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Experimental studies of REE fractionation during water–mineral interactions: REE release rates during apatite dissolution from pH 2.8 to 9.2

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Abstract

Rare earth elements (REE) release rates were measured during the open-system dissolution of natural apatite at 25 °C, $2.8<\mathrm{pH}<9.2$, and at ionic strengths ranging from 0.001 to 0.02 mol/kg. All inlet solutions were Ca, REE, and P free. In agreement with previous studies, apatite dissolution rates determined from outlet solution Ca concentrations decrease monotonically with increasing pH. Outlet solution molar REE/Ca ratios differ from that of the dissolving apatite during the experiments, this behaviour is interpreted to stem from dissolution or precipitation of minor quantities of rhabdophane ($\mathrm{REE(PO_4)} \cdot n\mathrm{H_2O}$). This interpretation is supported by solute speciation calculations, which indicate that REE are retained in the solid phase when the outlet fluids are supersaturated with respect to Nd-rhabdophane ($K_{\mathrm{sp}} \approx 10^{-24.5 \pm 0.5}$), but preferentially released when the outlet fluids are undersaturated with respect to Nd-rhabdophane. The relative concentrations of the REE in the outlet solutions suggest that the secondary rhabdophane is slightly enriched in light REE (Ce to Eu). The results of this study suggest that rhabdophane dissolution and precipitation during apatite–fluid interaction plays a major role in controlling surface and ground water REE signatures.

Keywords: Apatite dissolution; REE signatures; Rhabdophane precipitation

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1. Introduction

The overall goal of this study is the improved understanding of the behaviour of the Rare Earth Elements (REE) during low-temperature water–rock interaction. REE compositions of low-temperature natural solutions have received particular attention because of their potential as chemical tracers of natural fluid–rock processes (e.g., Sholkovitz, 1993; Öhlander et al., 1996; Johannesson et al., 1999; Ingri et al., 2000; Hannigan and Sholkovitz, 2001; Worrall and Pearson, 2001; Aubert et al., 2001; Felit-

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syn and Morad, 2002; Harlavan and Erel, 2002; Nelson et al., 2003). The REE compositions of such fluids are believed to be influenced by selective complexation in the fluid phase (Roaldset and Rosenqvist, 1971; Tang and Johannesson, 2003), secondary phase precipitation (Byrne and Kim, 1990, 1993; Zhong and Mucci, 1995; Liu and Byrne, 1997; Rasmussen et al., 1998; Harlov and Förster, 2003), and selective adsorption (Johannesson et al., 2000; Coppin et al., 2002). Distribution patterns of REE in minerals and rocks have been applied to the dating of minerals and bones (Hawkesworth and Calsteren, 1984; Grandjean-Lecuyer et al., 1993; Reynard et al., 1999), the correlation of rocks in sedimentary basins (Bouch et al., 2002; Ehrenberg and Nadeau, 2002; Fanton et al., 2002), deducing the paleo-chemistry of the oceans (Shaw and Wasserburg, 1985; Grandjean and Albarede, 1989), and to distinguish the biotic versus abiotic origin of minerals (Sano et al., 1999). The degree to which REE distribution patterns alter in response to low-temperature water–rock interaction affects strongly the accuracy of such applications.

The present study is focused on REE release rates during low-temperature apatite dissolution. Although apatite is present only as an accessory mineral in many low-temperature systems, its significance may be great as its far-from-equilibrium dissolution rates are far faster than those of many other REE-bearing minerals; compare, for example, the pH 2 apatite dissolution rate (10^{-7} mol/m^2 s, Valsami-Jones et al., 1998; Guidry and MacKenzie, 2003) with those of monazite (10^{-13} mol/m^2 s, Oelkers and Poitrasson, 2002), and the intermediate feldspars ($10^{-10.5}$ mol/m^2 s, Blum and Stillings, 1995; Oelkers and Schott, 1995). The ability of apatite to release REE to natural solutions during its dissolution was confirmed by the sequential leaching experiments of Harlavan and Erel (2002). Moreover, phosphate minerals with structures similar to apatite, zircon, and monazite are currently being considered as waste hosts for the storage of actinides extracted from nuclear waste (Wronkiewicz et al., 1995; Ewing, 1999); the knowledge of REE release rates from apatite can be used to better evaluate the potential of such waste hosts (Chapman and Smellie, 1986; Krauskopf, 1986). Towards an improved understanding of REE behaviour during low-temperature water–rock interaction, REE release rates have been measured during the 25 °C dissolution of natural apatite in open-system reactors as a function of pH. The purpose of this manuscript is to present the results of this experimental study and to use these results to illuminate the mechanisms controlling the REE evolution of low-temperature natural fluids.

2. Theoretical background

The standard state adopted in this study is that of unit activity for pure minerals and H_2O at any temperature and pressure. For aqueous species other than H_2O, the standard state is unit activity of the species in a hypothetical 1 molal solution referenced to infinite dilution at any temperature and pressure. Activities of solid-solution components are assumed to be equal to their mole fractions. All thermodynamic calculations on the present study were performed using PHREEQC (Parkhurst, 1998) together with the LLNL database after adding thermodynamic properties for REE solid phases taken from Runde et al. (1992) and Poitrasson et al. (2004).

Dissolution experiments were performed in the present study using open-system mixed-flow reactors. Steady-state apatite dissolution rates are computed from these experiments using measured outlet solution concentrations according to

$$r_{\mathrm{ap},i} = \frac{C_i F}{v_{\mathrm{ap},i} s} \tag{1}$$

where $r_{\mathrm{ap},i}$ [mol/cm^2 s] refers to the apatite dissolution rate based on the release rate of the ith element, C_i stands for the outlet concentration [mol/kg] of the ith element, F represents the fluid flow rate [kg/s], $v_{\mathrm{ap},i}$ denotes a stoichiometric coefficient equal to the number of moles of the ith element present in one mole of apatite, and s denotes the total apatite BET surface area [cm^2] present in the reactor. s was calculated by multiplying the powder's initial specific BET surface area by the mass of powder remaining in the reactor. The mass of powder remaining in the reactor was computed from mass balance considerations and the total Ca removed from the reactor via the outlet solution during the experiment. The saturation index of