

The role of clays in heterogeneous carbonate nucleation

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Our study was motivated by earlier observations of Mg-bearing calcite in Lake Balaton (Hungary), a typical shallow freshwater environment; we found that the calcite grains were associated with nm-sized flakes of the clay mineral smectite. In order to understand whether the smectite induced calcite nucleation and whether the possible templated nucleation influenced the composition and morphology of calcite, we performed both laboratory experiments and molecular dynamics (MD) simulations.

We precipitated calcite from filtered, supersaturated lakewater. Calcite precipitation started earlier in smectite-containing solutions than in the controls (solutions with no foreign material, and with kaolinite or diatoms). In addition, both the morphologies and Mg contents of calcite were similar to those typical of the particles formed in the lake, suggesting that calcite indeed heterogeneously nucleated on smectite, and its physical properties were affected by the foreign surface. MD simulations were performed in order to understand the atomic scale processes that favor calcite nucleation on smectite. We used a model solution with the same major ions and in ratios as observed in the lake, and studied the effects of three different surfaces, including montmorillonite (a member of the smectite group), kaolinite and graphene. In all three cases clusters of Ca^{2+} , Mg^{2+} and CO_3^{2-} ions formed in the solution between the layers. In the presence of montmorillonite, the clusters (1) were larger, (2) contained more Mg, and (3) attached to the surface in larger numbers than in the case of the other two materials. Thus, our MD simulations indicate a multistep process of calcite nucleation on smectite as a favorable surface, and with some interesting patterns of Mg incorporation into calcite nuclei.

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