

## Modelling continental weathering: from the lab to the field

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CO<sub>2</sub> consumption through continental silicate weathering at the watershed scale has been generally described as a parametric function of mean annual continental runoff and temperature, based on river chemistry. These mathematical expressions have been successfully used in numerical modelling of the evolution of the past geochemical cycles and climate. They have the advantage of integrating numerous processes (hydrologic, biospheric, and kinetic) and to rely directly upon field constraints, but they leave us without any access to the intimate processes of chemical weathering, and do not allow a hierarchization of its controlling factors. Here we present sensitivity tests performed with the WITCH numerical model which describes weathering in soil profiles through vertical multiple box modelling based on a rigorous description of mineral-water interactions. This model is coupled to a vegetation productivity model, and we explore the response of continental vegetation on weathering. We also test the impact of using laboratory-based kinetic weathering rates to estimate the main cation fluxes exported from the soil profile. We show that such method does not lead to any large overestimation of the CO<sub>2</sub> consumption, if the chemical affinity of reactions, and secondary minerals precipitation rates in soils are accurately accounted for. Sensitivity of the kinetic model WITCH to drainage and annual mean temperature is compared to the sensitivity expected from field parametric laws. Particularly, we show that parametric laws underestimate by one to two order of magnitude the weathering rates at low runoff (below 100 mm/yr), while the agreement is good at higher runoff. Although the specific contribution of the low runoff areas to the CO<sub>2</sub> consumption is low, they are typical of the weathering regime of 44 % of the total continental surface.

## 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) Cr<sup>III</sup><sub>aq</sub> 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 spheroidal-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 Cr<sup>III</sup> 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 Cr<sup>3+</sup> 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 Cr<sup>III</sup><sub>aq</sub> 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 Cr<sup>III</sup><sub>aq</sub>, was also confirmed by means of macroscopic experiments aiming at crystal growth of CaCO<sub>3</sub> into appropriate glass tubes filled with Cr(III)-doped hydrogel.