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Fractionation of Fe isotopes in soil suspensions at controlled redox conditions

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To evaluate the cause of fractionation of Fe isotopes in soils, understanding the influence of different redox conditions is of particular importance. A typical feature of e.g. Gleysols is a strong variation of redox conditions due to fluctuations of the groundwater table. A low groundwater table results in oxidising, a high groundwater table in reducing conditions, thus mobilising redox-sensitive elements like iron, arsenic, or manganese [e.g., 1]. At reducing conditions, iron is mobile in the divalent form (Fe^{2+}). Analytical investigation of bulk Fe isotope compositions in an extremely Fe-rich Gleysol (up to ca. 41 wt.-% Fe in the CrBg horizon) from NW Germany yielded $\delta^{57}Fe_{IRMM14}$ values of +0.28 ‰ (±0.03 2 s.d., Ah) to ca. -0.19 ‰ (±0.05 2 s.d., CrBg). In two experimental studies lasting up to ca. six weeks, three suspensions of the above-mentioned Gleysol (Ah, CrBg horizons) were run parallel at controlled redox conditions ranging from oxidising (E_H (pH 7) $>$ 550 mV), moderately reducing (E_H (pH 7) $\approx$ 330 mV), and reducing conditions (E_H (pH 7) $\approx$ 100 mV). Temperature, pH, and Fe concentrations were also recorded. The suspensions were stirred permanently to ensure homogenisation and avoid sedimentation. Solutions taken every other day from the suspensions were passed through 0.45 μm cellulose membranes. Nitric acid was then added to avoid precipitation of Fe compounds. Iron was separated from the matrix via anion exchange chromatography. Iron isotope measurements were carried out on the Neptune MC-ICP-MS at Universität Bonn, Germany, using copper for mass bias correction [e.g., 2]. The results for the Ah horizon show that the Fe isotope compositions vary with respect to the redox conditions. We noted light δ^{57}Fe values of ca. -0.4 ‰ in the solutions at moderately reducing conditions, and δ^{57}Fe values of around -1.1 ‰ for reducing conditions. At oxidising conditions, δ^{57}Fe values slowly increased from +0.3 ‰ to nearly +1.0 ‰ at the end of the experiment. As expected, Fe^{2+} concentrations in the solutions increased substantially at reducing conditions. For the Ah, this results in a preferential mobilisation of ^{54}Fe into aqueous solutions at reducing conditions, leaving the bulk residue enriched in heavy Fe isotopes. For the CrBg horizon, the amount of iron in solution did not change with respect to different redox conditions. The δ^{57}Fe values of the solutions showed little variation over the course of the experiment, and scattered around ±0.0 ‰ therefore being slightly lighter than the bulk material. Only when reducing conditions lasted several days, the δ^{57}Fe values nearly overlapped those of the soil material. We conclude that Fe mobilisation and isotope fractionation in soils depends on redox conditions and source composition, not solely on Fe abundance.

References

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