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Uranium and manganese diffusion in apatite

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Abstract

Diffusion of manganese and uranium has been characterized by Rutherford Backscattering Spectrometry (RBS) in fluorapatite. The following Arrhenius relation is obtained for Mn diffusion in natural Durango fluorapatite, for diffusion parallel to c:

$$D_{\mathrm{Mn}} = 5.4 \times 10^{-7} \exp\left(-288 \text{ kJ mol}^{-1}/RT\right) \text{ m}^2 \text{ s}^{-1}.$$

Mn diffusion normal to c appears to be similar to diffusion parallel to c, and diffusivities in natural and synthetic (free of significant amounts of REE or other minor constituents) apatites are the same within experimental uncertainties. Experiments run in air, where Mn is in a more oxidized state, yield diffusivities similar to those for experiments run in sealed silica capsules, which the above Arrhenius relation represents.

Uranium diffusion experiments over the temperature range 1000–1300 °C yield the following Arrhenius relation for diffusion parallel to c:

$$D_{\mathrm{U}} = 1.3 \times 10^{-6} \exp\left(-394 \text{ kJ mol}^{-1}/RT\right) \text{ m}^2 \text{ s}^{-1}.$$

Diffusion coefficients for transport normal to c are quite similar to those parallel to c. U diffusion experiments run in air, where U is most likely hexavalent, yield diffusivities about an order of magnitude slower than the Ni–NiO buffered experiments. Diffusivities of Mn are comparable to those established previously for Sr and are slightly slower than Pb in apatite. The similar diffusion rates for Sr and Mn, despite their significant differences in cationic radii, suggest that cation size does not exert strong influence on diffusion of divalent cations in apatite, a finding consistent with that previously observed for the trivalent REE. In contrast, cation charge does seem to influence diffusivities strongly in apatite (although Mn appears perhaps something of an exception). U diffusion (buffered at NNO) is about 4 orders of magnitude slower than Mn diffusion, and about 2 orders of magnitude slower than REE diffusion. The differences between U diffusivities in experiments run with the NNO buffer, when U is more likely in the tetravalent state, and in air, where U is hexavalent, are also consistent with this observation.

Keywords: Diffusion; Uranium; Manganese; Apatite; Rutherford Backscattering Spectrometry

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1. Introduction

Diffusion plays a significant role in the distribution of trace and minor elements within and among minerals in rocks exposed to elevated temperatures for extended periods of time. Although apatite exists primarily as an accessory phase, its ability to incorporate and potentially concentrate a range of minor and trace elements can make it a good indicator of granite petrogenesis (e.g., Sha and Chappell, 1999). Because apatite can survive episodes of crustal anatexis, inherited apatite cores in some cases can offer clues to the origins of crustally derived granites (Watson and Harrison, 1984). While accessory apatite is most often associated with crustal rocks, apatite can also be present in metasomatized upper mantle peridotites, representing up to 1% modal abundance (e.g., O'Reilly and Griffin, 2000) in those from continental lithosphere and to several tenths of a percent in sources from oceanic lithosphere (e.g., Hauri et al., 1993).

In previous work on apatite, we have measured Sr (Cherniak and Ryerson, 1993), Pb (Cherniak et al., 1991) and the REE (Cherniak, 2000) which have contributed to understanding of the importance of diffusion in influencing measured isotopic and chemical signatures of these elements. In this study, we investigate the diffusion of Mn and U in natural and synthetic fluorapatite.

Manganese is an important minor element in apatite, and can replace more than 10% of Ca (e.g., Deer et al., 1992), with Mn contents in some mantle apatites in the range of 290–1220 ppm (O'Reilly and Griffin, 2000). Mn plays an important role in the coloring of apatite as well as its luminescence (e.g., Mariano, 1988); fluorapatite can luminesce with as little as 40 ppmw Mn^{2+} (e.g., Filippelli and Delaney, 1993). It also has technological applications, since Mn-doped synthetic fluorapatite is used as a phosphor in fluorescent lamps (e.g., Butler, 1980; Blasse and Grabmaier, 1994, Waychunas, 2002). Both divalent and pentavalent Mn have been introduced into synthetic fluorapatite, with the former substituting for Ca (Okhubo, 1969) and the latter for P (Kingsley et al., 1965), where it can produce deep blue coloring of apatite (Gilinskaya and Mahskovetsev, 1995). Divalent Mn in apatite can occupy both Ca sites in apatite, as indicated by time-resolved luminescence studies of natural apatites (Gaft et al., 1997), but shows preference for Ca(1) sites (e.g., Hughes et al., 2004; Pan et al., 2002; Suitch et al., 1985), while Sr, for example, is strongly ordered into the Ca(2) site (Hughes et al., 1991).

U systematics in apatite are also important for several reasons. Apatite has long been used for U–Pb isotopic dating (e.g., Oosthuyzen and Burger, 1973), and U-series disequilibrium can be useful in dating young apatites (e.g., Farley et al., 2002; Amelin and Zaitsev, 2002). Phosphates such as apatite are also an important control on Th/U whole-rock ratios in meteorites (e.g., Goreva and Burnett, 2001). Since apatite is a possible ceramic matrix for storing actinides (e.g., Raicevic et al., 1999; Vance et al., 2000), characterizing transport of U in apatite is of some interest. In addition, tetravalent uranium can also be an activator for luminescence in apatite (e.g., Panczer et al., 1998), and observation of its variation in fine-scale zoning may aid in refining thermal histories if U diffusion rates are known.

Since we have, as noted above, measured diffusivities of other cations in apatite in previous studies (i.e., Cherniak et al., 1991; Cherniak and Ryerson, 1993; Cherniak, 2000), we can compare the present diffusion findings with those of divalent cations and those of other valences to assess the respective role of cation size and charge in influencing diffusivities in apatite. By using both natural and synthetic fluorapatite in experiments, we can also investigate whether the presence of various minor and trace elements (e.g., LREE) in natural apatite, and the differences in defect concentrations between natural apatite and flux-grown synthetic apatite, significantly affect cation diffusivities.

2. Experimental procedure

Mn diffusion coefficients were determined in a natural fluorapatite from Durango, Mexico, and a synthetic fluorapatite. The chemical composition of the Durango fluorapatite, as reported by Young et al. (1969), is $Ca_{9.83}Na_{0.08}Sr_{0.01}RE_{0.09}(PO_4)_{5.87}(SO_4)_{0.05}(SiO_4)_{0.06}(AsO_4)_{0.01}(CO_3)_{0.01}F_{1.90}Cl_{0.12}(OH)_{0.01}$. Among the rare earth elements, La, Ce, and Nd are each present in concentrations of a few thousand ppm. Although there can be significant chemical variation in individual specimens of this apatite, RBS analysis