

The aqueous geochemistry of the rare earth elements. Part XIV. The solubility of rare earth element phosphates from 23 to 150 °C

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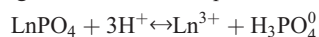
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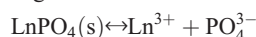
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Abstract

Rare earth element (REE) phosphates such as monazite and xenotime are important as ore minerals, potential hosts of radioactive waste, and target phases for isotopic dating. However, there are still insufficient thermodynamic data with which to model dissolution and precipitation of these phases in crustal fluids quantitatively. Therefore, the solubilities of end-member La(III)-, Nd(III)-, Sm(III)-, and Y(III)- phosphates were determined at 23 and 50 °C in NaCl–HCl and NaClO₄–HClO₄ solutions with pH_m from 0 to 2 and ionic strengths of 0.1, 0.5, 1.0, and 5.0 m. The solubility of Nd(III)-phosphate was also determined in chloride solutions at 150 °C. The La(III)- and Nd(III)-phosphates had the monazite structure, and Sm(III)-phosphate and Y(III)-phosphate had the rhabdophane and xenotime structures, respectively. The dependence of solubility on pH and chloride concentration, together with data from the literature, indicated that H₃PO₄⁰ and Ln³⁺ (where Ln³⁺ represents any free, hydrated trivalent REE ion) were the predominant species in our experimental solutions. At each ionic strength and temperature investigated, conditional equilibrium constants (*Q*_{s3}) were determined for reactions of the following type:



The conditional equilibrium constants determined at various ionic strengths were extrapolated empirically to obtain the equilibrium constants at infinite dilution (*K*_{s3}). These constants were then converted to solubility products (*K*_{s0}) for the following reaction:



using acid dissociation constants for H₃PO₄⁰ available in the literature. The values of log*K*_{s0} so obtained are:

	23°C	50 °C	150 °C
La	–25.7	–25.4	–
Nd	–25.8	–26.6	–30.8
Sm	–24.6	–24.8	–
Y	–27.9	–27.8	–

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These values are in reasonable agreement with the majority of those in the literature, with the exception of the values for Y(III)-phosphate, which are substantially lower. Our results, combined with data in the literature, suggest that the solubility products of REE phosphates are retrograde (i.e., decrease with increasing temperature) up to at least 300 °C. Moreover, the solubility of REE phosphate is quite low up to 300 °C, even at low pH and high chloride concentrations, confirming the robustness of these phases as hosts for radionuclides.

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1. Introduction

Quantitative modeling of the mass transfer of rare earth elements (REE), including yttrium, in the Earth's crust via aqueous fluids is dependent on the availability of several types of thermodynamic data, not the least of which are solubility products for REE-bearing minerals. However, solubility data for almost all geologically important REE-bearing minerals are lacking, even at standard conditions (cf. review by Wood, 2003).

Simple REE phosphates of the monazite and xenotime groups are important hosts of the REE in a variety of geologic environments (Clark, 1984; Mariano, 1989; Spear and Pyle, 2002). Monazite has the formula LnPO_4 , and is light REE-selective with a monoclinic structure, whereas xenotime has the formula YPO_4 , and is heavy REE-selective with an orthorhombic structure. Additional simple REE phosphates include rhabdophane ($\text{LnPO}_4 \cdot \text{H}_2\text{O}$; light REE-selective with a hexagonal structure) and churchite ($\text{YPO}_4 \cdot \text{H}_2\text{O}$; heavy REE-selective with a monoclinic structure). Note that Ln^{3+} is used here as a general symbol denoting any trivalent REE.

Monazite and xenotime are receiving considerable attention as target phases for U–Th–Pb geochronology in igneous, metamorphic, sedimentary, and hydrothermal environments (e.g., Harrison et al., 2002; Poitrasson et al., 2002; Willigers et al., 2002; Kositcin et al., 2003; Vielreicher et al., 2003, and references therein). The rare earth element phosphates have also been proposed as hosts for nuclear waste disposal owing to their physical and chemical durability, ability to resist metamictization, and capacity to contain actinides (Boatner et al., 1980, 1981; Boatner and Sales, 1988; Boatner, 2002; Ewing and Wang, 2002). Monazite, xenotime and, to a lesser extent, rhabdophane, occur as important REE-bearing minerals in a

variety of sub-economic to economic REE deposits of possible hydrothermal origin such as Lemhi Pass, Idaho/Montana (Anderson, 1961; Staatz, 1972; Wood et al., 1997; Gibson, 1999), Pea Ridge, Missouri (Nuelle et al., 1989; Kerr, 1998), Bayan Obo, China (Chao et al., 1992; Smith et al., 1999), Olympic Dam, Australia (Oreskes and Einaudi, 1990), and Steenkampskraal, South Africa (Andreoli et al., 1994). Clearly, knowledge of the solubility of REE phosphates in aqueous solutions over a wide range of temperature and pressure is crucial to a better understanding of the behavior of REE in crustal fluids.

The solubilities of REE and Y phosphates have been determined in a number of studies at or near standard conditions (25 °C, 1 bar). Previously reported, experimentally measured solubility products or K_{s0} values (see Eqs. (1) and (2) below for the definition of K_{s0}) are given in Table 1. Note that, in some cases, there are discrepancies of more than an order of magnitude in reported solubility products for a given REE. For example, for NdPO_4 , $\log K_{s0}$ values range from a low of -26.2 (Liu and Byrne, 1997) to a high of -24.65 (Rai et al., 2003), a range of ~ 1.5 log units. Some of these discrepancies arise because of differences in the structure, degree of hydration, and crystallinity of the REE phosphates studied (e.g., rhabdophane vs. monazite structure, and freshly precipitated vs. well-aged). Unfortunately, the nature of the REE phosphate used in solubility studies has not always been specified. Another problem is that, in some studies, dissolution was assumed to be congruent (i.e., the total REE concentration and the total phosphate concentrations were assumed to be equal, so that either REE or phosphate was not measured directly). A number of studies including ours suggest that this is likely an incorrect assumption. An additional source of discrepancies in published solubility products is the use of different activity coefficient

Table 1
Solubility products ($\log K_{s0}$) reported in the literature for REE and Y phosphates

Source	a	b	c		d		e	f	g	h			i
Temperature	25 (°C)	25 (°C)	25 (°C)	100 (°C)	25 (°C)	72 (°C)	25 (°C)	25 (°C)	25 (°C)	23 (°C)	50 (°C)	150 (°C)	23 (°C)
La	-25.0		-24.5±0.3		-26.2±0.5	-26.5	-25.4		-25.7±0.05	-24.70±0.15	-25.40		
Ce								-24.3	-26.2±0.15				
Pr				-26.0±1.0	-26.1±0.2	-26.5	-25.4		-26.4±0.30				
Nd			-25.9	-25.7±0.7	-26.0±0.1	-25.5	-25.4		-26.2±0.02	-25.83±0.05	-26.6	-30.81	-24.65±0.23
Sm					-26.0±0.1	-26.6	-25.3		-26.1±0.01	-24.55±0.19	-24.77		
Eu					-25.8±0.3	-26.4	-25.1	-24.2	-25.9±0.03				
Gd		-24.8			-25.4±0.2	-25.8	-24.7	-24.1	-25.6±0.12				
Tb					-25.1±0.03	-26.0	-24.4		-25.3±0.04				
Dy					-25.2±0.1	-25.7	-24.4		-25.1±0.13				
Ho					-25.6±0.5		-25.4		-25.0±0.13				
Er			-24.1	-25.5	-25.8±0.5	-25.9	-25.1		-25.1±0.11				
Tm					-26.1±0.1	-26.2	-25.4		-25.0±0.13				
Yb					-26.2±0.01	-26.3	-25.5	-23.3	-24.8±0.24				
Lu					-25.4±0.03	-26.0	-24.7		-24.7±0.31				
Y					-24.8±0.1				-25.02±0.08	-27.93 ^a	-27.82 ^a		
			21 °C		70 °C		200 °C			300 °C			
Nd (j)			-25.93±0.07		-27.13±0.12		-30.83±0.09			-35.29±0.56			
Gd (j)			-25.84										

(a) Tananaev and Vasil'eva (1963), extrapolated to infinite dilution by Byrne and Kim (1993); (b) Tananaev and Petushkova (1967), extrapolated to infinite dilution by Byrne and Kim (1993); (c) Jonasson et al. (1985); (d) Firsching and Brune (1991); (e) Firsching and Brune (1991), recalculated by Byrne and Kim (1993); (f) Byrne and Kim (1993); (g) Liu and Byrne (1997); (h) this study; (i) Rai et al. (2003); (j) Poitrasson et al. (2004).

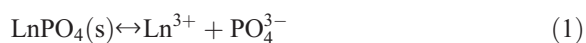
^a These values are probably too low owing to lack of attainment of equilibrium in the solubility experiments.

models. The activity of the trivalent Ln^{3+} ion is especially sensitive to the model employed for its calculation. Finally, there have been only a handful of measurements of solubility products at temperatures above 25 °C. Here we report solubility products of phosphates of La, Sm, and Y measured at 23 and 50 °C, and of Nd measured at 23, 50, and 150 °C, in an effort to improve the thermodynamic database for REE phosphates. We have carefully characterized the REE phosphates both before and after the experiments, and have directly measured both the REE and phosphate concentrations. Moreover, we have determined solubility products as a function of ionic strength, which permits an empirical extrapolation of the results to infinite dilution.

2. Theoretical considerations

In this study, we measured pH on the concentration scale and we define pH_m as $-\log m_{\text{H}^+}$. Solubilities of well-characterized phosphates were determined at low pH_m (0–2) in both chloride and perchlorate solutions of various fixed ionic strengths. The solubility experiments were conducted at low pH_m for several reasons. First, the solubility of REE phosphates is quite low at near-neutral pH_m , but increases with decreasing pH_m . Therefore, solubility measurements at low pH_m insured that the concentrations of REE and phosphate could be measured accurately. Measurements at low pH_m also insure that hydrolysis of the trivalent REE ions is negligible (cf. Baes and Mesmer, 1986; Wood et al., 2002, and references therein). Phosphate complexation of Ln^{3+} should also be negligible at low pH_m where strongly protonated forms of this ligand (H_3PO_4^0 and H_2PO_4^-) are predominant. Because the goal of this project was to determine solubility products, the ability to neglect hydrolysis and phosphate complexation simplifies the interpretation of the results. It should be noted that all previous solubility product determinations also have been carried out at low pH_m for similar reasons.

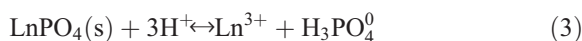
Neglecting possible waters of hydration in the solid REE phosphate, the solubility product of LnPO_4 refers to the reaction:



Assuming a pure end-member Ln-phosphate, the solubility product can then be written as:

$$K_{s0} = a_{\text{Ln}^{3+}} a_{\text{PO}_4^{3-}} \quad (2)$$

However, the dominant dissolution reaction at the low pH_m values measured should be:



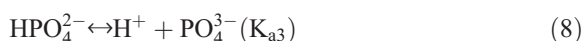
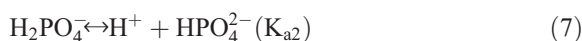
The equilibrium constant for this reaction may be written as:

$$K_{s3} = \frac{a_{\text{Ln}^{3+}} a_{\text{H}_3\text{PO}_4^0}}{a_{\text{H}^+}^3} \quad (4)$$

If total ionic strength of the solution is held constant, then activity coefficients will be approximately constant, and we can define a conditional equilibrium constant Q_{s3} for reaction (3):

$$Q_{s3} = \frac{m_{\text{Ln}^{3+}} m_{\text{H}_3\text{PO}_4^0}}{m_{\text{H}^+}^3} \quad (5)$$

Eqs. (4) and (5) illustrate that K_{s3} and Q_{s3} are very sensitive to uncertainties in H^+ ion activity or concentration, which may explain some of the discrepancies among solubility products reported in the literature. Our strategy to derive K_{s3} was to conduct solubility experiments at several fixed ionic strengths at each temperature, from which we obtained a Q_{s3} value for each ionic strength and temperature. The Q_{s3} values at each temperature were then extrapolated empirically as a function of ionic strength, as described below, to obtain K_{s3} at infinite dilution. The value of K_{s0} can be derived from the value of K_{s3} by adding the following dissociation reactions of phosphoric acid to reaction (3):



and combining equilibrium constants according to:

$$K_{s0} = K_{s3} K_{a1} K_{a2} K_{a3} \quad (9)$$

We conducted two separate sets of experiments. In one set, designed to determine the chloride dependence of solubility, pH_m was maintained nearly constant at approximately 1 using HCl, and the total

chloride concentration was varied from 0.1 to 5 m by adding the required amount of NaCl. In the second set, designed to determine the pH_m dependence of solubility, pH_m was varied from 0 to 2 using HClO_4 , and the total ionic strength was held constant by adding the required amount of NaClO_4 . Comparison of solubilities measured in NaCl and NaClO_4 media at approximately the same pH_m and ionic strength permits an additional assessment of the importance of chloride complexation.

Measurement of Q_{s3} for a series of fixed ionic strengths allowed us to calculate K_{s3} using an empirical method of extrapolation to infinite dilution. This extrapolation was accomplished using the following relationship:

$$\log Q_{s3}(I) = \log K_{s3} + \frac{A\Delta Z^2\sqrt{I}}{1 + \sqrt{I}} + CI + DI^2 + \dots \quad (10)$$

where K_{s3} is the equilibrium constant at infinite dilution, ΔZ^2 is the change in charges squared for reaction (3) (i.e., 6), A is the Debye–Hückel parameter, and C, D, \dots are adjustable parameters. The quantity $Q_{s3}(I)$ is the conditional equilibrium constant at the stoichiometric ionic strength I . The second term on the right in Eq. (10) is the Debye–Hückel term, which guides the extrapolation at ionic strengths lower than those at which measurements were made. The values of $\log K_{s3}$, C , and D were determined via regression analysis of the experimental data, in which $\log Q_{s3}(I) - \frac{A\Delta Z^2\sqrt{I}}{1 + \sqrt{I}}$ was the dependent variable and I was the independent variable. Sufficient adjustable parameters (C, D, \dots) were added so that Eq. (10) fits the experimental data within the experimental uncertainty to the highest ionic strength employed. A very similar approach was employed by Baes and Mesmer (1986), in their critical review of cation hydrolysis, to extrapolate hydrolysis constants to infinite dilution from ionic strengths similar to those employed in this study.

3. Experimental methods

3.1. Reagents

All reagents used in the experiments were of reagent grade, or better, and all solutions were

prepared by weight, employing 18-M Ω cm deionized water. The sodium chloride and sodium perchlorate employed were 99.98% and 99% pure, respectively. Neodymium-phosphate was synthesized by the method of Boatner et al. (1981) (see Cetiner, 2003 for details). Commercially available La-, Sm-, and Y-phosphates (purity 99.9%) in powder form were purchased from Alfa Aesar.

The solid phosphates were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM), before and after experiments. X-ray diffraction analysis showed no evidence of the presence of any other components. According to the XRD data, our La- and Nd-phosphates had the monazite structure. Samarium-phosphate and yttrium-phosphate yielded diffraction patterns consistent with the rhabdophane and xenotime structures, respectively. The XRD analyses of the LnPO_4 samples were virtually identical with respect to peak position both before and after the runs.

In addition, assays of the solids were obtained by dissolving 0.1–0.15 g of the LnPO_4 powder in concentrated sulfuric acid, followed by dilution and analysis for total Ln and P via ICP-AES to verify the stoichiometry of the starting material. The results, which are shown as molar P/Ln ratios in Table 2, confirmed that the LnPO_4 powders (with the exception of SmPO_4) used as starting material had the expected stoichiometry, within analytical precision, of approximately 5%. The SmPO_4 powder had a slightly lower Ln/P ratio of 0.92.

3.2. Experimental set-up

3.2.1. Low temperature

Experiments at low temperatures (room temperature and 50 °C) were carried out in 125-mL-capacity, high-density polyethylene bottles. Prior to the experiments, the bottles were soaked in an acid bath

Table 2
Molar Ln/P ratios in the initial Ln-phosphates used in the experiments

LnPO_4	Molar ratio Ln/P
LaPO_4	1.02
NdPO_4	0.96
SmPO_4	0.92
YPO_4	1.02

overnight and rinsed thoroughly with deionized water. Then 100 mL of the experimental solution was transferred to the bottles along with 100–150 mg of LnPO_4 in a powder form (solid/solution mass ratio of 0.001–0.0015). For the room-temperature (23 ± 2 °C) experiments, bottles containing the experimental charges were agitated on a shaking table. Experiments at 50 °C (± 0.2 °C) were conducted in a constant-temperature, shaking waterbath.

Before sampling, shaking was stopped and the solid was permitted to settle for about 15 min. Approximately 3 mL of the solution was withdrawn and forced through a 0.20- μm Nylon filter membrane. The filtered samples were acidified with 1.0 mL of concentrated HCl (Fisher ACS grade) and diluted to 10 mL in a volumetric flask. After mixing, solutions were then transferred to 10-mL polyethylene tubes for storage until analysis. Sampling was performed at regular intervals to check the evolution of pH_m and REE concentration until equilibrium was closely attained.

3.2.2. High temperature

At 150 °C (± 2 °C), experiments were conducted in 250-mL, gold- and glass-lined autoclaves. The maximum working temperature and pressure for these autoclaves are ~ 343 °C, and 37 MPa, respectively. Selected samples were analyzed for Fe and Au to monitor possible corrosion of the gold liner or the stainless steel autoclave. The concentrations of these metals were generally insignificant.

A quantity of 75–100 mg of $\text{LnPO}_4(\text{s})$ powder was loaded into a 2–3-cm length of Au tubing (4 mm OD, 3.8 mm ID), which was tightly crimped (but not welded) on both ends. The purpose of the crimped gold capsule was to minimize the potential for carryover of solid LnPO_4 when taking a fluid sample, while permitting the fluid to access the solid during the experiment. After adding the experimental solution, the system was pressurized to approximately 1.0–1.4 MPa and left overnight to check for leaks. The autoclave was heated in a nichrome resistance furnace. Temperature was measured using two external Chromel–Alumel thermocouples located at the top and the bottom of the autoclave. Thermal convection was stimulated by maintaining the bottom of the autoclave 2 °C higher than the top. Pressure was measured with an electronic

transducer. The precision of the pressure measurement was ± 70 kPa.

Samples were extracted from the vessel at temperature via Ti tubing and transferred using PEEK (polyetheretherketone) capillary tubing and PEEK microsplitter valves. The sampling arrangement, with the exception of the use of PEEK, was first suggested by Bourcier and Barnes (1987) and has been successfully employed by others in many hydrothermal experiments reported in the literature. Approximately 3 mL of the solution was withdrawn and syringe-filtered through a 0.20- μm PTFE (polytetrafluoroethylene) membrane. The filtered samples of solution were acidified with 1.0 mL of concentrated Fisher ACS certified HCl. Acidified samples were then diluted to 10 mL. Deionized water was used to wash the sampling line before and after each sampling session to avoid possible cross contamination.

3.3. Determination of pH_m

The pH_m of room temperature experimental solutions was measured in situ using a Ross combination glass electrode. Potentiometric measurements with glass electrodes actually register the activity of H^+ . However, if activity coefficients are maintained approximately constant by keeping the ionic strength constant, then pH_m can be directly measured. Therefore, to calibrate the pH electrodes for a given set of experiments at a given ionic strength, a series of standard HCl solutions of known molality (determined by titration against standard base) was prepared with the same constant ionic strength as the experiments. This procedure has the advantage of minimizing errors in pH_m measurement due to variations in liquid junction potentials and activity coefficients between the samples and the calibration standards. Some glass electrodes do not give accurate readings in the low- pH_m range. However, the response of our electrode was Nernstian, from pH 0 to 3. Moreover, at the low pH_m values of our experiments, it was possible to use titration with standard base to confirm the pH_m values obtained with the glass electrode. The two sets of values were in excellent agreement.

The quench pH_m of the solution samples from 50 and 150 °C experiments was measured in a few cases

to verify that protons were not irreversibly consumed during the run. These measurements verified that pH_m did not deviate from the initial values by more than $\pm 10\%$ during the experiments. Calculation of in situ pH_m for experiments at 50 and 150 °C was accomplished by solving the relevant mass-action, mass-balance, and charge-balance constraints for the concentrations of all aqueous species using a modification of the computer code EQBRM (Anderson and Crerar, 1993; Wood and Samson, 1998). Thermodynamic data for non-REE species were taken from SUPCRT92 (Johnson et al., 1992), supplemented by data for REE species from Haas et al. (1995). The calculated values of pH_m were relatively insensitive to the values of the stability constants for the REE species. Activity coefficients for charged species were calculated using the \hat{b} equation of Helgeson (1969):

$$\log \gamma = \frac{-Az_i^2\sqrt{I}}{1 + a_i^0B\sqrt{I}} + \hat{b}I \quad (11)$$

where z_i is the charge of species i and I is the true ionic strength of the medium, accounting for the formation of ion pairs. The values of the Debye–Hückel coefficients, A and B , at 50 and 150 °C and saturated water vapor pressure were obtained from Helgeson et al. (1981), and the \hat{b} deviation parameter was obtained from Helgeson (1969). The Debye–Hückel ion size parameters (a_i^0) were obtained from Langmuir (1997). Activity coefficients for neutral species were assumed to be unity. For additional details on the calculation of pH_m , the interested reader is referred to Cetiner (2003).

The use of the \hat{b} equation to estimate activity coefficients in the calculation of in situ pH_m values contrasts with the use of the empirical method (Eq. (10)) employed for extrapolating Q_{s3} values to infinite dilution. However, the empirical method, which is preferable to the \hat{b} method because it uses the actual experimental data as a function of ionic strength to guide activity coefficient corrections, cannot be employed in the calculation of pH_m values owing to a lack of data for conditional equilibrium constants for all the mass-action expressions (i.e., reactions) required in the calculation. In spite of the inconsistency this procedure introduces, we feel that it yields more accurate solubility products than, for

example, using the \hat{b} equation for all activity coefficient corrections.

3.4. Analytical methods

The HCl/HClO₄ content of all starting solutions was checked by triplicate potentiometric titration against certified standard base solutions. The concentration of Cl[−] before and after runs was verified by ion chromatography (IC) using a Dionex AI-450 model. A solution of 1.7 mM NaHCO₃/1.8 mM Na₂CO₃ was used to elute anions from an AS4A-SC column. The typical precision for these analyses was estimated to be within 5%.

Total Ln and P concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with an axial-view torch (Perkin Elmer Optima 3000 XL). Calibration standards for each analysis were made from certified standards of individual elements. Sets of three to five different concentrations of standards were used to establish a calibration curve. The correlation coefficients of the calibration curves were better than 0.999. Blanks and standard solutions were matched with the samples with respect to matrix (ionic strength and acidity). Blanks and standards of known concentrations were run periodically throughout each analytical run for quality control. The deviation from the known concentration was always less than 10%. Calculated detection limits were 0.06 mg L^{−1} for La, 0.08 mg L^{−1} for Nd and Sm, 0.03 mg L^{−1} for Y, and 0.1 mg L^{−1} for P. The analytical precision for ICP-AES in terms of the relative standard deviation (RSD) of replicate analyses was better than 5% for P, 2.5% for La, 2.9% for Nd, 2.7% for Sm, and 2% for Y. Selected samples with Ln concentrations near or below the detection limit of ICP-AES were analyzed at Washington State University using a Hewlett-Packard Model 4500 inductively coupled plasma mass spectrometer (ICP-MS).

4. Results

The temperature and initial solution composition of each experimental run, together with the equilibrium pH_m , REE and P concentrations, and molar Ln/P ratios, are given in Tables 3 (chloride) and 4 (perchlorate).

Table 3
Summary of experimental results in HCl+NaCl media at 23, 50, and 150 °C

Experimental conditions	Sample number	pH _m ^a	REE (mol kg ⁻¹ H ₂ O)	P (mol kg ⁻¹ H ₂ O)	Ln/P
<i>T</i> =23 °C	La-10.1-25	1.08	1.92E-03	1.91E-03	1.00
0.09 m HCl	Nd-10.1-25	1.06	4.05E-04	6.98E-04	0.58
0.01 m NaCl	Sm-10.1-25	1.08	1.81E-03	2.76E-03	0.66
	Y-10.1-25	1.08	2.64E-05	6.61E-05	0.40
<i>T</i> =23 °C	La-10.5-25	1.09	2.01E-03	2.33E-03	0.86
0.09 m HCl	Nd-10.5-25	1.07	4.95E-04	8.65E-04	0.57
0.41 m NaCl	Sm-10.5-25	1.09	1.65E-03	2.46E-03	0.67
<i>T</i> =23 °C	La-11-25	1.12	2.53E-03	2.69E-03	0.94
0.09 m HCl	Nd-11-25	1.09	5.37E-04	8.61E-04	0.62
0.91 m NaCl	Sm-11-25	1.09	2.05E-03	2.77E-03	0.74
	Y-11-25	1.08	2.91E-05	7.10E-05	0.41
<i>T</i> =23 °C	La-15-25	1.27	3.16E-03	4.05E-03	0.78
0.09 m HCl	Nd-15-25	1.23	6.07E-04	1.07E-03	0.57
4.91 m NaCl	Sm-15-25	1.28	4.08E-03	7.13E-03	0.57
	Y-15-25	1.22	6.05E-05	1.39E-04	0.44
<i>T</i> =50 °C	La-10.1-50	1.06	7.66E-04	9.39E-04	0.82
0.09 m HCl	Nd-10.1-50	1.05	2.18E-04	2.17E-04	1.00
0.01 m NaCl	Sm-10.1-50	1.07	1.54E-03	1.52E-03	1.01
	Y-10.1-50	1.05	3.79E-05	7.07E-05	0.54
<i>T</i> =50 °C	La-11-50	1.10	1.45E-03	1.81E-03	0.80
0.09 m HCl	Nd-11-50	1.08	3.47E-04	4.13E-04	0.84
0.91 m NaCl	Sm-11-50	1.10	1.35E-03	1.63E-03	0.83
	Y-11-50	1.08	5.45E-05	9.37E-05	0.58
<i>T</i> =50 °C	La-15-50	1.25	3.91E-03	4.66E-03	0.84
0.09 m HCl	Nd-15-50	1.20	6.16E-04	8.53E-04	0.72
4.91 m NaCl	Sm-15-50	1.24	2.99E-03	3.58E-03	0.84
	Y-15-50	1.19	1.55E-04	2.08E-04	0.75
<i>T</i> =150 °C					
0.09 m HCl					
0.01m NaCl	Nd-10.1-150	1.05	9.96E-07	1.27E-05	0.08
0.41m NaCl	Nd-10.5-150	1.07	2.04E-06	4.53E-06	0.45
0.91m NaCl	Nd-11-150	1.09	6.28E-06	6.05E-04	0.01

^a pH_m values given in italics were calculated as described in the text. All other values were measured.

4.1. Attainment of equilibrium

Approach to equilibrium was from undersaturation and was indicated by the lack of change of REE concentration with respect to time. Representative plots are given for all the REE phosphates studied at 23 and 50 °C in Fig. 1. For La, Sm, and Nd, it is evident that at 23 °C, concentrations remained constant after about 15–20 days, whereas at 50 °C, concentrations were more or less constant throughout the experiment (here the first sample was taken 2–3 days after the start of the experiment). However, for some sets of solution compositions and temperatures, the concentration of Y had not completely leveled off even after 40 days. For each experimental run, we report in Tables 3 and 4 the average of the REE

and P concentrations, respectively, of all samples taken after 20 days. Ideally, the best way to demonstrate attainment of equilibrium would be to reverse the experiments (i.e., to also approach equilibrium from supersaturation). We did not attempt to reverse our experiments out of concern that solids formed on precipitation from supersaturated solution would not have the same structural or hydration state as the starting material. Clearly, the rate of attainment of equilibrium in solubility experiments depends on a number of factors including temperature, pH, ionic strength, degree of crystallinity (aging), surface area (particle size), efficiency of agitation, and solution–solid ratios. However, the time required to attain apparent solubility equilibrium (i.e., constant concentration after 15–20 days at 23

Table 4
Summary of experimental results in HClO₄+NaClO₄ media at 23 and 50 °C

Experimental conditions	Sample number	pH _m ^a	REE (mol kg ⁻¹ H ₂ O)	P (mol kg ⁻¹ H ₂ O)	Ln/P
<i>T</i> =23 °C	La-P1-25	0.96	1.28E-03	4.13E-03	0.31
0.1 m HClO ₄	Nd-P1-25	0.99	2.98E-04	3.04E-04	0.98
0.9 m NaClO ₄	Sm-P1-25	0.99	7.95E-04	4.47E-03	0.18
	Y-P1-25	1.01	5.33E-05	1.07E-04	0.50
<i>T</i> =23 °C	La-P1.5-25	1.52	3.65E-04	9.05E-04	0.40
0.03 m HClO ₄	Nd-P1.5-25	1.52	6.23E-05	6.10E-05	1.02
0.97m NaClO ₄	Sm-P1.5-25	1.51	2.36E-04	9.76E-04	0.24
	Y-P1.5-25	1.53	2.71E-05	9.29E-05	0.29
<i>T</i> =23 °C	La-P2-25	1.99	5.54E-05	5.09E-04	0.11
0.01 m HClO ₄	Nd-P2-25	1.92	1.17E-05	ND	–
0.99 m NaClO ₄	Sm-P2-25	1.92	3.01E-05	8.60E-04	0.04
	Y-P2-25	1.95	3.40E-06	6.38E-05	0.05
<i>T</i> =50 °C	La-P0-50	<i>0.003</i>	2.22E-02	3.33E-02	0.67
0.999 m HClO ₄	Nd-P0-50	<i>0.003</i>	2.68E-02	2.62E-02	1.02
0.001 m NaClO ₄					
<i>T</i> =50 °C	La-P1-50	<i>0.96</i>	1.23E-03	1.84E-03	0.67
0.1 m HClO ₄	Nd-P1-50	<i>0.99</i>	2.31E-03	2.13E-03	1.08
0.9 m NaClO ₄	Sm-P1-50	<i>0.99</i>	1.12E-03	1.44E-03	0.78
	Y-P1-50	<i>1.01</i>	1.35E-04	1.71E-04	0.79
<i>T</i> =50 °C	La-P1.5-50	<i>1.52</i>	2.20E-04	5.10E-04	0.43
0.03 m HClO ₄	Nd-P1.5-50	<i>1.52</i>	7.08E-05	7.42E-05	0.95
0.97m NaClO ₄	Sm-P1.5-50	<i>1.49</i>	1.51E-04	4.66E-04	0.32
	Y-P1.5-50	<i>1.53</i>	3.13E-05	7.03E-05	0.45
<i>T</i> =50 °C	Sm-P2-50	<i>1.91</i>	2.01E-05	2.28E-04	0.09
0.01 m HClO ₄	Y-P2-50	<i>1.94</i>	3.54E-06	4.30E-05	0.08
0.99 m NaClO ₄					

^a pH_m values given in italics were calculated as described in the text. All other values were measured. ND-not determined.

°C) for well-crystallized La-, Sm-, and Nd-phosphates in our experiments falls within the range deduced from other similar solubility studies in which vigorous agitation and low solid/solution mass ratios also were employed (Jonasson et al., 1985; Liu and Byrne, 1997; Rai et al., 2003; Poitrasson et al., 2004). Therefore, we believe that the attainment of a constant REE concentration after 15–20 days in our experiments represents a close approach to equilibrium, with the likely exception of the Y experiments. This conclusion is supported by the relatively close agreement of the solubility products we determined with those reported in the literature (except for Y) from experiments with longer periods of equilibration (see Table 1 and Section 5.3). The reason why YPO₄ appears to take longer to equilibrate with solution in our study than the other REE phosphates investigated, and in other YPO₄ experiments reported in the literature, may be related to differences in crystal morphology or surface area, among other possibilities.

4.2. Characterization of the solid phases and dissolution stoichiometry

As mentioned above, X-ray diffraction analysis showed no evidence of the presence of any other phases either before or after the Ln-phosphates had reacted with the solutions. Moreover, chemical analysis (Table 2) suggested that the Ln/P ratio of the initial solid was stoichiometric within analytical uncertainty for La-, Nd-, and Y-phosphates, and somewhat less than stoichiometric for Sm-phosphate. However, in the equilibrium solutions (Tables 3 and 4), P was almost always present in excess, in some cases by more than an order of magnitude (see also Fig. 2), irrespective of the REE, the nature of the medium (chloride vs. perchlorate), or whether the phosphate was purchased or synthesized in our laboratory. There is a greater tendency towards stoichiometry for the lower-pH experiments where the concentrations of both phosphate and REE are higher.

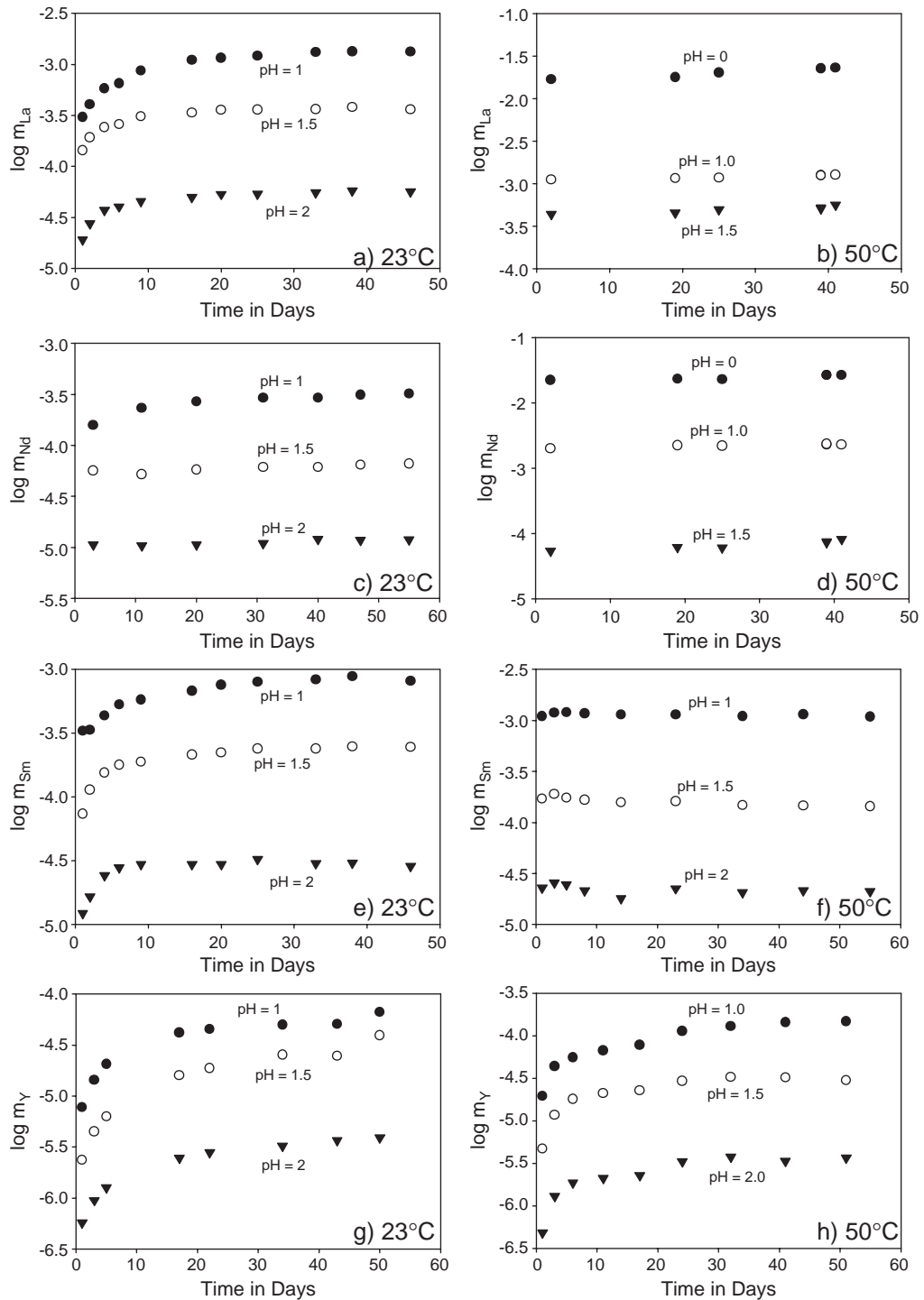


Fig. 1. Representative plots of the logarithm of the molality of REE concentration vs. time for phosphate solubility experiments in 1 m solutions of $\text{HClO}_4 + \text{NaClO}_4$ at various pH values and temperatures: (a) La, 23 °C; (b) La, 50 °C; (c) Nd, 23 °C; (d) Nd, 50 °C; (e) Sm, 23 °C; (f) Sm, 50 °C; (g) Y, 23 °C; (h) Y, 50 °C. The plots for solubility experiments in $\text{HCl} + \text{NaCl}$ solutions are very similar.

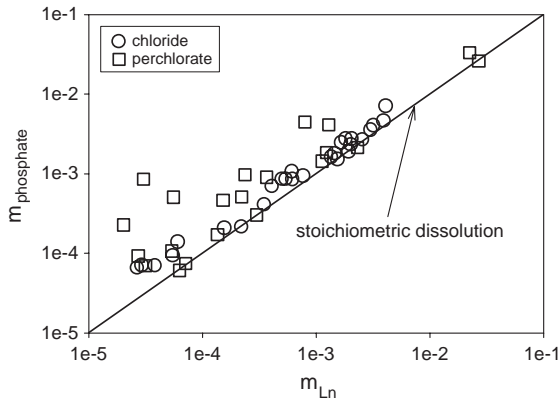


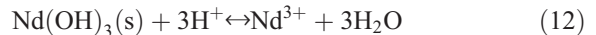
Fig. 2. Plot of the logarithm of the total phosphate concentration vs. the total REE concentration for all solubility experiments in this study. The straight line has a slope of unity and represents stoichiometric dissolution. Although some experiments plot on or near the stoichiometric dissolution line, most plot above the line (implying excess phosphate), and none plot below the line.

There are two possible explanations of the apparently non-stoichiometric Ln/P ratios in solution. The first is that the starting material may have contained a small amount of a phosphate impurity that is more soluble than the REE phosphate. Such an impurity may be a result of reagents used to synthesize the REE phosphates (many of the methods used to synthesize REE phosphates, including the one employed in this study, involve the use of ammonium phosphate, or some other soluble phosphate salt, at some point in the synthesis) (Boatner et al., 1981; Boatner and Sales, 1988; Boatner, 2002). The second is incongruent dissolution of the REE phosphate, resulting in a less-soluble REE-bearing phase. Possibilities for a less-soluble phase could include oxides, hydroxides, carbonates, or hydroxy carbonates.

Mass-balance calculations suggest that the amount of REE “missing” from solution (compared to phosphate) in the experiments is a relatively small proportion of the total REE in the starting material. For example, assuming that the REE deficiency in solution is attributable to the retention of REE oxide in the solid phase, calculations indicate that this oxide would represent on the order of 0.01 wt.% of the total initial solid material. Such a small proportion of a second phase could not be detected by standard X-ray diffraction methods. Moreover, if the secondary REE phase formed in the experiments lacked long-range order, then it would be even less likely to be detected

by XRD. Similarly, if the non-stoichiometric Ln/P ratios in solution are attributable to the presence of a more soluble phosphate impurity, the required amount of this impurity also would be too small to detect via XRD, and falls within the uncertainty of the bulk chemical analysis of the solid starting material.

It is possible to test the feasibility of the formation of a secondary hydroxide phase using equilibrium constants for the following reaction from Wood et al. (2002):



For an ionic strength of 0.1 mol kg⁻¹ at 25 °C, log*K* for the above reaction is 18.6. According to data from Table 3 for our experiment at 0.1 mol kg⁻¹ HCl+NaCl at 23 °C, the solution is undersaturated with respect to Nd(OH)₃(s) by approximately 20 orders of magnitude. The data of Wood et al. (2002) apply to well-crystallized Nd(OH)₃(s); the solubility of amorphous Nd hydroxide would be even higher. Thus, it seems unlikely that a hydroxide or oxide phase would form in the acidic solutions employed in our experiments. The formation of carbonate or hydroxycarbonate phases at these low pH_m values seems equally unlikely.

The fact that our solutions were strongly undersaturated with respect to the most probable secondary REE phases leads us to believe that the non-stoichiometric Ln/P ratios in solution result from the dissolution of a more soluble phosphate impurity in the starting material. The required amount of this impurity is too small to be detected by XRD or bulk chemical analysis. We also did not find any SEM evidence for the presence of an additional phase, but again the small amount required may have escaped detection. If a more soluble phosphate impurity were present, REE phosphate would have been the solubility-controlling phase, but the REE concentrations would have been suppressed by the common ion effect. If the actual measured dissolved REE and P concentrations are employed in the calculation of the solubility products, then the “excess” phosphate should not interfere with this calculation. Our interpretation is supported by the fact that the solubility products that we derive from our data are in reasonable agreement with those in the literature, with the exception of Y-phosphate (see Section 5.3). Our interpretation is also supported by the fact that

pre-conditioning of the starting material prior to an experiment by reaction with dilute acid solution or reuse of the starting material in successive experiments tended to reduce the degree of non-stoichiometry presumably because the soluble impurity was removed. Poitrasson et al. (2004) also noted an excess of P over REE in their experiments on REE phosphate solubility and attributed this non-stoichiometry to the presence of a small amount of a soluble phosphate impurity. In fact, they generally observed much smaller Ln/P ratios in solution than we did. Moreover, in the experiments of Firsching and Brune (1991) on Pr, Nd, Ho, and Er, the Ln/P ratio in solution was also consistently ≤ 1 (0.86–1.01). Thus, the presence of small amounts of phosphate impurities in Ln-phosphates may be a common occurrence, and experimental solubility products derived assuming stoichiometric dissolution could be significantly in error.

5. Discussion

5.1. Dependence of solubility on pH_m

The data presented in Tables 3 and 4 show that, as expected, the solubility of the REE phosphates decreases rather strongly with increasing pH_m . Within experimental uncertainty, the observed dependence of solubility on pH_m is consistent with reaction (3) being the solubility-controlling reaction. This confirms the expectation, based on known acid dissociation constants, that $H_3PO_4^0$ is the predominant phosphate species, with a smaller contribution by $H_2PO_4^-$. Note that, in calculating the values of Q_{s3} , we subtracted the relatively small concentration of $H_2PO_4^-$ from the total phosphate concentration to obtain the actual concentration of $H_3PO_4^0$. The observed pH_m dependence of solubility also confirms that Ln^{3+} is not significantly hydrolyzed.

5.2. Calculation of solubility products

The conditional equilibrium constant for reaction (3) (i.e., Q_{s3}) for each of the REE studied at each temperature and chloride concentration was calculated from Eq. (5). The value of $m_{Nd^{3+}}$ was assumed to be equal to the total measured molal concentration of Nd.

The value of m_{H^+} was calculated from the measured value of pH_m , and $m_{H_3PO_4^0}$ was calculated from the total measured phosphate concentration pH_m and the conditional dissociation constants of phosphoric acid given by Mesmer and Baes (1974). The resultant conditional equilibrium constants for reaction (3) for each of the REE studied at each temperature and ionic strength are given in Table 5. The extrapolation of Q_{s3} values to infinite dilution to obtain K_{s3} is illustrated in

Table 5
Calculated values of the conditional stability constant for reaction (3)

REE	Temperature (°C)	Stoichiometric ionic strength (mol kg ⁻¹)	Log Q_{s3}
La	23	0	-3.01
		0.1	-2.28
		0.5	-2.14
		1.0	-1.91
		5.0	-1.13
	50	0	-3.76
		0.1	-3.02
		1.0	-2.37
		5.0	-1.02
		Nd	23
0.1	-3.46		
0.5	-3.24		
1.0	-3.16		
5.0	-2.53		
50	0		-4.96
	0.1		-4.23
	1.0		-3.64
	5.0		-2.71
	150		0
0.1		-7.76	
0.5		-7.85	
1.0		-5.17	
Sm		23	0
	0.1		-2.16
	0.5		-2.22
	1.0		-2.07
	5.0		-0.73
	50	0	-3.13
		0.1	-2.48
		1.0	-2.45
		5.0	-1.29
		Y	23
0.1	-5.61		
1.0	-5.53		
5.0	-4.44		
50	0		
	0.1		-5.48
	1.0		-5.14
	5.0		-3.94

Fig. 3, which shows the degree of fit of Eq. (10) to the data at 23 °C. The fits are equally good at the other temperatures investigated. Note that a term in I^2 was required to fit all the data. The derived values of K_{s3} (i.e., $\log Q_{s0}$ at $I=0$) also are given in Table 5. Values of the solubility product (K_{s0}), derived as described in Section 2, are given in Table 1.

5.3. Comparison of measured solubility products to previous work

From Table 1, our results for the solubility products of the REE phosphates can be directly compared to those reported in the literature. Our value for K_{s0} at 23 °C for La-phosphate is identical to the value given by Jonasson et al. (1985) at 25 °C within the quoted uncertainties. Our value is also quite close to the value given by Tananaev and Vasil'eva (1963), and to the value of Firsching and Brune (1991) as recalculated by Byrne and Kim (1993). However, the original value given by Firsching and Brune (1991) is almost two orders of magnitude lower than ours. Our value is

exactly one order of magnitude higher than that given by Liu and Byrne (1997). Firsching and Brune (1991) are the only authors who have reported a solubility product of La-phosphate for a temperature above 25 °C. Their data show a decrease in the solubility product between 25 and 70 °C, which is smaller than the decrease we found between 23 and 50 °C.

Our value of K_{s0} at 23 °C for Nd-phosphate is within 0.2 log units of the values given at 25 °C by Jonasson et al. (1985) and the original value given by Firsching and Brune (1991), and is 0.4 log units lower than the value of Firsching and Brune (1991) as recalculated by Byrne and Kim (1993) and 0.4 log units higher than the value of Liu and Byrne (1997). Very recently, Poitrasson et al. (2004) have reported a value of $\log K_{s0} = -25.93 \pm 0.07$ at 21 °C, which compares very well with our value of $\log K_{s0} = -25.82 \pm 0.05$ at 23 °C. On the other hand, Rai et al. (2003) recently reported a value of the solubility product for NdPO₄, which is about an order of magnitude higher than all the others given in Table 1. Rai et al. (2003) may have measured the solubility

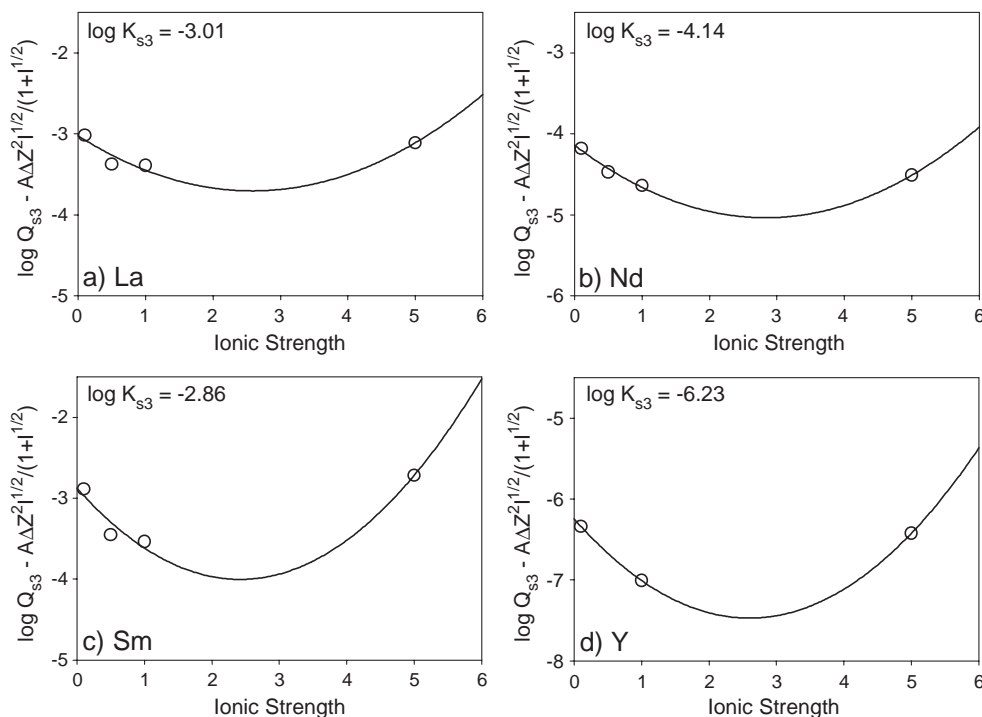


Fig. 3. Representative plots of $\log Q_{s3}(I) - \frac{A\Delta Z^2 \sqrt{I}}{1 + \sqrt{I}}$ vs. I at 23 °C for: (a) La; (b) Nd; (c) Sm; and (d) Y. The intercept of each curve yields an estimate of $\log K_{s3}$.

of a less crystalline form of NdPO_4 , resulting in the higher solubility product. As for the temperature dependence of K_{s0} for NdPO_4 , Firsching and Brune (1991) report a small increase in the solubility product with increasing temperature, whereas we find a substantial decrease with increasing temperature. On the other hand, as in our study, Poitrasson et al. (2004) find that the solubility product of NdPO_4 decreases strongly with increasing temperature (Fig. 4). This finding, coupled with the weak complexation of Ln^{3+} by chloride to at least 150 °C, implies that monazite exhibits retrograde solubility, at least over the range of temperatures investigated by us and Poitrasson et al. (2004) (i.e., up to 300 °C). Retrograde solubility of monazite to at least 300 °C also was predicted based on thermodynamic calculations by Wood and Williams-Jones (1994). Unfortunately, although our data and the data of Poitrasson et al. (2004) both show that K_{s0} for NdPO_4 decreases with increasing temperature, the trends diverge with increasing temperature, such that at 150 °C (the highest temperature we measured), our K_{s0} value is nearly two orders of magnitude smaller than the value interpolated from the data of Poitrasson et al. (2004) at 70 and 200 °C. The discrepancy at 50 °C is probably within the combined experimental uncertainties. However, the discrepancy at 150 °C is outside the stated uncertainties; it may be related to potential errors in measured phosphate, as our experiments at 150 °C consistently yielded the lowest Ln/P ratios (Table 3). Other possible sources of the discrepancy could be differences in the way activity coefficients or pH or both were determined;

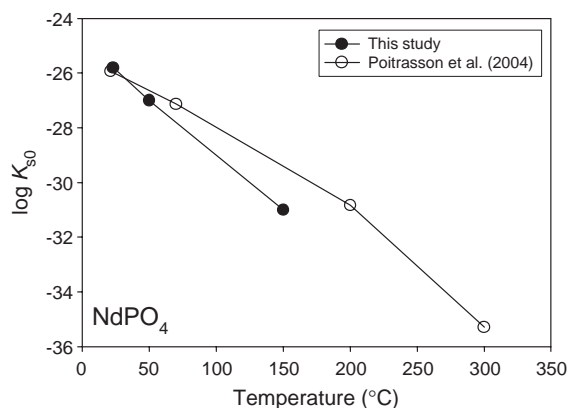


Fig. 4. Plot of $\log K_{s0}$ vs. temperature for NdPO_4 , comparing the results of this study to those of Poitrasson et al. (2004).

as mentioned in Section 2, calculated values of K_{s0} are very sensitive to uncertainties in these quantities. The disagreement between our study and that of Poitrasson et al. (2004), and the continued lack of solubility data for REE phosphates in general at elevated temperatures indicate the need for more experimental measurements. Nevertheless, it appears that the solubility products of NdPO_4 and LaPO_4 at standard conditions are now comparatively well-established.

Very few measurements of the solubility product of Sm-phosphates have been reported. Our value at 23 °C is about 1.5 log units larger than the original values given by Firsching and Brune (1991) and Liu and Byrne (1997), but only about 0.8 log units higher than the value recalculated by Byrne and Kim (1993). The higher value we obtain compared to that of Firsching and Brune (1991) could be due to the fact that our Sm-phosphate was apparently hydrated (i.e., had the rhabdophane structure), whereas the Sm-phosphate of Firsching and Brune (1991) may have had the monazite structure. However, the Sm-phosphate employed by Liu and Byrne (1997) had the rhabdophane structure but still yields a lower solubility product by about 1.5 log units.

To our knowledge, there have been only three measurements of the solubility of YPO_4 —ours and those of Firsching and Brune (1991) and Liu and Byrne (1997). Our value of K_{s0} for this phosphate at 23 °C is almost three orders of magnitude lower than those of Firsching and Brune (1991) and Liu and Byrne (1997) at 25 °C. Our value is also much lower than the values of K_{s0} reported in Table 1 for heavy REE phosphates, which should have the xenotime structure and behave similarly to YPO_4 . Thus, our value for YPO_4 may be in error. Given the relatively good agreement of our solubility products for La-, Nd-, and Sm-phosphates with those in the literature, it is curious that the solubility product for YPO_4 should be in error by such a large margin. However, as mentioned above, the concentrations of Y often did not level off with respect to time as clearly as was the case for the other phosphates, which suggests that equilibrium was not attained in our experiments with Y. However, the experiments of Liu and Byrne (1997) on YPO_4 had a similar duration to ours, but apparently resulted in a higher solubility product. This finding may indicate different rates of attainment of equilibrium in the two sets of experiments, possibly due to

different grain sizes/surface areas The Y experiments were also distinguished in consistently exhibiting the greatest deviation of the Y/P ratio from unity (Tables 3 and 4), with P often more than twice the concentration of Y. Finally, YPO_4 was the only Ln-phosphate studied, the solubility of which apparently had a slightly prograde temperature dependence. For all these reasons, we believe that our solubility products for YPO_4 are suspect.

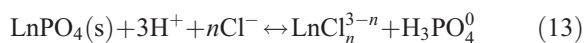
5.4. Effect of chloride on the solubility of REE phosphates

We conducted solubility experiments in both perchlorate media (presumed to be weakly complexing; Johansson, 1974) and chloride media. Chloride complexes of the trivalent REE and Y are known to be quite weak at temperatures less than ~ 150 °C (Wood, 1990a,b; Haas et al., 1995; Gammons et al., 1996, 2002; Migdisov and Williams-Jones, 2002). Because chloride complexation of Ln^{3+} ions is weak, we did not make an explicit correction for chloride complexation in the derivation of the solubility product. Rather, an empirical extrapolation of the equilibrium constant for reaction (3) to zero ionic strength was employed to account implicitly for weak complexation effects.

We used a variety of approaches to validate the assumption that chloride complexation can be ignored. First, we conducted a special set of experiments in which the solubilities at 23 °C of all four REE phosphates in 0.999 m HCl+0.001 m NaCl solutions were compared with those in 0.999 m HClO_4 +0.001 m NaClO_4 solutions (Table 6). In other words, the relative solubilities of the REE phosphates in chloride and perchlorate (presumably non-complexing) solutions were compared directly at the same

ionic strength, temperature, and pH_m . For La, the solubilities are nearly identical in chloride and perchlorate solutions, and for Nd and Y, the solubilities in chloride solutions are only 17% and 8% higher than those in the perchlorate solutions, differences that are within or only slightly outside the combined analytical uncertainties. The data for Sm in Table 6 appear to be anomalous, with the difference being more than a factor of two. However, overall the data imply that chloride complexation of the trivalent REE is weak at 23 °C. This conclusion is in excellent agreement with data in the literature for the stability constants of REE-chloride complexes at standard conditions (Wood, 1990a,b; Gammons et al., 1996, 2002; Migdisov and Williams-Jones, 2002).

A second check on the assumption that chloride complexation is weak enough to ignore is based on an evaluation of the chloride dependence of the measured solubility. Assuming that H_3PO_4^0 is the predominant phosphate species, we can write a general solubility reaction, including chloride complexation:



The conditional equilibrium constant for this reaction can be written as:

$$Q_{s3n} = \frac{m_{\text{LnCl}_n^{3-n}} m_{\text{H}_3\text{PO}_4^0}}{m_{\text{H}^+}^3 m_{\text{Cl}^-}^n} \quad (14)$$

Taking the logarithm of this expression and differentiating with respect to $\log m_{\text{Cl}^-}$ (holding pH_m constant) yields:

$$\frac{\partial (\log m_{\sum \text{Ln}} + \log m_{\text{H}_3\text{PO}_4^0})}{\partial \log m_{\text{Cl}^-}} = n \quad (15)$$

where $m_{\sum \text{Ln}}$ is the total analytical concentration of REE or Y in solution. Thus, the slope of a plot of $(\log m_{\sum \text{Ln}} + \log m_{\text{H}_3\text{PO}_4^0})$ vs. $\log m_{\text{Cl}^-}$ should yield an estimate of n , the average chloride ligand number of the dissolved REE species. In our case, this is only a rough estimate because ionic strength was not held constant as chloride was varied.

Calculated estimates of n , the average ligand number, as derived from Eq. (15) are given in Table 7, and some representative plots of $(\log m_{\sum \text{Ln}} + \log m_{\text{H}_3\text{PO}_4^0})$ vs. $\log m_{\text{Cl}^-}$ are shown in Fig. 5. The

Table 6

Comparison of REE phosphate solubilities in perchlorate and chloride media at 23 °C, 1 mol kg^{-1} total ionic strength, and 0.999 mol kg^{-1} H^+ (i.e., $\text{pH}_m \approx 0$)

Ln	Ln (mol kg^{-1}) perchlorate	Ln (mol kg^{-1}) chloride	$\text{Ln}_{\text{Cl}^-}/\text{Ln}_{\text{ClO}_4^-}$
La	1.65E–02	1.63E–02	0.988
Nd	7.39E–03	8.64E–03	1.169
Sm	1.25E–02	2.65E–02	2.120
Y	1.54E–04	1.67E–04	1.084

Table 7

Estimates of n obtained from the chloride dependence of the solubility data

LnPO ₄	T (°C)	n
LaPO ₄	23	0.35±0.08
	50	0.83±0.21
NdPO ₄	23	0.24±0.02
	50	0.63±0.09
	150	2.2±1.9
SmPO ₄	23	0.48±0.25
	50	0.38±0.31
YPO ₄	23	0.41±0.25
	50	0.63±0.26

calculated errors on the n values represent the standard error of the slope given by regression analysis, and do not include errors resulting from the variation in ionic strength. In general, the value of n will not be constant as a function of chloride concentration if stepwise complexation occurs; it should increase with chloride concentration as the number of chloride ions bound to the Ln³⁺ ion increases. However, over the range of chloride

concentration investigated in this study, a single straight line was sufficient to fit the data (except for Nd at 150 °C, where the data show significant scatter), implying a relatively constant value of n . Because the ionic strength was not held constant as chloride concentration was varied, the values of n given in Table 7 include the non-specific effects of ionic strength (i.e., activity coefficients) in addition to the formation of chloride complexes. In the case of reaction (3), increased ionic strength should favor increased solubility from activity coefficient effects alone. Thus, the values of n given in Table 7 overestimate the degree of complexation of the REE by chloride.

Nevertheless, taking all these issues into account, the values of n for all the REE at 23 °C indicate that the predominant species for all the REE investigated is the uncomplexed ion Ln³⁺, with a possible small contribution from the first chloride complex LnCl²⁺. The fact that n appears to be constant (i.e., a straight line fits the data well) suggests that the contribution of LnCl²⁺ is indeed very minor, and that the apparent

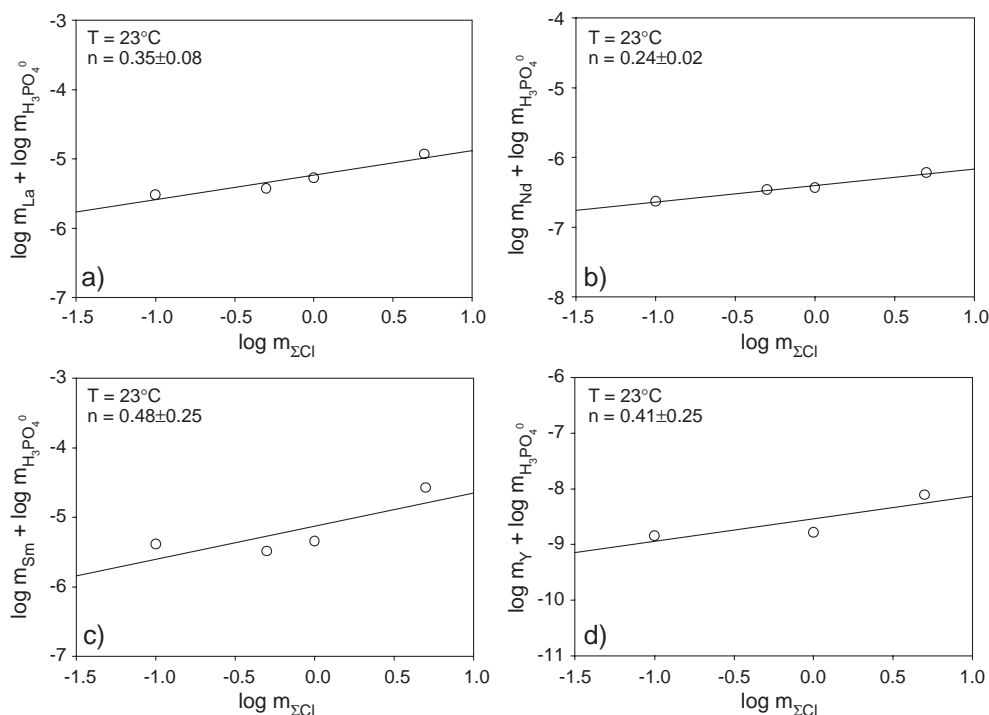


Fig. 5. Representative plots of $(\log m_{Ln} + \log m_{H_3PO_4})$ vs. $\log m_{\Sigma Cl}$ at 23 °C for: (a) La; (b) Nd; (c) Sm; and (d) Y. These plots yield estimates of the value of n in Eq. (15).

increase in solubility with chloride concentration at 23 °C may be a result of activity coefficient effects alone.

At 50 °C, the values of n tend to increase, but they remain less than 1.0. This possibly indicates an increased proportion of LnCl^{2+} , consistent with the expected increase in stability of the chloride complexes with increasing temperature. Nevertheless, the Ln^{3+} ion still probably represents a significant proportion of the REE, especially at the lower chloride concentrations. The value of n for Nd at 150 °C is significantly larger than at the lower temperatures, but the uncertainty of this estimate is quite large. Moreover, the data are not well fit by a simple straight line when plotted as $(\log m_{\text{Ln}} + \log m_{\text{H}_3\text{PO}_4})$ vs. $\log m_{\Sigma\text{Cl}}$. There may be a problem with the measured phosphate concentrations for the experiments at 150 °C inasmuch as they range over two orders of magnitude, whereas the Nd concentrations range over less than one order of magnitude over the range of chloride concentrations investigated. Moreover, the Nd concentrations increase systematically with increasing chloride concentration, but the phosphate concentrations vary non-systematically (Table 3). It appears as although the phosphate concentrations for the 0.1- and 1.0-m experiments may be too high. The value of n depends on the phosphate concentration as implied by Eq. (15), so any errors in the determination of phosphate concentration would contribute to errors in the estimation of n . The results of Gammons et al. (1996) suggest that the average value of n between 0.1 and 1.0 mol kg^{-1} chloride should be between 0 and 1.0 at 150 °C. Thus, even at 150 °C, the degree of complexation of Nd^{3+}

by chloride in our experiments is relatively small, especially as the chloride concentration decreases.

We carried out one final set of calculations to investigate the effect of chloride complexation on the solubility of REE phosphates over the range of temperatures investigated in this work. Using the values of K_{s3} for NdPO_4 at infinite dilution determined in this study, the stability constants determined by Gammons et al. (1996) for Nd(III)–chloride complexes, the Helgeson b equation for activity corrections, and the pH, total chloride, and H_3PO_4^0 concentrations of our experiments, we calculated a theoretical concentration of Nd in each of our experimental solutions assuming equilibrium with NdPO_4 . These values are compared with the actual measured values in Table 8. It should be noted that very similar results are obtained if the Nd(III) stability constants of Migdisov and Williams-Jones (2002) are used. This similarity is expected because the two sets of stability constants are in very good agreement.

At 25 °C and 50 °C, the calculated and measured concentrations of Nd agree satisfactorily, given the possible sources of error, even at the higher total chloride concentrations. The maximum deviation is a factor of three, with the measured values generally, but not always, greater than the calculated values. It is also clear from these calculations that, at 25 °C and 50 °C, chloride complexes represent less (and in most cases much less) than 50% of the total REE concentration. The abovementioned possible error in total measured phosphate concentration may account for the much poorer agreement between calculated and measured Nd concentrations at 150 °C. A

Table 8
Comparison of calculated and measured solubilities of $\text{NdPO}_4(\text{s})$

Temperature	m_{NaCl}	pH_m	$m_{\text{H}_3\text{PO}_4}$	$m_{\text{Nd}^{3+}}$ calculated	$m_{\text{NdCl}^{2+}}$ calculated	m_{NdCl_2} calculated	$m_{\Sigma\text{Nd}}$ calculated	$m_{\Sigma\text{Nd}}$ measured
25	0.1	1.05	6.98E–04	2.42E–04	8.11E–06	–	2.50E–04	4.05E–04
	0.5	1.05	8.65E–04	3.34E–04	3.22E–05	–	3.66E–04	4.95E–04
	1	1.05	8.61E–04	4.36E–04	6.92E–05	–	5.05E–04	5.37E–04
	5	1.15	1.07E–03	5.00E–04	3.62E–04	–	8.62E–04	6.07E–04
50	0.1	1.05	2.17E–04	1.24E–04	5.56E–06	–	1.29E–04	2.18E–04
	1	1.05	4.13E–04	1.49E–04	3.09E–05	–	1.79E–04	3.47E–04
	5	1.15	8.53E–04	1.07E–04	1.02E–04	–	2.09E–04	6.16E–04
150	0.1	1.05	1.27E–05	2.23E–06	9.03E–07	1.74E–08	3.15E–06	9.96E–07
	0.5	1.05	4.53E–06	1.21E–05	1.22E–05	7.05E–07	2.49E–05	2.04E–06
	1	1.05	6.05E–04	1.24E–07	1.95E–07	1.89E–08	3.37E–07	6.28E–06

See text for details.

potential problem with the measured total phosphate concentration is also indicated by the fact that, whereas the measured Nd concentration increases steadily with increasing chloride concentration, the calculated Nd concentration increases from 0.1 to 0.5 m chloride, but then drops to a much lower value at 1.0 m chloride. An erroneously high phosphate concentration for the 1.0-m experiment would result in an anomalously low calculated Nd concentration.

When all sources of error are considered, the relatively good agreement between calculated and measured solubilities of NdPO₄ in chloride solutions suggests that a model employing our value for K_{s3} with the stability constants for Nd(III)–chloride complexes from Gammons et al. (1996) yields reasonably reliable solubilities for NdPO₄ in low-temperature brines. If we employed K_{s3} values derived from the measurements of Poitrasson et al. (2004), the calculated NdPO₄ solubilities would be identical to those calculated by our model at 25 °C, but would be somewhat higher at 150 °C. The important point brought out by these calculations and the discussion in this section is that, at the low temperatures of our experiments, increased NaCl concentration should have only a modest effect on the solubility of REE phosphates such as monazite.

The conclusion that chloride complexation has little effect on REE phosphate solubilities at low temperatures should not be construed to mean that such complexes are always unimportant in nature. Several studies have demonstrated that the stability of REE–chloride complexes increases dramatically with increasing temperature (Wood, 1990a,b; Haas et al., 1995; Gammons et al., 1996, 2002; Migdisov and Williams-Jones, 2002). Thus, we can expect that, at temperatures above ~200 °C, the solubilities of REE phosphates such as monazite and xenotime could be increased significantly in highly saline fluids owing to the formation of chloride complexes. However, experiments by Ayers and Watson (1991) at 800–1100 °C and 1.0–2.8 GPa and by Devidal et al. (1998) at 450–800 °C and 200 MPa seem to suggest a very weak dependence of the solubility of monazite even at elevated temperatures. This finding may indicate that increased ion pairing of chloride with Na⁺ and H⁺ with increasing temperature may partially offset the increase in the stability of REE–chloride complexes. In a subsequent paper, we will explore the effect of

chloride concentration on the solubility of Nd-phosphate at temperatures up to 300 °C, using currently available thermodynamic data.

In the previous paragraphs of this section, we have provided a number of lines of evidence to suggest that, at the temperatures and chloride concentrations of our experiments, the formation of chloride complexes has a comparatively small effect on the solubility of the REE phosphates. The relatively close agreement (except for Y) among the solubility products we determined in chloride media with those reported in the literature (which have generally been determined in media other than chloride solutions) further supports that chloride complexation is sufficiently weak and that our empirical extrapolation adequately accounts for the effects of chloride complexation.

5.5. Enthalpy of formation of REE phosphates

Recently Ushakov et al. (2001) have determined the enthalpy of formation of REE phosphates using oxide–melt solution calorimetry. It was therefore of interest to compare these enthalpies with those derived from the temperature dependence of the solubility of the REE phosphates. Assuming that the enthalpy of reaction (3) is a constant over the short temperature range investigated in our study, we can obtain $\Delta_r H^\circ$ for reaction (3) from the slope of a plot of $\log K_{s3}$ vs. $1/T$ according to the van't Hoff relationship:

$$\log K_{s3,T} - \log K_{s3,T_r} = \frac{-\Delta_r H^\circ}{2.30259R} \left(\frac{1}{T} - \frac{1}{T_r} \right) \quad (16)$$

The plot for Nd is shown in Fig. 6. The enthalpies of reaction (3) for La, Nd, Sm, and Y are given in Table 9. Using the enthalpies of formation of the Ln³⁺ ions and H₃PO₄⁰ (recall that $\Delta_f H^\circ(H^+) = 0$ by convention) at 25 °C and 1 bar from SUPCRT92 (Johnson et al., 1992), the enthalpy of formation of LnPO₄ can be calculated from $\Delta_r H^\circ$ according to:

$$\Delta_f H^\circ(\text{LnPO}_4) = \Delta_f H^\circ(\text{Ln}^{3+}) + \Delta_f H^\circ(\text{H}_3\text{PO}_4^0) - \Delta_r H^\circ \quad (17)$$

These estimates of $\Delta_f H^\circ$ have relatively high uncertainties owing to the small number of temperatures investigated (three in the case of Nd, and two each in

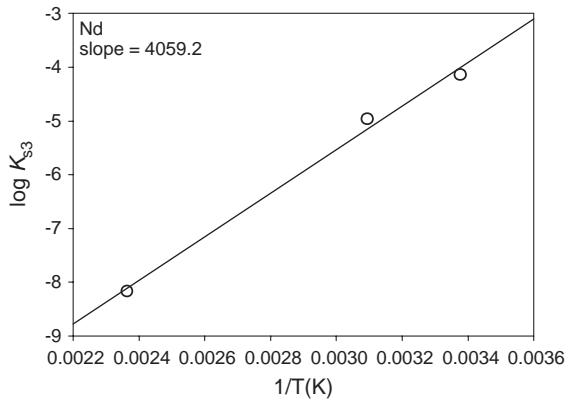


Fig. 6. Plot of $\log K_{s3}$ vs. $1/T$ for Nd-phosphate.

the cases of La, Sm, and Y). The uncertainty shown for Nd in Table 10 simply represents the standard error of the fit to the data in Fig. 6; it does not include other possible sources of uncertainties such as uncertainties in the values of K_{s3} or in the enthalpies of formation of the Ln^{3+} ions and H_3PO_4^0 . Moreover, derivation of $\Delta_f H^\circ(\text{LnPO}_4)$ from the temperature dependence of equilibrium constants normally is considered to be less accurate than direct calorimetry.

The estimates of $\Delta_f H^\circ(\text{LnPO}_4)$ from this study are given in Table 10 where they are compared with the calorimetrically derived values of Ushakov et al. (2001), those derived by Poitrasson et al. (2004) from temperature dependence of their solubility measurements, and two other sets of enthalpies reported in the literature (Ousoubalyev et al., 1975; Marinova and Yaglov, 1976). The values reported by Ousoubalyev et al. (1975) also were determined via calorimetry. Details on the derivation of the enthalpies of formation reported by Marinova and Yaglov (1976) are sketchy, but it appears that the enthalpies were calculated using solubility products of Ln(III)-phosphates from the literature (source not reported), and entropies of the phosphates estimated via an additivity algorithm. In general, our derived values of the enthalpy of formation of LaPO_4 , NdPO_4 , and SmPO_4 , are similar to, but somewhat less negative than, previously published estimates. Our enthalpy of formation of YPO_4 is more negative than the value quoted by Ushakov et al. (2001). The difference here may be a result of lack of attainment of equilibrium in our solubility experiments involving YPO_4 .

5.6. REE phosphates as a host for nuclear waste and geochronological studies

The implications of our results on the solubility of REE phosphates to economic geology, geochronology, and nuclear waste disposal will be explored more fully in a subsequent paper. However, our results do support conclusions of previous studies that, in the absence of strong complexing agents, the solubilities of REE phosphates are relatively low, even at low pH. The low solubilities of REE phosphates help explain their ubiquity as hosts of REE and actinides in a variety of geological environments. It therefore seems likely that the solubility of REE phosphates will limit REE mobility in many geologic situations. Our results also support the possible use of REE phosphates as host phases in the disposal of nuclear waste. The observed retrograde solubility over temperature ranges likely to be encountered in a geological nuclear waste repository suggests that these phases are even more resistant to modification by heated groundwaters than by cool groundwaters.

Our studies do not directly address the leaching of radionuclides such as Th, U, Pu, or their decay product Pb, from REE phosphate structures. Eyal and Olander (1990) and Olander and Eyal (1990a,b) showed that U and Th were more soluble than the monazite host. Moreover, Teufel and Heinrich (1997) and Seydoux-Guillaume et al. (2002) both concluded that resetting of the U–Th–Pb isotopic systems took place via dissolution–reprecipitation mechanisms. However, the REE phosphates remain quite resistant to leaching of actinides and Pb under most circumstances. It should be noted that the dissolution of minerals such as monazite and xenotime may be accelerated by radiation damage from the decay of U and Th (Petit et al., 1985). However, U- and Th-rich REE phosphate minerals are rarely found in a

Table 9

Enthalpies of the reaction: $\text{LnPO}_4(\text{s}) + 3\text{H}^+ \leftrightarrow \text{Ln}^{3+} + \text{H}_3\text{PO}_4^0$ at 25 °C derived from this study

Phosphate	$\Delta_f H^\circ$ (kJ mol ⁻¹)
LaPO_4	-51
NdPO_4	-78 ± 4
SmPO_4	-18
YPO_4	3

Table 10
Enthalpies of formation of LnPO₄ from the elements at 25 °C

Phosphate	$\Delta_f H^\circ$ (kJ mol ⁻¹) ^a	$\Delta_f H^\circ$ (kJ mol ⁻¹) ^b	$\Delta_f H^\circ$ (kJ mol ⁻¹) ^c	$\Delta_f H^\circ$ (kJ mol ⁻¹) ^d	$\Delta_f H^\circ$ (kJ mol ⁻¹) ^e
LaPO ₄	-1947	-1970.7±1.8	-	-1942	-1962
NdPO ₄	-1907±4	-1968.4±2.3	-1928	-1930	-1941
SmPO ₄	-1962 ^f	-1965.7±2.4	-	-1925	-1933
YPO ₄	-2008	-1987.7±1.7	-	-	-

^a Derived in this study from the temperature dependence of $\log K_{s3}$.

^b Derived by Ushakov et al. (2001) using oxide–melt solution calorimetry.

^c Derived from the temperature dependence of solubility by Poitrasson et al. (2004).

^d Derived by Ousbalyev et al. (1975) by calorimetry.

^e Derived by Marinova and Yaglov (1976) using solubility products and estimated entropies of LnPO₄.

^f Derived assuming SmPO₄, but this phosphate actually had the rhabdophane structure as described in the text.

metamict state, apparently because the radiation damage anneals quickly at comparatively low temperatures (Boatner, 2002; Ewing and Wang, 2002). Thus, thermodynamic and kinetic experiments carried out on Th- and U-poor REE phosphates may nevertheless be applicable to phosphates containing high quantities of radioactive elements and their daughter products.

6. Conclusions

The solubilities of end-member La-, Nd-, Sm-, and Y-phosphates have been determined in perchlorate and chloride media at 23 and 50 °C (and 150 °C for Nd) and low pH_m (0–2). Lack of change of concentration with time suggests close attainment of equilibrium (except for YPO₄) after 15–20 days, in agreement with most studies in the literature. Independent analyses of total REE and total phosphate demonstrate that Ln/P ratios are consistently ≤1.0, probably resulting from the presence of small amounts of soluble phosphate impurities remaining from the synthesis of the REE phosphates. Other recent studies have indicated a similar excess of phosphate. This imbalance should not affect the determination of solubility products if recognized and taken into account, but previous solubility studies based on an assumption that $\sum \text{REE} = \sum \text{PO}_4$ may need to be reevaluated.

The dependence of solubility on chloride concentration is weak at 23 and 50 °C. It is stronger at 150 °C, but more poorly constrained. Relatively weak complexation of the Ln³⁺ ions by chloride is

implied by our data and data from the literature. We employed an empirical extrapolation of the equilibrium constant to infinite dilution for the predominant REE phosphate dissolution reactions, and this procedure appears to have accounted adequately for the minor degree of chloride complexation. Solubility products at standard conditions derived from our work are in reasonable agreement with those given in the literature (except for Y). There are fewer measurements at elevated temperatures, and the agreement among the results of our study and those in the literature is poorer than at standard conditions, demonstrating the need for further measurements of REE phosphate solubilities at elevated temperatures.

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References

- Anderson, A.L., 1961. Thorium mineralization in the Lemhi Pass area, Lemhi County, Idaho. *Econ. Geol.* 56, 177–197.
- Anderson, G.M., Crerar, D.A., 1993. *Thermodynamics in Geochemistry: The Equilibrium Model*. Oxford University Press, Oxford, United Kingdom. 588 pp.

- Andreoli, M.A.G., Smith, C.B., Moore, J.M., Ashwal, L.D., Hart, R.J., 1994. The geology of the Steenkampskraal monazite deposit, South Africa: implications for REE–Th–Cu mineralization in chamoekite–granulite terranes. *Econ. Geol.* 89, 994–1016.
- Ayers, J.C., Watson, E.B., 1991. Solubility of apatite, monazite, zircon, and rutile in supercritical aqueous fluids with implications for subduction zone geochemistry. *Philos. Trans. R. Soc. Lond.*, A 335, 365–375.
- Baes Jr., C.F., Mesmer, R.E., 1986. *The Hydrolysis of Cations*. Krieger Publishing Company, Malabar, FL. 489 pp.
- Boatner, L.A., 2002. Synthesis, structure, and properties of monazite, pretilite, and xenotime. In: Kohn, M.J., Rakovan, J., Hughes, J.M. (Eds.), *Phosphates—Geochemical, Geobiological, and Materials Importance, Reviews in Mineralogy and Geochemistry*, vol. 48, pp. 87–121.
- Boatner, L.A., Sales, B.C., 1988. Monazite. In: Lutze, W., Ewing, R.C. (Eds.), *Radioactive Waste Forms for the Future*. Elsevier, Amsterdam, pp. 495–564.
- Boatner, L.A., Beall, G.W., Abraham, M.M., Finch, C.B., Huray, P.G., Rappaz, M., 1980. Monazite and other lanthanide orthophosphates as alternate actinide waste forms. In: Northrup Jr., C.J.M. (Ed.), *Scientific Basis for Nuclear Waste Management*, vol. 2. Plenum, New York, pp. 289–296.
- Boatner, L.A., Beall, G.W., Abraham, M.M., Finch, C.B., Floran, R.J., Huray, P.G., et al., 1981. Lanthanide orthophosphates for the primary immobilization of actinide wastes. Management of Alpha-Contaminated Wastes: Proceedings of the International Symposium. International Atomic Energy Agency, Vienna, pp. 411–422. IAEA-SM-246/73.
- Bourcier, W.L., Barnes, H.L., 1987. Ore solution chemistry-VII. Stabilities of chloride and bisulfide complexes of zinc to 350 °C. *Econ. Geol.* 82, 1839–1863.
- Byrne, R.H., Kim, K.H., 1993. Rare earth precipitation and coprecipitation behavior. The limiting role of PO_4^{3-} on dissolved rare earth concentrations in seawater. *Geochim. Cosmochim. Acta* 57, 519–526.
- Cetiner, Z.S., 2003. Experimental investigation of the solubility of the REE phosphate minerals monazite/xenotime and chloride complexation in hydrothermal solutions at 23 °C, 50 °C, and 150 °C and saturated water vapor pressure. Unpublished Ph.D. thesis, University of Idaho. 154 pp.
- Chao, E.C.T., Back, J.M., Minkin, J.A., Yinchen, R., 1992. Host-rock controlled epigenetic, hydrothermal metasomatic origin of the Bayan Obo REE–Fe–Nb ore deposit, Inner Mongolia, PRC. *Appl. Geochem.* 7, 443–458.
- Clark, A.M., 1984. Mineralogy of the rare earth elements. In: Henderson, P. (Ed.), *Rare Earth Element Geochemistry, Developments in Geochemistry*, vol. 2. Elsevier, Amsterdam, pp. 33–61.
- Devidal, J.L., Gibert, F., Kieffer, B., Pin, C., Montel, J.M., 1998. A new method for solubility measurement: application to NdPO_4 system in H_2O – NaCl – HCl hydrothermal fluids. *Min. Mag.* 62A, 375–376.
- Ewing, R.C., Wang, L., 2002. Phosphates as nuclear waste forms. In: Kohn, M.J., Rakovan, J., Hughes, J.M. (Eds.), *Phosphates—Geochemical, Geobiological, and Materials Importance, Reviews in Mineralogy and Geochemistry*, vol. 48, pp. 673–699.
- Eyal, Y., Olander, D.R., 1990. Leaching of uranium and thorium from monazite: I. Initial leaching. *Geochim. Cosmochim. Acta* 54, 1867–1877.
- Firsching, F.H., Brune, S.N., 1991. Solubility products of the trivalent rare-earth phosphates. *J. Chem. Eng. Data* 36, 93–95.
- 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 at 25 °C 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. In: Hellmann, R., Wood, S.A. (Eds.), *Water–Rock Interactions, Ore Deposits, and Environmental Geochemistry: A Tribute to David A. Crerar*, Geochemical Society Special Publication, vol. 7, pp. 191–207.
- Gibson, P., 1999. Origin of the Lemhi Pass REE–Th deposits, Idaho/Montana: Petrology, mineralogy, paragenesis, whole-rock chemistry and isotope evidence: Unpublished M.Sc. thesis, University of Idaho. 320 pp.
- 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.
- Harrison, T.M., Catlos, E.J., Montel, J.-M., 2002. U–Th–Pb dating of phosphate minerals. In: Kohn, M.J., Rakovan, J., Hughes, J.M. (Eds.), *Phosphates—Geochemical, Geobiological, and Materials Importance, Reviews in Mineralogy and Geochemistry*, vol. 48, pp. 523–558.
- Helgeson, H.C., 1969. Thermodynamics of hydrothermal systems at elevated temperatures. *Am. J. Sci.* 267, 729–804.
- Helgeson, H.C., Kirkham, D.H., Flowers, G.C., 1981. Theoretical predictions 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 molar properties to 600 °C and 5 kbar. *Am. J. Sci.* 281, 1249–1516.
- Johansson, L., 1974. The role of the perchlorate ion as ligand in solution. *Coord. Chem. Rev.* 12, 241–261.
- Johnson, J.W., Oelkers, E.H., Helgeson, H.C., 1992. SUPCRT92: a software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species and reactions from 1 to 5000 bars and 0° to 1000 °C. *Comput. Geosci.* 18, 899–920.
- Jonasson, R.G., Bancroft, G.M., Nesbitt, H.W., 1985. Solubilities of some hydrous REE phosphates with implications for diagenesis and seawater concentrations. *Geochim. Cosmochim. Acta* 49, 2133–2139.
- Kerr, I.D., 1998. Mineralogy, chemistry and hydrothermal evolution of the Pea Ridge Fe-oxide deposit, Missouri, USA, Unpublished M.Sc. thesis, Windsor, Ontario: University of Windsor. 113 pp.
- Kositcin, N., McNaughton, N.J., Griffin, B.J., Fletcher, I.R., Groves, D.I., Rasmussen, B., 2003. Textural and geochemical

- discrimination between xenotime of different origin in the Archaean Witwatersrand basin, South Africa. *Geochim. Cosmochim. Acta* 67, 709–731.
- Langmuir, J., 1997. *Aqueous Environmental Chemistry*. Prentice-Hall, Inc., New Jersey.
- Liu, X., Byrne, R.H., 1997. Rare earth and yttrium phosphate solubilities in aqueous solution. *Geochim. Cosmochim. Acta* 61, 1625–1633.
- Mariano, A.N., 1989. Economic geology of rare earth minerals. In: Lipin, B.R., McKay, G.A. (Eds.), *Geochemistry and Mineralogy of Rare Earth Elements*, Reviews in Mineralogy, vol. 21, pp. 309–337.
- Marinova, L.A., Yaglov, V.N., 1976. Thermodynamic characteristics of lanthanide phosphates. *Zh. Fiz. Him.* 50, 802–803.
- Mesmer, R.E., Baes Jr., C.F., 1974. Phosphoric acid dissociation equilibria in aqueous solutions to 300 °C. *J. Solution Chem.* 4, 307–322.
- Migdisov, A.A., Williams-Jones, A.E., 2002. A spectrophotometric study of neodymium(III) complexation in chloride solutions. *Geochim. Cosmochim. Acta* 66, 4311–4323.
- Nuelle, L.M., Day, W.C., Sidder, G.B., Seeger, C.M., 1989. Geology and mineral paragenesis of the Pea Ridge iron ore mine, Washington County, Missouri; origin of the rare-earth element and gold-bearing breccia pipes. *U.S. Geol. Surv. Bull.* 1989, A1–A11.
- Olander, D.R., Eyal, Y., 1990a. Leaching of uranium and thorium from monazite: II. Elemental leaching. *Geochim. Cosmochim. Acta* 54, 1879–1887.
- Olander, D.R., Eyal, Y., 1990b. Leaching of uranium and thorium from monazite: III. Leaching of radiogenic daughters. *Geochim. Cosmochim. Acta* 54, 1889–1896.
- Oreskes, N., Einaudi, M.T., 1990. Origin of rare earth element-enriched hematite breccias at the Olympic Dam Cu–U–Au–Ag deposit, Roxby Downs, South Australia. *Econ. Geol.* 85, 1–28.
- Ousbalyev, I., Batkybekova, M., Yousoufov, V., Kydynov, M., 1975. Les propriétés des phosphates et des iodates des éléments des terres rares. Fourth International Conference on Chemical Thermodynamics (Montpellier, France, August 26–30, 1975), pp. 217–223.
- Petit, J.-C., Langevin, Y., Dran, J.-C., 1985. Radiation-enhanced release of uranium from accessory minerals in crystalline rocks. *Geochim. Cosmochim. Acta* 49, 871–876.
- Poitrasson, F., Hanchar, J.M., Schaltegger, U., 2002. The current state and future of accessory mineral research. *Chem. Geol.* 191, 3–24.
- Poitrasson, F., Oelkers, E., Schott, J., Montel, J.-L., 2004. Experimental determination of synthetic NdPO₄ 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.
- Rai, D., Felmy, A.R., Yui, M., 2003. Thermodynamic model for the solubility of NdPO₄(c) in the aqueous Na⁺–H⁺–H₂PO₄[–]–OH[–]–Cl[–]–H₂O system. *J. Radioanal. Chem.* 256, 37–43.
- Seydoux-Guillaume, A.-M., Paquette, J.-L., Wiedenbeck, M., Montel, J.-M., Heinrich, W., 2002. Experimental resetting of the U–Th–Pb systems in monazite. *Chem. Geol.* 191, 165–181.
- Smith, M.P., Henderson, P., Peishan, Z., 1999. Reaction relationships in the Bayan Obo Fe–REE–Nb deposit Inner Mongolia, China: implications for the relative stability of rare-earth element phosphates and fluorocarbonates. *Contrib. Mineral. Petrol.* 134, 294–310.
- Spear, F.S., Pyle, J.M., 2002. Apatite, monazite, and xenotime in metamorphic rocks. In: Kohn, M.J., Rakovan, J., Hughes, J.M. (Eds.), *Phosphates—Geochemical, Geobiological, and Materials Importance*, Reviews in Mineralogy and Geochemistry, vol. 48, pp. 293–335.
- Staatz, M.H., 1972. Geology and description of the thorium-bearing veins, Lemhi Pass Quadrangle, Idaho/Montana. *U.S. Geol. Surv. Bull.* 1351. 94 pp.
- Tananaev, I.V., Vasil'eva, V.P., 1963. Lanthanum phosphates. *Russ. J. Inorg. Chem.* 8, 555–558.
- Teufel, S., Heinrich, W., 1997. Partial resetting of the U–Pb isotope system in monazite through hydrothermal experiments: an SEM and U–Pb isotope study. *Chem. Geol.* 137, 273–281.
- Ushakov, S.V., Helean, K.B., Navrotsky, A., Boatner, L.A., 2001. Thermochemistry of rare-earth orthophosphates. *J. Mater. Res.* 16, 2623–2633.
- Vielreicher, N.M., Groves, D.I., Fletcher, I.R., McNaughton, N.J., Rasmussen, B., 2003. Hydrothermal monazite and xenotime geochronology: a new direction for precise dating of orogenic gold mineralization. *Soc. Econ. Geol. Newsl.* (53), 1–15.
- Willigers, B.J.A., Baker, J.A., Krogstad, E.J., Peate, D.W., 2002. Precise and accurate in situ Pb–Pb dating of apatite, monazite, and sphene by laser ablation multiple-collector ICP-MS. *Geochim. Cosmochim. Acta* 66, 1051–1066.
- Wood, S.A., 1990a. The aqueous geochemistry of the rare earth elements and yttrium. Part I. Review of available low temperature data for inorganic complexes and the inorganic REE speciation of natural waters. *Chem. Geol.* 82, 159–186.
- Wood, S.A., 1990b. The aqueous geochemistry of the rare earth elements and yttrium. Part II. Theoretical predictions of speciation in hydrothermal solutions to 350 °C at saturated water vapor pressure. *Chem. Geol.* 88, 99–125.
- Wood, S.A., 2003. The geochemistry of rare earth elements and yttrium in geothermal waters. In: Simmons, S.F., Graham, I. (Eds.), *Volcanic, Geothermal and Ore-forming Fluids: Rulers and Witnesses of Processes Within the Earth*, Society of Economic Geologists Special Publication, vol. 10, pp. 133–158.
- Wood, S.A., Samson, I.M., 1998. Solubility of ore minerals and complexation of ore metals in hydrothermal solutions. In: Richards, J.P., Larson, P.B. (Eds.), *Techniques in Hydrothermal Ore Deposits Geology*, Reviews in Economic Geology, vol. 10, pp. 33–80.
- Wood, S.A., Williams-Jones, A.E., 1994. The aqueous geochemistry of the rare earth elements and yttrium. Part IV. Monazite solubility and REE mobility in exhalative massive sulfide-forming environments. *Chem. Geol.* 115, 47–60.
- Wood, S.A., van Middlesworth, P., Gibson, P., Ricketts, A., 1997. The mobility of the REE, U and Th in geological environments in Idaho and their relevance to radioactive waste disposal. *J. Alloys Compd.* 249, 136–141.

Wood, S.A., Palmer, D.A., Wesolowski, D.J., Bénézech, P., 2002. The aqueous geochemistry of the rare earth elements and yttrium. Part XI. The solubility of Nd(OH)₃ and hydrolysis of Nd³⁺ from 30 to 290 °C at saturated water vapor pressure with

in-situ pH_m measurement. In: Hellmann, R., Wood, S.A. (Eds.), *Water–Rock Interactions, Ore Deposits, and Environmental Geochemistry: A Tribute to David A. Crerar*, Geochemical Society Special Publication, vol. 7, pp. 229–256.