

The effect of PO₄ 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 PO₄, which is essential materials for biological systems acts a stabilizer of ACC and an inhibitor of calcite growth. However, there were little literature about PO₄ effect on vaterite formation and dissolution. In this paper, we investigated the formation and dissolution process of vaterite PO₄ containing from the incubation time for vaterite nucleation and polymorph change during precipitation.

We prepared supersaturated calcium carbonate solution containing PO₄ ions by mixing CaCl₂, Na₂CO₃, KH₂PO₄, NaCl and tris-aminomethane solutions. pH was buffered at 8.2-8.3 by tris-aminomethane to simulate body fluid. Concentration of Ca and CO₃ ions were adjusted at 10 mM at initial. We adjusted concentration of PO₄ ion at various values, 0-125 uM, to investigate dependence on PO₄ 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 PO₄ 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 PO₄ concentration as proportional to cube low of PO₄ concentration, and reached about 1500 sec at 10 uM in PO₄ concentration. Vaterite spherulites remained after 2 hours without collapsing. On the other hands, in more than 15 uM PO₄ 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 PO₄ act as an unstabilizer for vaterite.

In previous works, it was suggested that PO₄ act as a stabilizer for ACC. This mechanism can be interpreted from our experiments as follows; PO₄ inhibited to vaterite nucleation and maintain high calcium carbonate concentration in solution, so ACC survived from dissolution for a long time.

Keywords: vaterite, PO₄, phase transition, additive effect

Development of an Advanced Phase-Shift Interferometry to measure dissolution rate and phenomena of insoluble minerals

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From the point of views of the safety of radioactive waste disposal, dissolution of bentonite as engineered barrier and/or rock system surrounding waste as natural barrier is one of the key issues. Nevertheless, the understanding of the dissolution mechanisms in dissolution of very insoluble minerals is still insufficient. Therefore, an advanced Phase-Shift Interferometry (PSI) was developed to resolve dissolution process on a molecular level. The advanced PSI is distinguished by the some features, such as white light source for illumination, large working distance of the object lens, and so on. It allows the direct, simultaneous, and high speed measurement of dissolution of minerals. This high speed and high resolution observation shorten the observation period, and decrease the influence of disturbance of experimental condition. These are strong advantages for understanding the dissolution mechanism. For example, biotite dissolution rate of the order of $1\text{E-}11$ mol/m²/s was measured in the period of 4 days to 20 days by means of conventional method. It was measured by means of the advanced PSI within 12 hours.

Keywords: Phase-Shift Interferometry, insoluble mineral, dissolution rate, dissolution phenomena

Direct observation of nucleation and dissolution processes in a solution using a TEM

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Since nucleation is a fundamental event to determine size, number and morphology of produced crystals, nucleation process must be clarified to form products efficiently. Direct approach to understand nucleation would be an atomic scale in-situ observation. A transmission electron microscope (TEM) may be a most powerful tool. Unfortunately, however, we can prepare limited experimental condition in a TEM and only have a few reports concerning in-situ observation of a nucleation process so far. In particular, since TEM needs a high vacuum, crystallization experiment in a solution was impossible. Recently, formation process of platinum nanoparticles from a solution was observed using a specially designed cell in a TEM [1]. Disadvantages of this noble method are difficulties of high-resolution observation and changing the temperature. Recently, we overcame the disadvantage by using ionic liquid, which has negligible vapor pressure and does not charge up by electron beam due to their relatively higher electron conductivity. Ionic liquid has been used for direct observation of organic materials such as protein and sea weed using mainly scanning electron microscope or occasionally TEM observations. Here, we report successful in-situ observation of nucleation, growth and dissolution processes of sodium chlorate in an ionic solution.

Supersaturated ionic solution of sodium chlorate was prepared on a TEM grid. After controlled induction time, sodium chlorate crystals nucleated and grew under TEM observations with an acceleration voltage of 200kV (Hitach H-8100 placed at the Tohoku University). Ionic solution could be observed stably under normal electron irradiation condition. Nucleated sodium chlorate crystals were floated with the Brownian motion. When two crystalline particles contacted, they fused together to be a larger single crystalline particle. Produced nanocrystals of sodium chlorate were heated up and were observed their dissolution process using a TEM with an acceleration voltage of 300 keV (H-9500 placed at the Hitachi Hitec). The nanocrystals were not only dissolved but also grown even in the totally dissolving system, i.e., most probably undersaturated condition.

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Keywords: Nucleation, nanoparticle, dust, in-situ observation, electron microscope, ionic liquid

The growth mechanism of needle-like aragonite crystal

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Calcium carbonate (CaCO_3) is one of the most studied minerals among the barely soluble substances, since precipitation of CaCO_3 is a widely occurring process in biomineralization as well as in manufacturing process of industrial materials. For example, its needle-like crystals with high aspect ratios have been used as fillers to improve mechanical properties of paper and polymer materials [1]. To control the morphology or polymorph of CaCO_3 crystal, the effect of additives on the crystallization of CaCO_3 has been studied [2]. However, the growth mechanism of calcium carbonate crystals has been poorly understood yet. Understanding of the growth mechanism is important for constructing materials with morphology and function as we aim.

With respect to the needle-like crystals, two types of crystallization mechanism have been considered. One is VLS (vapor-liquid-solid) mechanism, which has been observed in formation of Si whisker [3]. Another is Frank mechanism with spiral dislocation, which is considered as a formation mechanism of NaCl whisker from solutions [4]. In this study, we synthesized needle-like aragonite crystals from solution. In order to understand the growth process of the needle-like aragonite crystal, we observed the tip of it in details by using electron microscopy.

We synthesized needle-like aragonite crystal by pouring Na_2CO_3 solution into the 40 ml of CaCl_2 solution with the rate of 1 mL min^{-1} . We stopped the inflow when the total volume of poured Na_2CO_3 solution reached 40 ml. The mixed solution was stirred at 300 rpm for about 3 h. The concentrations of CaCl_2 and Na_2CO_3 solutions are the same; we considered two cases of 0.005 and 0.05 mol/l. We controlled the temperature of solution at constant as 25, 50 and 80 deg C during precipitation. The morphology and the size of the precipitates were observed by scanning electron microscopy (SEM), and their crystalline phases were identified by X-ray diffraction (XRD).

The crystals obtained in the experiment were mainly needle-like aragonite and spherules of vaterite. The length of needle-like aragonite was about 2 -20 micrometers. The aspect ratio was estimated from 5:1 to 20:1. For vaterite, the size was about 2-5 micrometers. The total amount of precipitated crystals definitely depended on the concentration of initial solutions: many precipitates for higher concentration and few precipitates for lower concentration. The reaction temperature obviously affected the crystalline phases; aragonite was mainly crystallized at 80 and 50 deg C, on the other hand, vaterite particles appeared at 50 and 25 deg C. The morphologies were also affected by the reaction temperature. Vaterite changed from circular disc to sphere according to the decrease of reaction temperature from 50 deg C to 25 deg C. It was also seen that the higher the reaction temperature, the larger the aspect ratio of needle-like aragonite.

By detailed SEM observation, we showed that the needle-like aragonite has multi-step on the tip, which seemed higher than monomolecular step. Based on the experimental results, possible growth mechanism of needle-like aragonite was proposed.

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Effect of bacteria on calcite precipitation

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Calcite precipitation with/without bacteria was studied in two fields; Ogachi and Matsushiro. At Ogachi, two types of bacteria were mixed with carbonated water and passed through a column filled with glass beads. Calcite precipitation was observed in one column. At Matsushiro, hot spring water saturated with carbonate was also passed through a column and aragonite was detected in the column.

Keywords: calcite, bacteria, precipitation, hot spring, rate

The microgravity effect in colloidal phase separation

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Colloidal crystals are considered in the application to photonic crystals. The gravitational sedimentation method attracts great attention because of simplicity. It is thought that crystallization of colloidal crystals is caused by Kirkwood-Alder transition because of the repulsive interaction. However, to the colloidal dispersions in the conditions of low particle concentration and low ionic strength, void structure was generated 1) or gas-liquid-solid phase separation occurred 2). These phenomena cannot explain by only the repulsive force. The facts suggested the existence of a long-range attractive interaction between particles in spite of their repulsive pair potential. So, these results are very important.

The colloidal phase separation which arises in a gravity sedimentation process was reported 3). After like-charged colloidal particles sediment on glass substrate, colloidal particles cause gas-liquid-solid phase separation. A long-range attractive interaction between particles is required in order to bring out this phenomenon. However, in this experiment, when the phase separation of like-charged colloidal particles occurs, particles are always close to a glass substrate according to the gravity effect. Therefore, the interaction which works between particle-particles or between glass substrate-particles may be influenced by the gravity. So, in order to eliminate gravity effect, we experimented under microgravity.

3 μm polystyrene particles (Thermo scientific) were used. The density was 1.05 g/cm^3 . We compared the colloidal sample which was deionized one month or more by using Bio-Rad ion-exchanger resin and the untreated sample. Under the ground, the colloidal dispersion of 0.015 vol % was enclosed with the angle cell (10 mm x 10 mm x 47 mm), and 24 hours was settled. The angle cells were installed in the airplane. Then, the colloidal accumulations were observed in the microgravity environment about 20 seconds.

We measured the position change of colloidal particles. The diffusion coefficient by Brownian motion was calculated from these data. The diffusion coefficient of deionized sample was $0.082 \mu\text{m}^2/\text{s}$ and untreated sample was $0.137 \mu\text{m}^2/\text{s}$. On the other hand, the diffusion coefficient obtained from the Stokes rule was $0.14 \mu\text{m}^2/\text{s}$. The untreated sample was well in agreement with the diffusion coefficient obtained from the Stokes rule. When the value of a deionized sample and an untreated sample was compared, the direction of a deionized sample has a small value of a diffusion coefficient. In the deionized sample, we found a sign of the long range attractive interaction.

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Keywords: colloidal crystal, phase separation, microgravity, diffusion coefficient

Theoretical analysis of atomic process on the growth surface

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In order to understand formation process of minerals, it is important to analyze the atomic process on the growth surface. First-principles calculation of the growth surfaces is useful for this purpose, and is often used for semi-conducting materials. Recent progress of computer technology would make it applicable for more complex system such as minerals, which will provide more realistic information for the mineral growth in the atomic scale.

Here, as an example of this kind of approach, incorporation process of nitrogen (N) into GaAsN grown under a hydrogen atmosphere was analyzed. GaAsN with small N content has the zinc blende structure, and in this system it is difficult for nitrogen (N) to be incorporated into the solid owing to the large difference in the bond lengths of Ga-N and Ga-As. Therefore, we first determined the stability of reconstructed GaAs(001) surfaces absorbed by hydrogen (H) in dependence on chemical potentials of the constituent elements, and we found that two hydrogenized structures appear when the partial pressure of hydrogen is high. Then energies needed for N substitution to the As site were calculated. The results suggest that N is more easily substituted to surface sites bonded with H, which could be the origin of H-related defects. We are planning to apply this approach to actual mineral system.

Keywords: First-principles calculation, growth surface, surface reconstruction

Development of 3-D interferometer and refractive index matching cell for crystal growth

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It is known that the crystal growth mechanism in the solution changes as the supersaturation increases. When the crystal is growing in the supersaturating solution, the solute concentration at an interface between crystal and solution is smaller than that of the bulk solution because the crystal grows by incorporating solute in a solution. Since local concentration distribution at the interface can cause instability of the form on the crystal surface, determination of the concrete concentration distribution at the interface is important to discuss the mechanism of the crystal growth. Therefore, to discuss the relation between the crystal growth mechanism and growth rate of the crystal, it is necessary to measure the concentration around the crystal-liquid interface, not of the bulk.

There are many reports concerning measurement of the concentration field, but many of them are two-dimensional (2-D) observations, namely, the object is observed only from one direction. The information obtained by the 2-D observations is integrated along the direction of the observation, so the local information, e.g., concentration distribution around the crystal-liquid interface, is not obtained.

To improve the disadvantage on the 2-D observation, a method of computer tomography (CT) has been adopted by some authors. By using the CT method, one can reconstruct the information of the three-dimensional (3-D) concentration field around the growing crystal based on 2-D observations obtained from several directions (3-D observation). Previous works of 3-D observations revealed the 3-D structure of solute convection around the growing crystal. However, there are quite a few observations of the concentration field at the interface between crystal and solution.

In the present study, we carried out 3-D observation to measure the 3-D concentration field very close to the crystal-liquid interface growing in solution quantitatively. We newly developed microscopic Mach-Zehnder interferometer.

For quantitative 3-D measurement of concentration field, we developed a 3-D microscopic Mach-Zehnder interferometer. 3-D observations can provide us the concentration distribution at an interface between the growing crystal and solution with high magnification and high sensitivity.

For the application of the 3-D observation by using our Mach-Zehnder interferometer, we measured the concentration field around a protein crystal growing in a solution. The growth rate of the protein crystal is quite low, so the decrease of concentration in solution should be much smaller. The interference fringes obtained are straight, but curved slightly only at a very narrow area close to crystal surface. In spite of the very small movements of the interference fringes, we successfully reconstructed the 3-D concentration field around the growing protein crystal.

To use the 3-D observation of the concentration field at a rough interface or the interface in early stages of crystal growth, it is important to raise the spatial resolution of 3-D microscopic Mach-Zehnder interferometer further. The spatial resolution of the 3-D observation depends on the number of view angles. As the number of the view angles, namely the number of the images of 2-D concentration field, increases, resolution of reconstructed 3-D concentration field image gets better.

To get many 2-D images, we prepared cylindrical growth cell. Usually, cylindrical cell is not able to use for the interferometer because the curvature of the cell bends the light beam. We will overcome this problem by using the refractive index matching method.

To avoid bending of the light beam, we put the matching liquid around the cylindrical cell. This liquid removes refraction and reflection of the light on the wall of the cylindrical cell so that the beam can pass through the cell straightly.

Step free energy of inorganic single crystal surface

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Specific surface free energy of inorganic single crystal was experimentally determined by contact angle of liquid droplet on the crystal surface, and compared with the equilibrium grown length of each face. The relationship between specific surface free energy of the faces of the individual crystal with the same index and the equilibrium grown length of the face was linear. The difference of the specific surface free energy for the face of the same index can be explained by the difference of step length on the crystal surface.

Keywords: crystal surface, crystal growth, free energy

Nanoscopic Approach for Carbon Sequestration

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Growth mechanism of calcium carbonate crystals for carbon sequestration has been studied in-situ by FM-AFM, TEM and phase-shift interferometry, those of which have never been employed in this field. It was found that controlling polymorphs of calcium carbonate crystals is the key issue for the efficient sequestration.

Keywords: crystal growth, carbon sequestration, calcium carbonate