Understanding biomineralisation of bone apatite for applications to toxic metal remediation: Preliminary results

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Metal immobilisation via insoluble phosphate mineral formation is emerging as a remediation technology of great promise. The potentially high reactivity of bone in conjunction with its potential to slowly release phosphate to solution, has led to bonemeal being considered as a promising source of phosphate for metal remediation. The wider adoption of the method by the remediation industry has been slow due to health concerns about the safety of cattle bone. However, health concerns are only related to the organic component of bone, which is not active in the remediation process and may hinder this process by restricting bone porosity and availability of active mineral sites. Heat treatment can remove the organic component of bonemeal, but will, if too intense, deactivate the mineral source of phosphate (apatite) by improving its crystallinity and thus reducing its solubility and active surface area. There is therefore a clear need to determine the nature of bone apatite recrystallisation /transformation during different heating regimes. Work is being conducted to measure such changes using *in-situ* XRD-PSD heating experiments to measure the dynamics of apatite recrystallisation/transformation at temperatures of up to 900ºC. Transmission electron microscopy (TEM), infrared and Raman spectroscopy is also being used to investigate changes in bone apatite crystals. This is part of a larger study, which aims to fully characterise the changes that occur in the inorganic and organic parts of bone using small angle X-ray scattering (SAXS), thermal analysis (thermogravimetry-differential scanning calorimetry; TG-DSC) and amino acid analysis. These methods will allow a complete picture of the evolution of both inorganic and organic components to be obtained.

Secondary ion mass spectrometry of hypermineralized bioapatite: Human enamel, whale rostrum, and whale bulla

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Tooth enamel of mammals as well as certain bones of whales (the "bottlenose" facial projection and the tympanic earbone) are the densest types of natural apatitic biocomposites. Because those materials contain almost no proteins, they are ideally suited for compositional analysis of their nanocrystalline mineral phase. We analyzed rostrum, bulla, and human enamel (deciduous molar) using a CAMECA ims 3f ion microprobe with a negative primary $^{16}O^-$ ion beam. The relative concentrations of Ca, P, C, F, Cl, Na, Mg, K, Rb, Sr, Y, Ba, La and Ce were derived from their positive ion signals under energy filtering conditions. NIST OHApatite (nominal Ca/P atomic ratio = 1.67) was used as a standard. Compared to NIST OHAp, all three hypermineralized tissues are deficient in Ca, with Ca/P ratios of 1.46, 1.57, and 1.61 for enamel, rostrum, and bulla, respectively. Whereas Na, Mg, K, and Sr are very low in the NIST standard (all below 70 ppm), they are very abundant in the natural bioapatites. Compared to the human enamel, the whale bones are enriched by a factor of 2 in Na and Mg (~ 1.3 and 0.7 wt%, respectively, for rostrum and bulla) and by a factor of 4 in Sr (~ 400 ppm for rostrum and bulla). There is a large difference in the F contents: 8000 ppm in rostrum, 260 ppm in bulla, and 126 ppm in enamel. Assuming that all the detected C exists in the form of carbonate, we found, as expected, high CO_3^{2-} for the bony tissues (5.9 and 4.8 wt% in rostrum and bulla), and only 1.6 wt% CO_3^{2-} in enamel.