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The effect of incorporated carbonate and sodium on the IR spectra of A- and AB-type carbonated apatites

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Abstract

The substitution of carbonate in apatites has been voraciously explored for more than 60 yr. However, the characterization of the sites of carbonate substitution in apatite by the frequently used identification method, infrared spectroscopy, is still incompletely understood. In a significant departure from previous studies, a recent IR study concluded that most of the carbonate in apatites resides in the channels, at least in apatites prepared at high temperature and pressure. A series of A- and AB-carbonated calcium and strontium apatites have been prepared by aqueous precipitation and by carbonation with CO_2 at 800 °C. The type of carbonate substitution—A- (substitution for hydroxide in the channel) or B- (substitution for phosphate)—was determined from the carbonate asymmetric stretch (ν_3) and out-of-plane bend (ν_2) regions in the IR spectra. The IR ν_3 and ν_2 regions were analyzed by peak-fitting using both four- and six-peak models for the ν_3 region. A correlation of the band position of the high-frequency A-type carbonate band frequency with weight percent carbonate was observed for the calcium apatites, whereas a correlation of the band positions of both the low- and high-frequency B-type carbonate bands with carbonate weight percent occurs for the strontium apatites. The high-frequency member of the A-type carbonate ν_3 region for the calcium apatites showed the greatest variation with a change in the composition (A- or B-type) of carbonate. The lower frequency observed for the A-type ν_3 band of those calcium apatites with the greatest carbonate content suggested the importance of carbonate clusters in the unit cell of highly carbonated apatites. Correlations of band frequencies with sodium content were weaker than those for carbonate, even though carbonate and sodium were correlated with each other in the calcium apatites. Analogous observations on the IR band frequencies in potassium-containing carbonated apatites, in which the potassium content is low, also suggest that carbonate content is the primary driver for the interactions that produce an overlap of A-type peaks with those in the B-type region. This conclusion is further strengthened by the lack of a correlation of the frequencies of A-type carbonate in strontium apatites in which the carbonate content is low.

A comparison of the IR carbonate ν_3 region of the calcium apatites with that of apatites prepared under high pressure and temperature indicates that this region is very similar for both types of syntheses. Thus, previous conclusions about the distribution of A- and B-type carbonate likely should be valid for most synthetic calcium apatites formed under a wide range of temperature and pressure conditions.

Keywords: Apatite, IR, carbonate, carbonate correlation with IR frequencies, peak-fitting, A-type carbonate, B-type carbonate