Structural effects on incorporated water in carbonated apatites†

JENNIFER E. GOLDENBERG1, ZACHARY WILT1, DEMETRA V. SCHERMERHORN1, JILL D. PASTERIS2 and CLAUDE H. YODER1,∗

1Department of Chemistry, Franklin and Marshall College, Lancaster, Pennsylvania 17603, U.S.A.
2Department of Earth and Planetary Sciences, Washington University in St. Louis, St. Louis, Missouri 63130-4899, U.S.A.

ABSTRACT

Confirmation of structural H2O in apatites using 2H solid state NMR spectroscopy has been followed by the determination of the number of molecules of H2O per unit cell (MPUC) using thermal gravimetric analysis (TGA) in 10 series of carbonated apatites [CMApX; M10d(P04)6X2 = MApX] containing the divalent cations (M) calcium, strontium, barium, and lead, and monovalent anions (X) OH−, F−, and Cl−. For many of the series, the average MPUC ranges from ca. 1.5–2.5 and is independent of the concentration (wt%) of carbonate. For other series, the average MPUC is as low as ca. 0.8 or as high as ca. 4.0. We have found for six of the series, i.e., those in which carbonate predominantly (>90%) substitutes for phosphate that the average MPUC correlates with cation and anion atomic radii, with unit-cell axial lengths, and, especially, with our calculations of the void space available in the c-axis channels.

We speculate that the volume of the channels in apatites affects the ability of H2O to occupy channel sites. In most low-temperature apatites of the type M10d(P04)6X2 that have been studied, carbonate prefers to substitute for phosphate (B-type substitution) rather than for monovalent anions in channel sites (A-type substitution), although computer simulations indicate that carbonate is more thermodynamically stable in the channel sites rather than the phosphate sites. In apatites with nearly total B-type carbonate substitution, there is no relationship between the number of molecules of H2O in the channels and the weight percent carbonate in the apatite. This lack of correlation would be expected when there is no competition within the channel between H2O and carbonate occupancy. In apatites with greater channel volumes, however, we infer that increased ease of carbonate incorporation in the channels also increases competition between H2O and carbonate. The originally incorporated amount of H2O is diminished to accommodate the thermodynamically favored carbonate ion substitution in the channels. We further speculate that these scenarios are most easily rationalized by incorporation of H2O early in the formation of nascent crystallites of apatites formed in aqueous solution, with carbonate entering the newly formed channels later and, in some cases, with difficulty.

Keywords: Water, carbonate, apatite, Rietveld, channel

INTRODUCTION

The association of water with apatites has long been recognized but the presence of incorporated molecular H2O has only recently been verified by the determination of D2O in the apatite structure and identification of the D2O by IR, Raman, and 2H solid state NMR spectroscopy (Yoder et al. 2012c; Pasteris et al. 2014). The presence of this molecular species in the c-axis channels of apatites may be a factor in the preference of synthetic low temperature (~100 °C) apatites for B-type carbonate substitution for phosphate, despite the likely thermodynamic preference for substitution of the channel ion via A− or mixed AB-type carbonate substitution (Peroos and de Leeuw 2006). The charge imbalance caused by B-type substitution of CO32− or HPO42− for PO43− typically leads to anion vacancies in the channel site. Hydrogen-bonding of H2O to phosphate oxygen atoms as well as charge-dipole interactions may help stabilize structures in which many of the channel anions have been removed. Finally, the presence of channel H2O may account for rehydroxylation of initial carbonated, hydroxyl-deficient apatites that undergo thermal decarbonation (Pasteris et al. 2012).

We have continued our exploration of structurally incorporated H2O by synthesizing carbonated apatites of calcium, strontium, barium, and lead containing the monovalent anions OH−, F−, Cl−, and Br−. The amount of structural H2O in 76 synthesized carbonated apatites (CMApX) has been determined by thermogravimetric analysis (TGA), and the cell parameters of a subset of these apatites have been determined by Rietveld analysis of X-ray diffraction data. Our objective has been to identify structural parameters and lattice interactions that are responsible for the number of H2O molecules incorporated in the unit cell.

* E-mail: claude.yoder@fandm.edu
† Special collection papers can be found on GSW at http://ammin.geoscienceworld.org/site/misc/specialissuelist.xhtml.