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Formation mechanism of domain structure and defect of goethite surface

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Goethite (alfa-FeOOH) is one of the most common iron (oxyhydr)oxide minerals in surface environment of Earth and has huge specific surface area due to the small particle size. The surface of goethite plays an important role in many chemical reactions, e.g., adsorption, dissolution and precipitation, and thus their mechanism and kinetics are studied in detail using synthetic goethite. However goethite occurring in natural environment shows wide range of crystallinity (Kuhnel et al., 1975) and it is known that many properties, e.g. *a*-dimension of the unit cell and OH bending mode, are affected by the crystallinity (Schwertmann et al., 1985). Goethite with low crystallinity shows multidomain structure and weak hydrogen bonds owing to the -OH defects in the crystal structure and those characteristics accelerate the dissolution and adsorption rates (Strauss et al., 1997). In this study, we investigate the surface morphology and the ratio of surface hydroxyl group to oxygen, [-OH]/([-O] + [-OH]), of goethite with varying crystallinity and discuss the formation mechanism of multidomain structure and OH defects.

Goethite in this study was synthesized using ferric nitrate ($Fe(NO_3)_3$-$9H_2O$) and potassium hydroxide (KOH) as starting materials, according to Schwertmann et al. (1985). The dark brown precipitate, which is amorphous ferric oxide called ferryhydrite, was aged for 70 days at 4 oC (G-04), 30 days at 30 oC (G-30), 10 days at 50 oC (G-50) and 3 days at 70 oC (G-70). All products were washed with pure water, dried in nitrogen atmosphere and indentified as goethite by powder XRD analysis. The morphology of these goethite were observed using AFM and specific surface area were measured with 11-points BET method. X-ray photoelectron spectroscopy (XPS) was employed to analyze the ratio of surface hydroxyl groups to surface oxygen.

AFM observations revealed that all goethites have acicular morphology, however, goethite aged at high temperature has larger particle size (> 1000 nm), higher aspect ratio and monodomain structure. On the other hand, goethite aged at low temperature has smaller particle size (< 200 nm), lower aspect ratio and multidomain structure. This observation well agrees with TEM observation by Schwertmann et al. (1985). XPS analysis revealed that the ratio of surface hydroxyl group to oxygen, [-OH]/([-O] + [-OH]), was higher for the goethite aged at higher temperature.

Transformation of ferrihydrite into goethite proceeds in three stages (Cornell et al., 1989; Yuwono et al.): (1) crystallization of goethite nanoparticles from ferrihydrite nanoparticles, (2) oriented attachment of goethite nanocrystals and (3) development of crystal morphology by aging. In aging at high temperature, ferryhydrite nanoparticles crystallize rapidly and completely, and thus oriented attachment occurs without misalignments. As a result, goethite aged at high temperature has monodomain structure and high aspect ratio. On the other hand, in lower temperature, ferrihydrite crystallizes into goethite nanoparticles slowly and incompletely, hence aggregation of the goethite nanoparticles has many misalignments. The multidomain structure, OH defects and low aspect ratio of goethite aged at low temperature arise from the misalignments within the aggregate of nanoparticles as a precursor of aged goethite.

Keywords: crystallinity, crystal morphology, particle size, AFM, XPS

DNA nano-structure formation and the interpretation based on crystal growth theory

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The DNA molecule is now attracting attention as a new self-assemble material. The reason why DNA is used for self-assembly is that DNA molecule has calculation capability. Many nanostructures have been produced using DNA, for example, DNA tile (Winfree and Seeman, 1998). DNA tile is a complex molecule, which is composed of some single strand DNA (ssDNA). Each tile has some sticky ends (a part of some exposed bases). The complementary sticky end spontaneously makes hydrogen bond and grow to large ordered structure (DNA tile crystal) as the solution cools down. This process is termed as self-assembly, in other words, crystallization. Although DNA tile has potential as computer, there are some problems. The most important matter is presence of error (misfit crystallization). In order to reduce this error, many types of DNA tiles have been designed. However, it is difficult to completely prevent the assemble error. For synthesis of DNA tile crystal without the assemble error, we carried out experimental study of DNA tile formation and interpreted the result based on crystal growth theory.

First, we chose T-motif as DNA tile, which is able to grow on the electrically-charged Mica surface like two dimensional crystal, and measured its growth rate using DNA origami as a seed crystal with atomic force microscopy. The growth rate of T-motif crystal on Mica substrate was about 4.30 [monomers/minute].

In the second experiment, we observed T-motif crystals synthesized on the Mica surface for various conditions (temperature and concentration). We found that the nucleation temperature of the T-motif crystal was about 41.5 [deg. C.], which did not depend on the concentration significantly in a range of 2~10 [nM]. From this result, we assumed that the T-motif crystal growth can be considered to be melt growth. In order to understand the growth mechanism, we calculated the step free energy beta [J/m] and melting point Tm [deg. C.] under the assumption that the number density of crystals on the Mica surface is proportional to the two-dimensional nucleation rate. When the melting point is assumed to be 50 [deg. C.], the calculated step free energy was about 4.21×10^{-13} [J/m]. The calculated step free energy of T-motif crystal is similar to that of Lysozyme crystal (8.9×10^{-13} [J/m]).

We also observed the morphological change of T-motif crystals depending on the growth condition. In the highest supersaturation condition in this study (T-motif concentration is 10 [nM] and temperature is 38 [deg. C.]), the morphology of the T-motif crystal was similar to dendrite crystal. In other cases, the morphology was found to be polygonal shape. The reason why the T-motif crystal becomes dendritic in the highest supersaturation condition is considered to relate to the thermal stability of the sticky end binding. In low supersaturation, many T-motif units bind only at a site with two sticky ends. In contrast, in the highest supersaturation, the T-motif unit can bind to anywhere. We calculated the difference of Gibbs free energy in two conditions; one match bond of sticky end or two matches. We found that when the driving force exceeded the critical point, the T-motif crystal has possibility to be formed as dendrite. Using the critical driving force, we calculated the temperature at which the T-motif dendrite crystal was formed. In this calculation, the temperature of dendrite formation is 41.8 [deg. C.] when the melting point is assumed to be 50 [deg. C.]. On the other hand, experimental result shows that T-motif dendrite form in 38 [deg. C.]. The inconsistency between the theory and the experiments should be resolved in the future, however, our study is an important first step to describe the growth mechanism of the T-motif crystal based on the theory of crystal growth from melt phase.

Keywords: DNA tile, Crystal growth

The morphological relationship of octacalcium phosphate and its precursor: the role of intermediate phase

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Octacalcium phosphate (OCP) is the precursor of hydroxyapatite (HAP) which is main component of human tissue. HAP crystals which form through OCP are pseudomorph of OCP. Thus, the investigation of OCP morphological decision is connected with the later phase, HAP morphological decision. In around neutral pH solution, amorphous calcium phosphate (ACP) is precipitated as an initial solid phase at supersaturated calcium phosphate solution. Wherein, we investigated the formation process of characteristic morphology of OCP from ACP in solution.

We prepared 1 mol/L CaCl2 and 0.5 mol/L KH2PO4 solutions which were also buffered by tris amino methane, and 0.15 mol/L tris amino methane-HCl buffer solution. These three solutions were gently blended without starring to observe the morphological connection between initial phase and later phase through the materials evolution of calcium phosphates precipitations in solution by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). (The total concentration is Ca = 0.075 mol/L, PO4 = 0.045 mol/L, tris amino methane = 0.015 mol/L, 32C, initial pH = 7.7) Immediately after blending, white indeterminate precipitates were emerged and formed gel-like structure which was maintained for 40 minutes after blending. The solution pH was gradually decreasing around 4 until 40 minutes later. In FE-SEM and TEM observation, the gel-like structure was consisted of sphere-like ACP particles with 100 nm in diameter and ACP spherulites with 3-20 micro meter in diameter. In proceeding time, fiber-like beat-tri calcium phosphate crystals (TCP) were emerged in gel-like structure and ACP sphere particles were vanished. 3 minutes later, ACP spherulites transformed through TCP like phase. 6-12 minute later, the TCP like phase spherulites transformed spherulites which composed of both of single OCP crystal and TCP polycrystals. TEM dark field image showed OCP and TCP domains were mingled. Finally, the spherulites transformed into single OCP crystals with maintain their whole spheritic morphology until 40 minutes later. These observations suggested that OCP is pseudomorph of ACP. In below 7 pH solution, it suggested that through TCP like phase, morphology of OCP crystals was maintaining initial phase morphology, ACP.

Keywords: octacalcium phosphate, morphology, precursor, phase transition, pseudomorph

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In situ measurement of dissolution and growth velocities of $Ca(OH)_2$ for CO_2 trapping

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In these latter days, CO_2 capture and storage (CCS) has attracted considerable attention as a greenhouse gas mitigation option against global warming problems. CCS is a technique to confine captured CO_2 to underground or sea for a long time. One of the trapping strategies is a mineralization of CO_2, into calcite ($CaCO_3$) for instance. Since calcite is a stable polymorph of calcium carbonate on the earth, it is expected to trap CO_2 during a long term. To produce calcite, it has been investigated as a convincing reaction that calcium hydroxide ($Ca(OH)_2$) crystal reacts with liquid containing $CO_3{}^{2-}$ (Lacker et al., 1995). However we do not know how long the transformation takes for $Ca(OH)_2$ crystal to calcite because there is no date of the growth and dissolution velocities of $Ca(OH)_2$ crystal. The purpose of this study is to solve the growth and dissolution mechanism of $Ca(OH)_2$ crystal by 'in situ measurement of these velocities of it'.

We adopted Phase-Shift Interferometer (PSI) for the measure of normal growth and dissolution rates of $Ca(OH)_2$. Since PSI has extremely high spatial resolution as a few nm in vertical direction, it can detect ultra-slow normal velocity of crystal surface ($\sim 10^{-5}$ nm/s). We put a $Ca(OH)_2$ crystal in a solution which is adjusted from -0.46 to 0.29 in supersaturation by mixing 4 liquids (0.25 M $CaCl_2$, 0.50 M NaOH, 2.0 M NaCl solution and pure water which is completely degassed), and then measured the normal growth or dissolution rate of (001) face of the $Ca(OH)_2$ crystal.

We expect that the growth pattern was multi-nucleation in supersaturation > 0 by normal growth rate depending on supersaturation because the normal growth rate rises sharply at a specific supersaturation. We obtained that step edge energy of two dimensional nucleus formed in multi-nucleation condition was $1.093*10^{-11}$ J/m by fitting into a theoretical formula for the first time. The value was smaller than that of calcite on (10-14) obtained from the previous work (Teng et al., 2000). The result is probably one of the reason that $Ca(OH)_2$ crystal grows by multi-nucleation in the range of the low supersaturation.

In addition, on the basis of the result of $Ca(OH)_2$ normal growth and dissolution rate, toward CO_2 mineral trapping we could predict how $Ca(OH)_2$ crystal behaved during dissolution in $Ca(OH)_2$-calcite crystals system on the condition that calcium ion concentrations (supersaturation) were $[Ca^{2+}] > 10^{-2}$, $10^{-4.5} < [Ca^{2+}] < 10^{-2}$ and $[Ca^{2+}] < 10^{-4.5}$ M and that hydroxide and carbonate ion concentration and temperature were constant.

We inferred that the behavior of $Ca(OH)_2$-calcite crystals when they co-exist in the solution and found that calcite can grow sooner or later even if the solution is initially undersaturated for calcite. From these results, we concluded that the behavior of $Ca(OH)_2$ crystal could be predicted in the various supersaturation systems understood the normal growth and dissolution rates as a function of supersaturation and CO_2 mineral trapping is enough to enable using $Ca(OH)_2$ crystal, which is an important candidate material for CO_2-storage in the future.

Keywords: calcium hydroxide, calcium carbonate, mineral trapping, multi-nucleation

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Carbon Sequestration

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Carbon sequestration will be discussed.

Keywords: Carbon Sequestration, Crystal Growth, Dissolution