マグマにおける結晶成長と結晶中の累帯構造
Crystal growth in magmas and zoning profiles in crystals

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There are countless documents describing various types of chemical zoning in crystals of groundmass minerals to phenocrysts in igneous rocks including plutonic to volcanic rocks. However, the origins of such zoning patterns have been still controversial to lead the quite different interpretations of formation processes of rock textures. In this talk, after briefly reviewing theoretical works of crystal growth in terms of chemical zoning in crystals, I argue the significant influence of rate law of crystal growth on the zoning profile and discuss that the growth rate is controlled by the interplay with nucleation process through the mass conservation.

The relationship between crystal growth and zoning profile was studied theoretical first by Tiller et al (1953) in metallurgy, who derived the zoning profile under the steady state condition with constant growth rates. Smith et al (1995) derived the analytical solution for time-dependent problem with constant growth rates. Lasaga (1982) obtained the representative expressions for the solution to more general cases with time-dependent growth rate as function of composition at the interface, suggesting that the oscillatory zoning cannot be formed in a binary system such as plagioclase (anorthite and albite). On the basis of his numerical model, L'Heureux (1993) argued that the effective portioning coefficient between melt and crystal controls the occurrence of oscillatory zoning in a binary system. Recently, Gorokhova et al (2013) suggested that the multicomponent inter-diffusions play an important role in the development of oscillatory zoning as well as natural zoning pattern observed in eruption products. In these previous works, the coupling between the crystal growth and nucleation processes has not been taken into account. In the disequilibrium crystallization such as natural magmatic crystallization during volcanic eruptions, the nucleation process controls the supersaturation for crystal growth which, in turn, results in characteristic zoning profile through the mass conservation of crystallizing components and rate law of crystal growth. For instance, if we assume the constant nucleation rate, then the growth rate is found to be inversely proportional to time owing to the scaling arguments. Calculated zoning profiles well account for the observed zoning profile and core compositions as function of size for plagioclase microlites formed by the decompression-induced crystallization during explosive volcanic eruptions. Finally, I suggest that experimental reproductions of zoning profiles in systems effectively involving the nucleation process help our understanding for the natural crystallization processes especially in highly disequilibrium systems.

キーワード：結晶成長、累帯構造、核形成
Keywords: crystal growth , zoning profile, nucleation

気相から固相への多段階核生成の分子動力学シミュレーション
Multistep Nucleation from Vapor-to-Solid in Molecular Dynamics Simulations

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核生成過程は、理工学の幅広い分野で重要なプロセスであるが、分子レベルでの理解は未だ限られている。これまで我々は気相からの核生成過程の分子動力学（MD）シミュレーションを行い、相変化の様子を調べてきた[1,2]. MD計算では3重点以下のさまざまな温度下で計算しても、凝縮核は液相であることを示していた. このような現象はオストワルドの段階則として考えられ、初めに生成した過冷却液滴の凝縮核は、ある段階で安定相である結晶になることが期待される．我々は最大1500万の希ガス（Lennard-Jones分子）を用い，3重点以下の温度で気相から液相への核生成および液滴からの結晶化という多段階核生成過程のMD計算を行った。粒子数、体積、エネルギー(NVE)一定の系で，凝縮核が結晶化するには長い待ち時間が必要なため, 数億ステップ（実時間で数μs）の計算を行った. 計算には並列計算用の分子動力学計算コード(LAMMPS)を用い、国内外の並列計算機(チューリッヒ大、国立天文台）を利用した。MD計算の結果、気相分子から準安定相である過冷却液滴が多数生成し、その後に過冷却液滴内の一部分から核生成が始まり短時間で結晶核が広がり全体が結晶化する様子が得られた。液滴の結晶化はすぐには起きず、ある程度大きく成長してから起きること、生成されたナノ結晶は5回対称性を持つ正20面体、十面体の準結晶, 面心立方格子(fcc)に富む結晶,六方最密重点構造(hcp)に富む結晶が混在していること、また結晶化する際には蒸発を伴うことなどが明らかになった。

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キーワード：結晶化、分子動力学計算、核生成
Keywords: crystallization, molecular dynamics simulation, nucleation

溶液透過型電子顕微鏡によるリゾチームタンパク質の結晶化初期過程の動力学的研究

Dynamical study of initial stage of lysozyme protein crystallization by liquid-cell transmission electron microscopy

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Crystallization from solution has a key to understand geochemical processes of the earth and to synthesize functional materials. The primary stage of crystallization, called nucleation, has an important role to generate a new phase in an ambient phase. The following process is called crystal growth, which a formed crystalline nuclei grow continuously. To understand these processes in molecular scale, one of the powerful methods is direct observation of their dynamics in real-time by various microscopies. Crystal growth is well examined by in-situ observation using various advanced optical and scanning microscopies. On the other hand, nucleation process have been studied by indirect methods such as dynamic light scattering and spectroscopic methods, because nucleation process occurs at nano-scale and finishes within a few seconds and, therefore, nucleation is difficult to visualize by microscopy.. These indirect measurements suggest that nucleation is more complex process, for example, prenucleation clusters and dense liquids are formed before crystals appear. These primary particles may have critical role for nucleation of crystals, however, direct evidence is still poor because of difficulties to observe it. Recent advancement of nano-fabricate technique provides us the cells to observe liquids by transmission electron microscopy (TEM). This technique give us a chance to unveil the complex process of nucleation of minerals in nano-scale spatial resolution and real time. Here we adopt this technique to observe the nucleation process of protein lysozyme crystals. The dynamics of protein crystallization is relatively slower than that of inorganics due to their large molecular weight.

Optimizing the crystallization condition of lysozyme for TEM observation, we succeeded in observing three phases of lysozyme, amorphous and two crystalline phases. In addition, we caught the moments of nucleation of orthorhombic crystal which is the most stable phase in our crystallization condition. We measured the size evolution of nucleated particles with time, and found that the growth rate of the particle immediately after nucleation is surprisingly rapid, several hundred nm s^{-1}, which is two-three orders of magnitude faster than that of bulk lysozyme crystals. After this, growth rate is suddenly decreased, and facet faces appeared. Within several seconds from the particle appeared, growth rate became several nm s^{-1} which is the same as that of the bulk crystal at same supersaturation. Direct analysis of the nucleated particle suggests that the initial state of the nucleated particle is non-crystalline phase, and it transforms into the crystalline phase.

キーワード：その場観察、透過型電子顕微鏡、核生成、結晶化、タンパク質結晶
Keywords: In situ observation, Transmission electron microscopy, Nucleation, Crystallization, Protein crystal

溶解する炭酸カルシウム近傍におけるpH変化の２次元イメージング
2D imaging of pH change around calcium carbonate crystals during dissolution

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To understand the growth and dissolution mechanism of minerals, the pH monitoring of a solution is a useful technique. Actually a number of the previous studies has performed the pH measurements of bulk solution during the growth. However, to clarify the detail process on the surface, regional change of pH just above the crystal surface should be monitored. In the present study, we have tried to obtain two dimensional images of pH change around $CaCO_3$ crystals which inorganically grows or dissolves, by using the fluorescent probe 8-hydroxypyrene-1,3,6-trisul-fonic acid (HPTS) which has been applied for the research on the biogenic calcification of foraminifers. As a result, we succeeded to visualize the two dimensional distribution of pH around dissolved $CaCO_3$ crystal and its change with time, where pH increases above its surface. The results obtained by this technique may provide new insights into not only inorganic growth/dissolution mechanism of $CaCO_3$, but also the vital effect on the biomineralization by comparing with the results for bio-related process.

キーワード：pH、炭酸カルシウム、溶解
Keywords: pH, calcium carbonate, dissolution

プラズモンナノ粒子の円偏光光学捕捉により誘起される塩素酸ナトリウム結晶化におけるキラリティの偏り

Chiral asymmetry in $NaClO_3$ Chiral Crystallization Induced by Circularly Polarized Laser Trapping of Plasmonic Nanoparticles

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Chirality, the property that a certain 3D structure is not superimposable on its mirror image, is a fundamental characteristic prevailing in various natural hierarchies. Living organisms preferentially select only left-handed amino acids, despite the thermodynamic equality of mirror isomers. The significant chiral bias in living organisms is known as “homochirality”, and its origin is a great puzzle on the evolution of life. Among various hypothesizes which proposed to explain the origin of biohomochirality[1-3], the extraterrestrial scenario attributes the origin to enantioselective decomposition of chiral organic compounds on a meteorite by exposure to circularly polarized light (CPL), which asymmetrically interacts with chiral matters, emitted from a neutron star.[3] Therefore, asymmetric phenomena induced by CPL irradiation is of great interest from the viewpoint of earth science. Many previous studies on photosynthesis of chiral molecule have proven that asymmetric interaction between CPL and chiral matter, i.e. circular dichroism (CD), induces slight chiral bias in enantiomeric ratio of reaction products[4].
Chiral crystallization, in which chirality spontaneously emerges in the course of crystallization, has been received attention from the viewpoint of emergence of chirality. The exploration of physical factors that induce a significant chiral bias in chiral crystallization should provide implications for the origin of biohomochirality. However, light-based chiral bias in chiral crystallization still remains unreported. The conceivable reason is that CD is intrinsically small. Here, we provide the first demonstration of a statistically-significant chiral bias in sodium chlorate (NaClO3) chiral crystallization induced by CPL irradiation with the help of CD enhancement by localized surface plasmon resonance (LSPR) of silver nanoparticles (AgNPs), which is caused by electronic state chiral materials coupled with the collective oscillation of free electron on the surface of metal nanoparticles.
A continuous-wave (CW) CPL green laser (wavelength is 532 nm, laser power is 940±5 mW, ellipticity is 93%) was focused onto the air-liquid interface of the undersaturated $NaClO_3$ solution (6 microlitter) containing AgNPs by using a 60× objective lens (NA = 0.9) equipped on an inverted polarized light microscope. We repeated crystallization and chirality identification of the $NaClO_3$ crystal 150 times by using *l*-CPL and 150 times by using *r*-CPL, respectively. The number of the resulting enantiomorphs was counted. The crystallization dynamics was examined by *in-situ* microscopic observation of Raman scattering and polarized image.
Upon the laser irradiation, aggregates of the AgNPs occasionally floated on the air-liquid interface were

trapped at the focal spot because of optical trapping. Crystallization was induced simultaneously with the optical trapping of AgNPs. The observation of Raman scattering showed that crystallization occurred at the moment when surface-enhanced Raman scattering (SERS) [5] active particle was optically trapped, showing that the excitation of LSPR plays significant role for nucleation [6]. As the result of counting the given enantiomorphs, the crystallization using *l*-CPL(*r*-CPL) yielded *l*-enantiomorph 55(93) times and *d* -enanitomorph 95(57) times, respectively[7]. These results indicate that the "dominant" enantiomorph can be switchable by changing the handedness of incident CPL, i.e. enantioselectivity. This chiral bias is statistically significant because the number of the "dominant" enantiomorph deviates 99% interval of the binomial distribution B(n,p) = B(150, 0.5), where n is the number of trials and p is the probability that the "dominant" enantiomorph crystallizes out. The chiral bias, which was approximately 25% in crystal enantiomeric excess, is much higher than that in typical enantiomeric excess in photosynthesis ranging from 0.5 to 2% [8].

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