



Preliminary results upon crystallization of the (Co,Ca)CO₃ solid solution

D. Katsikopoulos, A. Fernández-González and M. Prieto

University of Oviedo, Spain (dionisis@geol.uniovi.es / Tel: +3498 510 5774)

Introduction

In this work, the interaction of Co(2+) with calcite is investigated, having as main intentions to characterize the (Co,Ca)CO₃ solid solution (ideal or non-ideal), to evaluate the way in which composition at nucleation depends on supersaturation, and finally to examine the chemical and morphological evolution of crystals during growth.

Experimental Methods

The growth of calcite in the presence of Co(2+) was studied at 25°C using both precipitation and silica gel experiments. In precipitation experiments, small crystals of the (Co,Ca)CO₃ solid solution were precipitated. In order to achieve precipitation of different solid phase compositions, 50 ml of solutions with different ratios of CaCl₂ and CoCl₂ were used. The CaCl₂-CoCl₂ aqueous solutions were added in a vessel that contained 50 ml of a continuously stirred solution of 0.05 M Na₂CO₃. The crystals were then recovered using a 0.65 μm filter and dried in an oven at approximately 39°C. In the case of crystals grown in gel, the aqueous reactants (CaCl₂-CoCl₂, Na₂CO₃) were introduced in two vertical reservoirs separated by a column of silica hydrogel, which occupied the horizontal branch between them, constituting in such a way a double diffusion system (U-tube). The silica gel was prepared by acidification of a Na₂SiO₃ solution (Merck, sp. gr.: 1.059 g/cm³) with HCl (1N) until a pH = 5.5 was obtained. In all cases, one of the reactant's reservoirs was filled with 8 ml of 0.5M Na₂CO₃ and the other with 8 ml of solution with different ratios of CaCl₂ and CoCl₂. Crystals were then separated from the gel by dissolving it in a 1M NaOH solution.

Results and discussion

An X-ray powder diffraction analysis carried out for precipitation experiments showed

the growth of a Co-rich amorphous phase from aqueous solutions high in cobalt ($\text{Co}^{2+}/\text{Ca}^{2+} > 3:5$). This phase dominates over crystallinity in the precipitates preventing the definition of unit cell parameters at the Co-rich side of the solid solution. A detailed IR Spectroscopy showed that the amorphous matter corresponds to a cobalt carbonate hydrated substance ($\text{CoCO}_3 \cdot n\text{H}_2\text{O}$). For solid phase compositions near the CaCO_3 endmember ($\text{Co}^{2+}/\text{Ca}^{2+} < 2:5$) the X-ray diffraction patterns were indexed in the R-3c space group of the Hexagonal-Scaleno-hedral class and the cell parameters were calculated using X'Pert Plus version 1.0. Despite the fact that variation of unit cell parameters with solid phase composition is almost linear, experimental unit cell volumes were plotted above the theoretical line of the cell volumes of the pure endmembers suggesting a non-ideal solid solution. Large crystals grown in gel were mainly homogenous and enriched in Ca with the mole fraction of cobalt carbonate (XCoCO_3) always below 0.2. Nevertheless, some of them exhibited a clear compositional zoning with a CoCO_3 -rich core surrounded by CaCO_3 -rich regions. Crystals that grown in gel were also examined using a scanning electron microscope (SEM) revealing a wide variety of crystal morphologies as a function of different $\text{Co}^{2+}/\text{Ca}^{2+}$ ratios in initial solutions.

Conclusions and Future Work

So far, experimental data of this system is suggesting a non-ideal solid solution, while the low degree of cobalt incorporation in crystals is indicating the presence of a miscibility gap near the CaCO_3 endmember. Therefore, calorimetric experiments at the Ca-rich side of the solid solution should be carried out, so that the excess thermodynamic parameters, and consequently the limits of a possible miscibility gap could be determined.