A FUN SURVEY OF THE MYSTERY OF APATITES

Masayuki Okazaki

Professor Emeritus, Hiroshima University

(Received April 21, 2012; Accepted April 23, 2012)

I had a chance to visit Kohama Island in Okinawa this March, where a beautiful coral reef expanded continuously near the sea shore. It is well known that coral is composed of inorganic calcium carbonate (Aragonite). We can find red and blue coral in addition to a popular white coral. I don't know how they are colored. We admire the surprising colorful nature. Shells are also composed with calcium carbonate and keep a number of shapes and colors as well.

On the other hand, we human beings are supported by bone and our daily metabolism. It is said that mammals selected phosphate instead of carbonate when they landed on the shore from the sea. However, fish still have skeletons, which are composed of calcium phosphate, hydroxyapatite. Fish scales are also composed of hydroxyapatite. Therefore, it appears that an additional secret is hidden in this phenomenon.

Bone is famous as a vital mineral safe. Phosphate is stored and used as a source of the life energy, ATP and a genetic component. A gene carries biological information in a form that must be precisely copied and transmitted from each cell to all of its progeny. Genes are made of DNA. A DNA chain is a long, unbranched polymer, composed of only four types of subunits (Albert B et al.: Molecular Biology of the Cell, 3rd Ed., Garland Publishing, New York, 1994). These are the deoxyribonucleotides containing the bases adenine (A), cytosine (C), guanine (G), and thymine (T). The nucleotides are linked together by covalent phosphodiester bonds that join the 5' carbon of one deoxyribose group to the 3' carbon of the next. The four kinds of bases are attached to this repetitive sugar-phosphate chain almost like four kinds of beads strung on a necklace. Inorganic phosphate (Pi), which is a stable ion formed from phosphoric acid, contributes to the formation of the phosphodiester. Phosphate ester can form between a phosphate and a free hydroxyl group. These inorganic phosphates are supplied from bone hydroxyapatite.

Fundamentally, hydroxyapatite in the calcium phosphate group is the most stable in the solution. Phosphoric acid dissociates at each of the three steps in the solution. Therefore, hydroxyapatite with

PO_4^{3-} and OH^- apt to precipitate there, differing from other calcium phosphates. At the alkali condition, PO_4^{3-} ions mostly exist with excess OH^- ions. Stoichiometrical ion balance is maintained in the ideal crystal. However, a number of apatites with different physico-chemical properties exist, which can confuse us. The naming of "apatites" is very suitable.

Fig. 1 Stereo-structure model of hydroxyapatite. Upper: computer graphic model of hydroxyapatite unit cell projected on the X-Y plane.

Lower: schematic model of hydroxyapatite showing columnar Ca and screw axis Ca.

When CO_3^{2-} ions substitute into the PO_4^{3-} positions, ionic balance is broken. Even if other mono-valent cations such as Na^+ substitute as a representative ion for Ca^{2+} , crystal stability is decreased. Therefore, a small amount of substitution of CO_3^{2-} ions happens to increase the solubility greatly. This is well known as the susceptibility of caries in the dental field. On the other hand, fluoride has been contributing to the prevention of caries.

Hydroxyapatite (Fig. 1) has two columnar axes of Ca. These axes contribute to make hydroxyapatite crystals stable. On the contrary, since the axes are not single, the center of the crystal is sometimes blurred. We tend to make a crucial mistake in understanding the properties, because it is difficult to decide which of the defects of Ca^{2+} ions in the left or right axis affects the occurring phenomena, when compared with a single axis. This is likened to an axis of the human mind. If we have two minds or purposes, we sometimes lose the way, not being able to decide which one to follow. Probably, even in hydroxyapatite crystals, similar affairs may occur. The shift of OH^- ions from stable positions was established by Key et al. (Nature 204: 1050-1052, 1964). The shift of 0.03 nm is approximately 5 % of the c-axis dimension (0.688 nm) of hydroxyapatite. This value is enough to create an imperfection in the crystal, contrary to fluorapatite's.

We reported the dislocation of fluoridated hydroxyapatite synthesized using a multi-step fluoride supply system. (Okazaki M et al.: Biomaterials 20: 1303-1307, 1999). High-resolution transmission electron microscopy showed a slender hexagonal shape similar to homogeneous hydroxyapatite in cross-sections perpendicular to the c-axis and the structural damage in the core of the crystal, although no boundary of step-like layers was observed. Some lattice imperfections and line dislocation (Fig. 2), were found in the core composed of many white spots, while crystal lattices in the outer layer were arranged almost perfectly.

I hope someone continues to explore the mystery of apatites, in which infinite seeds of research exist.

Fig. 2 Dislocation of hydroxyapatite crystal.

Upper: schematic model of a line dislocation.

Lower: magnified HR-TEM photo of multilayer fluoridated hydroxyapatite. Arrows show a line dislocation running downward.