

## Specific Surface Free Energy of Celestine

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The morphology of crystal is determined by the stability of each crystal face. Especially, Wulff's relationship is well known: growth length of the crystal face is proportional to the specific surface free energy (SSFE) of the crystal face. Though SSFE is theoretically discussed, experimental determination of SSFE is very few. We calculated the SSFE of some single crystals using contact angle of liquid droplets. We observed some sulfates such as, gypsum, anhydrite, and barite. This time we observed celestine ( $\text{SrSO}_4$ ), and determined the SSFE of natural and polished face in order to discuss stability of each face. Though natural celestine crystal do not have (001) face, the natural celestine crystal was cut and polished in order to produce (001) face. SSFE of (210) and (001) faces were 25.3 and 51.2 mN/m. SSFE of (210) face was much smaller than that of (001) face, indicating that (210) face is more stable than (001) face. Dispersion component which causes van der Waals force and polar component which causes permanent dipole moment interaction of SSFE were obtained separately. Dispersion and polar component for SSFE of (001) face was 47.9 and 3.3 mN/m, respectively. On the other hand, they were 13.0 and 12.3 mN/m for the SSFE of (210) face. (001) face of celestine is considered to be neutral face and the dispersion component for the interaction between liquid and solid is dominant. Though contact angle of liquid is macroscopic value, we can discuss microscopic, as atomic scale structure of crystal face.

Keywords: celestine, surface free energy

## On the relation between the origins of aragonite and transition temperatures to calcite

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Aragonite, a polymorph of  $\text{CaCO}_3$ , is less stable than calcite in the ambient condition, but commonly forms with both biological and geological origins. In particular, aragonite as the biominerals seems important in the geoscience fields because it constitutes the fossils of hard tissues or becomes a carbon reservoir in the carbon cycle near the surface of the earth. Hence, it is interesting to know how the mineralogical stability is different between aragonites with different origins. For this purpose, we have investigated the transition temperatures of various biogenic aragonite to calcite by heating, using high-temperature XRD, as well as geological and synthetic ones. Among 21 specimens, almost biotic aragonites showed a transition temperature 60-100C lower than geological and synthetic ones. However, the shells of land snails (three species were examined) showed almost the same transition temperature as abiotic aragonites. Accordingly, it cannot be concluded that the biotic aragonite is always less stable than geological ones. Besides, aragonite of a coral showed an onset temperature of the transition around 40C lower than the other biotic aragonites.

Keywords: aragonite, calcite, phase transition, biomineral, X-ray diffraction

## In situ AFM study on crystal growth of barite

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Barite ( $\text{BaSO}_4$ ) is the most abundant mineral of barium and occurs in a wide variety of geologic environments that span geologic time from the Early Archean to the present. Because of its low solubility ( $K_{sp} = 10_{-9.99}$  at 25C) in water, the dissolution and precipitation of barite control the concentration and mobility of Ba in ground and surface water. Barite is also a common scale mineral, and its formation, with its low solubility in water, is almost inevitable in industrial water, oil, and gas-production systems. Because  $\text{Ra}^{2+}$  and  $\text{Ba}^{2+}$  are of similar ionic radius and electronegativity, some  $\text{Ra}^{2+}$  is incorporated into the barite crystal structure during its precipitation. Therefore, water including radioactive Ra ions produced from oil, gas, and geothermal wells or from U mine wastes, which contain an array of radioactive nuclides, including  $^{226}\text{Ra}$ , may precipitate radioactive barite.

Many in situ and ex situ AFM studies on the dissolution reactions of the barite (001) surface have been conducted to elucidate the processes involved and problems mentioned above. However, information on microscopic growth reactions of barite in aqueous solutions is sparse. Here we report the results of a preliminary experiment performed by in situ AFM observations of the growth behavior on the (001) surface of barite in supersaturated  $\text{BaSO}_4$  solutions at 25C.

The barite sample was obtained from the Stoneham Barite Deposit in Colorado, USA in the form of a single optically clear crystal. The barite crystal was cleaved parallel to the (001) cleavage plane with a sharp knife blade immediately before the AFM observations. The  $\text{BaSO}_4$  aqueous solution was prepared by mixing  $\text{Na}_2\text{SO}_4$  and  $\text{Ba}(\text{NO}_3)_2$  solutions consisting of analytical grade chemicals and deionized water immediately before the AFM observations. The degree of supersaturation and ionic strength were calculated using the program PHREEQC. In situ observations of the barite growth were performed by a Nanoscope III with a Multimode SPM unit (Digital Instruments) operating in contact-mode AFM (CMAFM) on a vibration isolation platform in a temperature- and humidity-controlled room. The cleaved barite crystals were first reacted with deionized water at 25C to ensure stable AFM scanning conditions and obtain reliable AFM images. We then replaced the water with  $\text{BaSO}_4$  solution in the fluid cell and began observing the growth process on the barite (001) surface at 25C. Deionized water and  $\text{BaSO}_4$  solution flowed through the fluid cell at a constant rate of 0.6 ml/h, controlled by a syringe pump.

The growth behavior on the barite (001) surface at 25C appeared to begin with the advancement of the initial step edges and filling in of the etch pits formed in the water before the  $\text{BaSO}_4$  solution was injected. The advancing fronts of the steps were not angular but rather irregular, wavy, or rounded. Under higher supersaturation conditions ( $>S = 13$ ), circular sector-shaped two-dimensional (2D) nuclei were observed slightly later than the advancement of the initial step edges. These sector-shaped islands are defined by half-layer steps (3.6 Å) parallel to [120], [1-20] and a curved step edge tangent to [010]. The advance rate of the curved step was approximately 5 times that of the [120] step.

Other growth behavior observed on the barite (001) surface included the formation of prismatic or bladed growth ledges and growth hillocks and spirals. The prismatic growth ledges were formed at kinks or faults at multi-layer steps and were elongated along the [010] direction with curved edges. The growth hillocks and spirals were also elongated along the [010] direction and displayed a bow-shaped form. The morphology of the growth hillocks and spirals was very similar to that of the deep etch pits formed in NaCl solutions at room temperature or in water at 60C, that is, under the conditions that promote barite dissolution.

Keywords: crystal growth, barite, atomic force microscopy, two-dimensional nucleus, spiral growth

## Dissolution Rate of Crystals in Solution

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Compared to growth mechanism of crystals, dissolution mechanism has not been studied so well because the phenomena has been regarded as the reverse process of crystal growth. However the phenomena is not so simple as often has been observed in coupled-dissolution and precipitation. This mechanism has been applied to the interpretation of natural mineral dissolution or replacement, it would be important for the selection of polymorphs or chirality during dissolution of medicine or some other materials, as well as natural minerals. Some examples will be shown based on the precise dissolution rate of crystals by interferometry for discussion.

Keywords: crystal growth, dissolution mechanism, spiral growth, nucleation, crystallization, phase-shift interferometry