UV femtosecond laser ablation applied to stable Fe isotopes in BIFs

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Here we present *in situ* stable Fe isotope measurements in Precambrian banded iron formations (BIFs) using our in-house built laser ablation system which consists of a frequency-quadrupled fs laser operating at a wavelength of 196 nm and a multicollector-ICP-MS. The short pulse length turns the ablation process away from thermal pathways preventing artificial fractionation and minimizing matrix dependency (Horn and von Blanckenburg, 2007). The accuracy of this method has been verified for different types of matrices giving a reproducibility of 0.1‰ (2SD) for the $^{56}Fe/^{54}Fe$ ratio (Horn *et al.*, 2006). BIFs are fine-grained chemical sediments which are the product of initial precipitation from seawater and subsequent diagenetic and metamorphic processes. All of these processes involve redox reactions, dissolution and precipitation of Fe resulting in fractionation of Fe isotopes. In order to investigate these processes, we have determined the Fe isotope composition of single Fe-oxide and Fe-carbonate crystals by spot analyses at 30 microns resolution in different thin sections of low-grade metamorphosed BIFs. Small-scale isotopic variations of up to 0.9‰ in $\delta^{56}Fe$ within single layers exist for hematite as well as for magnetite. Furthermore we detect isotopic zonation in magnetite crystals as small as 30 microns which becomes heavier in their Fe isotope composition towards the rim. These heterogeneities suggest variable relocation of Fe on a sub-millimeter scale during diagenesis and metamorphism. Fe-carbonates have also been investigated. Although crystal sizes are often less than 25 microns and Fe contents are low giving only low Fe signal intensities, we have found that variations in chemical composition have little influence on the Fe isotopic composition. Both, Fe-oxides and Fe-carbonates show constant average Fe compositions over all layers within a thin section. Since also magnetite and Fe-carbonate exhibit a constant relative difference of ca. 0.9‰, either a diagenetic process with the same precursor material must have established these isotope equilibrium fractionations or, alternatively, fluid sources were distinct but pathways to the Fe-carbonate and Fe-oxide were steady with time. These results illustrate that the study of stable Fe isotopes at high spatial-resolution have the potential to gain a better understanding on the mechanism of BIF formation and the Precambrian Fe cycle.

References

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Potassium partitioning in the lowermost mantle from ab-initio computations

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Partitioning of radioactive isotopes in the Earth's interior is of great importance to the thermal and dynamic state and evolution of the Earth as radioactive decay provides an important source of energy for mantle dynamics. As a consequence, enriched (or depleted) reservoirs in the mantle can influence the energy balance in geodynamics. The recently discovered phase transition in $MgSiO_3$ from perovskite (pv) to post-perovskite (ppv) in the lowermost mantle provides the possibility for an enriched or depleted zone at the base of the mantle. Therefore, the partitioning of radiogenic isotopes among the phases of the lower mantle is of central importance in geochemistry and geodynamics of the deep Earth. Here we take a first step in addressing this issue by considering the partitioning of potassium between pv and ppv by performing *ab-initio* computations.

We have set up computations for a coupled substitutions of K and Al or Fe^{3+} (**M** ion) for 2 Mg on the A site, and evaluate the energetics of a $(Mg_{30},K,M)Si_{32}O_{96}$ composition in the pv and ppv structure. We compare the energetics of the following reactions for both pv and ppv to compute the enthalpy of formation:

$$(Mg_{30},K,M)Si_{32}O_{96} +2MgO \rightarrow Mg_{32}Si_{32}O_{96} + 1/2\ K_2O + 1/2\ M_2O_3.$$

The computations are performed with the VASP package using the projector augmented wave method for the static lattices of the high pressure phases in the reaction above. We use the generalized gradient approximation to the exchange and correlation potential. Structures are optimized for internal and external degrees of freedom at constant volume, and we assume that the **M** and K ions are at A positions directly adjacent to one another. Computations are performed for a wide compression range, reaching pressures of the CMB.

Slightly above 100 GPa we predict that $D_K<1$, implying that K partitions preferably into the ppv phase. Increased temperatures would decrease the magnitude of preferred differentiation. This makes a K enriched layer at the base of the mantle a possibility. It is clear, however, that the effect of other phases stable in the lower mantle (Ca-pv and mw) must be considered in a full assessment of K distribution in the lower mantle.