

The Re and Os contents in molybdenite were measured by isotope dilution mass spectrometry at the University of Bristol, UK. Samples were handpicked under a binocular microscope and then ground using an agate mortar and pestle.

Samples were dissolved using a modified Carius tube technique based on the method of Shirey and Walker [1]. Approximately 50 mg of molybdenite sample was added to a glass Carius tubes. These tubes were then chilled using dry ice and accurately weighed ^{185}Re and ^{190}Os isotopic tracers and inverse aqua regia (3 ml HCl and 9 ml HNO_3) were added to the tubes. The tubes were welded closed and placed in sealed steel pipes in an oven for ~60 hours at 230°C to ensure sample dissolution and sample-spike equilibration. Samples were refrigerated prior to tube opening.

The Re and Os is separated from the dissolved sample using solvent extraction techniques based on Birck et al., [2] and Cohen and Waters [3] respectively. Samples were pipetted from the opened Carius tube and added to 10 ml carbon tetrachloride (CCl_4) in a Teflon beaker. The carbon tetrachloride extracts the OsO_4 and the Re remains in the inverse aqua regia. Osmium was extracted from the carbon tetrachloride using HBr. In this reaction OsO_4 is reduced by the HBr to form OsBr_6^- which was then dried down overnight at 120°C. Osmium was further purified by microdistillation [2]. OsBr_6^- drydowns were dissolved using an additional 6 μl HBr placed on the inside of a cap for a conical Teflon beaker and was dried down at 90°C. Twenty μl of HBr was added to the apex of the conical Teflon beaker and 50 ml of a chromic-sulfuric acid mixture was added onto the OsBr_6^- drydown on the inside of the cap. The conical beaker was assembled, wrapped with aluminum foil three-quarters of the way up the beaker, and micro-distilled for three hours at 90°C. In this step the Os is oxidized to OsO_4 , which moves as a volatile up to the HBr-filled beaker apex where it is again reduced to OsBr_6^- . The OsBr_6^- solution was then dried down at 120°C. The purified Os sample was then loaded using 1 μl HBr onto Pt-filaments and 0.7 μl of $\text{Ba}(\text{OH})_2/\text{NaOH}$ activator was added on top of the sample. Purified Os samples were run as OsO_3^- ions by negative thermal ionization mass spectrometry (N-TIMS) with a Thermo Finnigan Triton. Isotopes were sequentially measured using a secondary electron multiplier.

For the Re purification chemistry, the Re-bearing inverse aqua regia was dried down overnight at 120°C. The Re drydown was then dissolved in 2 ml of 2N HNO_3 by heating to 120°C overnight. The Re- HNO_3 solution was then added to a centrifuge tube to which 2 ml 3-methyl-1-butanol (iso-amylol) was also added. The centrifuge tube was sealed and shaken for 2 minutes and then centrifuged for 4 minutes at 4000 rpms. Using Teflon pipettes, the iso-amylol was extracted into a second centrifuge tube containing 2 ml of HNO_3 . This was then sealed and shaken for 2 minutes and then centrifuged for 4 minutes at 4000 rpms. The HNO_3 was removed and another 2 ml of HNO_3 was added. The centrifuge tube was sealed and shaken for 2 minutes and then centrifuged for 4 minutes at 4000 rpms. Again, the HNO_3 was removed and 2 ml of MiliQ H_2O was added. The centrifuge tube was sealed and shaken for 2 minutes and then centrifuged for 4 minutes at 4000 rpms. The Re-bearing MiliQ H_2O was extracted to a Teflon beaker and an aliquot of 0.2 ml was dried down at 120°C. The purified Re sample was then loaded using 1 μl HBr onto Pt-filaments and 0.7 μl of $\text{Ba}(\text{OH})_2/\text{NaOH}$ activator was added on top of the sample. Purified Re samples were run as ReO_4^- ions using negative thermal ionization mass spectrometry (N-TIMS) with a Thermo Finnigan Triton. Total procedural blanks were 1.8 and 3.2 pg for Os and <5 pg for Re. Blank corrections have negligible effects on the calculated ^{187}Re and ^{187}Os concentrations. Deconvolution of the Os isotope data (blank and common Os correction) follows a similar method to that described in Markey et al., [4], but for a single rather than double spike.

Two procedural blanks and one Henderson molybdenite standard (27.656 ± 0.022 Ma, Markey et al., [5]) were also run with each of the Don Manuel molybdenite samples.

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

References

1. Shirey, S.B.; Walker, R.J. Carius tube digestion for low-blank rhenium-osmium analysis. *Analytical Chemistry* **1995**, *67*, 2136-2141.
2. Birck, J.L.; Barman, M.R.; Capmas, F. Re-Os isotopic measurements at the femtomole level in natural samples. *Geostandards newsletter* **1997**, *21*, 19-27.
3. Cohen, A.S.; Waters, F.G. Separation of osmium from geological materials by solvent extraction for analysis by thermal ionisation mass spectrometry. *Analytica Chimica Acta* **1996**, *332*, 269-275.
4. Markey, R.; Hannah, J.L.; Morgan, J.W.; Stein, H.J. A double spike for osmium analysis of highly radiogenic samples. *Chemical Geology* **2003**, *200*, 395-406.
5. Markey, R.; Stein, H.J.; Hannah, J.L.; Zimmerman, A.; Selby, D.; Creaser, R.A. Standardizing Re–Os geochronology: a new molybdenite reference material (Henderson, USA) and the stoichiometry of Os salts. *Chemical Geology* **2007**, *244*, 74-87.