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

JILL DILL PASTERIS1,*, CLAUDE H. YODER2 AND BRIGITTE WOPENKA1

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

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% CO3, synthesized in H2O or D2O. 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 H2O 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 Ca10–x[(PO4)6–x(CO3)x](OH)2–x·nH2O, 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

INTRODUCTION

About 55–60 wt% of human bone is mineral, far in excess of the accompanying ~30 wt% collagen and ~10–15 wt% water (Rogers and Zioupos 1999). Its mineral component accounts for much of the load-bearing capacity of bone and also acts as a chemical reservoir of biologically important ions, such as calcium, phosphorus, and magnesium (Skinner 1987; Weiner and Wagner 1998; Rogers and Zioupos 1999; Glimcher 2006). Remarkably, however, there presently still remain analytical and conceptual challenges to understanding both the crystalline structure and composition of bone mineral. The analytical challenges are linked to the extremely small size of the plate-like crystallites of carbonated hydroxylapatite in bone, which are about 2 nm thick and tens of nanometers in the other two directions (Weiner and Wagner 1998; Glimcher 2006; Rey et al. 2009), and their intimate association with an approximately equal volume of the protein collagen. The conceptual challenge comes from the lack of a coherent model of the chemical-structural entity “bone mineral,” which is an inorganic compound, yet grows in a biological (aqueous) environment and responds on biological time scales. The history of research in this field during the past 60+ years (Beever and McIntyre 1946; McConnell 1962; Blitz and Pellegrino 1971; LeGeros et al. 1978; Skinner 1987; Elliott 2002; Cho et al. 2003; Wilson et al. 2006a, 2006b; Glimcher 2006; Rey et al. 2009; Pasteris 2012) reveals an increasing understanding of specific details of the structure and chemistry of bone mineral. Despite all of these analytical studies, however, the exact nature of the mineral component of bone is not yet completely defined.