



## **Crystallisation behaviour of carbonate solid solutions**

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Considerable experimental work on the solid solution partitioning of divalent metals into calcite can be found in the geochemical literature. These works are of particular interest in the study of water-rock interactions that involve carbonate minerals and in environmental assessment of metal ion behaviour. Here, we present a review of recent experimental work carried out on this kind of systems, which includes: 1) nucleation behaviour of carbonate solid solutions from aqueous solutions, 2) reaction paths and generation of compositional patterns during crystal growth, 3) surface precipitation of solid solutions by interaction of dissolved metals with carbonate minerals.

Nucleation experiments widely demonstrate that, at high supersaturation rates, the substituting ions tend to incorporate to the nuclei in a ratio that significantly deviates from the equilibrium distribution coefficient. Here, we present examples of different nucleation behaviours for various carbonate solid solutions. After nucleation, crystal and aqueous solution compositions tend to vary as growth proceeds and this evolution is recorded in the crystal as a concentric compositional pattern. Concentric zoning provides a record of the changes in the crystallisation conditions during growth. From these patterns, the growth history of the crystals can be observed retrospectively, and those factors that can be influenced by the evolution in the bulk fluid composition can be separated from those that promote the development of oscillatory zoning. We show different examples in which oscillatory zoning is associated with near-surface fluctuations during the growth process. Finally, we consider the uptake of metals on carbonate minerals by surface precipitation of solid-solution layers. We revise the methodology needed to study this phenomenon, which includes considering structural, thermodynamic, nanotopographic, and kinetic factors. Nanoscale observations are shown to be especially relevant to understand the growth behaviour of solid-solution crystals.