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From clusters to crystals: Unraveling the Mn-driven dolomite puzzle

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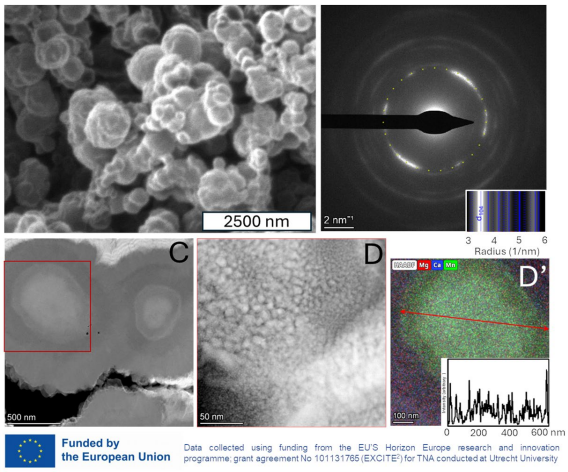
An emerging perspective suggests low-temperature dolomite formation begins with a non-classical pathway, where initial homogeneous nucleation forms amorphous Ca-Mg carbonate, subsequently reorganizing into high-Mg calcite nanoparticles with ordered nanoscale domains, before transitioning to substrate-mediated crystal growth. In contrast, heterogeneous (classical) nucleation is entirely surface-mediated, with microbial biofilms acting as nucleation templates that can trap impurities while binding Ca^{2+} and Mg^{2+} and other ions, thus leading to composite precursors with a predominantly disordered Ca-Mg lattice distribution. Aging driven by dissolution and reprecipitation can promote the growth of Ca-enriched phase with incipient $R\bar{3}$ superstructure[1]. This study investigates the role of manganese cycling in dolomite formation, following the hypothetical framework of Petrash et al.[2]. Sectorial chemical zoning in Neogene dolomite reveals Mn^{2+} incorporation via heterogeneous growth, sensitive to local redox or reservoir size variations. Cryogenian glacial weathering intensified manganese ocean input, driving primary productivity, redox buffering, and syngenetic shallow-water dolomite formation[3-4] . To test this link, we induced electrochemical redox cycling of millimolar Mn (~240 cycles over 48h) in a pH-stat-controlled dolomite-oversaturated electrolyte. The electrolyte was carboxylated and maintained at Mg:Ca≈6, pH≤pKa2, and 25°C . Samples were synthesized via cyclic voltammetry using a dual chamber H-cell membrane reactor and prepared using FIB-SEM milling for STEM characterization. Mg-Ca-Mn carbonate spherulites formed in the surface of our working electrodes, and exhibit Mn-enriched cores and Mg-rich cortices. Selected area electron diffraction of the cortices reveals d-spacings consistent with protodolomite exhibiting near-stoichiometric composition: d_{101} (4.029Å), d_{104} (2.88(1)Å), d_{110} (2.40Å), d_{113} (2.19Å), d_{202} (2.01Å), and d_{116} (1.79Å). While protodolomite formation in low-temperature experiments is occasionally observed without manganese cycling, these instances typically involve microbial mediation or non-framework ionic interactions with catalytic or desolvating effects. In contrast, we document substantial and rapid crystallization, resulting in abundant surface precipitates. These findings suggest that manganese cycling plays a crucial role in heterogeneous dolomite nucleation and cation ordering, warranting further investigation of the underlying kinetics.

References

[1] Wenk et al. (1993) American Mineralogist 78, 769-774.
[2] Petrash et al. (2015) Chemical Geology 404, 27–40.
[3] Zhang et al. (2021) Chemical Geology 584, 120502.
[4] Hu et al. (2022), Chemical Geology 609, 121065.



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