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Research Paper

In situ compressibility of carbonated hydroxyapatite in tooth dentine measured under hydrostatic pressure by high energy X-ray diffraction

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ABSTRACT

Tooth dentine and other bone-like materials contain carbonated hydroxyapatite nanoparticles within a network of collagen fibrils. It is widely assumed that the elastic properties of biogenic hydroxyapatites are identical to those of geological apatite. By applying hydrostatic pressure and by *in situ* measurements of the *a*- and *c*- lattice parameters using high energy X-ray diffraction, we characterize the anisotropic deformability of the mineral in the crowns and roots of teeth. The collected data allowed us to calculate the bulk modulus and to derive precise estimates of Young's moduli and Poisson's ratios of the biogenic mineral particles. The results show that the dentine apatite particles are about 20% less stiff than geological and synthetic apatites and that the mineral has an average bulk modulus $K=82.7$ GPa. A 5% anisotropy is observed in the derived values of Young's moduli, with $E_{11} \approx 91$ GPa and $E_{33} \approx 96$ GPa, indicating that the nanoparticles are only slightly stiffer along their long axis. Poisson's ratio spans $\nu \approx 0.30$–0.35, as expected. Our findings suggest that the carbonated nanoparticles of biogenic apatite are significantly softer than previously thought and that their elastic properties can be considered to be nearly isotropic.

1. Introduction

Carbonated hydroxyapatite (cHAp) mineral, known as dahllite, is the mineral found in bone and is one of the main constituents of dentine, the bulk-forming bio-composite material in teeth. Dahllite mineral deposits surrounding dental tubules form "peritubular dentine" (Fig. 1a and b) columns running through the tissue. The rest of the matrix of dentine is stiffened by cHAp particles (Johansen and Parks, 1960), surrounding the organic mesh, essentially composed of collagen

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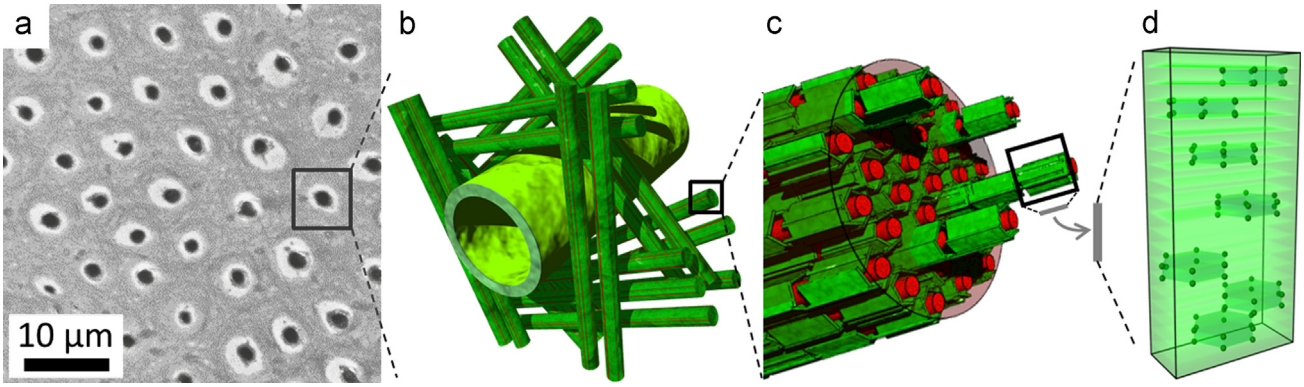

Fig. 1 – Dentine microstructure: (a) Scanning electron microscope micrograph of a polished section of dentine obtained from the crown part of a tooth exhibiting tubules surrounded by a thick layer of mineral (peritubular dentine, white rings) and suspended in the mineralized collagen matrix (intertubular dentine: light grey). (b) Schematic representation of typical dentine microstructure (not drawn to scale).Tubules lined with mineral (light green) are surrounded by a matrix of mineralized collagen fibres (dark green). These in turn are made of clusters of mineral-containing nanofibrils, with the long plate axis corresponding to the collagen axis (c). The mineral particles in dentine (d) are compositionally similar to the mineral of bone, carbonated hydroxyapatite (dahllite); the *c*-axis of the apatite crystals corresponds to the long particle axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

protein nanofibrils (Jantou-Morris et al., 2010; McNally et al., 2012). The mineral and fibres combine to form the mineralized collagen fibre matrix of dentine ("intertubular dentine"), which resembles the matrix found in other members of the bone family of materials (Weiner and Wagner, 1998).

Similar to all particle-reinforced composite materials and specifically similar to bone (Almer and Stock, 2007, 2005), the intimately attached organic phase (mainly collagen type 1) and cHAp particles carry the stress and deform jointly, when loaded by an external force (Deymier-Black et al., 2012, 2010). In this manner, strain energy is distributed throughout the dentine structures. The mineral provides stiffness in compression and thus the elastic properties of cHAp are of paramount importance for the rigidity and structural performance of the tissue. This has been shown in numerous models of bone and dental tissues (Bar-On and Wagner, 2012; Gao et al., 2003; Hellmich et al., 2004; Jäger and Fratzl, 2000; Vercher-Martínez et al., 2015; Zuo and Wei, 2007).

It is technically very challenging to measure and derive the mechanical properties of biogenic hydroxyapatites. Consequently much of what is known is based on measurements of geological or other large-scale apatite samples. Relevant measurements reported for both cHAp and fluorapatites are summarized in Table 1. Initially, ultrasonic testing methods were employed to measure the apatite elastic constants (Bhimasenachar, 1945; Gilmore and Katz, 1982; Katz and Ukraincik, 1971; Sha et al., 1994; Tofail et al., 2009; Yoon and Newham, 1969) requiring either large naturally-occurring samples, compacted pellets or sintered powders. Many of these were measured under high pressure so as to remove the effects of porosity on the acoustic signals (*e.g.* (Gilmore and Katz, 1982)). More recent *in silico* (simulation) approaches rely on calculating apatite elastic constants by atomic modelling using force fields (Menéndez-Proupin et al., 2011; Mostafa and Brown, 2007), *ab initio* techniques (Menéndez-Proupin et al., 2011; Ren et al., 2013; Snyders et al., 2007), theoretical tensile test modelling (Ching et al., 2009), and density functional theory computations (Li et al., 2015). Other work provided information about the bulk modulus and the zero-pressure volume of the apatite unit-cell, using a combination of X-ray diffraction and high-pressure experiments (Brunet et al., 1999; Matsukage et al., 2004). All the above have generated a consensus about estimates of Young's modulus of apatite mineral, on the order of 115–125 GPa. By extrapolation, similar apatite moduli can even be estimated from correlations between indentation modulus and mineral content measurements reported in teeth (Angker et al., 2004), from which the mineral is predicted to have a stiffness of 132 GPa.

However, a curious discrepancy emerges, when examining more direct mechanical measurements obtained using classic techniques listed in Table 2, including nanoindentation (Snyders et al., 2007; Viswanath et al., 2007), and micromechanical three-point bending tests (Teraoka et al., 1998). While indentation measurements on geologic or synthetic apatites report the same high modulus range as mentioned above, indentation along enamel rods known to be composed essentially of biogenic cHAp (90∼95 vol% (TenCate, 1998)) revealed lower stiffness, even when indenting specifically along the known crystal texture corresponding to the stiffer cHAp *c*-axis. The lower 85–95 GPa range of reported indentation moduli (Ang et al., 2010; Craig et al., 1961; Habelitz et al., 2001; Xu et al., 1998; Yilmaz et al., 2015) is typically attributed to the composite nature of enamel, known to contain minute amounts of organic material (Ge et al., 2005), found in the so-called interrod-regions between adjacent mineral clusters. Thus, assuming that the dentine bone-like nanoparticles and enamel mineral are made of similar cHAp, it is possible that tooth mineral is significantly less stiff than synthetic or other naturally occurring cHAp.

To address this question, we performed direct measurements of the compressibility of hydroxyapatite nanoplatelets of tooth dentine, which we use to gain insight into other elastic properties of biogenic cHAp. We use X-ray