

Precise and accurate lead isotopic analysis of fast transient signals by laser-ablation MC-ICP-MS

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Fluid percolation effects transport of chemical constituents and heat in the Earth's interior; hence, the source of such fluids are of great relevance. Lead isotopic compositions are particularly sensitive as a fluid source tracer. Synthetic fluid inclusions of known Pb and Tl isotopic compositions (SRM 981 and SRM 997) have been used to establish the LA-ICP-MS analytical protocol for precise and accurate Pb isotopic measurements, including mass 204, of fast transient signals.

Instrumental mass bias correction was effected within-run by using Tl either provided by the sample itself or admixed to the laser ablation aerosol via desolvated nebulization. Interference correction was most prominent for Hg on mass 204, which was effected based on the measured ²⁰²Hg intensity and the natural ²⁰²Hg/²⁰⁴Hg ratio that was transferred to its mass-biased state for correction based on the measured ²⁰³Tl/²⁰⁵Tl ratio. The external precision achieved on SRM610 glass converges to ± 110 ppm (2 SD) for ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb ratios and to ± 320 ppm (2 SD) for Pb isotope ratios normalized to mass 204 (n=18). Uncertainties on inclusion-to-inclusion reproducibility (n=11) approached 0.07% and 0.14% 2SD, respectively. These results are accurate. Considerable fractionation at the laser ablation site does not affect analytical accuracy, given controlled ablation of the entire fluid inclusion and integration of the entire transient signal.

Magmatic-hydrothermal fluid inclusions typically contain several thousand µg g⁻¹ Pb, translating into about 0.1 - 0.2 ng of Pb available for the analysis of individual ellipsoidal inclusions 40x40x30 µm in size. Acceptably reproducible results (±1 ‰ and 5 ‰, respectively) were obtained for inclusions containing as little as 0.005 ng Pb with the current setup using Faraday detectors, demonstrating the potential of our analytical protocol for low amount fast transient signals.

Molybdenum isotopes as proxy for redox conditions during weathering

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In recent years molybdenum isotopes in marine sediments and seawater have become widely recognized as potential tracers of past redox conditions. The particularly interesting aspect of the geochemical behavior of Mo isotopes is their potential to quantify regional or even global scale (paleo-) ocean redox conditions. Molybdenum is the most enriched trace metal in the oceans and its main speciation, molybdate, shows a conservative profile in the water column. Under oxidizing conditions, Mo is removed from the water column by adsorption to (Fe-) Mn oxy-hydroxides. In reducing depositional settings it is precipitated as particle reactive oxythiomolybdates. These processes are thought to produce a strong fractionation of Mo isotopes in the modern oceans that depends on the relative proportions of oxidized and sulphide-rich sedimentation. The modern Mo isotope composition of seawater is ca. 1 permil/amu heavier than authigenic Mo under oxidizing conditions. Reducing sediments have Mo isotope compositions from intermediate to compositions approaching seawater. The latter observation has been used for reconstruction of paleo-redox conditions, because as a consequence of isotope mass balance, the Mo isotope composition of seawater should vary with changes in the ratio of oxic to anoxic sedimentation in the oceans. However, some of the variables in the Mo isotope budget are still poorly constrained. One of these variables is the isotope composition of the riverine input. Therefore, focus has shifted on constraining the Mo input to the oceans. Here we present Mo isotope data from a variety of weathering profiles. Exciting preliminary results suggest, that the Mo isotope composition in these profiles is strongly controlled by redox conditions. Horizons that experience periodic reducing conditions, show strong enrichment in light Mo isotopes. This might be due to repeated cycling of Mn oxyhydroxides during these transition from oxic to anoxic conditions. However, due to large possible pH/Eh variations in weathering profiles relative to the marine environment, a number of different speciations of Mo should be stable during weathering. This allows for a variety of fractionation processes. Further research can prove if Mo isotopes are a valuable proxy for weathering conditions.