

Primary shape and nanomechanical properties of natural Fe-colloids studied by AFM and SEM

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Natural colloids and nanoparticles are involved in a multitude of biogeochemical and physicochemical processes and act as mobile reactive carriers [1]. Interactions with each other and with the immobile phase not only affect hydraulic properties, but may change geometric, mechanic and physicochemical properties of the pore network and its interfaces. Of particular importance are the nanoparticulate mineral-organic mixed phases, formed either by the way of heterogeneous nucleation, sorption or co-precipitation [2][3]. We studied natural colloids sampled from soils subjected to redoximorphosis combining Scanning Electron Microscopy, Energy-Dispersive X-ray Spectroscopy and Atomic Force Microscopy. We identified three types of material, i.e. bulky Fe-aggregates, linear-aligned Fe-aggregates and flat, circular, soft and adhesive patches, presumably pure organic in nature. The majority belongs to the bulky-type with mean sizes around 50nm. Yet they are formed of much smaller subunits. The linear-aligned aggregates, presumably representing the subunits of the bulky aggregates, have mean diameters around 20 nm with large variety of lengths. They seem to be "chained" along linear structures, which we hypothesize to be of biotic origin. Thus, biotic material may be important in the geometric structuring of the aggregation process of natural colloids.

[1] Totsche & Kögel-Knabner (2004) *Vadose Zone Journal* **3(2)**, 352-367. [2] Eusterhues *et al.* (2008) *Environ. Sci. Technol.* **42**, 7891-7897. [3] Eusterhues *et al.* (2011) *Environ. Sci. Technol.* **45**, 527-533.

Sequential extractions as a tool to investigate stable metal isotope fractionation between soil pools

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Stable isotope ratios contain information about sources and transformations in the biogeochemical cycle of metals in the environment. The recent development of high-precision methods to resolve metal isotope fractionation (e.g., Fe, Hg) now allows to apply these new isotope tracers to a variety of natural systems and sample matrices including soils. Biogeochemical metal cycling in soils plays an important role in chemical weathering processes, nutrient dynamics, and the fate of pollutants in terrestrial ecosystems.

The stable isotope signature of bulk soil samples can be assessed relatively easily by analysing total digest solutions. However, metals in soil samples are often present in various "pools" which can have very different histories and chemical properties. Thus, valuable information on isotopic differences between soil pools and fractionation between them is lost by analyzing only the isotope signature of bulk samples. Sequential chemical extractions are an established tool to separate metal pools from natural samples. However, the application of sequential extractions in stable isotope studies bears the risk of introducing fractionation artifacts during the extraction procedure. Thus, a careful method development is required to assess the suitability of specific extraction steps.

Here, we present iron isotope ($\delta^{56}\text{Fe}$) and mass-dependent (MDF) and mass-independent (MIF) mercury isotope ($\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$) data from sequential extractions of different environmental samples measured by MC-ICP-MS. Newly-developed extraction methods were able to trace the evolution of secondary iron phases in young initial soils from a granitic glacier forefield, revealing that the imprint of a kinetic isotope effect during silicate weathering is preserved in pedogenic minerals. Mercury isotope ratios of sequential extracts from contaminated mine samples demonstrated that isotopically-distinct Hg pools exist within different tailing materials, exhibiting strong positive MDF and small negative MIF signatures in the more soluble extraction steps relative to the bulk isotopic composition. Future applications as well as potential limitations and pitfalls of sequential extraction methods in metal isotope studies will be discussed.