APATITE STRUCTURES

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Apatites have the formula, $Ca_{10}(PO_4)_6X_2$, with X commonly OH, F or Cl. The apatite lattice is very tolerant of substitutions and vacancies, for example Ca can be replaced by Sr, Pb and Na, and PO_4 by AsO_4 and VO_4. Apatites are widely distributed as accessory minerals in igneous rocks and in small quantities in most metamorphic rocks. Rock phosphates (microcrystalline apatite) of biological origin are the starting material for phosphate fertilizer manufacture; synthetic apatites are used as phosphors in fluorescent light tubes; and impure microcrystalline hydroxyapatite (HAP) forms the mineral (bioapatite) of bones and teeth.

Precipitated CO_3-free apatites and bioapatites have a variable molar Ca/P ratio (from *ca.* 1.5 to *ca.* 1.7). Rock phosphates and bioapatite typically contain several percent CO_3 which increases their chemical reactivity (rate of dissolution in acids and ease of thermal decomposition). This is sometimes advantageous, sometimes deleterious. The CO_3 seems mainly to replace PO_4 ions. Models for the variable Ca/P ratio and CO_3 substitution have been proposed, but not established by XRD. As precipitated apatites are generally of submicron dimensions, we have undertaken Rietveld structure refinements (*The Rietveld Method*, ed R.A. Young, Oxford University Press, 1995) of dental enamel and synthetic analogues to try to establish these details. Data was collected, usually over 24h, using an INEL-CPS 120 position sensitive detector and CuK alpha-1 monochromatic radiation.

By comparison with Holly Springs HAP, dental enamel (typically 3 wt % CO_3) exhibits a 3.6% decrease in apparent PO_4 tetrahedral volume, a reduction in P-O2 bond length and a reduction in P and Ca2 occupancies. Synthetic Na-free precipitated CO_3 apatites (3-4 wt% CO_3) display a 3.2% decrease in PO_4 volume and slight reduction in P and Ca2 occupancies, but all P-O bond lengths decrease. These changes can be attributed to CO_3 replacing PO_4, although the difference in P-O bond behaviour is still to be explained. Na-containing precipitated CO_3 apatites can contain up to 22 wt% CO_3 (compared to Na-free, max 10 wt% CO_3). The PO_4 tetrahedral volume decreases with increasing CO_3 and the occupancies of P and Ca1 fall. More generally, a plot of PO_4 tetrahedral volumes against P occupancies from a variety of sources (sound and carious dental enamel, and synthetic precipitated CO_3 apatites) decreases in an approximate linear fashion.

This work was supported by the Medical Research Council grant G9824467