Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

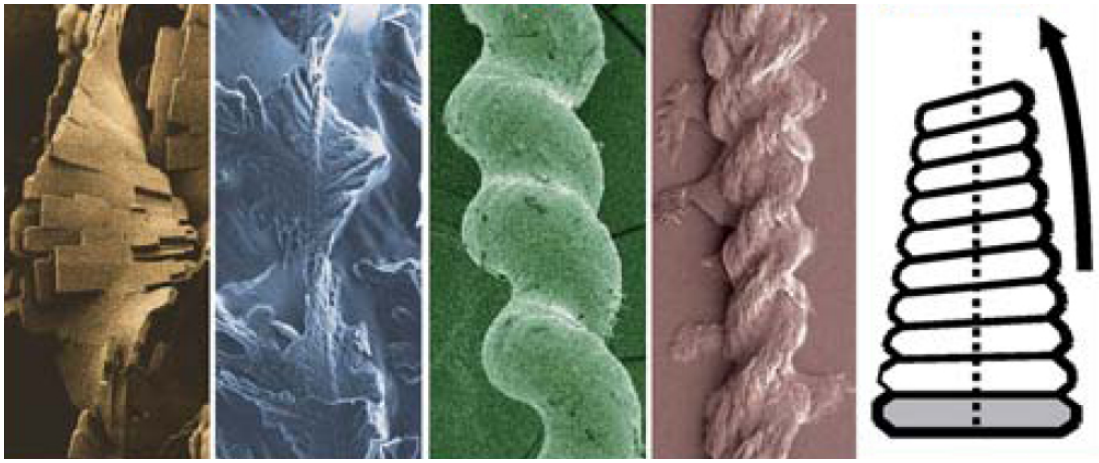
MIS31-01 会場:101B 時間:5 月 19 日 11:00-11:30

拡散場における結晶のねじれ成長
Emergence of helical morphologies with crystals: twisted growth under diffusion-limited conditions

今井 宏明 [1*]
Hiroaki Imai[1*]

[1] 慶應義塾大学理工学部
[1]Faculty of Science and Technology, Keio University

Twisted crystals are widely observed in natural minerals and artificial materials. However, the formation mechanism for most of the helical morphologies is quite complicated and, thus, remains to be explained. Here, the twisted growth of inorganic and organic crystals under a diffusion-limited condition is described after detailed observation of the backbone structures and the chirality tuning of the helices. The helical structures were formed in a gel matrix with various inorganic and organic crystals having low crystallographic symmetry, such as triclinic, monoclinic and orthorhombic systems. The backbone was composed of a twisted stacking of tilted units regardless of the presence of molecular chirality. The particular morphologies depending on the stacking mode of the units were controlled by the gel density. The formation of the helices was attributed to the specific crystal growth under a mild diffusion-limited condition. The handedness of the helices was precisely tuned with specific interaction between the surface of the helical crystals and the chiral molecules in the matrix.



Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

MIS31-02 会場:101B 時間:5 月 19 日 11:30-11:45

ケミカルガーデン反応と地下環境科学
Chemical garden reaction and underground environmental science

佐藤 久夫 [1*]
Hisao Satoh[1*]

[1] 三菱マテリアル株式会社
[1]Mitsubishi Materials Corporation

私たちの物質文明を下支えしているのは物質科学である。その創造された物質の中でも最も大事なものの一つとして、建築材料であるセメント物質が挙げられる。セメントは水酸化カルシウムであるポートランダイト結晶と、 クリンカーであるエーライト、ビーライトなどの可溶性ケイ酸塩の水和過程でできるケイ酸カルシウム水和物 C-S-H で構成される。このセメント水和反応によってダムに求められる止水性が生まれ、粒子の超微細組織によってビルやトンネルに求められる高い圧縮強度が得られるが、それらは、セメント空隙中でおこるナノスケールの結晶成長によって生み出されるものである。

C-S-H は結晶構造が厳密には決定されておらず、短周期の非晶質部とトバモライト結晶部の混合体であると考えられている (Pellenq et al. 2009)。その結晶成長過程では、過飽和度に応じて結晶形態が変化することが多く先行研究によって明らかになっている (Cartwright et al., 2002)。低過飽和条件では膜状からチューブ状の植物様の構造体を作るとされており、この反応はケミカルガーデン反応として知られている。

この反応は Ca2+やそれに類する Me2+の供給がケイ酸溶液中にあれば起こるが、溶解中の岩石表面においても起きることがわかった。その反応はアルカリ溶液が岩石亀裂を通過すれば常に起こるが、反応生成物のモル体積が増大するため、溶液の通水は最終的には阻止（クロッグ）される。この性質がセメントの高い止水性を生み出しているが、岩石においても、アルカリ環境下ではセメントと同様に止水性能があると考えられる。

今回の実験では、差圧一定の元で花崗岩表面に設けた人工亀裂へアルカリ溶液を通水させて流量測定をモニターし、結果的に生じた C-S-H を回収、観察し、形成過程を結晶成長の観点から考察した。現在、地下環境における多くの反応は、人工的な建造物に使用されているセメントによるアルカリ地下水が関与するが、その将来予測には C-S-H の成長挙動の知見が必要となる。

キーワード: C-S-H, アルカリ溶液, ナノ構造, ケミカルガーデン
Keywords: C-S-H, alkaline solution, nano texture, chemical garden

Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

MIS31-03 会場:101B 時間:5 月 19 日 11:45-12:00

炭酸カルシウム成長における不純物の影響についての理論的検討
Impurity effect for the formation mechanism of $CaCO_3$ polymorphs: ab initio study

川野 潤 [1*], 佐久間 博 [2], 永井 隆哉 [3]
Jun Kawano[1*], Hiroshi Sakuma[2], Takaya Nagai[3]

[1] 北海道大学・創成, [2] 東京工業大学・院理工, [3] 北海道大学・院理
[1]Hokkaido University, [2]Tokyo Institute of Technology, [3]Hokkaido University

The formation process of calcium carbonate polymorphs has been extensively investigated because of its importance in both geological and biological environments. Recently, it has been pointed out that the surface energy difference among polymorphs could determine their stability field, so that it becomes more important to analyze in detail their surface structures and the incorporation process of atoms and molecules into the growth surfaces.

In the present study, first-principles calculation of aragonite (001) surface was performed to theoretically analyze its surface structure and growth process. Especially, here we focused on the case in which Mg^{2+} ion substitutes for Ca^{2+} site as an impurity. Because, different from Ca^{2+}, smaller Mg^{2+} is unstable in the nine-fold cation positions of aragonite, it can hardly incorporate into bulk aragonite crystal. However it is expected to be able to substitute for Ca^{2+} site in the surface bulk. Our simulation results show that Mg^{2+} can incorporate into Ca^{2+} sites in the surface with lower substitution energy than that for bulk, but Mg^{2+} on the aragonite surface considerably affects the surface structure. This suggests the possibility that Mg^{2+} could play an important role for aragonite formation and growth.

キーワード: aragonite, 表面構造, 第一原理計算
Keywords: aragonite, surface structure, first-principles calculation

Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

MIS31-04 会場:101B 時間:5 月 19 日 12:00-12:15

非接触原子間力顕微鏡による溶液結晶成長のナノ観察
Atomic Resolution Investigation in Liquid by Frequency-Modulation (Non-Contact) AFM

長嶋 剣 [1*]
Ken Nagashima[1*]

[1] 北海道大学低温科学研究所
[1]Institute of Low Temperature Science, Hokkaido University, Japan

High resolution Frequency-Modulation AFM (FM-AFM) imaging had been limited to a vacuum environment. Fukuma et al. (2005) succeeded in obtaining true atomic resolution in a liquid by FM-AFM [1]. Subsequently, insoluble crystals have been mainly observed in liquid by FM-AFM. However, to observe the soluble crystals with atomic resolution is very important for discussing about mechanism of crystal growth process. We observed soluble crystals such as alkali halide or protein crystals [2].

FM-AFM images were obtained using a modified commercial AFM (Shimadzu, SPM-9600) with open fluid cell. We intentionally observed the soluble crystals in undersaturated solution at first. However, the concentration of solution gradually increased because of evaporation of water. Therefore, dissolution, near equilibrium, or growth conditions could be observed depending on time. By using this method, crystal growth speed of vertical direction was suppressed and atomic resolution images could be obtained.

In the case of KCl(100) cleaved surface in solution, we could observe periodic structure, in which the wavelength is 6.29 A. Therefore, only one kind of atom was considered to be imaged in liquid environment as well as ultrahigh vacuum environment.

In the case of lysozyme (110) in solution, the surface unit cell (black rectangle in fig. 2b, 11.2 x 3.8 nm) involves four molecules with the four unique orientations, which make two kinds of zigzag structures (circles and triangles) along the [001] direction. We obtained the AFM images with the individual four molecules in the unit cell and the image have higher resolution than images obtained by conventional contact mode or amplitude-modulation (tapping) mode AFM[3].

[1] T. Fukuma rt al., Appl. Phys. Lett. 87, 034101 (2005).
[2] K. Nagashima et al., J. Vac. Sci. Technol. B 28, C4C11 (2010).
[3] J. H. Konnert et al., Acta Crystallogr. D 50, 603 (1994).

キーワード: AFM, 結晶成長
Keywords: AFM, Crystal growth

Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

MIS31-05 会場:101B 時間:5 月 19 日 12:15-12:30

無重力での結晶成長速度
Growth Rate of Crystals under Microgravity

塚本 勝男[1*]
Katsuo Tsukamoto[1*]

[1] 東北大学・院・理
[1]Grad. School of Science, Tohoku Univ.

２０１２年に国際宇宙ステーション ”きぼう ”の中で、水溶液から成長する結晶の成長速度と過飽和度の関係を５ヶ月間にわたり測定した。結晶はモデル物質としてリゾチームを用いた。