0.02	0.381	0.40	0.02
Lu	2.339	2.31	-0.03	0.277	0.25	−0.03

[a] Haas et al. (1995); [b] Gammons et al. (1996).

Table 6. Average ligand numbers obtained in this study vs. those derived from the estimates of Haas et al. (1995).

	200 °C, 1.0m ΣCl			**300 °C, 1.0m ΣCl**		
	HSS [a]	**this study**	**deviation**	**HSS [a]**	**this study**	**deviation**
La	1.23	1.62	0.39	1.50	2.16	0.66
Ce	1.29	1.23	−0.06	1.54	1.96	0.42
Pr	1.21	1.17	−0.04	1.44	2.34	0.90
Nd	1.16	0.99 [b]	-0.17	1.35	1.99 [b]	0.64
Sm	1.12	1.13	0.01	1.30	1.66	0.36
Eu	1.22	1.25	0.03	1.50	2.30	0.80
Gd	1.31	1.00	-0.31	1.61	1.96	0.35
Tb	1.24	1.55	0.31	1.53	1.86	0.33
Dy	1.32			1.67		
Ho	1.29	0.94	−0.35	1.62	1.68	0.06
Er	1.19	1.04	−0.15	1.48	2.17	0.69
Tm	1.20	0.85	−0.35	1.51	2.10	0.59
Yb	1.13	1.11	−0.02	1.41	2.17	0.76
Lu	1.04	0.81	−0.23	1.39	2.01	0.62

[a] Haas et al. (1995); [b] Gammons et al. (1996).

between these two species is governed by K_2, the stepwise formation constant for $LnCl_2^+$. In this case, the solubility data can be interpreted with only a very approximate knowledge of β_1, the first association constant. In contrast, derivation of estimates for β_2 were very strongly dependent on our initial guess of β_1, since β_2 also involves the dissociated Ln^{3+} species. The precision in log K_2 is virtually the same as that for log β_2 (based on the standard deviations). The mean value of log K_2 for 11 rare earth elements is 0.57±0.46. Again, this compares favorably with our previous result of log $K_2 = 0.35$ in the more detailed study of neodymium (Gammons et al., 1996).

Because of the complexity of the indirect solubility method, it is difficult to attach a precise uncertainty to the equilibrium constants reported in Table 4. A liberal estimate of error in the reported values for most of the elements of concern (excluding neodymium and lutetium) is ± 0.5 log units. Because it was possible to refine both β_1 and β_2 for lutetium, the recommended error in this case is lowered to ± 0.3 log units.

Attempts to derive equilibrium constants at 300 °C from the solubility data obtained in this study were unsuccessful. Again, the main problem was a lack of information over a sufficiently wide range of chloride concentration. In addition, the fact that the derived ligand numbers were close to 2 in many cases suggests that a single complex, the $LnCl_2^+$ species, was dominant in the 300 °C experiments. This being the case, it was not possible to derive either stepwise or cumulative formation constants with an acceptable degree of precision.

4. DISCUSSION

4.1. Comparison with Previous Work

The only high-temperature experimental study with which to compare our results is that of Gammons et al. (1996). Whereas Gammons et al. (1996) investigated the chloride complexation behavior of a single element (neodymium) over a wide range of experimental conditions, in the present study we have looked at all of the rare earth elements for a limited range of conditions. Our results reinforce the earlier conclusions of Gammons et al. (1996), and also show only minor systematic variations in REE-chloride complexation behavior across the periodic table. This is consistent with the lack of strong variation in β_1 of REE-chloride complexes at 25 °C, as reported in the literature. For example, the compilation of Millero (1992) shows only 0.35 log unit variation in log β_1 for all of the rare earth elements, with a trend to lower β_1 values for higher atomic number.

Using theoretical estimation methods, the stability of rare earth element complexes at elevated temperature was predicted by Wood (1990) and Haas et al. (1995). Wood (1990) used a combination of the isocoulombic technique and the electrostatic approach of Helgeson and co-workers to estimate the stability of the $LnCl^{2+}$species to 300 °C. Haas et al. (1995) derived HKF (modified Helgeson-Kirkham-Flowers equation of state) parameters for Ln^{3+}, $LnCl^{2+}$, $LnCl_2^+$, $LnCl_3(aq)$ and $LnCl_4^-$, from which it is possible to estimate stepwise or cumulative formation constants over a wide range of temperature and pressure. Gammons et al. (1996) showed that the agreement between their experiments and the theoretical predictions of Haas et al. (1995) was quite good up to approximately 200 °C. Above this temperature, both Haas et al. (1995) and Wood (1990) underestimated the degree of Nd-chloride complexation.

Table 5 compares our experimentally-derived estimates for log β_2 and log K_2 at 200 °C vs. those calculated using the HKF parameters in Haas et al. (1995). For 7 of the 10 elements in which β_2 and K_2 could be refined (not counting neodymium), the agreement between our work and that of Haas and co-workers falls well within our experimental error (± 0.5 log units). Exceptions include lanthanum, terbium, and holmium. With the data in hand, it is difficult to say whether the disparities for these elements are real, or an artifact of experimental scatter. However, in the absence of a theoretical justification for the anomalous behavior of La, Tb, and Ho, we are inclined to implicate our own experimental uncertainty to explain the discrepant results.

Because we were not able to derive stability constants at 300 °C, a direct comparison cannot be made at this temperature with the study of Haas et al. (1995). However, the results can be indirectly compared by computing average chloride ligand numbers for each rare earth element based on the cumulative formation constants calculated from the data in Haas et al. (1995). The aqueous speciation of each lanthanide was computed for a theoretical solution containing 0.9m NaCl, 0.1m HCl, and 10^{-5} molal ΣLn. The activity of free chloride and activity coefficients for all REE complexes were estimated using the same computer program employed to interpret our own solubility data. The speciation calculations were used to calculate average ligand numbers at 200 °C and 300 °C. The results, summarized in Table 6, show very good agreement at 200 °C, as expected. However, at 300 °C, the theoretically estimated ligand numbers are substantially lower than those obtained from our own experiments, by an average of ~ 0.5 units. In other words, the estimates of Haas et al. (1995) are apparently underestimating the degree of chloride complexation at 300 °C. This reinforces the conclusion of Gammons et al. (1996), who found that their own estimates of log β_2 for neodymium agreed with those of Haas et al. (1995) up to 200 °C, but began to deviate above this temperature. At 300 °C, log β_2 was found to differ by 1.74 log units (6.87 vs. 5.13, respectively, for the two studies). The qualitative results of the present study suggest that a similar comparison would be obtained if it were possible to derive stability constants for the other rare earth elements at 300 °C.

We conclude that Haas et al.'s estimates of the stability of the chloride complexes of the rare earth elements are valid up to 200 °C, but that their formation constants for the 1:2 species are underestimated at T > 200 °C. We suggest that these stability constants should instead be approximated by the experimentally-determined values reported in Gammons et al. (1996) for neodymium. The lack of any systematic differences in average ligand number with atomic number at 300 °C supports the idea that log β_2 for the REE do not deviate greatly at this temperature, as is the case at lower temperature.

4.2. Speciation of Rare Earth Elements in Seafloor Hydrothermal Fluids

Recently, Douville et al. (1999) have reported REE concentrations from deep-sea hydrothermal fluids from the Mid-Atlantic Ridge, the East Pacific Rise, and the Lau and Manus Back-Arc Basins. Chondrite-normalized plots of their data reveal a general light REE-enrichment coupled with a positive Eu anomaly. However, when normalized to the REE content of related plagioclase from altered basalt, the patterns become much flatter (although still slightly LREE-enriched) with much weaker Eu anomalies. Douville et al. (1999) carried out calculations of the distribution of REE species using stability constants derived from the HKF equation parameters in Haas et al. (1995). These calculations suggest that REE-chloride complexes are the most important REE species in solution. Douville et al. (1999) note that previous workers have shown that chloride complex stability decreases across the REE series from light to heavy, and that chloride complex stability increases strongly with temperature. They therefore suggest that the remaining LREE enrichment observed in their plagioclase-normalized REE patterns and the apparent increase in this LREE-enrichment with increasing temperature both reflect the influence of chloride complexation.

The results from our study, combined with calculations in Gammons et al. (1996), confirm that the REE-chloride complexes are likely to be the dominant species in the fluids studied by Douville (1999). There is no question that complexation of the REE by chloride increases in magnitude with temperature. In fact, REE-chloride complexes are probably even more dominant than suggested by the speciation calculations of Douville et al. (1999), because experimental work has shown that the HKF parameters of Haas et al. (1995) underestimate the stability of chloride complexes at T > 200 °C (Gammons et al., 1996; this study), and overestimate the stability of hydroxide complexes (Wood et al., this volume). Our data at 200 °C are consistent with a modest overall decrease in the stability of the REE-chloride complexes from light to heavy, which could partly explain the LREE-enrichment observed by Douville et al. (1999) in their plagioclase-normalized hydrothermal fluids. However, our data suggest that it is unlikely that chloride complexation alone can induce *strong* LREE-enrichment in hydrothermal fluids.

Our results also support the conclusions made by Wood and Williams-Jones (1994), and reiterated by Gammons et al. (1996), with respect to enrichments and depletions of REE in the alteration zones beneath ancient seafloor massive sulfide deposits. The extent of REE mobility in such deposits is difficult to explain without invoking unusually high water/rock ratios (> 1000) or fluid chemistries significantly different than modern deep-sea hydrothermal fluids.

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