Chemical Imaging of Interfaces and in Interphases in Tooth Enamel

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Tooth enamel is the hardest tissue in vertebrates. Optimized to withstand the forces of mastication, it is composed of hydroxylapatite (OHAp) nanowires, thousands of which are bundled into rods that are organized in a three-dimensional weave. During tooth development, a preformed organic matrix is thought to be integral to the biological control over the precipitation of an amorphous precursor phase, its transformation into hydroxylapatite, and the growth of individual OHAp nanowires in enamel. This matrix is degraded during enamel maturation, but a small amount of organics remains in the final biocomposite, where its presence and that of water affect the mechanical properties. Once the tooth has erupted, enamel is affected by caries (tooth decay), a chronic infectious disease that affects nearly 100% of adults worldwide.[1] Caries commonly begins with the demineralization of enamel by acids produced in plaque biofilms. It has long been known that the susceptibility of enamel to dissolution is greatly dependent on the presence of magnesium, carbonate, and fluoride ions. However, mapping the distribution of organic and inorganic 'trace' constituents is very challenging due to the complex 3D architecture, the importance of primarily low atomic number (Z) constituents, and the sensitivity of the sample to beam damage.

Laser-pulsed atom probe tomography (APT), an imaging mass spectrometry technique of unrivalled spatial resolution (< 0.2 nm) and chemical sensitivity, allowed us to dramatically improve our understanding of the complex chemistry and structure of nano-scale organic/inorganic interfaces.[2] Others and we have recently expanded the use of APT to apatitic biominerals.[3-5] We report here on our recent discovery, by APT and correlative techniques, of a Mg-rich amorphous intergranular phase in regular enamel, and of iron-rich intergranular phases in pigmented rodent enamel (Figure 1), and the dramatic influence that these intergranular phases have on enamel mechanical properties and its resistance to acid corrosion.[6] We further discuss the localization of residual organic macromolecules, carbonate, and water in the intergranular phases and discuss the differentiation between organic and inorganic carbon (Figure 2).[7]

References:
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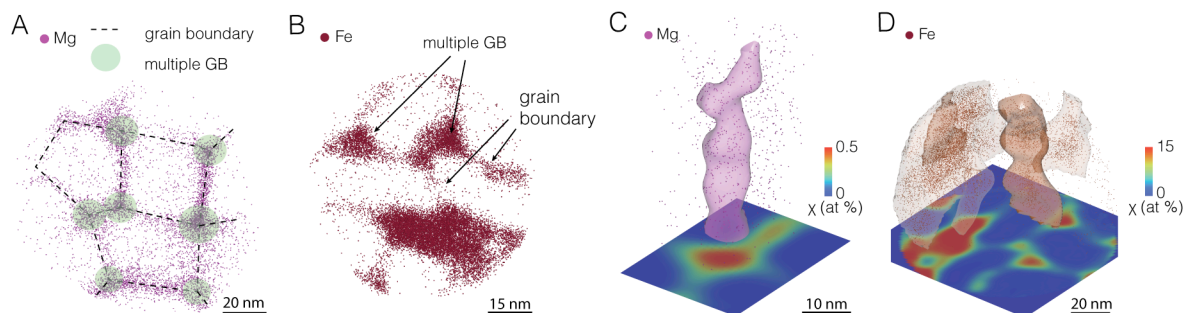
Figure 1. Atom probe tomography reconstructions of A: regular mouse enamel; B: pigmented rat enamel; C: multiple grain boundary in mouse enamel; D: amorphous interphase in pigmented rat enamel.
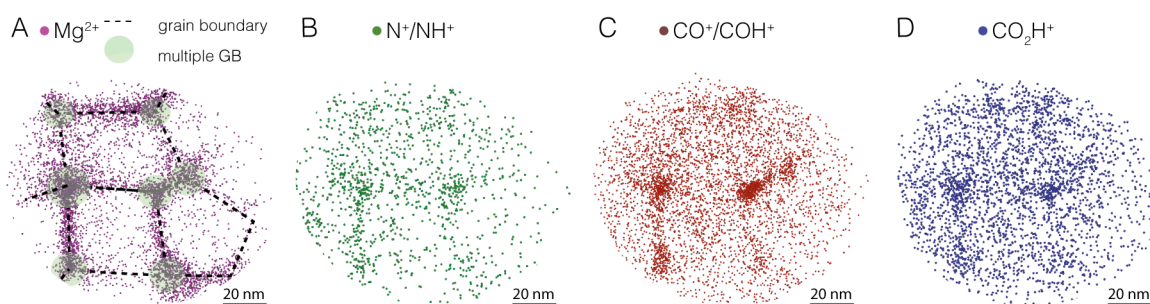

Figure 2. Atom probe tomography reconstruction of mouse inner enamel. A. Mg^{2+} segregated to simple and multiple grain boundaries. B. Nitrogen-containing ions that indicate the presence of biomacromolecules. C,D: CHO containing ions that can indicate both organic and inorganic carbon sources.