

The distribution of carbonate in apatite: The environment model

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ABSTRACT

The environment model is used to describe the location of carbonate in nine carbonated apatites containing varied percentages of carbonate and Na⁺, K⁺, or NH₄⁺ ions. Unlike the traditional model for carbonate substitution, which identifies different locations and orientations of the carbonate ion in the apatite structure, the environment model utilizes the different structural surroundings to describe the different types of carbonate. The A-type carbonate environment is assigned to channels lined only with calcium ions (A-channel configuration = Ca6) or to channels containing one Na⁺ or a vacancy (A'-channel configuration = Ca5Na or Ca5□), and the B-type carbonate environment is the surroundings of the replaced phosphate ion. The assignments are made by peak-fitting the carbonate asymmetric stretch region (ν_3) of the IR spectrum, following previously published criteria. These assignments lead to the conclusion that the percentage of channel carbonate (A- and A'-environments) is greater than that of B-type for each of these carbonated apatites. In general, the use of triammonium phosphate as the phosphate source in the synthesis produces apatites with larger amounts of channel carbonate (A- and A'-environments), while the use of sodium-containing phosphate reagents produces smaller amounts of channel carbonate.

The environment model provides explanations for the differences within IR and NMR spectra obtained for apatites containing a range of total carbonate content. The B-type appearance of the carbonate ν_3 region of the IR spectrum is found primarily in apatites containing sodium, which allows increased amounts of carbonation via co-substitution of Na⁺ with carbonate and creation of A'-environments with populations equal to that of B-type carbonate. The presence of ammonium or alkali metal salts with cations larger than Na⁺ results in the utilization of a charge-balance mechanism that produces vacancies rather than cation substitution in the channel. The carbonated apatites formed with primary utilization of the vacancy mechanism generally contain greater percentages of carbonate in the A-environment and carbonate IR spectra that contain an obvious high-frequency peak at about 1550 cm⁻¹. The multiple peaks in the solid state ¹³C NMR spectra previously observed for carbonated apatite are attributed to substitution in the A-, A'-, and B-environments rather than different stereochemical orientations of the carbonate ion.

Keywords: Carbonate apatite, environment model, infrared spectroscopy, NMR spectroscopy