

## The effect of PO<sub>4</sub> on vaterite formation and dissolution in solution

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Calcium carbonates are essential materials in biological beings as main component of hard tissue like shells. These calcium carbonate minerals are called as biogenic minerals. These minerals were formed from body fluid, which is a neutral-weak based solution, and the process is called as biomineralization. It is known that under neutral-weak based condition, amorphous calcium carbonate (ACC) is emerged from supersaturated solution as an initial solid phase and quickly transformed to vaterite by dynamic structural phase transition. Vaterite is intermediate and metastable phase. Calcite is formed later than vaterite, and as the calcite nucleates and grows further, vaterite begins to dissolve because of the following reason: calcite solubility is lower than that of vaterite, so solute concentration in solution drops below vaterite solubility with the growth of calcite. In this reason, in neutral-weak based solution, only calcite remains as the precipitate stably and other polymorphs will disappeared even if they precipitated at once.

However, in biological system, there were various metastable calcium carbonate polymorphs like ACC and vaterite that consist of biological structures. It is strongly suggested that some additives included in body fluid were controlling calcium carbonate nucleation and phase transitions. Especially, it was suggested that PO<sub>4</sub>, which is essential materials for biological systems acts a stabilizer of ACC and an inhibitor of calcite growth. However, there were little literature about PO<sub>4</sub> effect on vaterite formation and dissolution. In this paper, we investigated the formation and dissolution process of vaterite PO<sub>4</sub> containing from the incubation time for vaterite nucleation and polymorph change during precipitation.

We prepared supersaturated calcium carbonate solution containing PO<sub>4</sub> ions by mixing CaCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, KH<sub>2</sub>PO<sub>4</sub>, NaCl and tris-aminomethane solutions. pH was buffered at 8.2-8.3 by tris-aminomethane to simulate body fluid. Concentration of Ca and CO<sub>3</sub> ions were adjusted at 10 mM at initial. We adjusted concentration of PO<sub>4</sub> ion at various values, 0-125 uM, to investigate dependence on PO<sub>4</sub> concentration. We kept this solution at room temperature and atmospheric pressure with stirring to precipitate calcium carbonate. We sampled the precipitates every regular time intervals to observe their morphologies and to identify their phases by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). Also, we monitored Ca ion concentration in solution by using Ca electrode to detect the timing of nucleation of calcium carbonate crystals.

In less than 10 uM PO<sub>4</sub> systems, ACC particles of 10-100 nm in size emerged as an initial phase. With decrease of Ca ion concentration, vaterite spherulites of 0.5-5 um in diameter emerged. Incubation time till the detection of Ca ion concentration decrease elongated with increase of PO<sub>4</sub> concentration as proportional to cube low of PO<sub>4</sub> concentration, and reached about 1500 sec at 10 uM in PO<sub>4</sub> concentration. Vaterite spherulites remained after 2 hours without collapsing. On the other hands, in more than 15 uM PO<sub>4</sub> systems, there were no evidences for calcium carbonate crystalline nucleation till 2000 sec in Ca ion electrode and electron microscopy observation. As Ca ion concentration dropped after 2000 sec, small amount of vaterite spherulites and large amount of calcite crystals appeared. With proceeding time, the ratio of calcite to vaterite was increasing, and vaterite spherulites revealed halo structure. Suggesting dissolution of vaterite. Thus, it is suggested that PO<sub>4</sub> act as an unstabilizer for vaterite.

In previous works, it was suggested that PO<sub>4</sub> act as a stabilizer for ACC. This mechanism can be interpreted from our experiments as follows; PO<sub>4</sub> inhibited to vaterite nucleation and maintain high calcium carbonate concentration in solution, so ACC survived from dissolution for a long time.

Keywords: vaterite, PO<sub>4</sub>, phase transition, additive effect