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Molecular mechanisms controlling uptake of trace elements during calcite growth

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Growth and dissolution reactions of carbonate minerals are key processes that regulate the availability and fate of critical elements and substances on the Earth's surface. Much progress has been made in the field of crystal growth over the last two decades, establishing a new paradigm of multistep growth pathways in which non-monomer species can play crucial roles. Despite the wealth of information on nucleation and growth pathways obtained for a variety of minerals, the molecular mechanisms regulating the incorporation of trace elements into crystal lattice are still poorly understood. Elucidating the extent to which original solution conditions at the formation are stored in natural carbonate minerals and how the composition of a crystal can be controlled by growth processes are essential to interpret paleoenvironmental proxies and to control crystal purity in engineered procedures.

To address these challenges, we performed seeded calcite growth experiments using a chemostat reactor with varied amount of manganese, a representative impurity and a potential paleoenvironmental proxy. As Mn^{2+} is compatible with calcite lattice, we found large partition coefficients ($k_{Mn} > 1$) that are strongly inversely correlated with growth rate. Interestingly, the stable Ca isotope fractionation between the precipitated solids and solution is found to be invariant with $\{Mn^{2+}\}/\{Ca^{2+}\}$ and growth rate. These results challenge the classical partitioning behavior predicted by ion desolvation kinetics and the expected isotopic signatures of classical growth, possibly suggesting that the Mn-calcite growth involves the addition of Mn-rich, non-monomer species. However, it is equally important to consider the role of different crystallographic facets of calcite exhibiting distinct surface energies which can also vary with element substitution [1, 2], affecting the desolvation kinetics of ions, hence in turn controlling the impurity incorporation and growth mechanisms. We discuss the implications of these results and report new data from transmission electron microscopy performed at cryogenic conditions to shed light on the role of solution chemistry, calcite-solution interface, and growth pathway in controlling Mn uptake during calcite crystal.

References

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