In-situ observation of DCPD crystal (010) surface dissolution during transformation into HAP in solution

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Biomineralization is a biological process by which living organisms make use of organic matrix, such as peptides and proteins, to control the formation of functional minerals. The mineral brushite (DCPD) has been found under pathological conditions in kidney stones, some forms of arthritis, and caries. It has been proposed that brushite is a transient precursor for phase hydroxyapatite (HAP), which is the major inorganic component of bone and dental tissues. In recent years, the transformation mechanism from DCPD to HAP has attracted many attentions. The transformation from DCPD to HAP can be divided into two processes: dissolution of DCPD and precipitation of HAP. However, many researchers considered only the effect of interfacial energy on the transformation process from DCPD to HAP in solution and there were few literatures about kinetics of dissolution of DCPD. The purpose of this study is to reveal the details of fundamental process of the dissolution and the effects of bioorganic on the dissolution during transformation. For the purpose, we carried out in situ observations of dissolution of DCPD in solution by using the following microscopes. The phase shift interferometer (PSI) was used to measure the dissolution rate of DCPD crystal. Phase contrast microscope (PCM) and atomic force microscope (AFM) will be used to observe the change of crystal surface in atomic scale, e.g., the formation and growth of etch pit during dissolution process.

Firstly, we prepared the plate-like DCPD crystal around 2 mm in size by a simple precipitation method. The (010) surface of DCPD crystal during dissolution in solution has been in situ observed by PCM, PSI and AFM under different undersaturation, pH value, and concentration of Tris(hydroxymethyl)aminomethane. The reason why we chose Tris is that it is an organic compound and a primary amine, which can be widely used in biochemistry and molecular biology.

From in situ observation by PCM, we observed the triangle, quadrilateral, and trapezoidal etch pits on the (010) crystal surface under different conditions. We found that at the case of triangle etch pit, the step velocities, of [101], [-100] and [10-1] steps on the (010) surface are different in spite that the solution condition is the same. Especially, [-100] step has the fastest step velocity, which is opposite to the former report. It was also found that the step velocities increased evidently when two or three etch pits merged. In addition, the experimental data demonstrated that the dissolution rate normal to the (010) face became slower after adding Tris in solution. Therefore, it is considered that the effect of impurity on the crystal surface during dissolution process is very important, which may further change the crystal habit. Finally, these findings are helpful for us to further understand the mechanism of biomineralization.

Keywords: Biomineralization, DCPD crystal, dissolution, in-situ observation, etch pit