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

MICHAEL E. FLEET,* XIAOYANG LIU, AND PENEOPE L. KING

Department of Earth Sciences, University of Western Ontario, London, Ontario N6A 5B7, Canada

ABSTRACT

Carbonated hydroxylapatite (C-OHAp) and carbonate apatite (CAp; \(x \approx 0.5\)) in the composition series \(\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_{2-2x}\), \(x = 0.0–0.7\), \(y = 0.0–0.6\), 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 \(\text{PO}_4\) 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 \(P\overline{3}\); all other apatites studied have average structures with \(P\overline{6}_3/m\) 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 \(\text{OH}^-\) 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 \(\text{CaO}_x\) polyhedron, and rotation of the \(\text{PO}_4\) 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 \(\pm[001]\) and, thus, results in expansion of \(c\) (and contraction of \(a\)).