

Submerged atomic resolution imaging of hydration structure on calcite in the presence of the synthetic polypeptide

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Dehydration is an important growth rate-determining process in solution growth (Bennema, 1967). Recently, it has been suggested that hydration was eased by hydrophilic organic material from the result that the step velocity of calcite was increased by the addition of hydrophilic peptide (Elhadj et al., 2006). However, the influence of organic material on hydration has not been revealed. In order to verify the influence of the organic material on the hydration of the crystal surface visually, we tried in situ observation of hydration structure on calcite surface in atomic level during solution growth.

The observation was conducted by a recently developed high-resolution and low-thermal-drift Frequency Modulation AFM (FM-AFM) working in liquids (Fukuma et al., 2005). Hydration imaging was realized by force mapping of FM-AFM (Kimura et al., 2010). The probe is scanned on the vertical line to the crystal surface. Hydration layer is detected by the frequency shift due to the interaction of tip and water molecule. The supersaturated solution of CaCO₃ was prepared to be supersaturated for both calcite and aragonite at pH 8.1 and room temperature. A cleaved calcite crystal was glued to the bottom of an open fluid cell, and the solution was put on the surface. The synthetic polypeptide was adopted as organic material in our experiment. The synthetic polypeptide consists of fifteen amino acid residues including six aspartic acids periodically (Takagi and Miyashita, 2010). This polypeptide is considered as important material to control the polymorph of calcium carbonate in the field of biomineralization.

We obtained atomically image of lacy network of hydration on calcite (104) face. Water molecule formed four layers to be piled up alternately in the vertical direction of calcite surface. Water molecules were above gaps between calcium ions on calcite surface in the first and third layer. In the case of the second and fourth layer, water molecules were located above calcium ions. Furthermore, 3D hydration structure was constructed by multiple 2D hydration images which were taken at interval of 0.15 nm to the one direction. The hydration structure on each layer was described after construction of 3D image. As a result, it was confirmed that water molecules keep stable structure corresponding to the calcite surface structure until the height 0.5 nm above calcite surface.

Our result shows that the hydration can be visualized in the level that we can compare the structure in atomic resolution. It is strongly expected that the influence of organic material on hydration structure would be revealed.