Bioapatite: Where structure meets composition

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The nanometer scale of carbonate apatite crystallites in bone present a quandary: 1) Crystals growing uninhibited from a solution saturated with respect to that phase can become very large. 2) Bone crystals grow in body fluid saturated with apatite – otherwise, the fluid would resorb them. 3) So, how can bone crystals remain 10s of nanometers in size? Bone apatite contains 6-7 wt% CO_3^{2-}, mostly replacing PO_4^{3-}. Substitution of trigonal-planar CO_3^{2-} for tetrahedral PO_4^{3-} is a poor fit in geometry and charge balance. CO_3^{2-} incorporation strains the lattice, thereby increasing lattice energy, which we infer makes further crystal growth unfavorable. Thus, *composition affects structure*. In turn, the smaller a grain is, the greater is its surface area:volume ratio. Crystal surfaces have unsatisfied bonds, causing consequent re-alignment of neighboring atoms, thereby producing lattice distortion in the outer zones. In nanocrystals, such strained rinds can dominate their volume. Size-induced strain may be a major reason for the differences in properties between the nanocrystalline and macrocrystalline forms of chemically identical materials. Our group and others have shown that bone apatite is depleted in OH^- compared to synthetic hydroxylapatite. We postulate that lattice distortion caused by surface effects in bone nanocrystals may preclude incorporation of OH^- ions in the channel sites of this bioapatite. Thus, *structure affects composition*. Our proposed mechanism for the observed positive correlation between crystallite size and $[OH^-]$ is that CO_3^{2-} incorporation *indirectly* causes a decrease in OH^- concentration in bioapatite: Incorporation of carbonate strains the lattice, which constrains the crystallites to remain small, and makes OH-incorporation unfavorable. Note that this mechanism to account for an inverse correlation between $[OH^-]$ and $[CO_3^{2-}]$ in bioapatite is a plausible alternative to the suggestion that CO_3^{2-} *replaces* OH^- in the channel sites. Only structural-compositional analyses could distinguish between these mechanisms.

Nucleation and growth of nano-apatite: Applications to biomineralisation

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Calcium phosphate atomic cluster formation is the first step towards the nucleation of apatite, an important biomineral (bone, tooth). Formation of apatite at the atomic scale is believed to take place via the formation of a $Ca_3(PO_4)_2$ precursor. Very little is currently known about the nature and evolution (in saturated aqueous solutions) of this precursor, and how this may be affected/controlled by the presence of organic species.

Using the materials processing beamline, 6.2, at Daresbury Synchrotron Radiation Source for in-situ small-angle X-ray scattering (SAXS) experiments, we were able to monitor apatite nucleation and growth from supersaturated solutions at times scales of up to 30 minutes and at 10 second resolution. Our aim was to test the influence of a range of organic ligands (citrate, oxalate, osteocalcin) on nucleation and growth. Our preliminary observations suggest that organic ligands affect both the onset and the rate of crystal formation and growth, as well as the settling properties of apatite nucleating from a supersaturated solution. Compared to control experiments, the protein osteocalcin initiated early nucleation, whereas the organic ligands oxalate and citrate caused inhibition by delaying nucleation.

Initial shape analysis of the results suggests that, at least the particles forming in the presence of osteocalcin, have a distinctly flat pseudo-hexagonal appearance. These particles are well modeled using a disc like template. This in turn suggests an apatitic precursor early on in the particle growth process.