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Chemical Education

A CHIMIA Column

Topics for Teaching: Chemistry in Nature

Carnivores' Teeth: Inorganic Materials in Action

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Abstract: The replacement of hydroxy or phosphate ions in the naturally occurring inorganic material hydroxyapatite by carbonate ions leads to the properties of dental enamel and dentine that allow carnivores to cope with the stresses and forces involved in devouring their prey.

Keywords: Apatite · Carbonate apatite · Carnivores · Chemical education · Enamel · Teeth

Carnivores such as lions, leopards, tigers, jaguars and cheetahs possess specialized teeth appropriate for capturing, killing and eating their prey. The large canine teeth (Figs 1 and 2) are characteristic of a carnivore and are used to grasp and pull down prey. Molar and premolar teeth further back in the mouth comprise the *carnassial shear* (Fig. 2) and these are used to slice through raw meat. Inorganic materials play a key role in the structure and strength of teeth. We focus here on *enamel* which covers the surface of the exposed part of the tooth (the *dental crown*) and is the hardest part of a tooth, and on *dentine* which lies under the enamel and makes up the main part of a tooth.

Fig. 1. Male lion (Panthera leo) showing prominent canine teeth. ©Edwin C. Constable 2017.

Dental enamel is a form of *hydroxyapatite* and is the hardest mineralized tissue in a mammal's body. It comprises 96% inorganic material, 3% water and 1% organic material (non-collagen proteins – we return to *collagen* later). The naturally occurring mineral hydroxyapatite has the formula $Ca_{10}(PO_4)_6(OH)_2$, but replacement of hydroxide ion in the crystal lattice by fluoride or chloride ions leads to a family of minerals of general formula $Ca_{10}(PO_4)_6(OH,F,Cl)_2$. This latter nomenclature indicates that mixed compositions are possible. Tooth enamel hydroxyapatite differs from the natural mineral in having about 3–4 wt% of carbonate ion,[1] and its accommodation in the crystal lattice has been investigated by X-ray crystallography, elemental analysis, and infrared (IR), Raman and NMR spectroscopies.[1–3] Fig. 3 shows part of the 3-dimensional structure of hydroxyapatite with Ca^{2+} ions (in green), tetrahedral $[PO_4]^{3-}$ ions, and $[OH]^-$ ions. In Fig. 3, the 'sticks' between these building blocks are drawn to allow visualization of the 3-dimensional structure, and do not imply covalent bonds. Interactions between the ions are predominantly electrostatic. In enamel, $[CO_3]^{2-}$ ions substitute for both $[OH]^-$ and $[PO_4]^{3-}$ ions. Substitution of $[OH]^-$ or $[PO_4]^{3-}$ leads to Type A or Type B carbonate apatites (Type A CAp or Type B CAp), respectively. The low percentage of carbonate replacements in biological carbonate hydroxyapatites along with the extremely small crystal sizes are problematic for single crystal X-ray structural determinations for material originating from natural enamel. Much structural information has therefore been obtained from single crystals synthesized from carbonate-rich molten phases under conditions of high pressures and temperatures.[1,4]

Fig. 2. Cheetah (Acinonyx jubatus) showing the prominent canine teeth used for gripping prey during a hunt. The carnassials can be seen further back in the mouth and are used to cut and slice flesh into edible portions. ©Edwin C. Constable 2018.

The carbonate hydroxyapatite in mammalian enamel forms into thin crystallites which grow outwards from the enamel–dentine junction. Thousands of these crystallites assemble together to form rods with diameters in the range 2–10 µm. The arrangement of the rods within the layer of enamel covering the dentine varies with the type of mammal in order to cope with different forces when upper and lower teeth are brought together (*occlusal forces*).[5] The thickness of the enamel layer

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also varies and in lions it is rather thin, being only about 1 mm thick.[6] The distribution of carbonate in enamel differs on going from the outer edge of the tooth to the enamel–dentine junction. This generates a gradient in the mechanical strength across the enamel, and the mechanical properties can be investigated by using *nanoindentation*. This technique has been developed over the last few decades and allows the mechanical properties of materials to be measured at submicron levels.[7] Biomechanical analysis reveals an inverse relationship between the critical fracture load on a canine's tooth and the height of the tooth; when a dental crack reaches a certain critical length, there follows a catastrophic growth leading to fracture. Since carnivores such as lions and cheetahs have long canine teeth which experience significant forces, other factors must play a role in reducing fracture risks. Increased size of the base of a tooth is important, and the mechanical properties of the enamel are critical. In fact, dental enamel is intrinsically very brittle, with a toughness similar to that of glass. Thus, the formation of cracks in tooth enamel is common.

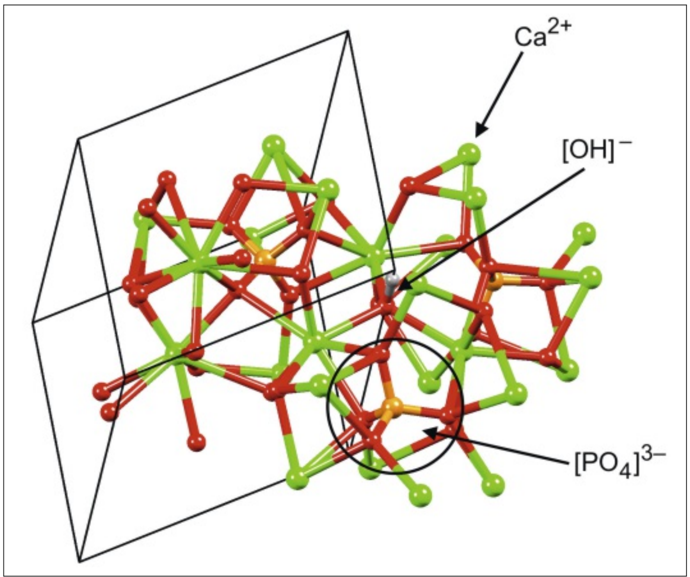

Fig. 3. The unit cell of hydroxyapatite with part of the 3-dimensional structure. Ca^{2+} ions are shown in green, the OH unit is directed along the crystallographic *c*-axis, and one $[PO_4]^{3-}$ ion is highlighted (P, orange; O, red). [Data: R.T. Downs, M. Hall-Wallace, The American Mineralogist Crystal Structure Database, *Amer. Mineral.* **2003**, *88*, 247.]

Enamel also contains inherent defects, most of which are associated with the enamel–dentine junction, and cracks in dental enamel tend to originate from these defects.[8] Extension of these enamel cracks into the dentine is prevented by the change in the mechanical strength across the enamel (see above).[6] The enamel–dentine junction itself exhibits an important mechanical gradient. The *elastic modulus* (a measure of the resistance of the material to being deformed elastically when under stress) changes from ≈95±15 GPa for inner enamel to ≈19±2 GPa for dentine.[1] Even so, for a lion, the mechanical stress of crushing bones increases the risk of tooth fracture, and broken teeth in large carnivores are common with more than 25% of natural populations having one or more fractured teeth. Among lions living in natural habitats, the canine teeth, followed by the carnassials, are most commonly broken.[10,11] The large change in elastic modulus on going from enamel to dentine is associated with a compositional change. Dental enamel and dentine comprise 96% and 79% carbonate hydroxyapatite, respectively. Dentine has a higher organic content consisting of *collagen* (a fibrous protein, Fig. 4) with long crystals of hydroxyapatite aligned relative to the protein chains so as to maximize resistance against load.

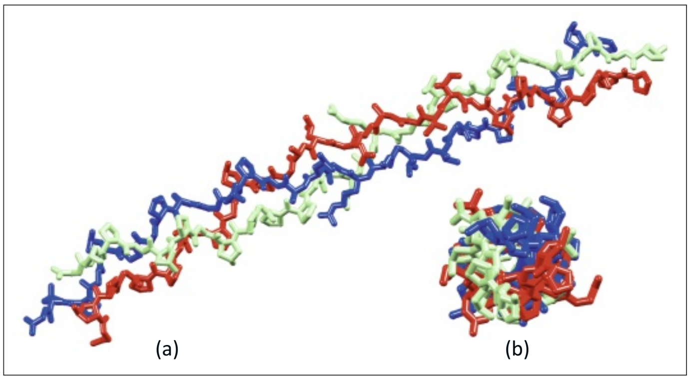

Fig. 4. Collagen is a fibrous protein. (a) The protein chains adopt helical conformations and three protein chains (shown in red, green and blue) combine to give a tube-like structure. (b) Looking down the tube-like collagen structure. [Data from the Protein Data Bank, PDB code 1BKV; H_2O molecules omitted.]

This column has highlighted how replacement of hydroxy or phosphate ions in the naturally occurring inorganic material hydroxyapatite by carbonate ions leads to the properties of dental enamel and dentine that allow carnivores to cope with the stresses and forces involved in consuming their prey.

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