Fe-isotope fractionation by plants and weathering in an Alpine glacier forefield.

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The investigation of stable iron (Fe) isotope variations in rocks, soils, and vegetation offers a promising new tool for tracing the biogeochemical cycle of iron in diverse ecosystems. Previous work in our group has shown that reductive and ligand-controlled dissolution of oxides in soils result in significant fractionation of Fe isotopes of more than 1 ‰ in $\delta^{57}Fe_{IRMM-014}$. The objective of this study is to investigate iron isotope fractionation during silicate weathering, plant uptake, and initial soil formation in an Alpine glacier forefield.

We selected the forefield of the Dammaglacier for this study, because it is located on a rather uniform body of granite (Aare massive, Central Switzerland). The retreat of this glacier has been well-documented for the past hundred years, which offers the possibility to study initial weathering processes along a well-defined chronosequence. Initial colonization of the forefield by plants is patchy, thus allowing a comparison of vegetated and non-vegetated spots of the same age. Fresh bedrock granite as well as soil samples of different age and the vegetation cover were analyzed for their Fe isotopic composition and other geochemical parameters. Since no published methods of processing plant materials for Fe isotope analysis were available, we developed and tested a procedure including dry-ashing followed by acid digestion and column chromatography for purification. Repeated preparation and measurement of an own internal reference material (*Rhododendron* leaves) gave a reproducibility of better than 0.15 ‰ in $\delta^{57}Fe$ (2SD). This is in the range of the precision (<±0.15 ‰ in δ^{57} Fe, 2SD) we achieve by standard-sample bracketing using the international iron isotope standard IRMM-014. The isotopic composition of the IRMM-014 is 0.10 ‰ lighter in δ^{57} Fe than the igneous rock baseline which is thought to be homogeneous to < ±0.05 ‰ in δ^{57} Fe. Measurements are done on a MC-ICP-MS (Nu Plasma) equipped with a desolvating nebuliser (MCN 6000, Cetac) to reduce argide interferences to insignificance.

Analysis of soil pH indicates geochemical changes within the first few years of exposure and a distinct influence of first plant establishment. Over a period of only 15 years, the soil pH drops from 5.5 to 4.9 in vegetation free locations, while it reaches pH 4.3 in vegetated spots. First Fe-isotope data (total Fe) reveal a lighter isotopic composition (~0.33 ‰ in $\delta^{57}Fe_{IRMM-014}$) of soil samples compared to the unweathered bedrock granite (0.5 – 0.6 ‰ in $\delta^{57}Fe_{IRMM-014}$). In between those samples, which represent vegetated and non-vegetated spots of 0-60 years of exposure, the differences are negligible. However,

a more strongly weathered soil (Cambisol) slightly off the forefield exhibits a further shift towards light Fe-isotopes in the A (0.14 ‰ in $\delta^{57}Fe_{IRMM-014}$) and B-horizons (0.12 ‰ in $\delta^{57}Fe_{IRMM-014}$). Separate analysis of different grain sizes in the B-horizon show a distinct enrichment of light isotopes in the clay size fraction (<2µm, -0.46 ‰ in $\delta^{57}Fe_{IRMM-014}$). Physical destruction and sieving of fresh rock material in the laboratory resulted in a lighter overall isotopic signature in the smaller grain size fractions.
Fe-isotope signatures measured in plants collected in summer 2006 on the glacier forefield cover a range between -1.19 and +0.40 ‰ in $\delta^{57}Fe_{IRMM-014}$. While roots show a comparatively low degree of fractionation (+0.1 to +0.4 ‰ in $\delta^{57}Fe_{IRMM-014}$), stems and leaves of different grasses reach up to -0.58 ‰ in $\delta^{57}Fe_{IRMM-014}$. In non-graminaceous plants a trend towards a lighter Fe-isotopic composition in compartments with lower iron contents can be detected.

The observed enrichment of light isotopes in the products of physical and chemical weathering may be due to a different isotopic composition and weathering stability of the main iron bearing minerals in the Aare granite, i.e. biotite and magnetite, and to Fe isotope fractionation induced by chemical weathering reactions. Apart from plant induced fractionation during uptake, this could also be an explanation for the lighter isotopic composition of some root systems. However, a quantitative interpretation of the observed variations in Fe isotope ratios will require a detailed investigation of the biogeochemical processes involved in Fe isotope fractionation.