CaCO₃ precipitation and aging in Co²⁺ bearing aqueous solutions

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Cobalt is a trace element in the Earth crust but it also is a toxic metal that can accumulate in some specific areas due to both natural and anthropogenic factors. Numerous studies have demonstrated that toxic elements can be removed from aqueous solution by its incorporation in mineral structures. In particular, the incorporation of divalent into the crystal structure of calcite has raised interest as a potential method for water decontamination.

It is known that the presence of Co^{2+} in water solution avoids the precipitation of calcite and promotes the precipitation of amorphous phases of calcium carbonate. However, the evolution of this amorphous phase and the eventual polymorphic transformations that occur after precipitation remain unknown.

In this work we have precipitated calcium carbonate at room temperature in the presence of different amounts of Co^{2+} . After precipitation, the obtained solid phase was aged in the remaining aqueous solution for two months. The aging process was monitored by analyzing both the aqueous solution and the aged solids after specific aging times. The evolution of the solids was followed by X-ray Powder Diffraction, Electron Microscopy and X-ray Spectroscopy. The aqueous solution was analyzed by ICP.

In all the experiments the initial solution is supersaturated for a number of crystalline phases: calcite, aragonite, vaterite, monohydrocalcite sphaerocobaltite ... However, it was observed that the first precipitate is a hydrated amorphous cobalt and calcium carbonate that quickly evolves to a mixture of calcite and amorphous hydrated cobalt and calcium carbonate. The evolution of this 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 after 4 days of aging. Aragonite and the amorphous phase coexisted in the aqueous solution at least after 30 days of aging. Finally, after 60 days, the crystalline phase Co₂CO₃(OH)₂ was identified in the solid together with aragonite.