NUCLEATION AND GROWTH OF THE (Mn,Ca)CO$_3$ SOLID SOLUTION IN DOUBLE DIFFUSION SYSTEMS

D. Katsikopoulos, Á. Fernández-González y M. Prieto

Dpto. de Geología. C/Jesús Arias de Velasco, s/n. 33005 Oviedo.

INTRODUCTION

At low temperatures, the limited miscibility and the formation of the -dolomite structure- double salt of kutnahorite, are the main features of the rhombohedral (Mn,Ca)CO$_3$ solid solution. In this work, is presented a thermodynamic equilibrium model for the (Mn,Ca)CO$_3$-H$_2$O system at 25°C based on the excess Gibbs energy (G^E) of McBeath et al. (1998), as well as experimental data upon nucleation of the solid solution from aqueous solutions.

THERMODYNAMIC EQUILIBRIUM

The G^E expression of McBeath et al. (1998) was used to calculate the activity coefficients of the solid phase components and the free energy of mixing function (G^M) of the (Mn,Ca)CO$_3$ solid solution. Using the common-tangents points of the G^M curve (Glynn and Reardon, 1990), two wide miscibility gaps have been calculated for $3.11 \times 10^{-8} < XMnCO_3 < 0.47196$ and $0.59584 < XMnCO_3 < 0.9999986$. The solutus curve of the Lippmann diagram is characterized by a eutectic and a peritectic point at X(Mn,aq) = 0.001108 and 0.06981 respectively.

EXPERIMENTAL

Nucleation and growth of the (Mn,Ca)CO$_3$ solid solution was studied under conditions of high supersaturation in silica hydrogel at 25°C. Three sets of experiments were carried out in U-shaped tubes of different lengths using Na$_2$CO$_3$, and MnCl$_2$-CaCl$_2$ aqueous solutions.

RESULTS AND DISCUSSION

Experimental results show that under conditions of high supersaturation, preferential partitioning of Mn^{2+} in the solid phase is softened relatively to equilibrium. The fact that measured manganese mole fractions (XMnCO$_3$) are not res-tricted 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 (Astilleros et al., 2002). Even so, the observed reaction paths corresponding to the growth process could be used to explain crystal-lization behaviour and Mn/Ca distribution coef-ficients in natural systems.
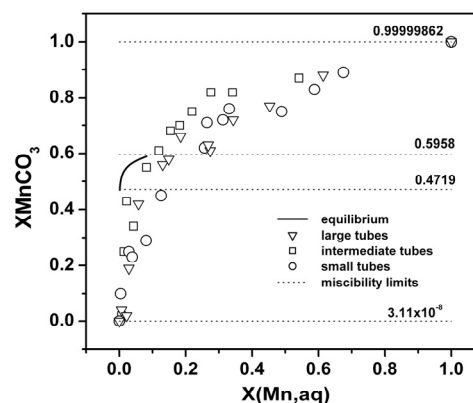

Figure 1: Roozeboom diagram.

Compositional profiles of crystals are characterized by alternations of Mn-rich and Ca-rich regions from the core to the rim, resulting in oscillatory zoning. Crystal morphologies are highly dependent on the Mn^{2+}/Ca^{2+} ratio in initial aqueous solutions.

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