Calcium carbonate precipitation induced by clay minerals

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The formation of calcium carbonate minerals in lakes is typically linked to biological activity; however, our previous results suggest that in a large, shallow lake smectite clay minerals facilitate the nucleation of Mg-bearing calcite [1]. Furthermore, nucleation and growth on the clay surface likely affects grain size and morphology.

In the present study we performed various laboratory titration experiments in order to understand the role of clay minerals in the formation of Mg-bearing calcite. Calcium carbonate phases were precipitated both in the presence and absence of kaolinite and montmorillonite. Nucleation was observed using a Ca ion selective electrode, and the precipitated materials were examined using transmission and scanning electron microscopies.

Homogeneous nucleation from a Mg-free solution produced mainly vaterite with a small amount of calcite; vaterite formed organized crystal aggregates with disk- or ring-shaped morphologies, and electron micrographs showed the attachment of ~5-nm units, presumably formerly amorphous nanoparticles, to the surfaces of crystals. In the presence of montmorillonite (1) Ca concentration in the solution was lower than in the bulk even before nucleation, suggesting that prenucleation clusters might have attached to the clay surface, and (2) nucleation started earlier and produced significantly more solid than both in the bulk and in the presence of kaolinite. Thus, montmorillonite, a member of the smectite group strongly enhanced calcite formation. Electron microscopy showed that calcite particles grew on the surfaces of montmorillonite flakes. In contrast, no significant enhancement of calcite formation was observed in the presence of kaolinite relative to the homogeneous case. Precipitation from Mg-bearing solutions also suggested an important role of montmorillonite, with implications for the formation of very high magnesian calcite and the dolomite problem.

[1] Nyirő-Kósa, I., Rostási, Á., Bereczk-Tompa, É., Cora, I., Koblar, M., Kovács, A., Pósfai, M. (2018), *Earth and Planetary Science Letters,* 496, 20-28. [2] This research was supported by NKFIH grants K116732 and BIONANO-GINOP-2.3.2-15-2016-0001.