

## Interaction of calcite with Cr(III) and evidence for direct inorganic formation of vaterite

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The interaction of freshly cleaved  $\{10\bar{1}4\}$  calcite surfaces with 100 mg/L (~2 mmol/L)  $\text{Cr}^{\text{III}}_{\text{aq}}$  solutions was investigated at room temperature under atmospheric conditions using *in-situ* AFM for a time-period of up to 20 min. It was observed that the initial typical nanoscale dissolution features (rhombohedral etch pits) are successively filled with matter up until the final overgrowth of spherical-like particle aggregates. *Ex-situ* experiments with variable time exposures (1 min, 20 min and 1 month) were also carried out in order to study the surface of the interacted calcite crystals using a combination of techniques. A detailed SEM-EDS, XRD and FTIR study of the experimental products revealed that the surface precipitates consist of amorphous  $\text{Cr}^{\text{III}}$  hydroxide/oxyhydroxide phases. EPMA (WDS) elemental maps on polished-thin sections of teeth-like material removed from the solid interface after long-term interaction (1 month) indicated the formation of a peculiar carbonate phase containing both Ca and Cr in variable concentrations. It should be noted that distinct Ca carbonate (or even hydroxycarbonate) solid phases containing Cr(III) are rather unknown in nature, except maybe the case of a meteorite. Preliminary computational investigations showed a difficulty of  $\text{Cr}^{3+}$  ions to be hosted in the calcite surface structure.

On the other hand, detailed XPS and Laser  $\mu$ -Raman studies of  $\{10\bar{1}4\}$  calcite surfaces interacted for 20 min with  $\text{Cr}^{\text{III}}_{\text{aq}}$  solutions indicated the presence of vaterite. In this case, the thickness of the Cr(III)-modified carbonate surface was investigated using accelerator-based techniques, namely <sup>12</sup>C-RBS. The formation of vaterite on the surface of calcite, and in general the direct inorganic formation of vaterite in the presence of  $\text{Cr}^{\text{III}}_{\text{aq}}$ , was also confirmed by means of macroscopic experiments aiming at crystal growth of  $\text{CaCO}_3$  into appropriate glass tubes filled with Cr(III)-doped hydrogel.