

Channel carbonate substitution in apatite: A new look with Raman and IR spectroscopy

J.D. PASTERIS^{1*}, C.H. YODER², M.M. BOLLMEYER²,
K.R. STEPIEN² AND S.N. DYBING¹

¹Dept Earth & Plan Sci, Washington Univ, St. Louis, MO
63130, USA (*correspondence: pasteris@wustl.edu)

²Dept of Chemistry, Franklin & Marshall College, Lancaster,
PA 17603, USA (claude.yoder@fandm.edu)

Background

The mineral component (40-60 wt%) of bone is carbonated (typically 4-8 wt% CO₃) hydroxylapatite. Based primarily on XRD and IR analyses, the model for 50+ years has been that CO₃²⁻ substitutes for channel OH⁻ ions (A type), PO₄³⁻ tetrahedra (B type), or both (AB type), and that B-type substitution greatly exceeds A-type[1]. Fleet [2] recently proposed, however, that overlap of IR bands in the ν₃ spectral region of sodium-bearing carbonated apatite (typical of bone) prepared at high temperature and pressure obscured the fact that A-type carbonate substitution in the channel was dominant.

Results

In an effort to evaluate the siting of the CO₃²⁻ ion in aqueously precipitated, bone-like, carbonated apatites, we have obtained Raman spectra in which there is little or no overlap of bands due to A- and B-type carbonate. We have compared Raman and IR spectra on the same high-temperature, well crystalline apatites to identify the corresponding A- and B-associated bands. We find a significant correlation of the stereochemical evidence between the techniques. Our spectral methodology developed on high-temperature apatites is now being evaluated for appropriate application to low-temperature aqueously precipitated apatites such as those in bone. Among the questions to be answered by ongoing experiments are (1) whether sodium incorporation affects carbonate partitioning between the A- and B-type sites and (2) whether incorporation of other monovalent ions such as K⁺ and NH₄⁺ cause the same or different effects as sodium in terms of structural and spectral responses.

[1] Elliott (2002) *Rev. Mineral. Geochem* **48**, 427-453.

[2] Fleet (2017) *Am. Mineral.* **102**, 149-157.