Quantifying the SIMS structural matrix effect

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Background

Determining absolute concentrations of trace elements by secondary ion mass spectrometry requires the use of one or more reference samples which are “matrix matched” to the material being analyzed. It is commonly posited that both the degree of crystallinity and the major element composition of a reference material influence its secondary ion yields, thereby affecting the determined relative sensitivity factors. This abstract reports on a project which quantifies the role played by sample crystallinity: the SIMS structural matrix effect.

Method

High purity disks of synthetic α-quartz and amorphous SiO_2 were purchased commercially. Special attention was given to obtaining samples with an optical polish with the surface roughness ≤10 nm. Both sample types underwent accelerator ion implantation in which the crystalline and amorphous samples were implanted during the same run, thereby assuring that both materials received identical ion fluxes (1e+14 ions/cm^2). Separate Quartz-glass pairs were implanted with ^{10}B, ^{27}Al and ^{47}Ti individually and the applied accelerating voltage was adjusted for each element so as to produce a maximum implant density at a depth below surface of ~200 nm.

Results

The results from single analyses on implanted pairs produced very similar depth profiles. The ratios of M^+ to $^{30}Si^+$ at peak concentration were similar in both the crystalline and amorphous samples (see table). These results have yet to be assessed for second order issues including ion channeling during implantation, target knock-on during SIMS analysis and sample intrinsic background.

Implant species	Quartz peak ($M^+/^{30}Si^+$)	SiO_2 glass peak ($M^+/^{30}Si^+$)
^{10}B	3.6E-3	3.8E-3
^{27}Al	3.8E-2	3.1E-2
^{47}Ti	2.8E-2	2.7E-2

Discussion

These preliminary results demonstrate that, at least in the case of SiO_2, the structurally induced SIMS matrix effect for crystal-glass pairs with identical major element compositions is <20 % for all of elements reported here. This conclusion is important because it suggests that the use of a chemically matched but amorphous reference material for SIMS mineral analyses would introduce a systematic error of only 10 to 20 percent.

How can we trace Fe isotope fractionation by weathering in soils?

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Stable Fe isotopes are fractionated during biogeochemical transformations of Fe in nature. Precise Fe isotope ratio measurements collected by several research groups using mainly MC-ICPMS have generated a substantial data set, which allows assessing natural Fe isotope variations and gaining insight into the underlying fractionation mechanisms. These studies have revealed both kinetic and equilibrium Fe isotope fractionations in laboratory systems and natural environments including soils. Hence, Fe isotopes represent a potential tool to trace past and present Fe cycling.

Iron occurs in soils in many different forms, and its transformations play an important role in weathering and soil formation. The oxidation of ferrous to ferric iron is one of the first steps in the weathering of primary silicate minerals under atmospheric conditions, which ultimately leads to the breakdown of the mineral structure. In contrast to other elements, Fe is usually not leached out of the system under oxic conditions, but precipitates immediately in the form of ferric (oxyhydr)oxide minerals. Thus, oxic weathering mainly produces in-situ re-distributions of Fe between different pools. Chemical extraction procedures are widely applied to separate specific Fe pools from soils. However, the success of these methods strongly depends on the mineralogy of the sample material, and they need to be calibrated carefully to obtain meaningful Fe pools and to avoid isotope fractionation artifacts. Therefore, we have tested whether grain size separation through physical methods might represent a suitable alternative approach to separate weathering products and residues in soils for Fe isotope analysis.

We will present Fe isotope data from an oxic Cambisol weathering horizon (Bw) on Aare granite (Switzerland). In this soil, weathering products (secondary Fe (oxyhydr)oxides) are enriched in the clay size fraction (<2 µm), whereas weathering residues (primary silicate minerals) are enriched in the sand size fraction (>63 µm). We performed and evaluated both physical and chemical separation methods in order to trace Fe isotope fractionation during weathering. The clay size fraction was found to be enriched in light Fe isotopes by more than -0.5‰ (reported as δ^{57}Fe) compared to the bulk digestion, whereas the sand size fraction was found to be enriched in heavy Fe isotopes by +0.2‰. An elemental and isotopic mass balance for Fe is consistent with a re-distribution of Fe within a closed system.

Our results show clear evidence for Fe isotope fractionation during weathering in soils causing enrichments of light Fe isotopes in weathering products and of heavy Fe isotopes in weathering residues. Potential fractionation mechanisms and implications for the interpretation and application of Fe isotope signatures in soils will be discussed.