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Exposing Advanced Building Strategies of Strongly Iron-Enriched Incisors

Vesna Srot[1], Birgit Bussmann[1], Julia Deuschle[1], Peter A. van Aken[1] Boštjan Pokorny[2,3] and Masashi Watanabe[4]

[1.] Stuttgart Center for Electron Microscopy, Max Planck Institute for Solid State Research, Stuttgart, Germany.
[2.] Environmental Protection College + Institute ERICo, Velenje, Slovenia.
[3.] Slovenian Forestry Institute, Ljubljana, Slovenia.
[4.] Department of Materials Science and Engineering, Lehigh University, Bethlehem PA, USA.

Teeth are an excellent example of optimally designed hybrid organic-inorganic nanoarchitectures composed of simple compounds. Typically, these simple building phases show exceptional mechanical property amplification when formed into constructions. Many natural materials are complex composites in which synergistic benefits of inorganic and organic components enhance the physical and mechanical properties [1]. The constantly growing incisors of rodents are a perfect example of natural organic-inorganic complex composite material. The front part of the incisor is covered by hard and resistant enamel, while softer dentin forms the bulk of the tooth, which is gradually removed due to the heavy gnawing, and hence forms self-sharpening device.

In the present study, the innovative microstructural adjustments combined with remarkable compositional adaptations in incisors of coypu (*Myocaster coypus* Molina) [2] were recognized by using advanced analytical and imaging transmission electron microscopy (TEM) techniques. Chemical analysis employing energy-dispersive X-ray spectroscopy (EDX) and electron energy-loss spectroscopy (EELS) has exposed a chemically diverse Fe-rich surface layer (Fe-SL) that is covering pigmented enamel (Fe-EN) (Fig. 1a). Three distinct compositional ranges based on the different Fe content were identified (Fig. 1b). The Fe-$L_{2,3}$ energy-loss near-edge structure (ELNES) obtained from areas with variable Fe concentration suggests that Fe in the Fe-SL is in predominantly 3+ valence state (Fig. 1b inset), while the O-K ELNES (Fig. 1c) exhibits three principal shapes that are strongly correlated with the Fe concentration. By combining all our findings, we have proven that three chemically, loosely separated amorphous phases, namely ferrihydrite (I), (**Fe**,Ca)-phosphate (II) and (**Ca**,Fe)-phosphate (III) phases and their intermixtures are present within the Fe-SL. The typical orange-brown coloration of the incisors is closely linked to the presence of the Fe-SL. The starting base layer of the Fe-SL shows a composition corresponding to ferrihydrite (Fh) as displayed on an energy-filtered TEM image (Fig. 2a). The underlying pigmented enamel (Fe-EN) consists of closely packed needle-shaped hydroxyapatite (HA) crystals that are arranged with a long axis towards the surface of the tooth. Chemically different material was discovered in the pockets within the Fe-EN (Fig. 2b,c). Chemical analysis through EDX and EELS demonstrates the existence of Fe-rich phase with Fe in 3+ valence state. Through fine spectral features of O-K ELNES we could assign the material within the pockets to ferrihydrite phase. The present results revealed close correlation between ideally tailored architecture and functionality in natural complex materials. Smart microstructural and compositional adjustments showed to be closely linked to the mechanical properties and functionality of natural materials [3].

References:

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[2] V. Srot *et al*., ACS Nano **11** (2017), p. 239.
[3] VS gratefully acknowledges Ms. Ute Salzberger (MPI-FKF) for tripod sample preparation.

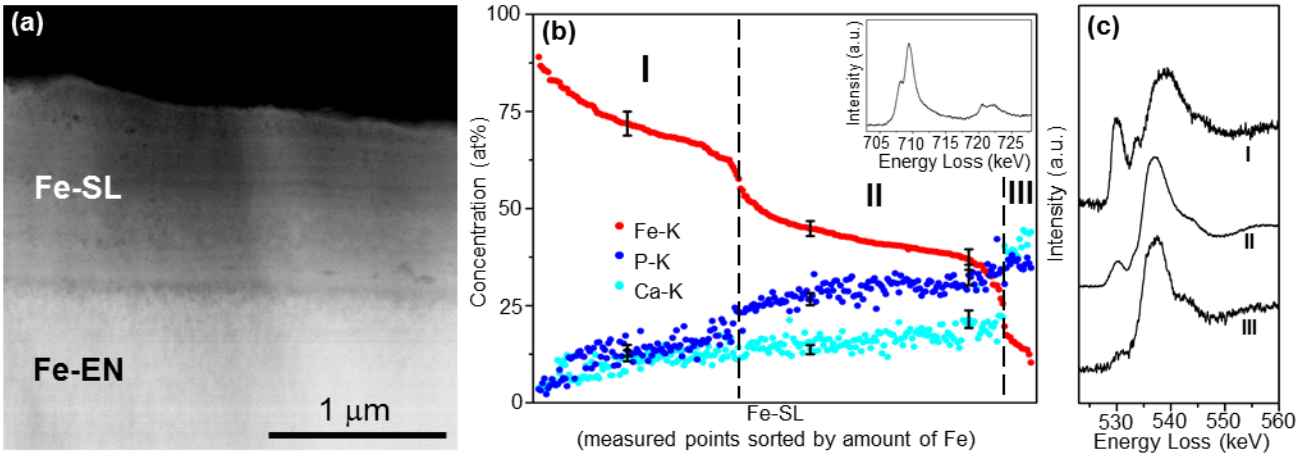

Figure 1. (a) HAADF-STEM image of the interface between the Fe-rich surface layer (Fe-SL) and Fe-rich enamel (Fe-EN). (b) EDX concentration data for Fe, P and Ca measured from different positions within the Fe-SL and sorted by Fe concentration. (c) O-K ELNES acquired from different positions within the Fe-SL with different Fe concentration.

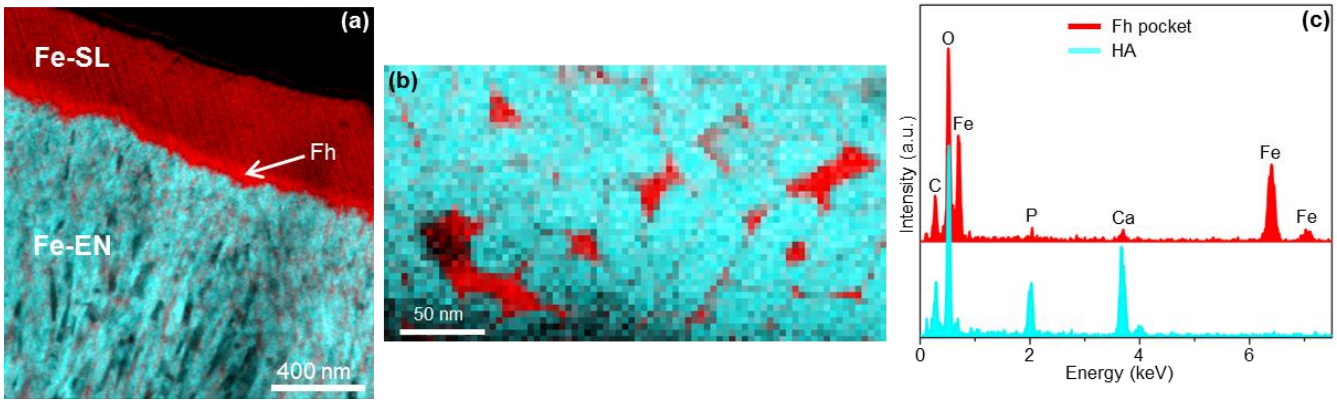

Figure 2. (a) EFTEM image of the interface between the Fe-SL and the Fe-EN with overlapped Ca (blue) and Fe (red) chemical maps. (b) Overlapped EELS elemental maps (Ca: blue and Fe: red) showing hydroxyapatite crystals and ferrihydrite filled pockets within pigmented enamel (Fe-EN). (c) EDX spectra acquired from hydroxyapatite crystals (blue) and ferrihydrite pockets (red).

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