

## 重力下における微粒子分散系の集団性と個別性 Collectivity and individuality of particle dispersion under gravity

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Collective motion of fine particles in liquid can be widely seen not only in engineering processes but also in natural phenomena such as water treatment [1], sediment transport [2], bio-convection [3] and lava convection [4]. It is well-known that the spatial variance of particle concentration brings about large-scale convection flow under gravity and sometimes it affects macroscopic motion of particles. In this study, of particular interest is whether collective or individual motion of particles reveals in liquid under the gravity field. The existence of concentration interface, which is an ambiguous interface between suspended particles and pure fluid, plays a significant role in these extreme behaviors.

Figure indicates the settling behaviors of stratified-suspended particles in a vertical Hele-Shaw cell filled with liquid [5]. In cases of small particle size with high concentration, the interfacial instability occurs at the lower concentration interface and the suspended particles behave as an immiscible fluid even though there is no distinct border with pure fluid [6]. Consequently the settling velocity is much faster than that of an isolated particle. On the other hand, in case of large particles with low concentration, the concentration interface is less distinct and the suspended particles settle individually. The transition from these collective to individual motions of suspended particles is controlled by the border resolution of concentration interface. We define the dimensionless parameter which describes the border resolution of concentration interface by the ratio of average particle distance  $d_p/\phi^{1/3}$  ( $d_p$ : particle diameter,  $\phi$ : concentration) to the dominant wavelength of the instability  $\lambda$ . As can be seen in Figure, the dimensionless parameter well describes the transition from fluid-like to particle-like behaviors. The suspended particles (and the interstitial fluid) perfectly behaves as continuum for  $d_p/\phi^{1/3}\lambda < 0.03$  and behaves individually relative to fluid for  $d_p/\phi^{1/3}\lambda > 0.2$  [5].

The similar collective motion of suspended particles has been studied on the settling of particle clouds in viscous fluid. Some researchers have suggested that the collective motion of particles in clouds can be explained by the swarm of Stokeslet [7]. They have found that the particle cloud behaves collectively when the flow generated by each particle (Stokeslet) enough screens the surrounding flow. If the above parameter is rewritten by number density of particles  $N$ , it is expressed as  $(6/\pi)^{1/3}/N^{1/3}\lambda$ . Therefore the border resolution of concentration interface express the discretization of space by Stokeslet  $1/N^{1/3}$  for a given lengthscale  $\lambda$ .

One more interesting similarity to previous study is the wavelength of instability. From the linear stability analysis of Rayleigh-Taylor instability on both miscible and immiscible interfaces of pure fluids [8], it is found that the dominant wavelength of miscible interface with no diffusion and immiscible interfaces with no interfacial tension are asymptotically close to constant value. The wavelength at concentration interface is also close to the asymptotic value [9]. From this point of view, the concentration interface can be interpreted both as the immiscible interface with no interfacial tension and the miscible interface with no diffusion.

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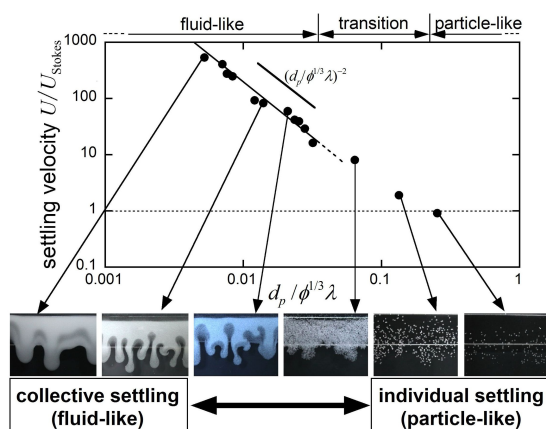


Figure 1: Collective and individual settlings of suspended particles in Hele-Shaw cell.

## セメント物質の逆ケミカルガーデン反応 Reverse chemical garden reaction of cementitious materials

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近年、ナノスケール鉱物学は星間ダストや小惑星由来の物質に知られる地球外物質からごく普通の工業生産物質であるセメントにまで広く拡張されている。ナノ物質における固有の性質は、(1) 核形成、(2) 自己組織化、(3) 組織の柔軟性の観点において特徴づけることができる。非常に一般的な工業物質であるセメントは、カルシウムケイ酸塩水和物 (C-S-H) のナノ粒子で構成されている。

最近、干渉計やナノ観察技術を使ったセメント物質の結晶成長実験が可能となった。水酸化カルシウムやそれ以上のアルカリ性溶液と反応するケイ酸塩から C-S-H を形成するセメント反応は、建設中やその後のビルで広く起きているものであり、同様の反応は、トンネルやダム、放射性廃棄物処分場などのコンクリート建造物と天然の岩石が接触している界面などでも予想される。

垂直走査干渉計を用いた岩石の高アルカリ変質実験は、C-S-H 沈殿の振る舞いが天然岩石における逆ケミカルガーデン反応によってもたらされることを明らかにした (Sato et al., in press)。このとき、岩石上の C-S-H の成長速度は非常に遅く、およそ  $2.4 \times 10^{-3}$  nm/s と観測された。その C-S-H の壁は半透膜のようにナノポアをもっていて、それを通して溶質のイオン選択が起きていることも確認された。

最近になって、我々は新たに開発された溶液反応電子顕微鏡観察装置 Poseidon による超微細観察手法をシリカヒューム (Elkem Microsilica 940-U, ~150 nm) と水酸化カルシウム飽和溶液における逆ケミカルガーデン反応の研究に適用した。その結果、この反応は数分から数十分の短期間で観察でき、シリカの水和 (体積膨張) で始まり、続いてひも状およびベール状の C-S-H 形成が起こることを明らかにした。ひも状 C-S-H の成長速度は  $4.5 \times 10^{-2}$  nm/s であり、これは続いて起こるベール形成のためのフレームネットワークとなるには充分速いものである。またこのベール状 CSH は時間と共に化学組成が Ca-rich へと変化することを FESEM-EDS 分析によって確認した。この観察した過程は、逆ケミカルガーデン反応、すなわちセメント固化反応の素過程と思われる。

超微細観察による C-S-H 成長の探究は将来の地下水環境のシミュレーションを改善するために役立つであろう。

キーワード: 逆ケミカルガーデン反応, セメント物質, C-S-H, 流体反応透過電子顕微鏡

Keywords: reverse chemical garden reaction, cementitious material, C-S-H, fluid reaction TEM

## 水溶液系における液体・液体転移の普遍的性質 General nature of liquid-liquid transition in aqueous organic solutions

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Contrary to the conventional wisdom that there exists only one unique liquid state for any material, there are growing experimental and numerical pieces of evidence for the existence of more than two liquid states in a single component substance. The transition between them is called liquid-liquid transition (LLT). LLT has attracted considerable attention because of its importance in the fundamental understanding of the liquid state. However, the physical nature of the transition has remained elusive. Particularly for water, the possible existence of LLT has special implications not only on its fundamental understanding, but also on a link of various thermodynamic and transport anomalies with critical anomaly associated with LLT. Here we reveal that 14 aqueous solutions of sugar and polyol molecules, which have an ability to form hydrogen bonding with water molecules, exhibit liquid-liquid transitions. We find evidence that both melting of ices and liquid-liquid transitions in all these aqueous solutions are controlled solely by water activity, which is related to the difference in the chemical potential between an aqueous solution and pure water at the same temperature and pressure. Our theory shows that water activity is determined by the degree of local tetrahedral ordering, indicating that both phenomena are driven by structural ordering towards ice-like local structures. This has a significant implication on our understanding of the low-temperature behaviour of water.

キーワード: 液体・液体転移, 水・水溶液, 過冷却液体・ガラス

Keywords: liquid-liquid transition, water and aqueous solution, supercooled liquids and glasses

## TEMによる溶液中結晶化過程の直接観察 Direct Observation of Crystallization Process in a Solution using Transmission Electron Microscopy

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Nucleation is a fundamental event that determines the size, number and morphology of produced crystals. Therefore, the nucleation process must be clarified to form products efficiently and to predict mineralization in various environments. The direct approach to understanding nucleation would be atomic-scale in-situ observation, for which a transmission electron microscope (TEM) would be a most powerful tool. However, the experimental conditions for TEM are limited, and there have been only a few reports on the in-situ observation of nucleation processes to date. In particular, since TEM needs a high vacuum, crystallization experiments in a solution are generally impossible. Recently, the processes of formation of nanoparticles and coalescence in a solution were finally observed using specially designed cells in a TEM [1-3]. However, live observation of the dynamics of the earliest stages of nucleation - those taking place before the formation of a stable crystal - had never been achieved before our recent work [4]. We overcame the difficulty by using an ionic liquid, which has negligible vapor pressure and is not charged up by the electron beam due to its relatively high electron conductivity, and by aiming to visualize the dynamics of nucleation under conditions very close to equilibrium, where the nucleation rate must be small but the conditions for TEM observation are more stable. We used two TEMs at an acceleration voltage of 200 kV (Hitachi H-8100, installed at Tohoku University, Japan) for the nucleation experiment and 300 kV (Hitachi H-9500, installed at Hitachi High-Technologies Corporation, Ibaraki, Japan) for the in-situ heating experiment.

An ionic solution could be observed stably under normal electron irradiation conditions as expected. Nucleation of sodium chlorate crystals was directly observed in the TEM at room temperature. Then, the sample was heated up in the TEM. The main results of the heating experiment were as follows:

1. Nanocrystals were not only dissolved but also newly formed even in the totally dissolving system, i.e., probably an under-saturated condition.
2. Both stable and metastable crystals nucleated independently of their respective solubility. However, metastable crystals were dissolved in a shorter residence time.
3. The total number of smaller particles decreased with the formation of new particles by the Ostwald ripening at or near equilibrium conditions.
4. High-density fluctuations may lead to nucleation even under equilibrium conditions.

We describe the ongoing results to elucidate the dynamics of nucleation at the nanoscale, as well as the growth, coalescence and dissolution of nanocrystals in a solution.

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キーワード: 核生成, その場観察, 透過電子顕微鏡, イオン液体

Keywords: Nucleation, In-situ observation, TEM, Ionic liquid



## NaClO<sub>3</sub> 溶液成長におけるアキラル-キラル多形転移を介したキラリティの発生と増幅 Emergence and Amplification of Chirality via Achiral-Chiral Polymorphic Transition in Sodium Chlorate Solution Growth

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キラリティは、自然界の様々な階層において普遍的に存在する概念である。両鏡像異性体の安定性は同じであるにも関わらず、地球上における生命は、片方の鏡像異性体（例えば、アミノ酸はL体、糖はD体）のみで構成されている。この現象は、ホモキラリティと呼ばれ、その起源と同一キラリティの増幅過程は原始地球環境における生命進化上の謎である。ホモキラリティの起源の1つとして、アキラルな物質のキラル結晶化が考えられている。塩素酸ナトリウム (NaClO<sub>3</sub>) は、アキラルな水溶液からキラル結晶する。NaClO<sub>3</sub> は立方晶系の結晶構造にキラリティを有する。NaClO<sub>3</sub> 水溶液を静置し、蒸発させ結晶を得ると両鏡像体は同数得られる。ところが、水溶液に攪拌を施すと、片方の鏡像体のみ得られることが Kondepudi らにより明らかにされた [1]。両鏡像体の熱力学的安定性は同じであるにもかかわらず、何故、キラリティが偏るのか、その機構は未解明である。後続の結晶化実験により、対称性の破れは結晶化初期で起きることが示唆されている。しかし、その初期過程を直接的に調べた研究はない。そこで、著者らは、NaClO<sub>3</sub> 結晶化初期過程の顕微鏡“その場”観察を試みた。その結果、キラル結晶の形成に先立ち、アキラルな単斜晶系の準安定相が現われることを明らかにし、2011 年度の地球科学連合大会で報告した。本研究では、さらに詳細なその場観察を試み、キラリティ発生過程と増幅過程を明らかにする。

22 °C で飽和な NaClO<sub>3</sub> 水溶液滴 (6 μl) をスライドガラス上で蒸発させ、蒸発により誘起される結晶化過程を偏光顕微鏡によりその場観察した。液滴の温度は、ペルチェ素子を用いて 22 °C に保たれた。偏光顕微鏡により複屈折の有無を検知し、立方晶か非立方晶かを判別し、キラル結晶とアキラル結晶を区別した。また、偏光顕微鏡により旋光性を検知し、キラル結晶の掌性を判別した。

アキラル結晶からキラル結晶への多形転移が観察された。その多形転移は、転移速度の違いにより 2 種類に分類できることがわかった。遅い転移はおおよそ 35 μm/sec で進行し (Fig. A)、速い相転移はおおよそ 2000 μm/sec の速さで進行した (Fig. B)。また、遅い相転移は、キラル結晶との接触により誘起されることがわかった。この接触誘起転移の場合、接触した結晶のキラリティと相転移の結果現れた結晶のキラリティは、同じであることがわかった。転移速度における 2 桁もの違いは、転移機構の違いが原因であると推測される。そのため、速い相転移と遅い相転移は、それぞれ、構造相転移と液相媒介相転移であると考えられる。構造相転移の場合、転移に要する活性化エネルギーは両鏡像体で等しいと推測されるので、両鏡像体は同確率で現われると考えられる。一方で、接触誘起の液相媒介相転移の場合、結果現われる結晶は、接触した結晶のキラリティを引き継ぐ。この特徴は、同一のキラリティの増幅過程であると考えられ、系のキラリティが偏る原因の 1 つであると考えられる。

これまで、キラリティの発現と増幅は、それぞれ、キラル結晶の一次核形成と、一次核形成により現れたキラル結晶を元にした二次核形成により解釈されてきた。それに対し、本研究では、結晶多形転移に基づいた新たなキラリティ発現・増幅機構が示唆された。

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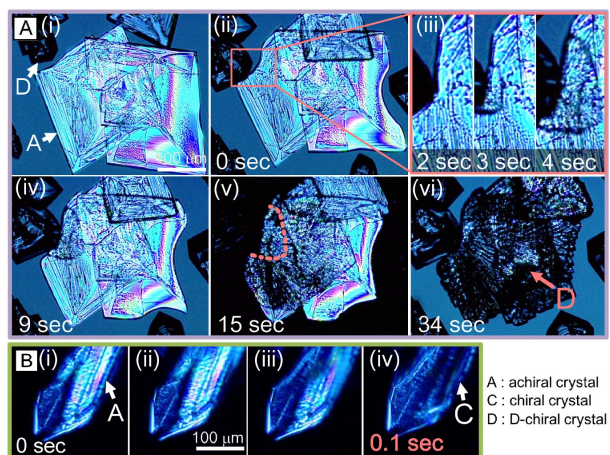
キーワード: 塩素酸ナトリウム, キラリティ対称性の破れ, キラル結晶化, 準安定相, 多形転移, その場観察

Keywords: sodium chlorate, chiral symmetry breaking, chiral crystallization, metastable phase, polymorphic transformation, in-situ observation

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## 炭酸カルシウム表面/クラスターにおける2価陽イオンの安定性に関する理論的考察 Theoretical analysis on the stability of divalent cations in the surface sites and clusters of calcium carbonate

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Formation process of calcium carbonate polymorphs, calcite, aragonite and vaterite has been extensively investigated, and impurity effect has been proposed as controlling phenomena in order to account for the formation of a particular polymorph. For example, it has been reported that an addition of  $Mg^{2+}$  in a solution inhibits calcite formation and promotes aragonite formation, however incorporation mechanism of this kind of impurities is poorly understood.

In general, smaller divalent cations than  $Ca^{2+}$ , like  $Mg^{2+}$ , cannot form solid solution with aragonite. However, the structure of a crystal surface or small cluster forming at an initial stage of crystal growth can be different from the bulk crystal because of its flexibility, and it can act as the site for incorporation of ions which is unstable in the bulk structure. In the present study, the stability of divalent cations, especially  $Mg^{2+}$ , (1) on hydrated aragonite surface and (2) in the cluster forming in an early stage of nucleation was investigated by quantum-chemical calculations, and the impurity effects on the formation of polymorphs were discussed.

The calculation results show that  $Mg^{2+}$  is easier to be incorporated into a small cluster, while the hydration energy of  $Mg^{2+}$  is higher than that of other divalent cations. This indicates that  $Mg^{2+}$  is difficult to be released from hydration shell, however, once released, it is easy to incorporate into the cluster. Atomic arrangement of these clusters including  $Mg^{2+}$  is different from that of additive-free  $CaCO_3$  clusters. Furthermore,  $Mg^{2+}$  on the aragonite surface considerably affects the surface structure and has an influence on the stability of aragonite. Thus, incorporation of  $Mg^{2+}$  into the clusters and surfaces sites should play an important role on the formation of the crystalline nuclei and the consequent crystal growth.

キーワード: 炭酸カルシウム, 不純物, 結晶成長

Keywords: calcium carbonate, impurity, crystal growth



## 固液界面の原子レベルその場観察によるカルサイトの水和構造に対する添加物効果の解明

### Atomic scale in situ observation of solid-liquid interface of calcite

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Calcium carbonate is one of common minerals on the earth. Calcium carbonate crystals are utilized industrially in various fields, so that the control of crystal growth is required. It has been known that organisms control the morphology and polymorph of calcium carbonate crystals by utilizing inorganic and organic additives in biomineralization. Understanding the additive effects on growth of calcium carbonate crystal is necessary to control the crystal growth.

The effect of additives on growth of calcite which is a stable polymorph of calcium carbonate has been investigated. The additive effect on calcite surface, such as incorporation of magnesium ions into calcite and pinning of step propagation by organic molecules has been confirmed. On the other hand, the additive effect on hydration of calcite has remained unclear even if that effect has been suggested by the measurement of growth rate of calcite in the presence of additives. Hydration affects adsorption and surface diffusion of ions on calcite surface. Also, the dehydration has been considered as rate-determining process in solution growth by the estimation of energy barriers of solution growth processes. Therefore, hydration is a key to control the kinetics of calcite growth.

Hydration at the vicinity of calcite surface has been measured by surface X-ray diffraction. Although this technique made the description of hydration structure clear, it does not show the local difference of hydration structure between on the terrace and the step front which is capture site of ions. Hence, we employed the newly frequency modulation atomic force microscopy (FM-AFM) for in situ observation of local hydration structure in atomic scale. This technique is expected to provide insight into the atomic scale distribution of hydrated water molecules in growth solution even at step front. This study describes the first in situ examination of the additive effect of organic molecules and magnesium ions on local hydration structure of calcite surface in atomic scale utilizing FM-AFM. The hydration images were compared with the growth rate of calcite measured using phase shift interferometry so as to validate the influence of hydration on the growth rate of calcite.

The findings are summarized as follows:

- (1) The synthetic polypeptide, even that with high hydrophilicity, does not affect hydration at the surface of calcite.
- (2) Combination of magnesium ions and the synthetic polypeptides provides a rigid hydration on calcite surface.
- (3) Magnesium ions and the synthetic polypeptides influence hydration and the surface pattern of calcite, respectively.
- (4) Structured water distribution eases the energy gap between the calcite surface and solution. As a result, the interfacial tension between the calcite surface and the solution is decreased.
- (5) Magnesium ions and the synthetic polypeptide act in unison to accelerate nucleation via changes in hydration structure.
- (6) Hydration contributes to interfacial energy between the calcite and the solution, but not for the adsorption of ions on the calcite steps.

This study demonstrated that additives affect the interfacial tension via altering hydration structure by application of FM-AFM for crystal growth experiment for the first time. Our results also showed that there is hardly any change in the adsorption of ions on calcite surface due to the hydration structure. That suggests that dehydration is not a rate-determining process, an observation that is contrary to the currently prevailing theory. The further observation of hydration of step front will be carried out by FM-AFM to demonstrate the effect of hydration on adsorption of ions. These findings indicate that the control of interfacial tension is possible utilizing the additive effect on hydration. That provides a new knowledge to regulate the polymorphism of calcium carbonate.

キーワード: カルサイト, 水和, 周波数変調方式原子間力顕微鏡

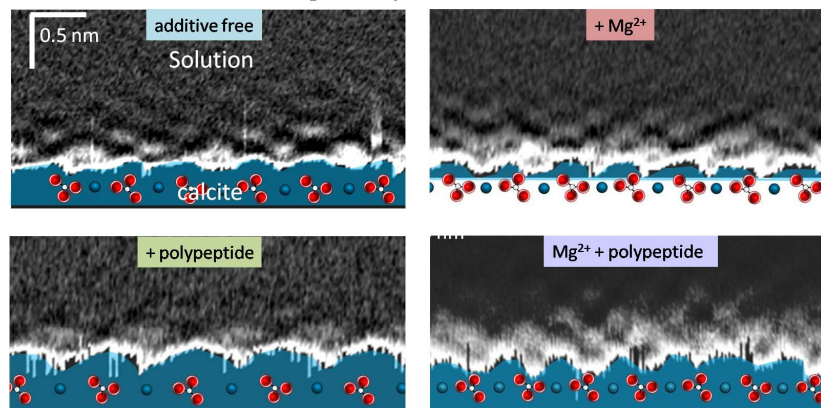
Keywords: Calcite, Hydration, FM-AFM

MIS36-07

会場:314

時間:5月1日 12:15-12:30

FM-AFM images of Hydration structure on calcite



## コロイド結晶成長における不純物の分配挙動 Impurity partitioning in colloidal crystallization

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Colloidal crystals are regarded as a promising tool to investigate diverse basic physical phenomena. We have applied this colloidal crystal to impurity partitioning in the melt growth. Since no research has been focused to detail partitioning behavior of colloidal crystals, the objective of the present work is to reveal a partitioning behavior during colloidal crystallization.

A few amount of impurities (2 percent) were doped to the colloidal dispersion, from which colloidal crystals were grown with convective assembly method. Polystyrene particles (PS) were used for fabricating colloidal crystals, and different sizes of PS and fluorescent bearing PS (w/fluor.) were doped as impurity particles.

In each particle size for two kinds of impurity, effective partition coefficient ( $k_{eff}$ ) were measured at various growth rates. Obtained  $k_{eff}$  gives  $k_0$  by using BPS plot. The  $k_0$  is decreased as the difference between the size of the impurity and the 500 nm host particle increased. The  $k_0$  of each w/fluor. was larger than that of the corresponding pure PS. Moreover, the value of  $k_0$  for the 520 nm w/fluor. surpassed unity, whereas the PS is always less than unity.

We have employed a Thurmond and Struthers (T&S) model (J. Phys. Chem. 57, 831 (1953)) to discuss the difference of  $k_0$  for PS and w/fluor. particles. T&S model shows  $k_0$  as;  $k_0 = \exp((\Delta G_{Tr} - \Delta H)/RT)$ . Here,  $\Delta G_{Tr}$  is free energy difference between the solid and liquid phases of an impurity at the transition temperature,  $T$ ,  $\Delta H$  is the excess enthalpy which is caused by incorporation of the impurity into the host material, and  $R$  is a gas constant. We have determined the phase transition volume fraction for PS and w/fluor. to evaluate the  $\Delta G_{Tr}$ . It was shown that  $\Delta G_{Tr}$  of w/fluor. is positive whereas PS is zero. This leads to larger  $\Delta G_{Tr} - \Delta H$  of w/fluor. than that of PS, which corresponds to larger  $k_0$  of w/fluor., and in a small  $-\Delta H$  range,  $k_0$  of w/fluor. surpasses unity. We have found the difference of  $k_0$  for different kinds of impurity particles, and succeeded in applying concept of T&S model to partitioning of colloidal crystals.

キーワード: コロイド結晶, 不純物分配

Keywords: Colloidal crystal, Impurity partitioning

## シュウ酸カルシウム一水和物 (100) 面上での氷核生成機構：分子動力学シミュレーション研究

### Mechanism of ice nucleation on (100) plane of calcium oxalate monohydrate: a molecular dynamics simulation study

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シュウ酸カルシウム一水和物 (Calcium Oxalate Monohydrate, COM) はシュウ酸カルシウム多形の中で熱力学的に最も安定である。COM は、地表、海底、大気中、隕石中、植物中、腎結石中などに存在する有機鉱物として知られている。これまで、COM は鉱物学や生物学、医学の分野における研究対象としてよく取り上げられてきた。

最近、石川らの実験により、ヨウ化銀や氷核バクテリアと同じように COM が氷核物質であること、COM 結晶の (100) 面が高い氷核性を示す面であることがわかってきた。COM の氷核生成促進機構の研究は、人工降雪剤の開発などとも関連して学問的にも実用的にも重要である。分子動力学 (MD) シミュレーションは、分子レベルでの氷核生成促進機構を調べるにあたり最適な手段である。そこで我々は、COM(100) 面による氷核生成促進機構を解明するための MD シミュレーションを行った。

シミュレーションにおいて、水分子間相互作用は Six-site model を用いて計算した。水分子- COM 間相互作用は Tommaso らが提案する COM モデルを用いて計算した。COM の <100> 方向には、二つの異なる分子層が交互に積み重なっている。一つはカルシウムイオンとシュウ酸イオンからなる正に帯電した Ox-1 層で、もう一つはシュウ酸イオンと水分子からなる負に帯電した Ox-2 層である。シミュレーションは、Ox-1 層と Ox-2 層に挟まれた過冷却水に対して実施した。温度は 268 K に設定した。合計で 4 ns 以上のランを実施した。シミュレーションは、Ox-2 層周辺における極性立方晶氷構造の形成を示した。しかし、六方晶氷構造の形成は見られなかった。詳しいシミュレーション結果は講演時に示す。

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キーワード: 結晶成長, 核生成, 氷, 有機鉱物, 計算機シミュレーション, シュウ酸カルシウム

Keywords: crystal growth, nucleation, ice, organic mineral, computer simulation, calcium oxalate

## 液中非接触原子間力顕微鏡による結晶表面での吸着分子観察 Observation of admolecule on the crystal surface in liquid by non-contact atomic force microscopy

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近年液中での非接触原子間力顕微鏡観察が盛んに行われている。我々はそれを用いてタンパク質結晶である正方晶リゾチーム (110) 面の溶液中観察を行った。非常に弱い相互作用力で高分解能像が得られるという特徴を活かし、分子分解能像や吸着分子等の観察を行うことに成功した。

原子間力顕微鏡 (AFM) による高分解能観察において最も重要なのは、如何にして弱い相互作用力で表面の情報を得るか、ということにある。これまで固液界面観察で主流であった接触方式 (コンタクト) や振幅変調方式 (タッピング) では nN オーダーの強い相互作用力によって画像化していたが、近年開発が進められている周波数変調方式による非接触原子間力顕微鏡 (NC-AFM)[1] では pN オーダーと弱い相互作用力により表面観察が可能である。この利点として、例えば原子 1 個や分子 1 個との間に働く弱い相互作用力によって画像化が可能であることがあげられ、高分解能観察や表面に弱い力で吸着している吸着分子観察への応用が期待できる。本発表ではタンパク質結晶である正方晶リゾチーム (110) 面の分子分解能観察 [2] や吸着分子観察を例にとって非接触原子間力顕微鏡の利点を紹介する。

### 謝辞

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[1] T. Fukuma et al., Appl. Phys. Lett. 87, 034101 (2005).

[2] K. Nagashima et al., J. Vac. Sci. Technol. B 28, C4C11 (2010).

キーワード: 原子間力顕微鏡, 結晶成長, 原子像, 吸着分子, タンパク質結晶

Keywords: AFM, Crystal growth, Atomic resolution image, Admolecule, Protein crystal



## 国際宇宙ステーションでのタンパク質結晶成長その場観察実験結果 In-Situ Observation of Protein Crystal Growth in The International Space Station

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In-situ observation of protein crystal growth was conducted at the international space station in 2012. Both growth rate and surface topography of lysozyme crystals vs supersaturation and purity of the solution were measured for the first time by interferometry in space. The differences from ground-based experiments became clear to answer the question "Why better crystal could be grown in space?".

キーワード: 結晶成長, 宇宙実験

Keywords: crystal growth, space experiment, microgravity

## 空気雰囲気下における Pt/C 触媒の SEM/STEM 同時その場観察 In situ simultaneous SEM/STEM observation of Pt/C catalysts in a gaseous atmosphere

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In order to gain fundamental understanding of the degradation mechanisms of Pt/C catalyst, there is an increasing demand on the nanostructural characterization using TEM. We have developed the humid-air supply system in TEM, H-9500 300 kV TEM and we have success the deterioration mechanism of fuel cell electrocatalyst<sup>1</sup>. Recently, we developed in situ simultaneous SEM/STEM observation technique for surface analysis of catalyst materials using a HF-3300 Cold-FE TEM with SEM/STEM function. We succeeded in visualizing of three-dimensional movement of the Pt particles on the carbon support in the gas atmosphere by this observation technique.

In situ simultaneous SEM/STEM observation of the platinum catalysts on carbon support (Pt/C; Pt: 29 wt.%) in the air conditions were carried out using HF-3300 equipped with the Cold-FE gun and the SEM/STEM function. A gas injection-heating specimen holder<sup>2</sup> was used for the Pt/C powder heating and gas injection. Pt/C powder mounted on the tungsten wire was heated to 200 deg C in a TEM, and then, while air was spraying (up to  $1.2 \times 10^{-2}$  Pa) from the injection nozzle to the Pt/C, the behavior of the Pt/C was recorded as the movie file. After the air injection at about  $1.0 \times 10^{-3}$  Pa, the coalescence growth between Pt particles on the carbon support was observed, and the Pt particles gradually started inserting into the carbon support. After that, most all of the Pt particles on the carbon support disappeared from the surface of the carbon support. And the carbon support structure was changing into a porous morphology.

We can observe that the behavior of the Pt particles on the carbon support was penetrated into the carbon support by in situ simultaneous SEM/STEM observation. These results demonstrate that the penetration of Pt particles to carbon support affects the degradation mechanism of a Pt/C electrocatalyst.

1. T. Yaguchi et. al., Journal of Electron Microscopy 60(3), 217-225, (2011)
2. T. Kamino et. al., Journal of Electron Microscopy 54(6), 497-503, (2005)

キーワード: 電子顕微鏡, その場観察

Keywords: electron microscope, in situ observation

晩期型巨星周におけるシリケートダストの低温結晶化：自由浮遊ナノ粒子の赤外スペクトルその場計測実験  
Low temperature crystallization of free-flying silicate nanoparticles investigated by in-situ IR measurement experiment

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Dust is typically 100 nm sized nanoparticles which can be observed ubiquitously in the universe. Dust forms from the high temperature gas in the out flow of evolved stars and dispersed into interstellar space. Silicate dust is one of the most abundant minerals in the universe including, shells around evolved stars [1], disks around young stars [2], comets [3] and so on. So its formation mechanism is the key process to understand the lifecycle of dust. Especially, 10  $\mu\text{m}$  IR band structure from 8  $\mu\text{m}$  to 12.5  $\mu\text{m}$  in wavelength arising from Si-O stretching provides us mineralogical character of silicate. The Infrared Space Observatory mission revealed the existence of crystalline silicates around evolved stars based on the 10  $\mu\text{m}$  band feature mainly attributed to amorphous silicate [4]. Numerous laboratory experiments to reproduce the observed spectra such as direct condensation [e.g. 5] and annealing of amorphous silicates [e.g. 6] showed variation in the IR spectra due to structure, chemical composition, temperature, size and shape, and proposed formation mechanisms of crystalline silicates. Nevertheless the scenario is not fully understood. One of the most important discrepancies concerning the dust formation process is a detection of an IR feature attributed to crystalline silicates at low temperature region, typically <300 K [1] in contrast to amorphous silicates at high temperature region [4]. Low temperature crystalline silicates cannot be explained by direct condensation or annealing involving high temperature process.

Recently, we have investigated new IR measurement technique for free-flying nanoparticles which enabled direct comparison with astronomical observation without KBr medium effects which pervert its band structure such as peak wavelength, FWHM and relative intensity [7]. Applying the new IR technique, we investigated condensation of Mg-bearing silicate from thermally evaporated magnesium and silicon oxide under the atmosphere of O<sub>2</sub> and Ar based on 10  $\mu\text{m}$  band.

*In-situ* IR measurement revealed initial condensates were amorphous or droplet of Mg-bearing silicate and its crystallization took place at <500 K. Furthermore, crystallization kept proceeding through lower temperature region. Produced particles showed core-mantle like structure, amorphous silica covered with polycrystalline forsterite observed by Transmission Electron Microscope.

Prevailing annealing experiments reported that 1000 K is required for crystallization of forsterite [8]. This critical discrepancy may be explained by nano size effects. When immoderately small particle nucleates, a particle takes metastable amorphous or droplet phase because of lower melting point of a nanoparticle [9] and larger diffusion coefficient of molecules in a nanoparticle distinct from in bulk [10]. In case the condensates were droplet due to the size effects, activation energy of crystallization is significantly low compared to amorphous [11]. We concluded such characteristic phenomena in nanometer scale enabled low temperature crystallization in the same way as the circumstellar environments.

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Keywords: astromineralogy, nanoparticle, experiment, IR

## 大規模MD計算による凝縮核生成エネルギーの導出および核生成率の新しいスケーリング

### Free energy of cluster formation and a new scaling relation for the nucleation rate

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核形成過程は、様々な分野で重要な役割を果たすが、分子レベルでの理解は未だ限られている。古典的核形成理論は、均質核形成の巨視的記述を与え、広く用いられているが、理論から得られる核生成率は実験や分子シミュレーションから得られる核生成率と何桁も一致しないことが示されている。我々は気相からの核生成過程を調べるため、大規模並列計算機を用いて 10 億から 80 億のレナード・ジョーンズ分子による分子動力学計算を行ってきた。これにより従来より 4 桁以上低い核生成率の現象を調べることが可能となり、これまで難しかった室内実験条件と同様の低過飽和状態での核生成過程を再現することに成功した (Deimand et al. J. Chem. Phys. 139,074309, 2013)。幅広い条件下での計算を行うことにより、核生成率の算出のみではなく、核生成の際のクラスター分布の詳細な情報を得ることが可能になった。本研究では大規模計算から得られたクラスター分布からクラスター形成のための自由エネルギーを算出した。ナノサイズの臨界核を形成するための自由エネルギーは従来の巨視的な見積りより大幅に小さくなり、これにより室内実験で得られる高い核生成率が説明できる。また自由エネルギーからクラスターの表面エネルギーのサイズ依存性を求めた。クラスターの表面エネルギーとバルクの表面エネルギーの比は温度によらず曲率のみに依存するという結果が得られた。得られた結果はクラスターの表面エネルギーのサイズ依存性が曲率に依存する Tolman の関係式を良く満たしていることを示す。算出した自由エネルギーを用いることにより任意の過飽和比に使える核生成率の表式が得られた。またこれらの結果を用いて核生成率および臨界核に関する新しいスケーリングの関係を見出した。新たなスケーリングは臨界核のサイズおよび  $\ln J^*/\eta$  が  $\ln S/\eta$  のみに依存することを示す ( $J^*$  は無次元核生成率、 $S$  は過飽和比、 $\eta$  は無次元のバルクの表面エネルギー)。得られたスケーリングの関係と分子計算および実験と比較したところ、このスケーリングの関係が幅広い温度や過飽和比において成り立っていることが分かった。

キーワード: 核生成, 分子動力学計算, 核生成率, スケーリング, 凝縮核, 自由エネルギー

Keywords: nucleation, molecular dynamics simulation, nucleation rate, scaling, free energy of cluster formation

## ガス中蒸発法におけるナノ粒子生成過程の高速偏光“その場”観察 High-speed polarized in-situ observation in a nucleation process of nanoparticles produced by the gas evaporation method

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The gas evaporation method has been investigated for more than half a century since the Kubo effect was reported (1962). There have been many studies on the produced nanoparticles mainly using a transmission electron microscope, which have elucidated the different physical properties of nanoparticles from those in bulk. On the other hand, there have been almost no reports on nucleation in smoke related to crystal growth. Recently, we achieved in-situ observation of the nucleation process in smoke using a double-wavelength Mach-Zehnder-type interferometer, which can determine the temperature and pressure at the nucleation simultaneously. A series of experiments clearly showed that smoke particles condense homogeneously only in a very high supersaturated environment [1-3]. In a preliminary experiment using tungsten trioxide, the smoke particles condensed with a degree of supersaturation as high as  $\sim 10^6$ . In this process, since evaporant is continuously supplied into the surrounding of the evaporation source, the flow of smoke after the nucleation and growth of nanoparticles has been simply considered as a consecutive process. The nucleation and growth of smoke particles should be a rapid process (ms order) due to high supersaturation, so the concentration of the evaporated vapor drastically decreases. However, the details of the formation process remain unknown.

In this study, we attempted to visualize the nucleation of nanoparticles and motion of smoke using a high-speed polarization image sensor (Photron Inc.) to clarify the details of the nucleation process of smoke particles. Since the sensor itself has pixels with micro-polarizers, a phase shift interferogram can be obtained in less than a millisecond because of the lack of mechanical movement free, and can therefore be applied to rapid phenomena such as nucleation in vapor phase. Here, we show the preliminary results of homogeneous nucleation of tungsten oxide from vapor phase.

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キーワード: 核生成, 偏光高速カメラ, その場観察

Keywords: Nucleation, High-speed polarized camera, in-situ observation



## フルイド反応 TEM を用いた炭酸カルシウム核生成過程の TEM 中 “その場” 観察 In-situ observation of nucleation process of calcium carbonate by the fluid-reaction TEM

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Recent studies have reported achievements of in-situ observation of the nucleation and crystallization studies using transmission electron microscope (TEM), and several new perspectives for non-classical pathway of crystallization [1-4]. Calcium carbonate generates a lot of attention because of complex nucleation due to appearance of various polymorphs in addition to availability for industrial materials such as paper and paint, and reservoir of carbon dioxide, and biomineralization. We also focus on the calcium carbonate in view of selection of polymorph in nucleation process. In case of nucleation from relatively higher supersaturated solution, nucleation of amorphous phase prior to crystalline phase has been known [5,6]. Kawano et al. have been reported an in-situ observation of solution-mediated phase transition from amorphous phase into crystalline phase under optical microscope [6]. The Ostwald law of stages has been believed to occur in many cases. Contribution of prenucleation cluster, which was confirmed by using the cryo-TEM [8], to the nucleation has also been reported [7]. However the generality or solution condition to take these processes is still not obvious.

Now, we have performed energetically a project to observe crystallization and dissolution processes in an aqueous solution using ionic liquid instead of water or the “Poseidon” (Protochips Inc.), which is a sample holder having a liquid cell for TEM observation. We call our TEM fluid-reaction TEM (FR-TEM), which is able to perform crystallization experiments in a solution including both methods. Here, we have been tried to observe whole the process of crystallization of calcium carbonate via amorphous phase using fluid-reaction TEM and actually observed a solid-state phase transition from amorphous phase into a crystalline phase by in-situ observation.

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キーワード: フルイド反応透過電子顕微鏡, その場観察, 炭酸カルシウム, 核生成  
Keywords: Fluid-reaction TEM, In-situ observation, Calcium carbonate, Nucleation

## “Poseidon”を用いた溶解過程のTEM中“その場”観察実験 In-situ TEM observation of dissolution processes in aqueous solutions using “Poseidon”

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Recently, we started a new project to observe crystallization and dissolution processes of crystals in a solution using two different methods under transmission electron microscope (TEM). To overcome the difficulties to introduce a solution into a TEM, Kimura et al. used ionic liquid to avoid evaporation of a solvent in the high-vacuum of a TEM [1]. As the result, several new insights were found: solubility-independent formation of polymorph; crystals do not dissolve smoothly but in a fluctuating manner; and new crystals form even in a totally dissolving system. Another advantage of this method is that the growing crystal does not have a hydrated layer on their surface. It has been believed that dehydration process has a largest potential barrier to incorporate a unit cell into the crystal. However, no one ever visualized the process and it has been totally veiled. The water free experiment using an ionic liquid may give us a new perspective on the dehydration process by comparison with experiments in general aqueous solutions. Now, we are forwarding a project to observe crystallization and dissolution processes in an aqueous solution in atomic-scale using the “Poseidon”, which is a sample holder having a liquid cell for TEM observation. We call our TEM fluid-reaction TEM (FR-TEM) including both solution growth experiments using an ionic liquid and the Poseidon.

Poseidon (Protochips Inc.) give us the opportunity to visualize the three-dimensional process with several advantages compared with previous works using an atomic force microscope, which is able to observe only two-dimensional, and an optical microscope, which has much less lateral resolution. Growth and dissolution processes at the first top layer (surface) of a crystal have been energetically studied long time using these tools. However, the detail process in atomic scale has been observed very limited. Therefore, the aims of our project is understanding of three dimensional nucleation including Ostwald law of stages based on phase determination by electron diffraction, determination of very slow dissolution rates, and dissolution process in terms of an influence of defects. Here, we will show the first pictures about the movements of nanoparticles and dissolution of amorphous silica and crystalline silicate samples.

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キーワード: フルイド反応透過電子顕微鏡, 溶解, その場観察

Keywords: Fluid-reaction TEM, Dissolution, In-situ observation

## モンモリロナイトの溶解における鉱物サイズ分布の変化 Mineral size distribution modeling during dissolution of montmorillonite

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In the geological disposal of radioactive waste, the waste is sealed by cement-based materials and bentonite-based material to prevent leakage into environment. The bentonite-based material protect the radioactive waste from the groundwater flow around the geological disposal area, so its low permeability should be maintained for a long term. The low permeability could be achieved by the swelling of montmorillonite in the bentonite-based material. However, montmorillonite will dissolve by a reaction with high-alkaline pore water, spoiling the low permeability of the bentonite-based material. In addition, precipitation of secondary minerals such as zeolite will promote the dissolution of montmorillonite through changes in composition of the pore water. In order to assess the long-term permeability of the bentonite-based material, it is necessary that the dissolution of montmorillonite and crystallization of secondary minerals are comprehended over a long time of several tens of thousands years.

In the pore water, there are numerous montmorillonite particles of various sizes. When montmorillonite of various sizes co-exists in the same solution, the smaller particle dissolves faster than the larger one because of the Thomson-Gibbs effect. The mean size of montmorillonite will increase gradually, leading to a delay of further dissolution. In addition, an evolution of size distribution is also important for the crystallization process of the secondary minerals, e.g., zeolite. Since zeolite is not present in the initial solution, the crystallization process is described in the nucleation and subsequent growth. Evolution of the size distribution of zeolite affects the dissolution of montmorillonite through changes in solution composition. This implies that the evolution of the size distribution of montmorillonite and zeolite should be considered to assess the long-term behavior of the permeability of the bentonite-based materials. However, in the previous chemical equilibrium calculations, the evolution of the size distribution has not been considered.

In this report, we numerically modeled the time evolution of the size distribution of montmorillonite due to dissolution according to a theoretical model described in Yao et al. (1993). The crystallization of zeolite was neglected as a first step. We consider the dissolution of montmorillonite in a closed system. The evolutions of the size distribution, bulk concentration of solution, and mean radius of montmorillonite were successfully calculated.

The model given in this report is a model in a closed system. On the other hand, the geological disposal environment is not a closed system because there is an actual mass transfer due to the flow of groundwater and diffusion. To couple the local mineral dissolution/crystallization and the global mass transfer, some chemical reaction-mass transfer calculation codes have been developed. However, these codes assumed chemical equilibrium, so the evolution of the size distribution of minerals did not considered. The evolution of the size distribution of minerals would significantly affect the long-term behavior of the permeability of the bentonite-based materials. Therefore, it is important to compare the calculation results of the model with the evolution of the size distribution and chemical equilibrium calculation result.

キーワード: モンモリロナイト, 溶解, 鉱物サイズ分布

Keywords: montmorillonite, dissolution, Mineral size distribution

## 結晶成長実験のための画像定量解析技術の最前線 Advanced techniques in the latest quantitative image analysis for crystal growth experiments

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結晶成長実験は、ナノスケールの小さな空間から、我々が肉眼で認識できる可視的空間スケールを対象としてきた。しかし、近年では、その空間スケールはさらに拡大し、地下深部まで、あるいは軌道上の宇宙空間までを対象とするように発展した。測定の世界では、従来より xyz- t の時空間においてスケーリング則が存在するが、最先端技術の発達によってその障壁を超えることが可能となった。

干渉計やレーザ顕微鏡は試料表面を損なわずに高速データ収集が可能のため、結晶成長の長時間解析や広範囲な表面形状の観察には非常に価値の高いツールである。一定の時間間隔で取得されたデータをオフライン処理することで、時間スケールは容易に変えることができ、真の成長を追跡できる時系列データとなる。これは無人で測定された国際宇宙ステーションでのリゾチーム実験データ (Tsukamoto et al., 2013) や氷界面の観察 (Sazaki et al., 2012)、粘土の溶解速度測定 (Satoh et al., 2003) の自動処理に有効であった。

また、観察視野のシフトで得られた大量のデータ断片をオフライン処理することで、空間スケールも容易に変えることができる。一般に個別測定データにはオフセットや歪みを含み、また手作業では生成されるデータ量に補正が追いつかないため、データ全体を最終的な解析に活用できないケースが多い。そこで、市販ソフトウェアに専用の処理を行うプラグインを加えたシステムを用いて一貫した正規化や接続面の補正を行うことで測定機に起因するアーティファクトを除去することを試みた。これにより、面全体の特徴を解析するための大規模縫合が実現された。

本講演では、実際の大量データの定量解析を試みた例を紹介する。

キーワード: 画像解析, 時空間スケール, 表面形状, 大規模縫合

Keywords: image analysis, time-space scale, topography, huge stitching

## 銀輸送体としての IP6 および銀ナノ構造の形成 IP6 as a silver carrier agent and formation of Ag nanostructures

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In recent years, people have become aware of the importance of natural organic materials in geological systems. It would be important to clarify the interaction between natural organic materials and metallic ions.

Phytic acid, known as inositol hexakisphosphate (IP6), or phytate,  $C_6H_{18}O_{24}P_6$ , is found within the hulls of nuts, seeds, and grains, and it is the principal storage form of phosphorus in many plant tissues, especially bran and seeds. IP6 is not digestible to humans and animals, and phytic acid chelates make unabsorbable certain important minerals such as zinc, iron, calcium and magnesium.

On the other hand, for many years, it has been known that silver works for its catalytic activities, anti-microbial activities, and used to avoid infections and prevent spoilage. Many researchers have focused on the anti-bacterial, ability to kill microorganisms and multi-functional properties of silver nano-particles.

In this study, it is demonstrated that IP6 plays a role as a metal carrier agent for the formation of metallic nanostructures. For the preparation of the IP6 with Ag elements (Ag-IP6), The commercial IP6 solution (50 %) was diluted with distilled  $H_2O$  at the  $H_2O$ :IP6 solution ratio of 9:1, then 1g of  $AgNO_3$  was added to the diluted IP6 solution of 100 ml, and long-term stabilized small Ag clusters were formed in the solution. A drop of the solution was dripped onto metallic substrates, then kept for the treatment time of 10 s to several min at room temperature. The solution was immediately dried using a gas burner or hot plate. Then, the reaction of the Ag-IP6 with several kinds of metals was examined. The structural and morphological properties of the Ag nanostructures were characterized by scanning electron microscopy (SEM) along with energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) with EDS. In addition, the surface condition of the Ag nanostructures reacted with Cu or Al and dried IP6 complexes was characterized by X-ray photoelectron spectroscopy (XPS) using a VG, ESCA-LAB Mk II with a non-monochromatized Al  $K\alpha$  source ( $h\nu = 1486.6$  eV). The energy calibration for a charge correction in the spectra was made using the C1s peak. The FTIR spectra of the dried IP6 complexes were measured using KBr disks. Each disc was composed of powders consisting of IP6:KBr=1:100. The spectra were recorded in the range of 400 to 1400  $cm^{-1}$ . Raman spectra were obtained using an NR-1800 triple Raman system with backscattering geometry using the SHG(532 nm) of a Nd:YAG laser as the excitation source. All measurements were carried out at room temperature. It was found that various kinds of Ag nanostructures were formed with additional metallic sources using the Ag-IP6. Ag nanostructures with the three-dimensional dendritic structures replaced by Cu and Mn, the two-dimensional dendritic structures replaced by  $CaSi_2$  and Mg, the two-dimensional fractal structures replaced by Fe, Ti, Al and Ni, the particles replaced by  $SrSi_2$  and the nanowires replaced by Mo and W were formed. It is noted that the IP6 plays an important role as a silver carrier agent to control the structure and morphology of the Ag nanostructures. In addition, the experimental results suggest that the structural evolution of the Ag-IP6 reacted with Cu takes place to form the Cu-IP6 complex. However, the reaction of Ag-IP6 with Al is not active.

The structural properties of the Ag nanostructures were examined, and the growth evolution of the nanostructures was discussed. The results would help us to understand the nanostructure formation by the reaction between natural organic materials and metals in nature.

Keywords: IP6, nanostructure, dendrite growth, silver



## 三次元干渉計の開発とそのタンパク質結晶成長への応用 Development and application of 3-D interferometer for analysis of the concentration field in protein crystal growth

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When the crystal is growing in a supersaturating solution, the solute concentration is decreasing towards the crystal/ solution interface because the crystal consumes solute in the solution as it grows. Due to this large vertical concentration gradient, buoyancy driven solutal convection develops. As a result, the distribution of concentration around the crystal become complicated compared to the case when there is no convection.

Thus, not only concentration gradient but also the flow and convection of the solution influences the state of the crystal surface. So that visualizing the whole concentration field of a crystal interface including convection is required.

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

To improve the disadvantage on the 2-D observation, a method of computer tomography (CT) has been adopted in this study. By using the CT method, we 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).

In this study, 3-D measurement of the concentration field with convection and without convection around inorganic and protein crystals was carried out to reveal the concentration distribution over the crystal surfaces. Normal growth rate of the face from points to points are also measured to discuss the effect of concentration distribution on the surface.

キーワード: 干渉計, リゾチーム, 対流

Keywords: interferometer, lysozyme, convection

## ステップ形状と成長速度から見た正方晶リゾチーム結晶の不純物吸着 Dependence of impurity adsorption on the step morphologies and growth rate of tetragonal lysozyme crystal

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High quality protein crystals are required to get the information of the 3-dimensional structure of protein molecules. Impurities, mainly dimer molecules, affect the quality of protein crystal strongly (Yoshizaki et al., 2006). In addition, it is known that the step morphology on {110} faces of the tetragonal lysozyme crystal is changed by impurities. Until now, a lot of space experiments were carried out to get high quality protein crystals under microgravity conditions (McPherson, 1993, etc.). However, the relevance between impurity effects and microgravity condition is not clear. In addition, the step morphology corresponding to the crystal external form is not observed in preceding studies.

We performed "in situ" observations under terrestrial environment and space environment using a tetragonal lysozyme crystal as the model protein. The purpose of this paper is to reveal "the influence of microgravity condition to the impurities adsorption on the {110} faces" and "the reason why the step morphology corresponding to crystal external form does not appear". We made it possible to observe the step morphology and to measure the face growth rate at the same time by using a Michelson type interferometer.

As a result of growth rate measurement, the face growth rate under microgravity condition was higher than that under terrestrial condition. An impurity works to suppress the growth rate of a crystal. Because the buoyancy-driven convection was suppressed under the microgravity condition, we assumed that the larger impurity-depletion-zone was formed around a crystal.

As a result of the observation of the step morphology, we succeeded in observing the lozenge shape step which was corresponding to an external form by a space experiment for the first time. In addition, the step morphologies were classified in four types. It is considered that the impurity adsorption on the crystal surface is different depending on the crystal orientation of the step.