



## **Influence of $\text{Co}^{2+}$ in $\text{CaCO}_3$ polymorphism.**

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Cobalt is a trace element in the Earth crust but also a toxic metal. Furthermore,  $\text{Co}^{2+}$  can accumulate in some specific areas due to both natural and anthropogenic factors and hence soils and groundwater can be contaminated. Numerous studies have demonstrated that toxic elements can be removed from aqueous solution by its incorporation in mineral structures. In particular, the uptake of divalent metallic cations in the crystal structure of calcium carbonates has been postulated as a valuable solution to resolve and / or reduce some environmental problems. Here, we have investigated the cobalt uptake during calcium carbonate precipitation at ambient conditions. It is well known that certain anions such as sulphate, chromate and selenite favour the precipitation of vaterite while other cations as  $\text{Sr}^{2+}$  or  $\text{Mg}^{2+}$ , avoid the calcite crystallization favouring the aragonite precipitation. Similar scenery can be depicted for  $\text{Co}^{2+}$  behaviour since the precipitation of both aragonite and a low crystallinity phase from aqueous solution have been described. However, the evolution of the polymorphic transformations after the precipitation of the phases remains unknown.

In the present work we have precipitated calcium carbonate at room temperature in the presence of a certain amount of  $\text{Co}^{2+}$ . Then, the precipitated solid has been aged in the remaining aqueous solution for two months. The experiment was carried out by mixing two different aqueous solutions: a) 50 mL of  $\text{CoCl}_2$  (0.02M) and  $\text{CaCl}_2$  (0.05M) and b) 50 mL of  $\text{Na}_2\text{CO}_3$  (0.05M). The aging process was monitored after 5 minutes, 1, 5, 24, and 48 hours and 4, 7, 30 and 60 days by analysing both the aqueous solution and the aged solids. The evolution of the different crystalline phases in the solid was followed by X-ray Powder Diffraction, their morphology was observed by Scanning Electron Microscopy and their chemical composition was analysed by Energy-dispersive X-ray Spectroscopy. Furthermore, the aqueous solution has also been analyzed for the entire aging time.

The initial solution is supersaturated for a number of crystalline phases that could precipitate: calcite, aragonite, vaterite, monohydrocalcite sphaerocobaltite... However, we have observed that the first precipitate is a mixture of calcite and hydrated amorphous cobalt carbonate. The evolution of this first solid with the aging time is complex. One of the most relevant changes takes place one hour after precipitation, when calcite dissolves and monohydrocalcite occurs together with the amorphous phase. This newly formed monohydrocalcite is also dissolved and aragonite precipitates 4 days after precipitation. Aragonite and the amorphous phase coexisted in the aqueous solution at least after 30 days of aging. Finally, after 60 days, the crystalline phase  $\text{Co}_2\text{CO}_3(\text{OH})_2$  was identified in the solid together with aragonite. This cobalt hydroxy-carbonate has never been reported to precipitate at room temperature.