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Iron Isotope Fractionation in Soils

Friedhelm von Blanckenburg (fvb@mpi.unibe.ch)

Isotopengeologie, Universität Bern, Erlachstrasse 9a, Bern, 3012, Switzerland

Vertical movement of Fe in soils is a common process. Fe enrichment or depletion leads to distinct chemical layering that is widely utilised to classify soil sequences. In Podzol soils, Fe and Al migrate downwards until they are precipitated into a dark-brown illuvial horizon. Processes that are thought to mobilise Fe in Podzols are downward transport of complexes of organic acids with Al and Fe, while the immobilisation is ascribed to either inorganic precipitation / adsorption of metal complexes caused by increasing metal / carbon ratios in the solution down the soil profile; or microbial degradation of the complex formers. In contrast, in soils affected by groundwater, such as gleys, Fe(II) moves upward from a reducing environment either inorganically by a change in redox conditions, or by microbial reduction of Fe. Fe is re-precipitated as Fe(III) in a more oxidising layer. Fe isotopes have the potential to characterise these inorganic and microbial processes, depending on their relative degrees of isotope fractionation.

Fe isotopes have been investigated in a Podzol formed in an alluvial soil sequence of the Maas catchment (the Netherlands). Soils consist to 95% of Fe-coated detrital quartz. Isotope measurements have been performed on a Nu-Plasma multicollector ICP-MS, using an Aridus desolvating nebuliser tuned to reduce isobaric ArX to Fe interference ratios to around 0.1 permille, where interferences are subtracted using on-peak background measurements of the acid used as solvent. ^{57}Fe, ^{56}Fe, ^{54}Fe, and ^{53}Cr are measured simultaneously, followed by ^{65}Cu and ^{63}Cu, the ratio of which is used for an initial instrumental mass discrimination correction. Sample runs are alternated with standard runs under the same conditions, and the sample's isotope ratios are calculated relative to the bracketing standards. It is found that the use of Cu-corrected bracketing standards results in the highest reproducibility (up to ca. 0.1 permille for the ^{57}Fe/^{54}Fe and ^{56}Fe/^{54}Fe ratio, respectively, and up to 0.05 permille for the ^{57}Fe/^{56}Fe ratio.

^{57}Fe/^{54}Fe ratio variations in the Podzol sequence are small with a ca. 1 permille difference between the surface Ah layer and the C-horizon, with highest values measured within the area of the dark illuvial horizon. At this stage there is no clear evidence for strong fractionation as predicted for microbial action. This points to either inorganic microbial immobilisation, or to quantitative microbial precipitation of Fe, producing an only marginally fractionated residue.

In a gley sequence formed in granitic alluvial sediments, bulk Fe is dominated by that contained in the minerals. However, leaching using various mild acids or reducing agents results in release of Fe from the oxidised layer that is lighter by more than 1 permille in ^{57}Fe/^{54}Fe. It is possible that Fe reduction in the reduced soil layer mobilised Fe(II) that is re-precipitated in the oxidised layer. This light Fe is then desorbed upon leaching in the laboratory. Further laboratory calibrations will shed light on the bacterial vs inorganic origin of such Fe isotope fractionation.