Crystal chemistry of Uranium and Thorium in apatites

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Understanding the crystal chemistry of actinides in the apatite structure is critical for the evaluation of its potential use and stability as a radionuclide sequestration and remediation agent. Because of its common occurrence and its high affinity for many radionuclides (i.e. U, Th, REE, $^{9\circ}$Sr, $^{9\circ}$Y, etc), apatite has been used in geochronological and petrogenetic studies for decades. Those studies provide important information for the performance and properties of actinide containing apatites in specific natural environments over geologic periods, which cannot be duplicated purely by laboratory studies. However, little is known about the mechanism of incorporation and structure response of apatite to substituent actinides. It is therefore fundamentally important to understand the substitution mechanisms and other intrinsic and external factors that control the chemical composition and structural variation in actinide containing apatites.

In this study, U and Th substituions into fluor- and chlor-apatites were examined by the complementary use of diffraction and spectroscopy techniques. Results from single crystal X-ray diffraction indicate that U and Th show a marked perfence for Ca2 site in fluorapatite, whereas they favor both Ca1 and Ca2 sites in chlorapatite. Extended X-ray Absorption Fine Structure (EXAFS) is used to obtain quantitative information about the local structure distortions around U and Th in both natural and synthetic apatites. The EXAFS fitting results show that U and Th partitions into the Ca2 site in fluorapatite and yielded a ~0.05 – 0.08Å decrease of average Ca2-O bond distances associated with local structure distortions which extend over the first O shell to the second P shell. The substitution of U/Th in the Ca2 site of fluorapatite causes an overtall shrinkage of the Ca2 site and potentially rotations of the PO_4 polyhedra that are linked with Ca2 site. We speculate that the preference of Ca2 site over Ca1 site in fluorapatite is to minimize distortion of the Ca1-PO_4 framework of the fluorapatite structure. U/Th is chlorapatite is currently under EXAFS investigation in which case different approaches are taken to model one absober in two structure sites.

Quantitative assessment of the bioavailability and toxicity of nanometal particles in aquatic environments: New methodologies

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Understanding bioavailability is a pre-requisites for understanding toxicity of nanomaterials in the aquatic environment. Yet only a few studies have begun to quantitatively address these processes. Bioavailability is defined by uptake rates from food and water, as well as loss rates from an organism. Knowledge of those rates for a species of animal will allow comparisons of nanomaterial formulations and modeling of potential for bioaccumulation at environmentally realistic concentrations. Quantifying the rates is possible in simple experiments that require a tracer. Here we show that metal nanomaterials can be synthesized with a unique stable isotope ratios then employed in such experiments. Recent results comparing Ag nanomaterials with different caps, ZnO nanoparticles and Ni nanoparticles in an aluminium oxide matrix, show that the biology of the organism, the characteristics of the nanomaterial and the interaction of the nanomaterial in the environment all combine to affect bioavailability and resultant toxicity, sometimes in unanticipated ways.