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Accommodation of the carbonate ion in apatite: An FTIR and X-ray structure study of crystals synthesized at 2–4 GPa

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ABSTRACT

Carbonated hydroxylapatite (C-OHAp) and carbonate apatite (CAp; $x \geq 0.5$) in the composition series $Ca_{10}(PO_4)_{6-y}[(CO_3)_{x+(3/2)y}(OH)_{2-2x}]$, $x = 0.0–0.7$, $y = 0.0–0.6$, have been synthesized at 2–4 GPa, and studied by FTIR spectroscopy and single-crystal X-ray diffraction. Three structural locations for the carbonate ion have been identified: (1) apatite channel, oriented with two oxygen atoms close to the *c*-axis (type A1); (2) close to a sloping face of the PO_4 tetrahedron (type B); and, (3) stuffed channel position (type A2). Type A1 and B carbonate are equivalent to type A and B CAp of bone and enamel, whereas type A2 is a high-pressure feature. In type A CAp, ordering of type A1 carbonate within the apatite channel results in space group $P\bar{3}$; all other apatites studied have average structures with $P6_3/m$ symmetry. Results for three new structures are: type A C-OHAp, $x = 0.14$, $y = 0.0$, $a = 9.4468(4)$, $c = 6.8806(4)$ Å, and R (residual index of structure refinement) = 0.025; type B C-OHAp, $x = 0.0$, $y = 0.17$, $a = 9.4234(2)$, $c = 6.8801(3)$ Å, and $R = 0.025$; and type A-B CAp, $x = 0.7$, $y = 0.5$, $a = 9.4817(6)$, $c = 6.8843(3)$ Å, and $R = 0.025$. A fourth structure analysis suggests that the type A-B CAp exchanges some of its channel carbonate with OH^- during room-temperature storage in nujol oil, with x and y reduced to 0.6 and 0.4, respectively. Local structural adjustments to accommodate the carbonate ion in the *c*-axis channel of OHAp include dilation of the channel, contraction of the $Ca1O_n$ polyhedron, and rotation of the PO_4 tetrahedron about the P-O1 bond. The progressive increase in the *a* unit-cell edge length with increase in carbonate content of type A CAp is readily attributed to the dilation of the apatite channel. Carbonate-for-phosphate substitution in OHAp (type B CAp) requires displacement of O3 along ±[001] and, thus, results in expansion of *c* (and contraction of *a*).