

Conjecturing Chemical Environment of Crystal Growth by AFM Observation of Polyhedral Micro-Etch Pits during Dissolution

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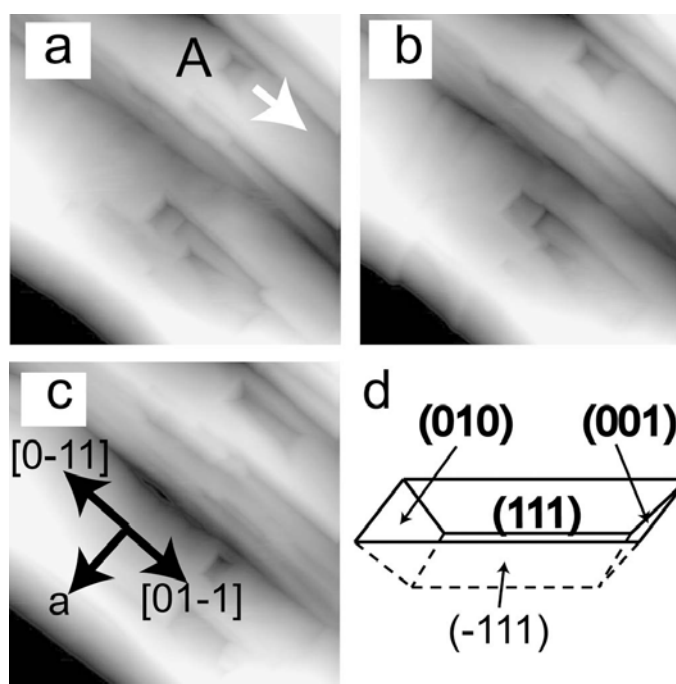
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Minerals take various growth forms in nature depending upon locality. The shapes of polyhedral crystals grown under thermodynamic control, rather than under kinetic control, reflect relative stabilities of the crystal faces surrounding the material in the given environments. If we know the relationship between the stability of each face of a crystal and the chemical and the physical conditions, we can describe in detail the environment of the mineral growth. However, it is not easy to obtain equilibrium forms of crystals by keeping a uniform growth environment for sufficiently long time.

On the other hand, shapes of small polyhedral etch pits formed at crystal faces during dissolution in solutions reflect relative stabilities of crystal faces

in the same condition, especially for less soluble crystals. The shapes of micro-etch pits can be analyzed in situ using atomic force microscopy (AFM). For example, the figure (reproduced from Ref.[1]) shows the AFM images ((a) 0 min., (b) 3min. (c) 10 min., full scale:2 micron sq.) observed at the (011) surface of anhydrite(CaSO_4 , orthorhombic, Amma) crystal in 0.01 mol/L Na_2SO_4 aq.[1]. With the etch pit denoted A in (a), less stable (001) front wall moved fast in the arrow direction, while the most stable (010) face forming the rear wall stayed nearly at the same position. The (010) face is much more stable because only one Ca-O ionic bond out of 8 is lost per each sulfate ion at the surface, while two bonds are lost per each sulfate at the (001) surface[2]. In 0.01 mol/L CaCl_2 aq., a sulfate poor condition, the (001) facets became even less stable and were totally lost with etch pits formed.

The (111) face is a so-called kink face usually expected to be unstable with ionic crystals. However, the figure clearly shows that {111} faces form stable sidewalls. The stability was explained by partial cancellation of positive charges of top Ca-layer by negative charges of O-atoms in the 2nd sulfate-layer. By analyzing profiles of etch pits formed at several different faces, we were able to explain the growth environments of natural crystal forms [1]. The same technique was applied to comparison of relative stabilities of crystal faces of carbonate minerals, aragonite (CaCO_3)[3, 4], calcite and cerussite (PbCO_3), in acidic aqueous solutions. Most natural aragonite crystals are considered to have been formed in alkaline solutions.



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