

SPECIAL COLLECTION: APATITE: A COMMON MINERAL, UNCOMMONLY VERSATILE

## Structural effects on incorporated water in carbonated apatites<sup>†</sup>

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### ABSTRACT

Confirmation of structural H<sub>2</sub>O in apatites using <sup>2</sup>H solid state NMR spectroscopy has been followed by the determination of the number of molecules of H<sub>2</sub>O per unit cell (MPUC) using thermal gravimetric analysis (TGA) in 10 series of carbonated apatites [CMApX; M<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>X<sub>2</sub> = MApX] containing the divalent cations (M) calcium, strontium, barium, and lead, and monovalent anions (X) OH<sup>-</sup>, F<sup>-</sup>, and Cl<sup>-</sup>. 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 H<sub>2</sub>O to occupy channel sites. In most low-temperature apatites of the type M<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>X<sub>2</sub> 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 H<sub>2</sub>O 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 H<sub>2</sub>O 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 H<sub>2</sub>O and carbonate. The originally incorporated amount of H<sub>2</sub>O 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 H<sub>2</sub>O 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