Biomaterials are synthetic compounds and composites that replace or assist missing or damaged tissue or organs. This review paper addresses Ca phosphate biomaterials that are used as aids to or substitutes for bones and teeth. The viewpoint taken is that of mineralogists and geochemists interested in (carbonated) hydroxylapatite, its range of compositions, the conditions under which it can be synthesized, and how it is used as a biomaterial either alone or in a composite. Somewhat counter-intuitively, the goal of most medical or materials science researchers in this field is to emulate the properties of bone and tooth, rather than the hierarchically complex materials themselves. The absence of a directive to mimic biological reality has permitted the development of a remarkable range of approaches to apatite synthesis and post-synthesis processing. Multiple means of synthesis are described from low-temperature aqueous precipitation, sol-gel processes, and mecanosynthesis to high-temperature solid-state reactions and sintering up to 1000 °C. The application of multiple analytical techniques to characterize these apatitic, frequently nanocrystalline materials is discussed. An online supplement details the specific physical and chemical forms in which synthetic apatite and related Ca phosphate phases are used in biomaterials. The implications from this overview are the enhanced recognition of the structurally and chemically accommodating nature of the apatite phase, insight into the effects of synthesis techniques on the specific properties of minerals (specifically apatite), and the importance of surface chemistry of apatite nanocrystals. The wide range of synthesis techniques, types of analytical characterization, and applications to human health associated with apatite are non-geological demonstration of the power of mineralogy.

Keywords: Apatite, Ca phosphate, biomaterial, synthesis, bone, hydroxylapatite, Review article

INTRODUCTION

The mineral component in bones and teeth is a highly carbonate-substituted, hydroxyl-deficient form of hydroxylapatite, Ca\(_{10}(PO_4)_6(OH)_2\). Bone and tooth are referred to biologically, geologically, and medically as biomineralized tissues or biomimetic materials. Intriguingly, however, they are not called “biomaterials.” For the past few decades the latter word has been reserved for synthetic materials, including those that contain apatite, that temporarily or permanently replace biological tissues in humans or other animals (Williams 1987). In the words of Donglu Shi, “Biomaterials are artificial materials utilized to repair, assist, or replace damaged or missing tissue or organs...biomaterials can be classified into four different categories: metals, ceramics, polymers, and composites” (Shi 2006, p. 211). By this definition, synthetic forms of apatite and related Ca phosphate phases used to assist diseased or damaged bone or tooth tissue are ceramics or bioceramics.

The increasing need for such synthetic replacements arises not only from an expanding population, but also from the increasing percentage of senior citizens. For example, over 1200000 hip and knee surgeries/replacements occurred worldwide in 2013. Although apatitic materials are not strong enough to be used alone in load-bearing situations, such as the hip joint, they are critical as coatings on those stronger biomaterials, enhancers of new bone growth, and implants that do not support heavy loads. As illustrated in Figure 1, modern applications include treatments related to bone fractures, bone defects, cranio-maxillofacial reconstruction, dental implants, and spinal surgery (Hench and Wilson 1993; Dorozhkin 2010; Heimann 2013).

The types of natural apatite in the body and the biological responses to them are a reflection of apatite’s range of mineralogical-geochemical properties. Multiple papers over the years have highlighted apatite’s remarkable chemical-structural adaptability (Beavers and McIntyre 1946; Hughes et al. 1989; Elliott 1994; Kohn et al. 2002; White et al. 2005) as revealed, for instance, by its ability to accept in solid solution up to half of the elements in the periodic table (Pan and Fleet 2002; Hughes 2015), to retain or recover its crystallinity even under assault from the decay of structurally incorporated radioactive elements such as uranium (Ewing and Wang 2002; Harrison et al. 2002; Fox and Shuster 2014), to form in large-volume apatite deposits through both low-temperature aqueous precipitation and high-temperature igneous crystallization (Knudsen and Gunter 2002; Ihlen et al. 2014), and to constitute two distinctly different types...