MINERALS IN THE HUMAN BODY

Synthesis and structure of carbonated barium and lead fluorapatites: Effect of cation size on A-type carbonate substitution†

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ABSTRACT

Substitution of carbonate has long been recognized in both synthetic and natural biologically and geologically precipitated forms of hydroxyapatite. Although the predominant substitution mechanism in all of the calcium members of the apatite group formed below 100 °C is substitution of carbonate for phosphate (B-type), small amounts of A-type substitution of carbonate in the channel sites also occur. The present study focuses on the effect of cation size on the type of substitution of carbonate in members of the apatite group. The barium and lead members offer a larger channel site, which potentially could stabilize A-type substitution. A series of carbonated barium and lead fluorapatites were synthesized in aqueous solution and characterized by powder X-ray diffraction, and infrared and Raman spectroscopy. Carbonate content was determined by combustion analysis.

Unit-cell parameters derived from X-ray diffraction showed that, as carbonate content increased, the a-axis length decreased and the c-axis increased slightly for carbonated barium fluorapatites (CBAaApF), whereas the lengths of both the a- and c-axes increased for CPbApF. The co-occurrence of two sets of peaks in the ν1 carbonate region of the infrared spectra of lead and barium carbonated apatites are strongly suggestive of both A- and B-type carbonate substitution. This interpretation is supported by Rietveld analysis of X-ray powder diffraction data, which confirms the presence of significant, but not dominant, A-type substituted carbonate ions. The variation in cell parameters as a function of carbonate substitution mode is discussed, and it is shown that B-type carbonate substitution need not be accompanied by a decrease in the a-axis in all apatites. The greater amount of A-type carbonate substitution in barium and lead fluorapatites compared to their calcium homologs can be attributed to: (1) the less negative enthalpies of hydration of the barium and lead ions relative to that of calcium, and/or (2) the greater amount of space available for the relatively large carbonate ions in the channels defined by these large cations. Thus, the substitution modes can be controlled by either thermodynamic or kinetic considerations.

Keywords: Apatite, type A-carbonate, Rietveld, infrared, barium apatite, lead apatite

INTRODUCTION

Only five cations form well-characterized end-member apatites. These elements are the alkaline earth metals Ca, Sr, and Ba, the Group 14 metal Pb, and the transition metal Cd (Pan and Fleet 2002; Flora et al. 2004). The barium and lead apatites are particularly interesting because they contain the largest cations [the six-coordinate ionic radii for Ba2+ and Pb2+ are 1.35 and 1.19 Å, respectively, whereas the radius of Ca2+ is 1.00 Å (Shannon 1976)] present in end-member apatites and therefore can provide information on how cation size affects the structure and other characteristics of apatites. Of particular interest are the carbonated forms of these compounds because of the biological importance of the carbonated calcium homolog (CCaApOH), which is the mineral component of bones and teeth, and the possibility that larger cations may influence the substitution mode of carbonate. The barium and lead apatites are also of interest because of their formation in the remediation of heavy metal spills using phosphate remediants (Nriagu 1984; Ruby et al. 1994; Traina and Laperche 1999). We have previously reported on the preparation and characterization of lead hydroxyl- and chlorapatites (pyromorphites) (Sternlieb et al. 2010) as well as barium hydroxyl- and chlorapatites (Yoder et al. 2012).

Carbonate can be incorporated in the apatite structure in two different ways. In A-type substitution, carbonate resides in the channels between the M(2) metal ions, as represented, for example, by the formula Ca10(PO4)6(CO3)2(F)2. In B-type substitution, carbonate replaces a phosphate ion. Both types of substitution require charge compensation due to the difference in charge between the carbonate ion and the ions it replaces. In A-type substitution the charge is generally compensated by the removal of two fluoride ions for each substituting carbonate. There

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