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Clarification of aragonite formation mechanism by in situ observation in atomic resolution

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Calcite and aragonite are polymorphs of the calcium carbonate ($CaCO_3$) crystal. Although aragonite is metastable at normal temperature and pressure, some bivalve shells contain prismatic calcite and nacreous aragonite simultaneously. Previous studies showed that organic matrices in shells control polymorphs of $CaCO_3$(Hare, 1963, Falini et al., 1996, Belcher et al., 1996). It was revealed that amino acids sequence is considered as one of the most effective chemical agents to active the formation of aragonite (Tsukamoto et al., 2004). Recently, it was confirmed that aragonite was nucleated in the supersaturated solution of $CaCO_3$containing the synthetic polypeptide, which consists of 15 amino acid residues and has six aspartic acids which are arranged periodically (Miyashita et al., priv. comm.). In their experiments, magnesium (Mg^{2+}) should be contained in the solution for aragonite nucleation.
In this study, we carry out a crystal growth experiments on a substrate of calcite single crystal (seed crystal). First of all, supersaturated solution of $CaCO_3$with the synthetic polypeptide and magnesium(supersaturation rate = 2.0, [Mg^{2+}]= 0.05M, the concentration of the polypeptide = 50 mg/l) was loaded on the seed crystal, then the surface pattern is observed. In order to observe the change of the surface pattern as the seed crystal grows, Atomic Force Microscopy (AFM) was employed. Secondly, the supersaturated solution of $CaCO_3$contains only synthetic polypeptide (Without Mg^{2+}) was loaded on another seed crystal, in order to explore the function of Mg^{2+}. Rectangular hillocks emerge on the surface of the face of calcite seed crystal in both cases with and without Mg^{2+}. The rectangular hillocks are very likely to be aragonite, because aragonite is orthorhombic and the space group is Pmcn. The rectangular hillocks fit the symmetry of aragonite.
Polymorphs of these hillocks are identified by in situ observation of the lattice pattern of the surface. Frequency Modulation AFM (FM-AFM) was employed to observe the surface of the hillocks in true atomic resolution. The lattice pattern changed from calcite pattern to aragonite pattern during one hour experiment with polypeptide and Mg^{2+}. On the other hand, the lattice pattern did not changed to aragonite pattern without Mg^{2+}.

Our results strongly suggest that the synthetic polypeptide cannot induce aragonite formation on calcite single crystal without Mg^{2+}, however, the shape of hillocks changed to that expected from the symmetry of aragonite. The relationship between the shape of hillocks and the lattice pattern could be a key to reveal the mechanisms of aragonite formation.

Keywords: biomineralization, synthetic polypeptide, calcite, aragonite,
Frequency Modulation Atomic Force Microscopy