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Quantitative Compositional Analysis of Fluorhydroxyapatite by Atom Probe Tomography

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Fluorhydroxyapatite crystals (FA) have been used to coat dental/medical implants because they are biocompatible and have bioactive properties, which include stimulating osteoblast-like cells and stem cells to produce mineral (bone) and inhibiting bacterial growth. The mechanism by which the FA crystals induce their bioactivity has yet to be established. Establishing the atomic structure and chemistry of these FA crystals may lead to understanding the mechanism of how FA crystals exert their bioactivity. As a first step towards this goal, the present study is to explore the chemical composition and chemical homogeneity of FA crystals.

The analysis of minerals and biological materials by atom probe tomography (APT) is a relatively recent possibility [1,2]. Preliminary data has already been published in [3], revealing a complex mass spectrum. Traditionally, APT is well suited for conducting materials but with the development of fast laser pulsing and focused ion beam milling, this technique has shown promises in analyzing poor conducting materials. Apart from high spatial resolution, APT typically offers very high and unbiased chemical sensitivity. However, careful calibrations of the analysis parameters (specimen temperature, laser pulse energy, repetition rate, etc.) are required to ensure that indeed unbiased chemical measurements are performed. In this work, we intent to show the possibility of analyzing fluorhydroxyapatite by APT quantitatively.

For FA synthesis, 2.5mM of EDTA-Ca-Na_2 /1.5mM of $NaH_2PO_4.H_2O$ (pH 6.0) was mixed with 0.05M of NaF (pH 7.0) and the reaction solution was autoclaved (121^{o}C , 2 atm) for 10 hours. The synthesized FA crystals are hexagonal with a c-axis of 10-20 µm and a cross section of 1-3 µm. Atom probe samples were prepared by lift-out technique using focused ion beam (FIB) milling. Hexagonal rods that are aligned perpendicular to surface (Figure 1 (a) and (b)) are selected for the lift-out procedure to create needle-shaped specimens with apex radius less than 100 nm (Figure 1c)). After sharpening, the surface of the specimen is cleaned by low energy (5 kV) Ga^+ ions to remove and minimize the damage caused by the 30kV Ga beam used during the milling procedure. APT analysis is carried out at different laser energies, detection rate of 0.003 atoms/pulse, pulse rates between 100 and 160 KHz, and base temperatures of <70 K. A mass spectrum obtained from 2.6 X 10^7 atoms is shown in Figure 2. Molecular ions are obtained from the evaporation process. Quantification of the crystal composition from such a mass spectrum requires proper deconvolution of peaks.

Issues and results on compositional quantification of fluorhydroxyapatite will be discussed with particular emphasis on the effects of analysis conditions.

References

[1] T. F. Kelly and D. J. Larson, Annual Review of Materials Research, 42 (2012) 1.

[2] K. Narayan, T.J. Prosa, J. Fu, T.F. Kelly and S. Subramaniam, Journal of Structural Biology 178 (2012) 98.

[3] L.M. Gordon, L.Trans, D. Joester, ACS Nano 6 (2012) 10667-10675

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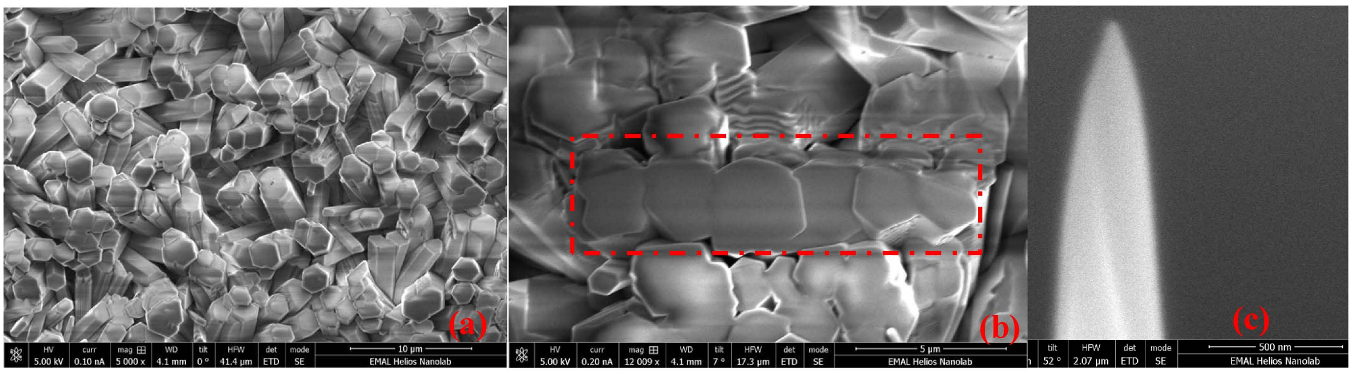

Figure 1. SEM images of (a) synthesized fluorhydroxyapatite (b) high magnification of the region selected for liftout with Pt deposition already performed (b) an APT specimen ready for analysis.

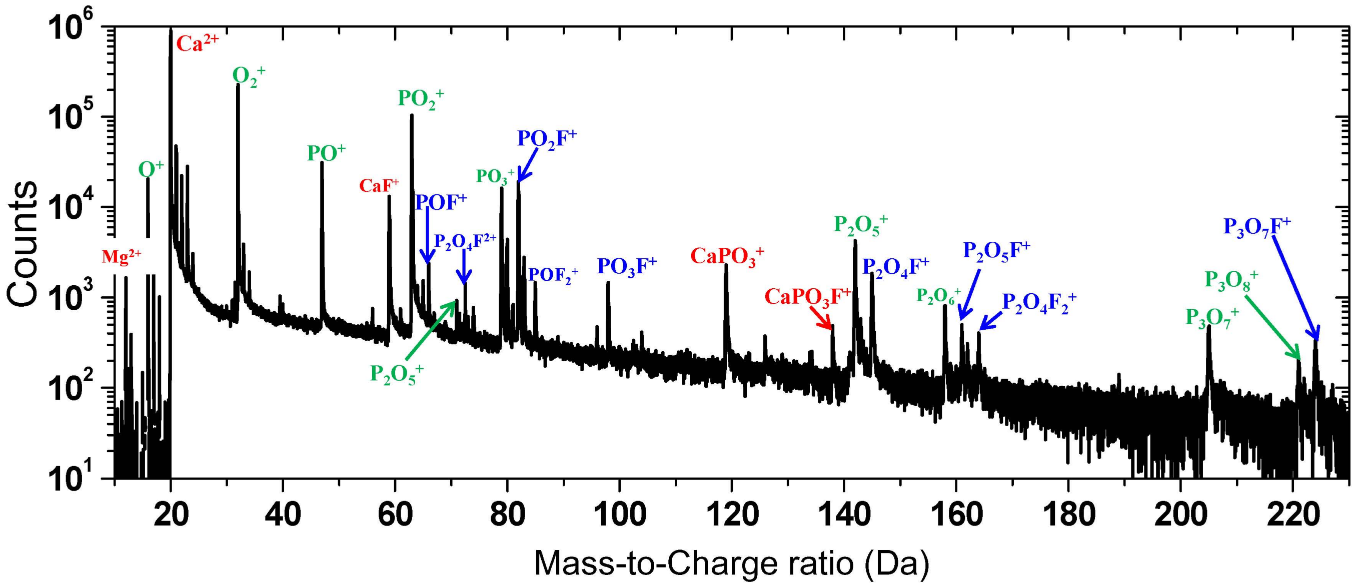

Figure 2. Mass spectrum from single rod of fluorhydroxyapatite crystal obtained from $2.6x10^7$ atoms.