RE-OS GEOCHRONOLOGY OF REFRACTORY METAL NUGGETS THROUGH ATOM PROBE MICROSCOPY.

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Introduction: Refractory metal nuggets (RMNs) are sub-micrometre metal alloys comprised of the highly siderophile elements (HSE) found in primitive carbonaceous chondrite meteorites [1]. RMNs are thought to be amongst the first phases to form in the protoplanetary disk [2]. However, recent observations have suggested that some may have a pre-solar origin [3,4]. The small size of RMNs has inhibited precise isotopic analyses capable of discerning between RMNs that formed in our Solar System and RMNs that formed in a pre-solar environment. A relatively new technique- atom probe microscopy (APM) - has the potential to extract isotopic information from small sample volumes (< 0.01 μm^3) [5]. However, a reliable approach for extracting isotopic information from the mass-to-charge-state-ratio (m/q) spectrum generated by APM has not been established. Here we apply APM and Negative Ion-Thermal Ionisation Mass Spectrometry (N-TIMS) to extract isotopic information from synthetic Re-Os bearing standards to develop a robust approach for isotopic analysis of Re and Os using APM that could be applied to RMNs.

Evaluation of the Method: The theoretical prescision of the APM technique, calculated from the uncertainties associated with the counting statistics, might discern isotopic differences > 40ε (2σ) which is sufficient to detect isotopic signatures of pre-solar grains. However, complications in the APM datasets such as peak ranging, hydride formation, complex ions, variable background, and peak overlaps increase the uncertainty of the technique and must be evaluated and corrected. Synthetic standard materials of pure Re and Os, as well as two complex HSE alloys comparable to RMNs made for the experiments of Schwander et al. [6]; both the original alloy and the final run product (henceforth HSE and SYN respectively) were analysed by both TIMS and APM. APM data reduction approaches were evaluated accounting for the factors described above. Corrected APM data yielded isotopic information in good agreement with TIMS. APM analysis of the pure Os sample produced a $^{187}Os/^{188}Os$ ratio of 0.142±0.003, (2σ) which is within 0.25% of the TIMS value of 0.1417±0.0002 (2σ). The pure Re and SYN samples were within 0.5% and 1% of the TIMS analysis respectively. However, the HSE samples had a 7% discrepancy between APM and TIMS. This may be due to a higher uncertainty associated with the deconvolution of the ^{187}Re-^{187}Os isobaric interference or an inherent isotopic heterogeneity within the original alloy that was then homogenised during the experiments of Schwander et al. [6]. Our APM approach robustly extracts isotopic information with respect to Re and Os for both pure elements and alloys with a comparable composition to RMNs. Therefore, we may apply our approach to similar samples for which isotopic information can only be extracted by APM, such as RMNs.

Isotopic analysis of RMNs: Seven RMNs were extracted from ultra-refractory inclusions in the Allende (1), Murchison (1), and ALH77307 (5) meteorites. Isotopic information for Re and Os were extracted from the APM data using the same methodology applied to the synthetic standards. The sensitivity of the current approach, while insufficient to discern a pre-solar isotopic signature, is sufficiently sensitive to evaluate the Re-Os decay system for these RMNs. The Re-Os systematics of these RMNs plot on a regression line consistent with that of the Solar System isochron of 4.56 Ga. This suggests that these RMNs, associated with high temperature inclusions, are likely to have a Solar System origin and formed within a reservoir that was already isotopically well mixed with respect to Re and Os.

While the RMNs here all appear to have a Solar System origin, this approach can in principle be used to demonstrate the origin and ages of pre-solar RMNs. Our approach can also be applied to evaluate the Re-Os geochoronology of other sub-micrometre Os rich phases *in situ*, which has several applications in both meteoritics and Earth sciences.

References: [1] Palme H. & Wlotzka F., 1976, *Earth and Planetary Science Letters*, 33:45-60 [2] Berg T. et al., 2009, *The Astrophysical Journal* 702:L172-L172. [3] Daly L. et al., in press, *Geochimica Et Cosmochimica Acta*. [4] Croat T. et al., 2013, *Meteoritics and Planetary Science*, 48:686-699 [5] Kelly T.F. & Larson D.J., 2012, *Annual Review of Materials Research*, 42:1-31. [6] Schwander D. et al., 2015, *Meteoritics and Planetary Science*, 50:893-903.