



## Crystallisation of (Ca,Mn)CO<sub>3</sub> from aqueous solutions

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The (Ca,Mn)CO<sub>3</sub>-H<sub>2</sub>O system has been investigated by a variety of experimental and theoretical studies. These studies have proved that in suboxic-anoxic marine pore waters, manganese concentration is controlled by the precipitation of (Ca,Mn)CO<sub>3</sub> solid solutions with a calcite-type structure and/or by the formation of ordered kutnahorite, CaMn(CO<sub>3</sub>)<sub>2</sub>, an isotype of dolomite. The presence of dissolved Mn<sup>2+</sup> influences the transformation of orthorhombic aragonite to rhombohedral (Mn,Ca)CO<sub>3</sub> solid solutions in aqueous solutions. In addition to its geochemical importance, the calcite-rhodochrosite series can have an environmental interest. The coprecipitation of Mn<sup>2+</sup> with calcite represents a potentially significant process of removing manganese in aqueous environments. The low solubility of rhodochrosite compared to calcite implies a strong preferential partitioning of manganese into the solid phase.

The non-ideality of this solid solution and the extent of its miscibility gaps have been fully discussed in scientific literature, but most of these aspects are not completely known. Based on the different ideality degrees of the calcite-rhodochrosite solid solution proposed by different authors, we suggest different thermodynamic models for the system (Ca,Mn)CO<sub>3</sub>-H<sub>2</sub>O. The calculated Lippmann diagrams are compared and their efficacy to explain the crystallisation behaviour in this system is discussed. We present experimental work on crystallisation of (Ca,Mn)CO<sub>3</sub> solid solutions from aqueous solutions. The experiments were carried out at high supersaturation in silica hydrogel. The main observed effects of supersaturation on crystallisation were: (i) the preferential partitioning of Mn<sup>2+</sup> towards the solid phase was less important than in equilibrium, but remains at high supersaturation levels and (ii) the miscibility tolerance became wider. The obtained precipitates were single crystals whose external morphology depends on the manganese content. The crystalline individuals developed a sharp concentric compositional zoning with superimposed oscillatory zoning.