

Carbonate apatite crystal chemistry

M. E. FLEET*

Earth Sciences, Univ. Western Ontario, London, Ontario
N6A5B7 (*correspondence: mfleet@uwo.ca)

The location and orientation of the carbonate ion in the c -axis channel (type A) and phosphate (type B) positions of carbonate hydroxylapatite (CHAP) have been determined and correlated with infrared spectra (Fig. 1), using crystals synthesized at high pressure and temperature from carbonate-rich melts [1]. Carbonate out-of-plane bend (ν_2) infrared band areas are in good agreement with site occupancies from X-ray structures, but the areas of the corresponding asymmetric stretch (ν_3) bands of sodium-bearing CHAP greatly overestimate the contribution of type B carbonate, owing to band overlap. In complex sodium-bearing AB carbonate apatites, A and B carbonate ions and Na cations form a discrete A-B-Na defect cluster, which is associated with a downward shift of about 50 cm^{-1} in the type A doublet band. This spectral interference accounts for the reported dominance of B carbonate in bone mineral and dental enamel [2].

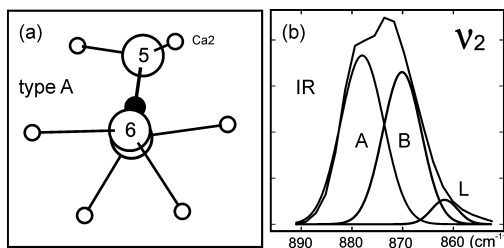


Figure 1: Na-AB CHAP; (a) channel carbonate ion; (b) composite ν_2 spectrum fitted with Gaussian components for channel (A), phosphate (B) and labile (L) carbonate.

The infrared spectra show that the hydrogencarbonate (bicarbonate) ion in Na-AB CHAP crystals is a channel species, as are its room-temperature decomposition products, type A carbonate and labile (L) carbonate, pointing to a possible role for the apatite channel in mediating acid-base reactions in the body.

Synthetic carbonate fluorapatite (CFAP) crystals show progressive conversion to the type B structure of francolite, the ore mineral of phosphorite. A weak feature in residual electron density maps is assigned to an interstitial fluoride anion, offering an explanation for the troublesome excess fluorine content of francolite: F-C interatomic distances are not consistent with a bonded fluor-carbon complex.

[1] Fleet & Liu (2009) *Biomaterials* **30**, 1473-1481. [2] Rey *et al* (2009) *Osteoporos Int.* **20**, 1013-1021.