

## X-ray structures of carbonate apatite

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The structural role of the carbonate ion in hydroxylapatite (OHAp) is reviewed. In recent studies, composite single crystals of carbonated OHAp and type A and A-B carbonate apatites [CAp;  $\text{Ca}_{10}(\text{PO}_4)_{6-y}(\text{CO}_3)_x+2y(\text{OH})_{2-2x-y}$ ] have been synthesized at 2-4 GPa, 1400-1500°C, and investigated by X-ray structure and FTIR spectroscopy.

Type A CAp (e.g.,  $x = 0.75, y = 0.0$ ) is characterized by IR bands at 1540 and 1455  $\text{cm}^{-1}$  and space group  $P-3$ . The carbonate ion is ordered along the apatite channel at  $z = 0.5$ , and single crystals are domain disordered with a multiplicity of six about the  $c$ -axis. Structure refinements have been made with the carbonate oxygens both unconstrained ( $R = 0.024$ ) and constrained to ideal carbonate ion geometry, with similar results. There are three structural locations for the carbonate ion in disordered type A-B CAp (e.g.,  $x = 0.7, y = 0.6$ ;  $P6_3/m$ ;  $R = 0.023$ ): A1 (of type A CAp) and A2 in the apatite channel, and B (IR bands at 1475 and 1410  $\text{cm}^{-1}$ ) representing carbonate substituting for the orthophosphate ion. The A2 carbonate ion (IR bands at 1570 and 1505  $\text{cm}^{-1}$ ) is in a stuffed channel position and appears to charge compensate carbonate-for-phosphate substitution at high pressure: it is selectively lost when type A-B CAp is annealed in air at low pressure. Both A1 and A2 carbonate ions are oriented nearly parallel to the  $c$ -axis, but A1 has two oxygen atoms close to this principal axis and A2 has only one. The B carbonate ion is located near to the sloping faces of the  $\text{PO}_4$  tetrahedron, but is not well resolved in the present X-ray structures.

Local structural adjustments to accommodate the carbonate ion in the  $c$ -axis channel of OHAp include dilation of the channel, contraction of the  $\text{Ca}_1\text{O}_n$  polyhedron, and rotation of the  $\text{PO}_4$  tetrahedron about the P-O1 bond axis. Carbonate-for-phosphate substitution requires displacement of the O3 oxygen atom along  $\pm[001]$ , and results in expansion of  $c$ .

## Complexity in the carbonate $\nu_3$ domain in fluorapatite

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Micro-FTIR and EMPA analysis (Tacker 2004) of large fluorapatite (FAp) crystals from pegmatites and carbonatites clarifies some of the issues involving the variability of literature values for carbonate peak positions. The asymmetric stretching vibration  $\nu_3$  for  $\text{CO}_3$  in apatite minerals is doubly degenerate, so the position and splitting of the  $\nu_3$  vibration ( $\nu_{3a}, \nu_{3b}$ ) should provide useful information about the distortion of the carbonate group and the environment of substitution. Peakfitting methods explicitly modelled peak overlaps.

A newly assigned Type A2 (Fleet et al. 2004) absorbance is observed in all specimens, as is the traditional Type A (A1 of Fleet et al. 2004). The low frequency peak diagnostic of Type B substitutions is observed, in single spectra, to have two  $\nu_{3a}$  components at  $\sim 1406$  (B1) and  $\sim 1424$  (B2)  $\text{cm}^{-1}$ . In some specimens, the corresponding  $\nu_{3b}$  peaks are resolved (1459 and 1449  $\text{cm}^{-1}$ , respectively). Using the data of Fleet et al. (2004) as initial conditions, spectra are described as combinations of A1 (1470, 1539  $\text{cm}^{-1}$ ), A2 (1498, 1574  $\text{cm}^{-1}$ ), B1 and/or B2 absorbances. Splitting of the  $\nu_3$  vibration is fairly constant ( $1\sigma = 2-7 \text{ cm}^{-1}$ ) for all four substitutions, an internal consistency suggesting the carbonate substitution mechanisms are similar in all specimens.

Only subtle differences emerge in comparison of FTIR of natural FAp with synthetic hydroxylapatites. The  $\nu_{3a}$  absorbance for A2 is shifted to slightly lower wavenumbers compared to the results of Fleet et al. (2004). Both B1 and B2 are reported in the literature regarding synthetic HAp, so the untenable substitution of  $\text{CO}_3\text{-F}$  for  $\text{PO}_4$  (Regnier et al., 1994) is unnecessary here. This leads to the inference that B1 and B2 represent (1) differing charge balance mechanisms and/or (2) replacement of different faces of the  $\text{PO}_4$  tetrahedron. Although charge balance achieved with paired cations cannot be ruled out entirely, results do not vary systematically with composition, and charge compensation with associated vacancies seems more probable.

### References

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