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Minerals in the Human Body

Molecular water in nominally unhydrated carbonated hydroxylapatite: The key to a better understanding of bone mineral†

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Abstract

Despite numerous analytical studies, the exact nature of the mineral component of bone is not yet totally defined, even though it is recognized as a type of carbonated hydroxylapatite. The present study addresses the hydration state of bone mineral through Raman spectroscopic and thermogravimetric analysis of 56 samples of carbonated apatite containing from 1 to 17 wt% CO_3, synthesized in H_2O or D_2O. Focus is on the relation between the concentration of molecular water (as distinguished from hydroxyl ions) and the concentration of carbonate in the apatite. Raman spectra confirm the presence of molecular water as part of the crystalline structure in all the aqueously precipitated carbonated apatites. TGA results quantitatively document that, regardless of the concentration of carbonate in the structure, all hydroxylapatites contain ~3 wt% of structurally incorporated water in addition to multiple wt% adsorbed water. We spectroscopically confirmed that natural bone mineral also contains structurally incorporated molecular H_2O based on independent analyses of bone by means of spectral stripping (subtracting the spectrum of collagen from that of bone) and chemical stripping (chemically removing the collagen content of bone prior to analysis). Taken together, the above data support a model in which water molecules densely populate the apatite channels regardless of the abundance of hydroxyl vacancies. We hypothesize that water molecules keep the apatite channels stable even when 80% of the hydroxyl sites are vacant (typical in bone), hinder carbonate ions from substituting for hydroxyl ions in the channels, and help regulate chemical access to the channels (e.g., ion exchange, entry of small molecules). Our results show that bone apatite is not a "flawed hydroxylapatite," but instead a definable mineralogical entity, a combined hydrated-hydroxylated calcium phosphate phase of the form $Ca_{10-x}[(PO_4)_{6-x}(CO_3)_x](OH)_{2-x}\cdot nH_2O$, where n ~ 1.5. Water is therefore not an accidental, but rather an essential, component of bone mineral and other natural and synthetic low-temperature carbonated apatite phases.

Keywords: Apatite, bone, molecular water, channel sites, Raman, thermogravimetric analysis