Investigating the site preference of U and Th in Cl, F, Sr apatites using single crystal X-ray diffraction

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Introduction

Apatite, $Ca_{10}(PO_4)_6(F,OH,Cl)_2$, can accommodate numerous substituents, including radionuclides of environmental concern (REE, U, Th). Scores of studies have focused on the crystal chemistry of apatite substituents. However, little is known about the mechanisms of incorporation and the structural response of apatite to U and Th, despite the fact that the presence of these elements in apatite has been used in geochronologic and petrogenetic studies for decades. We investigated the site preference of U and Th for the two Ca positions (Ca1 and Ca2) in the structure of apatite using X-ray structures of synthetic Cl-, F-, and Sr-apatites.

Results and Discussion

Crystal structure refinements (R = 0.0138 - 0.0267) were undertaken on synthetic Cl-, F-, and Sr-apatites. X-ray refinements of U doped fluorapatites indicate a marked preference of U for the Ca2 site. Values of $U_{Ca(2)}/U_{Ca(1)}$, calculated per individual site to account for the different multiplicity of the two Ca sites, is 7.5. Similarly, X-ray refinement of Th doped fluorapatites also suggests that Th substitutes in the Ca2 site with a $Th_{Ca(2)}/Th_{Ca(1)}$ value of 6.5. For the Th doped chlorapatite, results show that Th is essentially equally distributed between the two Ca sites. The X-ray refinement for Th doped Sr-apatites with end members F and Cl shows that Th is incorporated in both Ca1 and Ca2 sites with $Th_{Ca(2)}/Th_{Ca(1)}$ ratios from 0.58 to 1.5.

The result which indicates U substitutes in the Ca2 site in fluorapatite is not consistent with the site preference of U^{6+} in fluorapatite, which is Ca1 site (Rakovan et al, 2002). Because the oxidation state of U in our sample is unknown, we are preparing to undertake X-ray absorption spectroscopic studies in order to demonstrate the relationship between the site preference and local structure and valence of U and Th in apatite.

The role of apatite in controlling the REE composition of natural waters

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Among the many biotic and abiotic processes that are influenced by apatite, one which is commonly overlooked is its effect on natural water Rare Earth Element (REE) composition. Apatite's role in the REE content of natural waters is unique as it 1) has a relatively rapid dissolution/precipitation rate and 2) is a major mineralogical reservoir for both REE and phosphate. As such, apatite may be close to equilibrium in many systems and its dissolution can provoke the precipitation of sparingly soluable REE phosphate minerals such as rhabdophane ($REE(PO_4)\cdot nH_2O$).

Towards an improved understanding of the link between apatite and natural water REE content, apatite was dissolved in both open and closed system reactors at 25° C and $2<pH<10$ (c.f. Ragnarsdottir and Oelkers, 1998; Chaïrat et al., 2004). REE are preferentially released from the solid phase when the reactive fluids are undersaturated with respect to rhabdophane, but retained in the solid phase when the reactive fluids are supersaturated with respect to rhabdophane. The relative concentrations of the REE in the reactive solutions suggest that the secondary rhabdophane is enriched in Ce, Pr, and Nd compared to the other REE. Results of the experimental study have been used to estimate the precipitation rate of rhabdophane in the presence of apatite.

An internally consistent database of REE bearing aqueous species and minerals has been used together with measured rates to estimate both the concentration of REE in natural waters in equilibrium with apatite and rhabdophane, and time required to attain this equilibrium. Comparisions between calculated contentrations and those reported in the literature are used to identify those systems where the REE are controlled by this mineral-fluid equilibrium.

References

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