Composition of exopolymeric substances (EPS) associated with microbially-mediated high Mg-calcite and protodolomite

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The origin of dolomite—a common carbonate mineral—is the subject of an ongoing debate. Among different hypothesis, it has been proposed that extracellular polymeric substances (EPS) excreted by microbes contain specific organic molecules that facilitate the incorporation of magnesium in the carbonate minerals, probably by favoring Mg$^{2+}$ dehydration [1]. However, data on the composition of the EPS produced by (proto)dolomite-forming microbes are still limited, which hinder our understanding of their precise role in the mineralization. Here, we present the results of laboratory experiments in which we characterized the EPS associated with microbially-mediated carbonate minerals containing high mol% of Mg. Two *Virgibacillus* strains known to trigger Mg-rich carbonates formation, as well as a strain of *Bacillus licheniformis* that does not mediate mineral formation and can be used as a negative control, were grown under different salinities and temperatures. We characterized the EPS produced under different conditions by measuring total carbohydrate (TCHO), total protein (TP) content in addition to Fourier-transform infrared spectroscopy (FTIR) analysis. We report the formation of Mg-carbonates with a mol% Mg higher than 41% (i.e., potential dolomite precursor phases) exclusively in association with EPS rich in carbohydrates (TCHO > than 75% of the total EPS mass). Moreover, FTIR analysis of these EPS revealed the presence of protein secondary structures (e.g., β-sheets) known to favor mineral nucleation. These results suggest that, among the different constituents of microbially produced EPS, some organic molecules with specific functional groups (e.g., carboxyl and hydroxyl groups) may be of key importance for overcoming the kinetic barriers that else prevent the incorporation of Mg into carbonate minerals, a crucial step for the formation of dolomite in natural environments.