

Geochemical tracing of core-mantle interaction: High-precision W isotopic data on komatiites using TIMS

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It has been suggested that coupled suprachondritic ¹⁸⁷Os and ¹⁸⁶Os in some plume-derived picrites and komatiites may be best explained by a small contribution (<0.5-1%) of a component from the outer core in the mantle sources of these lavas. Tungsten is another siderophile element that might help tracing core-mantle interaction. The excess of ¹⁸²W (from the decay of short-lived ¹⁸²Hf during the first 60 Ma of solar system history) in the mantle relative to chondrites suggests that the core may have a deficit of ¹⁸²W relative to the mantle ($\epsilon_{182W} \approx -2$). A previous study of ¹⁸²W systematics of Hawaiian picrites that show suprachondritic ¹⁸⁷Os and ¹⁸⁶Os did not reveal resolvable deficits in ¹⁸²W at the 10-20 ppm level (Schersten *et al.* 2004). Because the effects of a 0.5-1 % core contribution on ¹⁸²W likely may be less than 30-40 ppm, external precisions better than 10 ppm (2σ) on ¹⁸²W/¹⁸⁴W or ¹⁸²W/¹⁸³W of lavas are required in order to resolve a core contribution. The goal of this project was to establish analytical protocols that allow the measurement of differences in the abundance of ¹⁸²W in komatiites at the 5-10 ppm level by negative thermal ionization mass spectrometry using the Johnson Space Center TRITON TIMS. Komatiites show W abundance excesses (relative to similar incompatible elements such as Ce or Th) that remain unexplained and the association of some komatiites with plume/LIP provinces may hint at an origin of the source rocks in the deep mantle. Results over a 3 month period yielded in-run precisions ($2\sigma_m$) of individual W standard runs between 4 and 6 ppm for ¹⁸²W/¹⁸⁴W and ¹⁸³W/¹⁸⁴W, respectively, and external precision (2σ) of 7 and 9 ppm on ¹⁸²W/¹⁸⁴W and ¹⁸³W/¹⁸⁴W, respectively (n=10). After 3 months, it was observed that standard runs were systematically shifted to higher values by 10-15 ppm for both ¹⁸²W/¹⁸⁴W and ¹⁸³W/¹⁸⁴W. Two aliquots of a 2.7 Ga Belingwe komatiite yielded the best in-run precision (± 6 ppm), and show values for ¹⁸²W/¹⁸⁴W that are within uncertainties of W standards run during the same time period. A single run for komatiite GOR 94-7 (Gorgona) shows an uncertainty of ± 17 ppm ($2\sigma_m$) and a ¹⁸²W/¹⁸⁴W value overlapping with standard measurements. The main limitations on high-precision ¹⁸²W measurements by N-TIMS are the influence of variable O isotopic compositions and minor Re oxide interferences on W oxide corrections. Normal W isotopic compositions and W abundance excess in these komatiites may reflect addition of crustal W during komatiite alteration.

Searching for selenium: *In situ* measurement in base metal sulfides

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To test the idea that most of the Se in rocks is located in base metal sulfide minerals (BMS), *in situ* Se concentrations in BMS would be useful. This is important for two reasons. Firstly, whole rock S/Se ratios have been used to model the formation of magmatic sulfide ore deposits. This approach is based on the idea that the whole rock analyse reflects the S/Se ratio of the BMS. Secondly, S and Se determination can be difficult and for Se, labor intensive. If Se could be determined *in situ* in BMS, then the whole rock Se would not be necessary.

Both whole rock Se and *in-situ* measurements of Se in BMS have been carried out on the BMS of the JM-reef of the Stillwater Complex and Merensky Reef of the Bushveld Complex.

In-situ Se is determined with a collision cell laser ablation (LA) ICP-MS (Thermo X7). Kinetic energy discrimination and a 50:50 mixture of H₂:H₂+He added to the collision cell minimize argide interferences. Sulfur is used as the ablation monitor. Detection limits range in the 1-5 $\mu\text{g/g}$ Se (depending on laser beam), although quite high in terms of ICP-MS, it fits the purpose for Se determination in sulfide where Se ranges from 50 to 1000 $\mu\text{g/g}$ Se. In order to better match the matrix, reference materials (RM) are Se-doped NiS beads (80-1000 $\mu\text{g/g}$ Se) made from a technique similar to fire-assay preconcentration. Se is determined independently by preconcentration on thiol-cotton and INAA. RM homogeneity is tested with SEM imaging, microprobe determinations and LA-ICP-MS repeated determinations within a single bead. Reproducibility is in the range of 10 % RSD (at 2σ) for more than 30 Se determinations on different NiS beads.

Mass balance calculations show that within analytical uncertainties all, Se is hosted in BMS. Furthermore, our results compare favorably with previous PIXE determinations of Se in BMS of the Merensky Reef. These results suggests that assuming that all Se is hosted in BMS to interpret S/Se is valid.