Particular effect of Mg^{2+} on hydration structure at calcite surface

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Magnesium ions (Mg^{2+}) affect the $CaCO_3$ crystal nucleation, morphology and growth/dissolution rate. Recently, the relation of hydration and these phenomena has been suggested. In this study, we conducted the three-dimensional (3D) observation of water distribution in the vicinity of calcite surface by using the frequency modulation atomic force microscopy (FM-AFM). We compared the molecular-scale change of water distribution in 100 mM Ca-, Sr- and $MgCl_2$ solutions to specify the effect of Mg^{2+} on water.

The eigenfrequency of silicon probe is shifted by the interactions with the surface atom and the water molecules in the vicinity of sample surface. The 2D/3D maps of frequency shift (Δf) represent the water density distribution namely hydration structure.

The 3D Δf maps revealed the characteristic change in the lateral water distribution in the 1st hydration layer in $MgCl_2$ solution. Analysing 3D water distribution, the hydration structures in $CaCl_2$ and $SrCl_2$ solutions were strongly affected by the calcite structure. However, the water in $MgCl_2$ solution was formed bcc structure. This structure was consistent with the 6 coordination of the 1st hydration shell of single magnesium ion. This result suggest that the Mg^{2+} distribute in the hydration layers of calcite surface. A previous MD simulation have reported that the Ca^{2+} distribute the out of the hydration layers of calcite surface compared with the monovalent ions [Ricci et al. (2014)]. On the other hand, Mg^{2+} may distribute in the hydration layers due to its lower hydration energy than Ca^{2+} and Sr^{2+}. This specific effect of Mg^{2+} on hydration structure strongly suggest the effects of hydration on the calcite growth and polymorphism.