Correlating microstructure and nanochemistry of human dental tissues

V Srot¹, B Bussmann¹, U Salzberger¹, CT Koch¹² and PA van Aken¹

¹. Stuttgart Center for Electron Microscopy, Max Planck Institute for Intelligent Systems, Stuttgart, Germany
². Institute for Experimental Physics, Ulm University, Ulm, Germany

srot@is.mpg.de
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Many living organisms have a remarkable ability to form a diversity of biominerals and a variety of structures. Many of these biominerals are composite or agglomerated materials, where an organic matrix and crystalline or amorphous minerals are linked together [1]. These exceptional combinations formed under particular conditions possess unique architectures and sophisticated compositions, which leads to highly improved materials characteristics compared to their inorganically formed mineralogical varieties [1, 2].

Human mineralized tissues, such as teeth and bones, consist of the inorganic Ca phosphate component hydroxylapatite (HA) and an organic component, mainly collagen. Biological HA is structurally and chemically very complex and it can be described as impure Ca-deficient carbonate-containing apatite modified mainly with magnesium, sodium, potassium and zinc [3]. Teeth consist of three unique dental hard tissues, enamel (E), dentine (D) and cementum (C). Their inorganic phase is based on HA, however they vary in Ca/P ratio and the concentration of minority elements.

Numerous dentinal tubules (DT) penetrate the dentine (D) and are surrounded by a wall of highly mineralized peritubular dentine (PD) and are separated by intertubular dentine (ID) [4].

In this study [5], permanent and primary human teeth were investigated. Enamel (E), dentine (D) and DT from different locations in the teeth were studied in detail by using energy-dispersive X-ray spectroscopy (XEDS) and electron energy-loss spectroscopy (EELS). P-L₂,₃, C-K, Ca-L₂,₃, N-K and O-K energy-loss near-edge structures (ELNES) were acquired at high energy and high spatial resolution using the Zeiss SESAM and VG HB501UX microscopes.

Bright field (BF) scanning transmission electron microscopy (STEM) images of enamel, dentine and DT are shown in Figure 1a-c. An annular dark field (ADF)-STEM image of an enlarged area of DT clearly shows a well mineralized PD that appears denser compared to the ID (Figure 1d). XEDS measurements were performed from several different areas in enamel (E), dentine (D, D₁-D₅) and cementum (C) and are marked in Figure 2a. For all measured positions the values of Ca, P and Mg atomic fractions were determined and the average Ca/P at% ratios are plotted against the average Mg/P at% ratios (Figure 2b). The Ca/P at% ratios of enamel (E) and dentine (D) are rather constant; however there is a variation of the Mg/P at% ratio. Different areas of ID show quite constant Ca/P at% ratios and only minor variations for the Mg/P at% ratios. On the other hand, the Ca/P at% ratios of PD are significantly lower than those of ID, which, in turn, feature higher and variable Mg/P at% ratio values. Our results measured in ID and PD plotted in Figure 2b suggest that magnesium is most likely incorporated in the HA lattice by substituting calcium. Overview EEL spectra from enamel (E) and dentine (D) acquired in the energy range between 125 eV and 575 eV containing P-L₂,₃, C-K, Ca-L₂,₃, N-K and O-K edges are shown in Figure 3a. C-K ELNES shown in Figure 3b were acquired from enamel (E), dentine (D), ID and PD. The main C-K edge signal acquired from enamel (E) is originating from the inorganic component. A sharp peak may be attributed to transitions to unoccupied \( \pi^* \) anti-bonding orbitals of CO₃²⁻ clusters [6]. A broader feature at around 300 eV could be ascribed to transitions to the unoccupied \( \sigma^* \) anti-bonding orbitals [6]. C-K ELNES from dentine (D) acquired in the near vicinity of the dentine-enamel junction. Spectra from ID and PD show identical positions of spectral features, although there are some noticeable differences in the peak intensities (marked with dotted lines in Figure 3b). Presented results are an important contribution to the understanding of differences in microstructure and chemical composition of mineralized human dental tissues as well as to the discussions of natural and synthetic organic-inorganic materials.
References

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Figure 1. BF-STEM images of enamel (a), dentine (b) and dentinal tubules (DT) separated by intertubular dentine (ID) and surrounded by peritubular dentine (PD) (c). In ADF-STEM image (d) an enlarged area is shown.

Figure 2. (a) Optical micrograph of a longitudinal section of permanent maxillary premolar with marked positions used for TEM sample preparation. (b) Ca/P at% ratio plotted against the corresponding Mg/P at% ratio measured from enamel (E), dentine (D), cementum (C), intertubular dentine (ID) and peritubular dentine (PD). The data shown in the diagram are based on XEDS spectra measured from 436 positions.

Figure 3. Overview EEL spectra from enamel (E) and dentine (D) are shown in (a). In (b) C-K ELNES from enamel (E), dentine (D), peritubular (PD) and intertubular dentine (ID) are presented. C-K ELNES of dentine (D) and ID appear identical. Differences in spectral features between ID and PD are marked with dotted lines.