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 substitutted 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 carbonate 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 ν3 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 ν3 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

INTRODUCTION

The apatite family of minerals has members (Ca hydroxylapatite) of biological necessity to vertebrates and ions, such as Ca, Sr, phosphate, and hydroxide, that can be easily substituted. These characteristics can be partially rationalized by the abundance of the constituent ions and the hexagonal structure containing close-packed phosphate ions and cations that form channels that can accommodate anions and neutral molecules (Hughes and Rakovan 2002). The possibility of ion mobility in the channel that gives rise to nutrition and acid-base regulation (Fleet 2017) makes it particularly intriguing. The carbonate ion is known to substitute for two hydroxide ions located in the channel (A-type substitution) and also for phosphate (B-type substitution) (Pan and Fleet 2002). At least two types of channel carbonate ions with different orientations have been identified by X-ray diffraction (Fleet 2015, 2017) and three different environments for channel carbonate have been postulated on the basis of IR spectra (Fleet 2017).

Carbonated Ca hydroxylapatite, a close approximation to the inorganic material that constitutes bones and teeth, has been thought to contain primarily B-type carbonate, with A-type contributing not more than 10–15% of the total carbonate (Elliott 1994). Those assumptions were challenged by Fleet (2017) in an analysis of the IR spectra of Na-containing apatite prepared at high temperature and high pressure. This disentanglement of the carbonate asymmetric stretch region (ν3) of the IR spectrum, a frequently used monitor of the types of carbonate in apatite, suggested that the use of spectral indicators of A-type carbonate must be replaced by careful band-fitting, especially in this complex region of the IR.

All of the alkaline earth metal cations except those of Be and Mg form apatites that are structurally homologous to those of Ca but with more voluminous channels. Strontium, the closest homolog to Ca, forms apatites that have been used to enhance bone remediation and are closely related in structure and properties to their biologically active Ca counterparts. It is natural to speculate therefore on the possibility of additional carbonate ion orientations in the Sr apatite channel or to propose different channel environments.

We have previously shown that the a-axial length for carbonated Sr hydroxylapatite increases with increasing carbonate substitution and that the carbonate asymmetric stretch region of