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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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 NaClO$_4$–HClO$_4$ 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 H$_3$PO$_4^0$ and Ln^{3+} (where Ln^{3+} 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:

$$LnPO_4 + 3H^+ \leftrightarrow Ln^{3+} + H_3PO_4^0$$
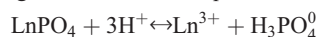
The conditional equilibrium constants determined at various ionic strengths were extrapolated empirically to obtain the equilibrium constants at infinite dilution (K_{s3}). These constants were then converted to solubility products (K_{s0}) for the following reaction:

$$LnPO_4(s) \leftrightarrow Ln^{3+} + PO_4^{3-}$$
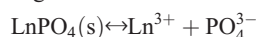
using acid dissociation constants for H$_3$PO$_4^0$ available in the literature. The values of logK_{s0} so obtained are:

	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.

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 ($LnPO_4 \cdot H_2O$; light REE-selective with a hexagonal structure) and churchite ($YPO_4 \cdot H_2O$; 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