

Determining the influence of the mineral matrix on thermal analysis of soil organic matter in bulk samples

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Thermal analysis has the potential to analyze the quality continuum of soil organic matter (SOM) in a quick and inexpensive way, most importantly without pre-treatment of the sample [1]. However, many soil mineral components also exhibit diverse thermal effects. There are different reactions related with the soil mineral matrix (e.g., clay dehydration) that could interfere in the interpretation of thermogravimetry (TG) and differential scanning calorimetry (DSC) results, affecting both weight loss and energy flux measurements, and leading to an over- or underestimation of parameters initially assigned to the thermal oxidation of soil organic matter [2].

To study the effect of the mineral matrix on thermal properties of SOM, five forest soils from conifer ecosystems of the western U.S. with different mineralogy but similar clay to organic C ratios were selected. One aliquot of each soil was treated with HF (10%) to remove minerals, while a second aliquot was treated with NaOCl (6%) to remove organic matter. Bulk soil, HF-treated and NaOCl-treated samples were then analyzed using a simultaneous thermal analyzer under: i) an oxidizing atmosphere (synthetic air, 30 mL min⁻¹) to assess the combustion characteristics of the organic material, and ii) an inert atmosphere (N₂, 30 mL min⁻¹) that suppresses combustion but allows the observation of other thermal reactions. All samples were re-run after each analysis to establish a baseline thermal signature.

Results obtained allowed for quantification of the influence of the mineral matrix on different parameters estimated for the thermal decomposition of SOM in bulk soil samples, and support the hypothesis that on a per-mass basis, the thermal reactions of organic matter are significantly greater than those of the mineral fraction. Thus, only a moderate concentration of SOM is necessary for the mineral phase to have a negligible effects on the DSC signal of bulk soil.

[1] Plante *et al.* (2009) *Geoderma* **153**, 1-10. [2] Rovira & Vallejo (2000) *Commun Soil Sci Plant Anal* **31**, 81-100

Modelling of a bentonite column experiment with CrunchFlow including new clay-specific transport features

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The porosity concept in bentonite has become an important issue since bentonite is foreseen as a confining and buffer material in high level radioactive waste repositories. The mechanisms associated to transport in the bentonite barrier play a critical role to characterize the chemical and mineralogical evolution of the repository near field.

As a consequence of the interest generated in the last years on this topic, the geochemical code CrunchFlow [1] has been recently implemented to take into account an explicit diffuse layer model associated to charged surfaces in clay systems.

A multi-component advective-diffusive ion transport experiment performed for 304 days at laboratory scale with a cylindrical column of a compacted MX-80 saturated bentonite was proposed as a benchmark experiment to test the new features in CrunchFlow. An artificial saline solution was infiltrated from one column end and the outflow solution was collected in syringes at the other end.

The Cl⁻ evolution in the experiment and the breakthrough of a non-reactive tracer were used to constrain the microporosity (diffuse layer) and macroporosity (free water) volume fractions and the transport parameters (advective flow rate and specific diffusion coefficients of aqueous species).

The chemical and mineralogical behaviour observed in the experimental system is rather complex. However, the model shows good agreement with the experimental results and demonstrates the relevance of the partition of the pore water in sub-volumes with different characteristics.

[1] Steefel (2009) CrunchFlow. Software for Modeling Multicomponent Reactive Flow and Transport. User's manual. Earth Sciences Division. Berkeley, CA. 91 pp.