

Sequestration of radionuclides and heavy metals by hydroxyapatite doped with Fe, Cu and Sn

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Apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH},\text{Cl})$ ($P6_3/m$, $Z=2$), is the most abundant phosphate mineral on Earth. The end-member hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ($P2_1/b$), is the primary mineral component in bones and teeth and tends to scavenge and sequester heavy metals in the human body. Hydroxyapatite has also been shown to be effective at sequestering radionuclides and heavy metals in geochemical systems (Dybowska et al., 2004). Hydroxyapatite has been the focus of many laboratory studies and is utilized for environmental remediation of contaminated sites (Moore et al., 2002). The crystal structure of apatite tolerates a great deal of distortion caused by extensive chemical substitutions. Metal cations (e.g. REE, actinides, K, Na, Mn, Ni, Cu, Co, Zn, Sr, Ba, Pb, Cd, Fe) substitute for Ca and oxyanions (e.g. AsO_4^{3-} , SO_4^{2-} , CO_3^{2-} , SiO_4^{4-} , CrO_4^{2-}) replace PO_4^{3-} through a series of coupled substitutions to preserve electroneutrality. Owing to the ability of apatite to incorporate "impurities" including actinides gives rise to its proposed use as a waste form for radionuclides. Recent work at Sandia National Laboratory demonstrated that hydroxyapatite has a strong affinity for U, Pu, Np, Sr and Tc reduced from pertechnetate (TcO_4^-) by SnCl_2 (Moore et al., 2002). Based on these earlier promising results, an investigation was initiated into the use of apatite-type materials doped with aliovalent cations including Fe, Cu and Sn as Tc-scavengers. Synthetic Fe and Cu-doped hydroxyapatite samples were prepared by precipitation of Ca, from Ca-acetate, and P, from ammonium phosphate. The Fe and Cu were introduced as chlorides into the Ca-acetate solution. Stannous chloride was used as a reducing agent and was apparently incorporated into the crystal structures of the hydroxyapatite samples in small, as yet, undetermined quantities. Their crystal chemical details and sorption properties will be discussed.

References

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Molecular Partnerships as a tool for engineering the morphology of hydroxyapatite

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The presence of hydroxyapatite in many biological systems is well documented because of the unique morphological forms which are expressed – the large hexagonal prisms in mammalian enamel, for example, or the small anisotropic tablets which populate the collagenous matrices of bone. The occurrence of these different crystallographic forms, and their associated chemico-physical characteristics provides a muse for crystal scientists seeking to develop new methodologies with which to engineer the exploitable properties of such minerals, e.g. catalysis, adsorption.

Here the chemical and sequence data extracted from the bio-organic species associated with bio-apatites were used to design a series of crystal growth additives whose activity was investigated in a crystallization assay. The results evidence the ability of specific additives to generate crystal morphs of apatite that duplicate those observed in biology. The molecular processes which facilitate this morphological tailoring have been resolved; specific molecular partnerships must exist between Ca^{2+} /additive complexes and the crystals in order for their habit and morphology to be re-engineered. In this presentation the identity and nature of these molecular partnerships will be discussed. The results offer an important insight into the processes of biological crystal formation and offer design prompts for the development of additives which might be deployed to engineer crystals of technological benefit.