

A-type carbonate in strontium phosphate apatites

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ABSTRACT

One of the most important characteristics of the apatite family of minerals is its ability to undergo substitution by ions such as sulfate and carbonate. The substitution of carbonate is particularly important because of the presence of carbonate in bone mineral and the recent suggestion that most of the substituted carbonate resides in the apatite channels (A-type substitution) rather than in place of phosphate (B-type substitution). The possibility of additional channel species or environments in carbonated Ca hydroxylapatite has been pursued via its Sr homolog, which is known to have a larger channel volume and a greater unit-cell *a*-axial length than its unsubstituted parent. Strontium hydroxyl-, chlor-, and fluorapatites, containing incorporated ¹³C-carbonate up to 7 wt%, were synthesized by aqueous precipitation reactions in the presence of Na, K, and ammonium counter cations. ¹³C-labeled carbonate was used to facilitate observation of the solid-state ¹³C MAS NMR spectra. Band-fitting of the IR carbonate asymmetric stretch ν_3 region required the use of eight bands, arranged as four doublets, that are interpreted as representing three channel environments (A-type substitution) and one B-type substitution. The carbonate ν_3 region of low Na, carbonated Sr hydroxylapatite contained the high-frequency limbs of the A-type doublets in the area between 1520 cm⁻¹ and the B-type region (1400–1360 cm⁻¹), whereas in the high Na analog the A-type doublets produced a broad high-frequency tail into the B-type region. Similar behavior was exhibited by the chlor- and fluorapatite analogs. Heating samples to 600 °C resulted in the loss of carbonate and conversion to A-type carbonate demonstrating the stability of A-type carbonate at higher temperatures.

Analysis of the populations of A-, A', and A'', and B-sites for the hydroxyl-, chlor-, and fluorapatites, prepared under both low Na and high Na conditions, revealed that high Na/carbonate ratios produce a larger amount of channel substitution, contrary to observations for Ca homologs. It is speculated that multiple A-environments also exist for Ca hydroxylapatite prepared by aqueous precipitation, which is consistent with Fleet's analysis of apatite prepared at high temperature and high pressure.

Keywords: Strontium, strontium apatite, apatite, IR, NMR, A-type carbonate