

Nucleation and growth of the (Mn,Ca)CO₃ solid solution in double diffusion systems

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Introduction

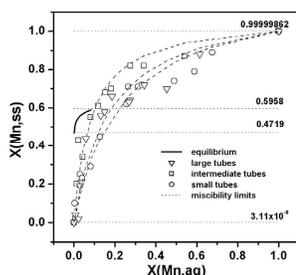
Nucleation and growth of the (Mn,Ca)CO₃ solid solution was studied under conditions of double diffusion in silica hydrogel at 25°C. Three sets of experiments were carried out in U-shaped tubes of different lengths using Na₂CO₃, and MnCl₂-CaCl₂ aqueous solutions.

Results and Discussion

Using the excess Gibbs energy function of McBeath *et al.*, 1998, two wide miscibility gaps were calculated.

Experimental results show that nucleation takes place under nonequilibrium conditions when a specific value of high supersaturation $\beta(x)$ is reached. Under these conditions, preferential partitioning of Mn in the solid phase has been observed. The fact that measured manganese mole fractions [X(Mn,ss)] are not restricted to the equilibrium miscibility range, can be attributed to kinetic factors. Moreover, since there is no agreement in bibliography upon the mixing properties of this solid solution, the miscibility limits at equilibrium are still under discussion.

Figure 1: Equilibrium values and experimental results plotted on a Roozeboom diagram.



Compositional profiles of crystals are characterized by alternations of Mn-rich and Ca-rich regions from core to rim, resulting in oscillatory zoning. Crystal morphologies are highly dependent on the Mn²⁺/Ca²⁺ ratio of initial aqueous solution. Even low concentrations of Mn²⁺ are capable of eliminating the {10-14} rhombohedron, by favoring the growth of rounded blocky crystals, spheres, and spherulites.

The observed reaction paths corresponding to the growth process could be used to explain crystallization behaviour and Mn/Ca distribution coefficients in natural systems.

References

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Late Archean biospheric oxygenation and atmospheric evolution

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High resolution geochemical analyses of organic-rich shale and carbonate through 350 m of the ABDP-9 core through the > 2,500 Ma Mt. McRae, Mt. Sylvania, and Wittenoom formations in the Hamersley Basin of northwestern Australia record changes in both the oxidation state of the surface ocean and in atmospheric composition. Carbonate $\delta^{13}\text{C}$ compositions through the strata vary systematically with lithofacies between 0 and -10‰, suggesting a strong carbon isotope gradient in Neoproterozoic seawater. High resolution sulfur-33 abundance data was obtained through a modified bulk powder EA combustion technique monitoring m/z 48, 49 and 50 on the SO analyte (Baublys *et al.*, 2004). Based on observations from SO analyses, we have additionally measured many samples by standard SF₆ techniques. We observe wide variations in $\delta^{13}\text{C}$, $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ through the stratigraphy with specific correlations between $\delta^{34}\text{S}/\Delta^{33}\text{S}$ and of $\Delta^{33}\text{S}/\Delta^{36}\text{S}$ that are temporally resolved. In the upper Mt. McRae Formation we see a change to negative $\delta^{34}\text{S}$ with positive $\Delta^{33}\text{S}$ that is interpreted to capture activation of the oxidative sulfur cycle, for perhaps the first time in Earth history. In the lower Mt. McRae the $\delta^{34}\text{S}/\Delta^{33}\text{S}$ and the $\Delta^{33}\text{S}/\Delta^{36}\text{S}$ relationships are different, and we interpret this as a change in atmospheric source reactions. The data suggest that oxygenation of the surface ocean preceded that of the atmosphere by 50 million years or more. Correlation of the time series sulfur isotope signals in northwestern Australia with equivalent strata from South Africa suggests that changes in the exogenic sulfur cycle recorded in marine sediments may have been global in scope, and linked to atmospheric evolution.

References

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