

MINERALS IN THE HUMAN BODY

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

ZACHARY WILT<sup>1</sup>, CAITLYN FULLER<sup>1</sup>, TAIA BACHMAN<sup>1</sup>, VICTORIA WEIDNER<sup>1</sup>, JILL D. PASTERIS<sup>2</sup>  
AND CLAUDE H. YODER<sup>1,\*</sup>

<sup>1</sup>Department of Chemistry, Franklin and Marshall College, Lancaster, Pennsylvania 17603, U.S.A.

<sup>2</sup>Department of Earth and Planetary Sciences, Washington University in St. Louis, St. Louis, Missouri 63130-4899, U.S.A.

### ABSTRACT

Substitution of carbonate has long been recognized in both synthetic and natural biologically and geologically precipitated forms of hydroxylapatite. 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 (CBaApF), whereas the lengths of both the **a**- and **c**-axes increased for CPbApF. The co-occurrence of two sets of peaks in the  $\nu_3$  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