

## **Mg-calcite formation in a freshwater environment (Lake Balaton): nucleation, growth, structure and composition**

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Lake Balaton can be regarded as a large scientific laboratory in which many interesting aspects of carbonate mineral formation can be studied, with relevance to the general understanding of nanoscale processes that govern crystal nucleation and growth in a natural aqueous system. The lake is extremely shallow for its size (on average 3.5 m deep and 70 km long), its calcareous water Mg-rich (with a Mg/Ca molar ratio ranging from (~1 to 4), typically displaying a chemical gradient along the W-E long axis of the lake, as a result of the main inlet and outlet being located at opposite ends. The bottom sediment is a soft grey mud, with 30 to 80% of it consisting of Mg-calcite, a mineral that precipitates from the water (Fig. 1a). We used SEM, TEM and STEM techniques to characterize this Mg-calcite, in order to obtain a better understanding of its formation and role in the ecosystem.

Freshwater calcite is known to nucleate on biological material, primarily on picoplankton (cyanobacterial) cells. In contrast, the Mg-calcite in Lake Balaton is closely associated with few-unit-cell-thick stacks of clay (smectite) layers (Figs. 1b and c), suggesting that it either nucleated on smectite or adsorbed to the clay flakes. Our laboratory experiments confirm that adding smectite to filtered lakewater dramatically induces Mg-calcite precipitation; thus, the nm-scale clay fragments likely serve as nucleation sites. Since the lake sediments are stirred up by even gentle winds, most of the time smectite particles are readily available for Mg-calcite nucleation. A special case occurs when the lake is frozen and even the clay particles can settle: only bacterial cells are available as nucleation sites (Fig. 2a), and encrustation of cells results in tube-shaped, porous Mg-calcite particles (Fig. 2b).

Mg-calcite that formed under „normal” conditions (i.e., nucleated on smectite) typically occurs in the shape of elongated, several  $\mu\text{m}$ -large, aggregate-looking particles (Fig. 2c). Even though they appear to be composed of many smaller crystals, SAED patterns suggest that the particles are perfect single crystals (Fig. 2d). The single crystalline nature of the particles probably results from a dissolution/reprecipitation process that preserves the original shapes of particles.

The Mg content of the calcite varies from 2 to 20 mol%, depending on the water budget (dilution) and geographical location in the lake. Mg-calcite that nucleated on bacterial cells is highly enriched in Mg; according to SAED patterns, Mg and Ca ions do not order in the structure. Our results provide new information on freshwater calcite nucleation and on the biologically assisted precipitation of high-magnesian calcite.

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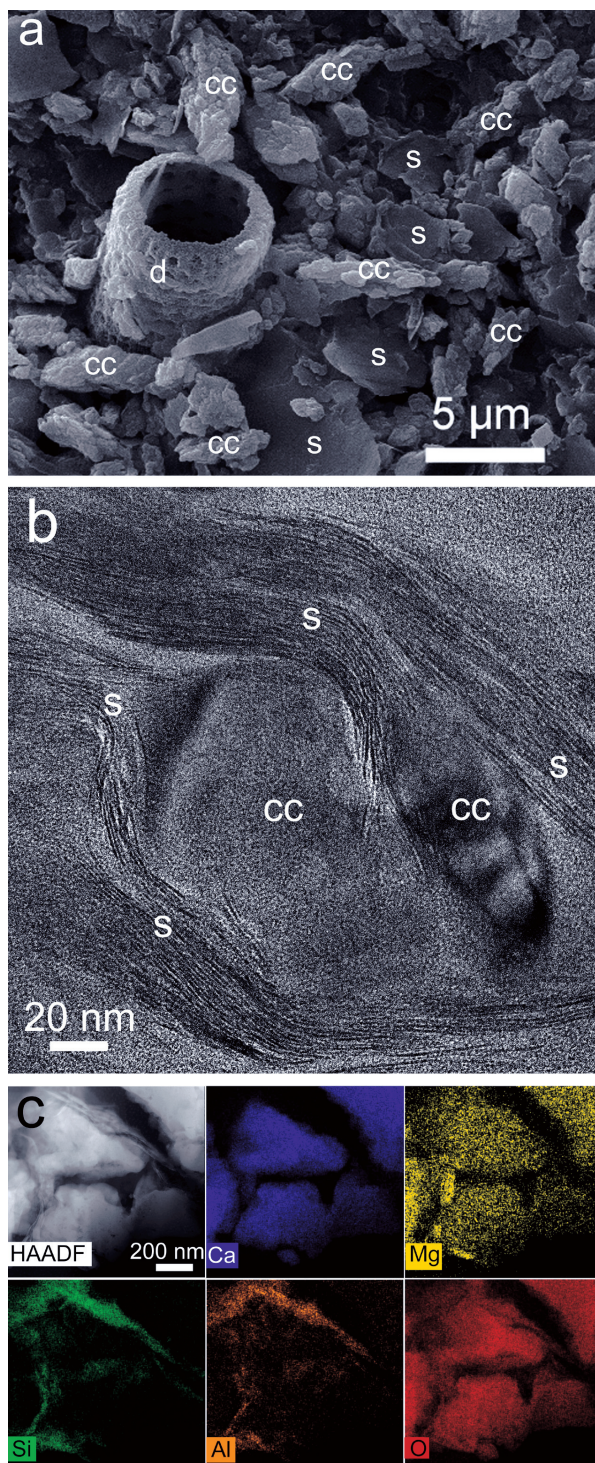


Figure 1. (a) SE image of typical sediment particles from the sediment of Lake Balaton (cc: Mg-calcite; s: clay minerals (mostly smectite); d: diatom fragment). (b) HRTEM image of nm-scale Mg-calcite particles enveloped by disordered stacks of smectite layers. (c) HAADF image and EDS elemental maps of Mg-calcite particles (containing Ca, Mg, O) enveloped by smectite layers (containing Si, Al, Mg and O).

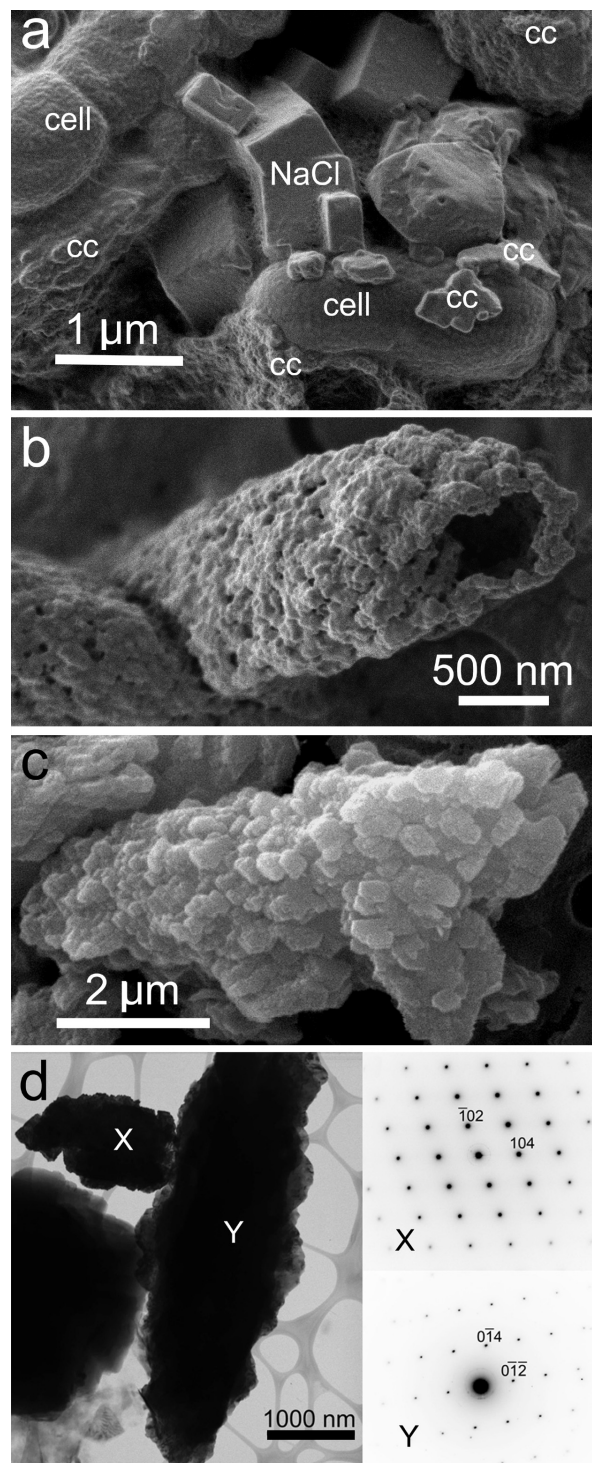


Figure 2. (a) SE image of bacterial cells, partially encrusted by Mg-calcite (cc) and (b) tubular, porous Mg-calcite particles, formed on the surfaces of cells from water collected from the ice-covered lake. (c) SE image of a typical Mg-calcite with a mesocrystal-like morphology. (d) TEM BF image and corresponding SAED patterns of Mg-calcite particles, confirming their single crystal character.