Experimental fluoridation of nanocrystalline apatite

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ABSTRACT

Biological apatite, i.e., the major component of teeth and bones, is a widely available source of nanocrystalline apatite. More information is needed about its chemical reactivity in the environment. In the present study, wafers of cross-sectioned dentin and enamel from a modern horse tooth were soaked in phosphate-buffered solutions with NaF concentrations ranging from 0.01 to 2 molar for periods of up to 14 days at about 19.5 °C. The samples were removed at intervals and analyzed by Raman microprobe spectroscopy. Additional, real-time, in-situ Raman spectroscopic analyses were made on some samples during their fluoridation reaction, using an immersible probe. All spectra were deconvolved and their spectral components analyzed for band position, width, and area. Spectral modeling indicates that fluoridation occurred by a kinetically controlled dissolution-reprecipitation process—bioapatite grains partially dissolved and released Ca and P to the F-bearing solution, which caused essentially end-member fluorapatite to nucleate and precipitate, gradually replacing some of the original bioapatite. The replacement process, i.e., fluoridation of the sample, progresses due to the difference in solubility between bioapatite and (highly insoluble) fluorapatite. The bioapatite in (more soluble) dentin reacted much faster and to a much greater extent than that in (less soluble) enamel. These results have implications for paleoenvironmental reconstruction based on the geochemistry of fossil teeth, heavy-metal remediation in soils and water through addition of phosphate phases, and the recommended methods for dental fluoridation in humans.

Keywords: Fluoridation, medical mineralogy, Raman spectroscopy, apatite, fossilization

INTRODUCTION

Biologically precipitated apatite [carbonated form of Ca₅(PO₄)₃(OH)], i.e., bioapatite, is of scientific interest for several reasons. It is the dominant phase in our bones and teeth, which historically has been called “dahllite,” although the IMA-approved name is carbonate-hydroxyapatite. The chemistry, including the isotopic composition, of bioapatite reflects the climate conditions under which its host animal lived, as well as the animal’s sources of water and food. Thus, when fossil bones and teeth are chemically analyzed, their isotopic composition can—in principle—reveal past climate conditions (Cerling and Sharp 1996; Koch 1998; MacFadden 2000; Kohn and Cerling 2002; Hoppe et al. 2004; Kohn and Law 2006; Zanazzi et al. 2007). Bioapatite also possesses the much-touted property of nanocrystallinity, and both bones and teeth are nanocomposites of apatite and organic molecules. It is well recognized that the smallest bioapatite crystallites form in bone and dentin and the largest ones in enamel. Determinations of specific sizes vary, but they typically are reported as about 2 nm thickness and tens of nanometers in the two other directions for dentin and bone crystallites compared to about 20 nm thickness and up to a micrometer length for enamel crystallites (Daculsi et al. 1997; Eppell et al. 2001; Skinner 2005; Glimcher 2006). Bioapatite becomes fluoridated in some well-recognized but incompletely understood processes, such as in the dentists’ recommended synthetic fluoridation of our teeth and the natural fossilization of animal bones and teeth.

Both natural and synthetic fluoridation of bioapatite lead to a product that is referred to, in bulk, as fluorapatite or carbonate-fluorapatite (IMA-approved term), which historically was known as “francolite.” The individual nanocrystals in such materials, however, typically are not analyzed separately to determine their specific chemistry or grain-to-grain homogeneity. Instead, research has focused on fluoride-induced changes in the bulk apatitic material—decrease in the solubility of tooth enamel, i.e., enhanced resistance to the acid attack that leads to tooth decay (LeGeros et al. 1985) and enhanced preservation of fossil bone and tooth material (Hassan et al. 1977; McClellan 1980; Zocco and Schwartz 1994; Michel et al. 1996; Bryant et al. 1996; Sharp et al. 2000; Fabig and Herrmann 2002; Truemann and Tuross 2002; Berna et al. 2004; Nemliher et al. 2004).

The present study involves the controlled synthetic fluoridation of cross-sectioned wafers of modern horse teeth. Because of the structure of a horse’s tooth, the wafer cross-sections reveal side-by-side the strongly contrasting types of bioapatite in dentin and enamel. The fluoridation process was monitored in real time by Raman spectroscopy, and the differences in response between dentin and enamel bioapatite were recorded.

MATERIALS AND METHODS

Materials

The materials used in the following experiments come from the molar of an ~3 year old horse. The molar was sawn into wafers 2 to 3 mm thick (Fig. 1) using an Isomet (Buehler Ltd., Lake Bluff, Illinois) saw outfitted with a diamond-edged...