American Mineralogist, Volume 103, pages 550–564, 2018

Nanocrystalline apatites: The fundamental role of water

Christophe Drouet[1,*,†], Maëlenn Aufray[1], Sabrina Rollin-Martinet[1,2], Nicolas Vandecandelaère[1], David Grossin[1], Fabrice Rossignol[2], Eric Champion[2], Alexandra Navrotsky[3], and Christian Rey[1]

[1]CIRIMAT, Université de Toulouse, UMR CNRS/INPT/UPS 5085, ENSIACET, 4 allee Emile Monso, 31030 Toulouse cedex 4, France
[2]Université de Limoges, CNRS, SPCTS, UMR 7315, Centre Européen de la Céramique, 12 rue Atlantis, 87068 Limoges cedex, France
[3]Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California Davis, 1 Shields Avenue, Davis, California 95616, U.S.A.

Abstract

Bone is a natural nanocomposite. Its mineral component is nanocrystalline calcium phosphate apatite, whose synthetic biomimetic analogs can be prepared by wet chemistry. The initially formed crystals, whether biological or synthetic, exhibit very peculiar physicochemical features. In particular, they are nanocrystalline, nonstoichiometric, and hydrated. The surface of the nanocrystals is covered by a non-apatitic hydrated layer containing mobile ions, which may explain their exceptional surface reactivity. For their precipitation in vivo or in vitro, for their evolution in solution, for the 3D organization of the nanocrystals, and for their consolidation to obtain bulk ceramic materials, water appears to be a central component that has not received much attention. In this mini-review, we explore these key roles of water on the basis of physicochemical and thermodynamic data obtained by complementary tools including FTIR, XRD, ion titrations, oxide melt solution calorimetry, and cryo-FEG-SEM. We also report new data obtained by DSC, aiming to explore the types of water molecules associated with the nanocrystals. These data support the existence of two main types of water molecules associated with the nanocrystals, with different characteristics and probably different roles and functions. These findings improve our understanding of the behavior of bioinspired apatite-based systems for biomedicine and also of biomineralization processes taking place in vivo, at present and in the geologic past. This paper is thus intended to give an overview of the specificities of apatite nanocrystals and their close relationship with water.

Keywords: Nanocrystalline apatite, water, hydroxyapatite, bone, DSC, cryo SEM, thermodynamics, enthalpy; Biomaterials—Mineralogy Meets Medicine