

## Dissolution/precipitation processes during low-temperature mineral weathering

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Low-temperature weathering of rock-forming minerals is critical for understanding earth-surface geochemical processes. Many of these minerals are reported to dissolve non-stoichiometrically, i.e. the elemental ratios in the solid are different to those in the fluid. This phenomenon is commonly called *incongruent dissolution*, and it is attributed to the preferential release of certain cations to the solution (due to differences in the bonding strength of the mineral components), leading to the formation of the so-called *leached layers* [1]. In this study, chemical analysis of the output solutions during mineral dissolution (dolomite, as an example of a mineral that reportedly dissolves 'incongruently' [2]) and in situ, nanoscale observations of the reacting surfaces using AFM are combined with the aim of establishing a realistic mechanism for the reaction. From our observations of the reacting surface we found no experimental evidence that supports the hypothesis of a preferential release of any of the cations. Moreover, our AFM results clearly indicate that the 'incongruent' behavior is the result of a dissolution-precipitation process, with the formation of a Mg-rich precipitate on dolomite dissolving surfaces. This process seems to be controlled by the composition of a boundary layer at the carbonate-fluid interface. Dissolution of the carbonate causes this fluid boundary layer to become supersaturated with respect to the secondary phase, which then precipitates.

[1] Busenberg E. & Plummer L.N. (1982) *Am. J. Sci.* **282**(1), 45–78. [2] Casey *et al.* (1993) *Nature* **366**, 253–256.

## Optimized hydrofluoric acid demineralization for quantitative isolation of soil organic matter

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Many analytical methods for chemical characterization of soil organic matter (SOM) require a precedent separation of SOM and soil mineral matrix [1]. For example,  $\delta^2\text{H}$  measurements of SOM are hampered by the interference of constitutional water of clay minerals [2]. During demineralization of soil samples with hydrofluoric acid (HF), the hydrolyzed fraction of SOM is frequently discarded. Moreover, neoformed fluorides after HF treatment are often removed with highly concentrated acids resulting in additional SOM hydrolysis. Particularly from subsoil horizons considerable amounts of SOM are lost because of demineralization (losses of organic carbon [ $C_{\text{org}}$ ] up to 70%).

In order to increase the  $C_{\text{org}}$ -recovery after HF treatment of soil samples and to minimize chemical alterations of SOM induced by the acid attack, we demineralized soil samples from three depth profiles. We used a new method involving density fractionation or dilute acid washings to reduce the amount of neoformed fluorides in SOM concentrates. Furthermore, we recovered the SOM dissolved in HF via precipitation of dissolved metals as hydroxides in the presence of sodium pyrophosphate to avoid coprecipitation of dissolved organic matter, followed by desalting the supernatant by means of dialysis.

Our results show that the new method allows for a better demineralization compared to established procedures, especially for subsoil horizons. We were able to minimize hydrolysis of SOM, double the C enrichment factors (ratio of  $C_{\text{org}}$  concentration after to that before treatment) and reduce  $C_{\text{org}}$ -losses to below 15%. We will discuss potential effects of the demineralization method on  $\delta^2\text{H}$  values of SOM.

[1] Gélinas *et al.* 2001 *Organic Geochemistry* **32**, 677–693.  
[2] Ruppenthal *et al.* 2010 *Geoderma* **155**, 231–241.