# CHARACTERIZATION AND CRYSTALLIZATION OF (Ca,Co)CO<sub>3</sub> SOLID SOLUTION

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### INTRODUCTION

One of the most important aspects in environmental geochemistry is the understanding and interpretation of the mechanisms governing the incorporation of impurities in the mineral structures during growth. As calcite is one of the most abundant carbonate minerals on Earth and cobalt a toxic metal (Lauwerys et. al. 1994), the study of the  $(Ca,Co)CO_3$  solid solution is of high importance. Although there are different works published, referring to morphological modification of calcite crystals by cobalt (Fernádez-Díaz et. al., 2006) (Braybrook et .al., 2002), the solid solution is not fully studied yet. In this work, the interaction of Co(2+) with calcite is investigated, having as main intentions to characterize the 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  $(Ca,Co)CO_3$  solid solution was studied at 25°C using precipitation experiments and crystallization in gels. In precipitation experiments small, homogenous crystals of the  $(Ca,Co)CO_3$  solid solution were precipitated according to the following reaction:

 $Na_2CO_3 + xCoCl_2 + (1-x)CaCl_2 \Leftrightarrow Co_xCa_{(1-x)}CO_3 + 2Na^+ + 2Cl^-$ 

In order to achieve precipitation of different solid solution compositions, 50ml of solutions with different ratios of  $CaCl_2$  and  $CoCl_2$  were used. The mother solutions were added in a vessel containing 50ml of a continuously stirred solution of 0.05M  $Na_2CO_3$ . The crystals were then separated from the solution using a 0.65µm filter and dried in an oven at approximately 39°C.

In the case of crystal growth in gel, the reactants 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 Na<sub>2</sub>SiO<sub>3</sub> solution (Merck, sp. gr.: 1.059 g/cm<sup>3</sup>) with HCl (1N) until a pH = 5.5 was obtained. Three sets of experiments carried out using parent solutions with different initial concentrations, and tubes with different horizontal branch lengths and diameters. In all cases one reactant reservoir contained 8 ml of 0.5 M  $Na_2CO_3$  and the other 8 ml of solutions with different ratios of CaCl<sub>2</sub> and CoCl<sub>2</sub>.

All experiments were stored in a constant temperature cabinet at  $25 \pm 0.1$  °C. The growth evolution of the crystals and the position in the gel column of the first nuclei (visible at x500 magnification) were then monitored. The total waiting period (t<sub>w</sub>), from the beginning of the experiment, until the first crystallites appeared, was noted. The experiments were stopped two months after nucleation observed in the intermediate and small U-tubes, and one month after nucleation observed in the large U-tubes. The crystals were then recovered by dissolving the gel in a 1 M NaOH solution.

### **RESULTS AND DISCUSSION**

An X-ray powder diffraction analysis carried out for precipitation experiments showed the growth of an amorphous phase from aqueous solutions high in cobalt (Fig. 1). This amorphous phase dominates over crystallinity in the precipitates preventing the definition of unit cell parameters for these diffractograms. Different cobalt oxides and hydroxides like Co(OH)<sub>2</sub>, Co(OH)<sub>3</sub>, and Co<sub>3</sub>O<sub>4</sub> have been assumed as potential constituents of this phase. For solid phase compositions near the CaCO<sub>3</sub> endmember the X-ray diffraction patterns were indexed in the R-3c space group of the Hexagonal-Scalenohedral class and the cell parameters were calculated using X'Pert Plus version 1.0. Also, as shown in Fig.1 the solid phase precipitated as pure CaCO<sub>3</sub> clearly corresponds to calcite (P1 experiment). An almost linear variation of unit cell parameters as a function of the solid phase composition was observed near the  $CaCO_3$  end-member (Fig. 2). Despite the fact that unit cell parameters vary linear with composition, experimental unit cell volumes plotted above the theoretical line of the cell volumes of the pure end-members (Fig. 3) suggesting a non-ideal solid solution.

In order to reduce the amorphous phase spread, all sequence of precipitation experiments repeated using NaHCO<sub>3</sub> instead of Na<sub>2</sub>CO<sub>3</sub> as a reactant, but also in that case, the degree of crystallinity from aqueous solutions high in cobalt was proved very low.

One of the main features of silica hydrogel experiments is the high supersaturation obtained, allowing the study of system behaviour under



Figura 1: Diffractograms of the precipitates (P1 to P12) and the reference diffractograms of  $CaCO_3$  and  $CoCO_3$ 



*Figura 2: Variation of unit cell parameters of crystal phase as a function of*  $CoCO_3$  *mole fraction* 



Figura 3: Experimental unit cell volumes plotted together with theoretical values of  $V_{cell}$  for the two end-members

nonequilibrium conditions. The supersaturation at nucleation in gel experiments can be assessed with the measured solid solution composition using the stoichiometric supersaturation function:

$$\beta(x) = \frac{\alpha(Ca^{2+})a(Co^{2+})a(CO_3^{2-})}{[x \cdot K_{CoCO_3} \cdot \gamma_{CoCO_3}]^x \cdot [(1-x) \cdot K_{CaCO_3} \cdot \gamma_{CaCO_3}]^{(1-x)}}$$

where  $x = X_{CoCO_3}$  and  $1 - x = X_{CaCO_3}$  are the mole fractions of the solid phase which vary between 0 and 1. Activity coefficients  $\gamma_{CoCO_3}$  and  $\gamma_{CaCO_3}$  of the pure endmembers were assumed equal to unity. The calculated high values of  $\beta$  show that the system is supersaturated with respect to the corresponding solid-phase compositions in all the gel experiments.

Larger crystals grown in gel are homogenous and enriched in Ca, in all the experimental sets, with the mole fraction of calcium carbonate always above 0.95. Nevertheless, some of them are revealing a compositional profile with a clear compositional zoning with a CoCO<sub>3</sub>rich core surrounded by CaCO<sub>3</sub>-rich regions. For solutions high in cobalt, a CoCO<sub>3</sub>-rich zone is also present near crystals rims. Examination of the crystals grown in the gel experiments in the SEM shows a wide variety of crystals morphologies as a function of different Ca<sup>2+</sup>/Co<sup>2+</sup> ratios in initial solution. Blocky hexagonal prismatic and needle like crystals are forming spherical aggregates with the presence of rhombohedra for high ratios of Ca<sup>2+</sup>/Co<sup>2+</sup>. For equal concentrations of Ca<sup>2+</sup> and Co<sup>2+</sup> in the initial solution crystal morphologies are dominated by rose-like multi crystals (Fig. 5). Crystallization from solutions high in Co<sup>2+</sup> and low in Ca<sup>2+</sup>, produces also spherical aggregates consisting of not very well formed crystals.

# CONCLUSIONS

The growth and dominance of the amorphous phase in precipitates from solutions high in cobalt prevents the definition of the crystal phase composition near the  $CoCO_3$  end-member. In order to overcome this problem, precipitation experiments in atmosphere of nitrogen have to be carried out. So far, experiments for this system are suggesting a non-ideal solid solution, while the existence of a possible miscibility gap between the pure end-members has to be clarified. This can be achieved by determining basic thermodynamic properties of the system like the free energy of mixing ( $G^E$ ) in precipitates.



Figura 5: (A) A rose-like aggregate and (B) a backscattering electron image for crystals grown in gel experiments

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