

バテライトの形成・溶解過程に対する PO₄ の影響 The effect of PO₄ on vaterite formation and dissolution in solution

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炭酸カルシウム鉱物は、生体にとって不可欠な物質であり、生物の殻などの硬組織の主要構成成分である。これらの組織を構成する鉱物は、生体鉱物と呼ばれ、生物の体液中から生成する。また、この作用の事をバイオミネラリゼーションという。生物の体液は、中性-弱塩基性の pH に保たれているため、バイオミネラリゼーションは、中性-弱塩基性溶液からの結晶成長作用とみなすことが出来る。

中性-弱塩基性の溶液中で Ca と CO₃ を混合し過飽和溶液を作成した場合、アモルファス相 (ACC) が初成相として晶出し、その後構造相転移により、バテライトへと相転移する。バテライトは、中間相及び、準安定相であり、さらにより安定なカルサイトが核形成、成長する。溶解度のより低いカルサイトが形成すると、溶液の濃度がバテライトの溶解度より低くなるためバテライトは、不安定になり溶解する。他の多形についても同様であり、中性-弱塩基性溶液中においては、溶解度の最も低いカルサイトが安定相として最後まで残る。[1]

しかし、生体内には ACC やバテライトのような準安定相、不安定相が存在しており、組織を形成している。これらの準安定相が安定的に存在出来る理由として、生物体液に含まれるいくつかの添加物が炭酸カルシウム多形間の相転移をコントロールしていることが強く示唆されている。この中でも、生体必須元素である PO₄ は、ACC を安定化させ、カルサイトの成長を阻害するという研究が報告されている。[2] しかし、ACC からカルサイトへ相転移する際に中間相として晶出するバテライトの安定性に関して、PO₄ の影響を調べた研究は殆ど存在していない。本研究では、PO₄ 濃度を変化させた系においてバテライトの形成過程、及び溶解過程の開始時間、及びそれらの過程の経過時間、及びその様式を測定し、PO₄ の影響を定量的に測定した。

実験手法を以下に述べる。まずは、CaCl₂、Na₂CO₃、NaCl、KH₂PO₄、トリスアミノメタン溶液を規定量混合することにより、含 PO₄ 過飽和炭酸カルシウム溶液を作成した。PO₄ 濃度は、イオン強度一定に保持したまま、0-125 μ M まで変化させた。Ca・CO₃ 濃度は、10 mM とし、pH 値はトリス緩衝により 8.2-8.3 で一定に保たれた。この溶液中を室温、常圧で攪拌し、炭酸カルシウムを晶出させ、一定時間ごとにサンプリングし、晶出物の多形、モルフォロジーの時間変化を走査型電子顕微鏡 (SEM)、透過型電子顕微鏡 (TEM)、粉末 X 線回折法 (XRD) にて観察、同定を行った。また、Ca イオン電極を用いて、溶液中の Ca イオン濃度モニタリングを行い、固相晶出に伴う Ca イオン濃度の減少を測定することで、核形成待ち時間の算出を行った。

PO₄ 濃度 10 μ M 以下の系では、混合直後に 10-100 nm 程度のサイズの ACC が晶出し、150 秒程度経過後に、Ca イオン濃度の減少と共に溶液は白濁し、その直後のサンプルでは直径 0.5-5 μ m 程度のバテライトの球晶が観察された。以後 2 時間経過しても、バテライト球晶は崩壊することなくそのままの形で存在していた。バテライトの晶出時間は、PO₄ 濃度の 3 乗に比例して増加し、PO₄ 濃度 10 μ M の系では、1500 秒前後になった。このことから、PO₄ はバテライトの核形成を抑制することが示唆される。PO₄ 濃度が 15 μ M 以上の系では、混合直後に ACC が晶出した後、2000 秒前後の間は Ca イオン電極モニタリングにおいて激しい変化が観察されず、電顕においても結晶相が観察されなかった。その後、少量のバテライトと、カルサイトの菱面体の結晶が観察された。さらに時間が経過すると、XRD によるピーク比の対比より、カルサイトの量比が増大することが分かった。また、SEM・TEM 観察により、バテライト球晶が中空構造を示し、溶解している様子が観察された。以上の観察結果より、PO₄ 濃度 15 μ M より高い系では、バテライトの溶解が観察されたため、PO₄ はバテライトの安定性を低下させるという事が示唆された。

従来の報告では、PO₄ が ACC の安定性を高めるということが示されている。この結論は、本実験結果より、次のように解釈できる。PO₄ が、次に晶出するバテライトの核形成を抑制することにより、溶液の濃度が高いまま維持されるため、ACC が長時間安定に保持される。

[1]: J. D. Rodriguez-Blanco et al., *Nanoscale*, 2011, 3, 265

[2]: S. Bentov et al. *J. Struc. Biol.*, 2010, 171, 207

キーワード: バテライト, PO₄, 相転移, 不純物効果

Keywords: vaterite, PO₄, phase transition, additive effect

難溶性鉱物の溶解速度及び溶解現象観察のための位相シフト干渉計の開発 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 $1E-11$ 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.

キーワード: 位相シフト干渉計, 難溶性鉱物, 溶解速度, 溶解現象

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

溶液成長における核生成と溶解過程のTEM中“ その場 ”観察 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.

[1] H. Zheng et. al., Science 324 (2009) 1309.

キーワード: 核生成, ナノ粒子, ダスト, その場観察, 電子顕微鏡, イオン液体

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

針状アラゴナイト結晶の成長メカニズム 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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バクテリアの関与による方解石沈殿現象の実験的研究 Effect of bacteria on calcite precipitation

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バクテリアが及ぼす炭酸塩鉱物沈殿への影響の評価と定量を目的とし、炭酸塩鉱物飽和度が高い温泉や地下水を調査し、バクテリアの種の同定を行い、そのバクテリア種を用いて、沈殿速度の検討を行う。試験方法は、飽和度を調整した溶液中に、石英板を一定期間浸して、付着する炭酸塩鉱物を定量する。この際、バクテリアを添加したものと、無添加のもの（殺菌したもの）の炭酸塩鉱物沈殿速度の比較検討を行う。

現在までに、富山県東部地域に湧出する温泉を調査し、生存しているバクテリアについて検討を行った。図. 1はバクテリア群衆構造（DGGE バンドパターン）を示し、一つのバンドが一つの種に相当し、バンドの色が濃いほどバクテリアが多いことを意味する。この結果から、温泉によってバクテリア種が異なることがわかった。このうち No.6 の温泉は石灰華を形成している。今後は各温泉のバクテリアのクラスター分析を行うとともに、No. 6 の温泉に生息するバクテリアの種の同定を行う予定である。

キーワード: 方解石, バクテリア, 沈殿, 温泉水, 速度

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

コロイド相分離現象における微小重力効果 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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キーワード: コロイド結晶, 相分離, 微小重力, 拡散係数

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

結晶表面における元素取り込み過程の理論的解析手法 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.

キーワード: 第一原理計算, 成長表面, 表面再構成

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

結晶成長過程の解明に向けた三次元干渉計および屈折率マッチングセルの開発 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.

無機酸化物単結晶表面におけるステップ自由エネルギー Step free energy of inorganic single crystal surface

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無機酸化物単結晶の表面自由エネルギー密度を液体接触角から求め、結晶各面の成長距離との関係を求めた。同じ面指数をもつ面でも結晶によってその表面自由エネルギー密度が異なり、結晶面と表面自由エネルギー密度との間に一次の関係が見られた。この表面自由エネルギー密度が結晶によって異なる原因として、結晶面でのステップ自由エネルギーの影響があると考えた。さらにステップ長の厳密な見積もりによってステップ自由エネルギー密度の評価を行う。

キーワード: 結晶表面, 結晶成長, 自由エネルギー

Keywords: crystal surface, crystal growth, free energy

二酸化炭素削減のナノレベルからのアプローチ 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.

キーワード: 結晶成長, 二酸化炭素削減, 炭酸カルシウム

Keywords: crystal growth, carbon sequestration, calcium carbonate