Precise measurement of selenium isotopes by HG-MC-ICPMS using 76-78 and 78-82 double-spikes

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Selenium (Se) stable isotopes are a new geochemical tracer (e.g., [1]) that can be used to understand the redox evolution of the Earth, as Se displays multiple oxidation states and similar chemical behaviour to sulphur. Previous studies have already demonstrated that Se stable isotopes have the potential to constrain the redox evolution of the Earth's ocean and atmosphere through time using sulfide and Se-rich sedimentary records (e.g. black shales, [2]). However, the Se isotope compositions of the Earth's mantle and other major chemical reservoirs remain poorly constrained, partially due to the very low abundances of Se in mantle rocks (typically 3-100 ppb, [3]) and multiple analytical challenges (e.g. low sensitivity, interferences). In order to address these issues we have focussed on the development of a new method to measure Se stable isotopes ($\delta^{82/78}$Se; per mil deviation relative to Se NIST SRM 3149) to high precision.

Selenium has six stable isotopes and therefore is a good candidate for isotope analysis using a double spike approach, which has the additional advantage that it can correct for any stable isotope fractionation that may occur during sample processing. We have calibrated both ^{76}Se-^{78}Se and ^{78}Se-^{82}Se double spikes. Analyses were conducted on a Thermofisher NeptunePlus MC-ICPMS using an ESI hydride generation introduction system. Sensitivity is over 1000V/ppm; a measurement typically requires 25 ng of natural Se. For each integration, argon dimer isobaric interferences on masses 76 and 78 and germanium atomic interferences on mass 74 and 76 were corrected by measuring masses 80 and 73 respectively. Mass 75 was also monitored to correct for the arsenic hydride interference on mass 76. The 2 s.e. error for a single analysis typically ranges from 0.015 to 0.025 ‰ (n = 80) for $\delta^{82/78}$Se using the ^{76}Se-^{78}Se spike. Our long term reproducibility and accuracy were estimated by multiple analyses of the Se Merck standard [4] over numerous different analytical sessions, resulting in a mean $\delta^{82/78}$Se value of 0.99 ± 0.042 ‰ (n = 47; 2 S.D.), which is in excellent agreement with previous studies [4].

[1] Rouxel et al., *GCA* **66**, 18 (2002); [2] Wen et al., *GCA* **75** (2010); [3] Lorand et al., *CG* **278** (2010); [4] Carignan et al., *CG* **242** (2007).