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

MIS31-01 Room:101B Time:May 19 11:00-11:30

# Emergence of helical morphologies with crystals: twisted growth under diffusion-limited conditions

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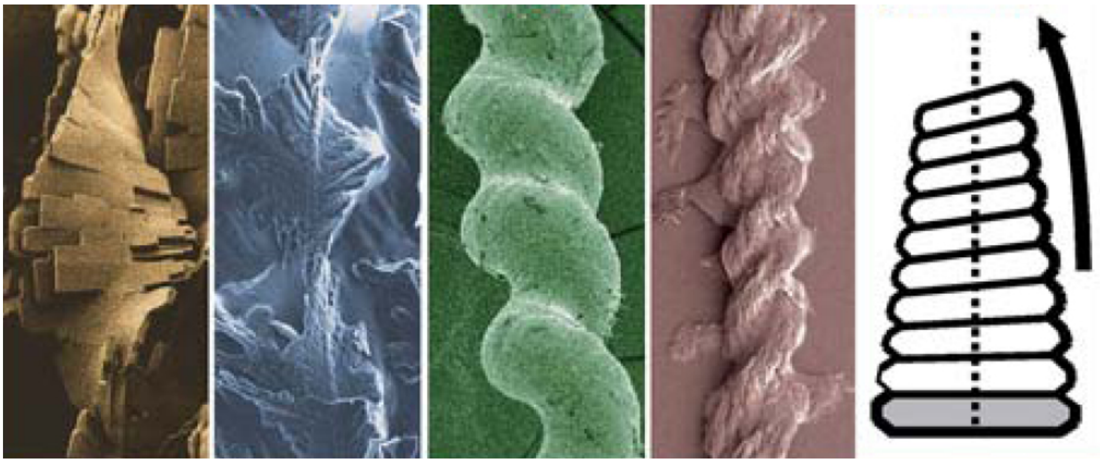
Twisted crystals are widely observed in natural minerals and artificial materials. However, the formation mechanism for most of the helical morphologies is quite complicated and, thus, remains to be explained. Here, the twisted growth of inorganic and organic crystals under a diffusion-limited condition 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.



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MIS31-02 Room:101B Time:May 19 11:30-11:45

# Chemical garden reaction and underground environmental science

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Our civilization is based on material science. One of the most important material created in our civilization is cement for many buildings. Cement consists of Ca(OH) (portlandite) and hydration products of calcium silicate hydrate (C-S-H) resulted from hydration of crinker minerals such as alite and belite. This hydration reaction produces function of water stopping and mechanical strength on the cement utilized for dams, urban buildings and tunnels. This function is created by nano-scale crystal growth in the cement pores. The C-S-H is not well-understood crystallographically. The latest model proposes that the structure of C-S-H includes both glass-like short-range order and crystalline features of tobermorite (Pellenq et al., 2009). During crystal growth of C-S-H, the growth form changes from layered to hollow as a function of supersaturation, which is widely known as chemical garden reaction.

This reaction occurs when the silicate solution includes Ca2+ or other Me2+ ions, and also on natural rock in the alkaline solution. If the C-S-H occurs on natural fractures in which alkaline solution flows, the solution flow can be clogged finally.

Laboratory experiment reproduced C-S-H growth on synthetic rock fracture by flow of alkaline solution at a constant pressure gradient. Nano-scale observation revealed the growth texture of C-S-H and its function. This can serve important information for prediction of our future condition of underground environment that may be affected by alkaline groundwater including cement leachates.

Keywords: C-S-H, alkaline solution, nano texture, chemical garden

MIS31-03 Room:101B Time:May 19 11:45-12:00

# Impurity effect for the formation mechanism of $CaCO_3$ polymorphs: ab initio study

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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.

Keywords: aragonite, surface structure, first-principles calculation

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MIS31-04 Room:101B Time:May 19 12:00-12:15

# Atomic Resolution Investigation in Liquid by Frequency-Modulation (Non-Contact) AFM

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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).

Keywords: AFM, Crystal growth

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MIS31-05 Room:101B Time:May 19 12:15-12:30

# Growth Rate of Crystals under Microgravity

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Growth rate vs supersaturation of lysozyme has successfully been measured for 5 month under microgravity condition in the international space station ”KIBO” in 2012. These data clearly shows why the quality of crystals grown under microgravity is improved.