

## A multimodal in situ approach reveals molecular pathways for manganese substitution in growing calcite

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Carbonate minerals are crucial in aqueous and soil geochemistry as regulators of critical and toxic element availability. Despite recent advances in the field of crystal growth and the wealth of information on multistep pathways, how and to what extent a given growth pathway affects the incorporation of trace elements into growing minerals remains elusive, even for well-studied minerals such as calcite.

In this work, we investigated the mechanism by which manganese, a representative natural impurity in carbonate minerals, is incorporated into growing calcite crystals using a custom-built chemostat reactor. Seeded growth experiments were performed in the presence aqueous  $Mn^{2+}$  while maintaining a constant solution pH and temperature with quasi-constant solution composition and saturation index ( $SI = 0.8$ ) with respect to calcite. We used in situ time-resolved small-angle X-ray scattering (SAXS) to monitor interfacial growth, by successfully isolating scattering due to interfacial processes from that due to bulk of the crystals, and combined with in situ Raman and static light scattering to constrain the relevant SAXS models. This combination of bulk scattering techniques overcomes drawbacks of surface-sensitive scattering methods that rely on the reflection from atomically smooth surfaces and are therefore not suited to capture the broad range of processes observed here.

Our results revealed a formation of 15-20 nm Mn-bearing amorphous calcium carbonate (Mn-ACC) particles on the surface of growing calcite at  $[Mn^{2+}]/[Ca^{2+}] = 0.1$ . These particles rapidly reorganize to porous and polymeric mass fractal structures that undergo intermittent and likely local crystallization events. These crystallization events can result in local atomic reorganization and hence modifies the chemical composition at the growing front of calcite. Knowledge obtained on how “non-classical” growth units such as Mn-ACC are involved in crystal growth not only provides new mechanistic insight of trace element uptake in different classes of carbonate (bio)minerals but also provides a useful basis to inform predictive models for trace element partitioning in carbonates. These results also demonstrate that multimodal in situ time-resolved scattering techniques enable the characterization of interfacial growth on bulk minerals, thus