Journal of Conference Abstracts
Volume 5(2), 601


# Laser Ablation ICP-MS Analysis of Molybdenites – Implications for Re-Os Geochronology

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The Re-Os geochronometer is potentially a powerful tool for dating formation ages of mineral deposits, particularly where the age of Re-bearing mineral phases such as molybdenite or pyrite can be related to discrete episodes of hydrothermal activity (e.g., Stein et al. 1998a). Molybdenite is used most widely because it is ubiquitous in many ore deposits and contains relatively large concentrations of Re and negligible initial Os. Thus, ages may be calculated simply as: $T= \{\ln[(^{187}Os/^{187}Re) + 1]\}/\lambda$ where $\lambda$ is the decay constant for $^{187}Re$. An outstanding issue in Re-Os molybdenite geochronology is whether or not the system can be disturbed or reset by subsequent events. Evidence from hydrothermal experiments (McCandless et al. 1993, Suzuki et al. 2000) suggests that Re may be preferentially lost from molybdenite. In contrast, multiple analyses of molybdenites from individual deposits produce a narrow range of reproducible ages, suggesting that the Re-Os system is robust in molybdenite (e.g. Raith and Stein in press, Stein et al. 1998b).

Most previous measurements for Re-Os molybdenite geochronology have been made by conventional NTIMS or ICP-MS analysis, which utilise 20-200 mg bulk samples. Laser ablation ICP-MS has not been used extensively but possesses the spatial resolution required to assess mobility of Re and $^{187}Os$ on a fine scale within molybdenite grains. We have therefore used this method to study Re and $^{187}Os$ inhomogeneities in molybdenite and explore the implications for isotopic dating.

The instrument is a VG PlasmaQuad 2S+ ICP-MS with a sensitivity of at least 1-5 x$10^4$ cps/ppm coupled to an in-house built 266 nm NdYAG laser, located at Memorial University. Molybdenites of variable Re content and known NTIMS Re-Os ages were exposed to a stationary 10 Hz defocused laser beam while the sample stage was rastered, producing a rectangular (200 x 200 x 100 microns) ablation pit on the exposed grain surface. The rastering procedure achieved a stable analyte signal for at least 180 seconds. The total amount of ablated material from each site was ca 0.02 mg, i.e. 1000 - 10000 times less than the amount used for a typical TIMS analysis. Raw $^{187}$(Re+Os) and $^{187}Re$ counts were corrected for multiplier dead time and gas blank. Measured $^{187}$(Re+Os)/ $^{187}Re$ ratios were corrected for instrument mass bias using measured $^{186}W/^{184}W$ ratios of a 15 ppb W solution that was simultaneously aspirated to the plasma. $^{187}Os/^{187}Re$ ratios were calculated after stripping the appropriate amount of $^{187}Re$ from 187 mass peak intensity, determined from the natural $^{187}Re/^{185}Re$ ratio of 1.6738. This correction is a source of large uncertainty on the Re-Os ages, as it yields errors of <10% (2- $\sigma$) only for molybdenites containing more than 2 ppm radiogenic Os (i.e. molybdenites with [age (Ma)] * [Re (ppm)] > 2 x $10^5$), reducing its utility as a dating tool relative to ID-NTIMS.

Concentrations of Re vary by an order of magnitude between analysed points within a single molybdenite grain and there is no relation between Re content and distance from the margin of the grain. In addition, Re concentrations change by a factor of 3 on a 100 micron scale (i.e. within a single raster analysis). This variation is even more pronounced on sections perpendicular to the cleavage and it may correspond to alternate layers of 2H and 3R molybdenite polytypes with the later being usually richer in Re (Newberry 1979, McCandless et al. 1993). The spatial resolution of the laser probe and large errors in the $^{187}Os/^{187}Re$ ratio did not allow us to relate variations in Re content across the cleavage to variations in age. However, variations in ages between individual ablation sites are larger than the analytical error and may reflect decoupling of Re and Os on the scale of a single molybdenite grain. In a recent laser ICP-MS study of molybdenite crystals from the Aittojärvi deposit in Finland, Re and $^{187}Os$ were clearly decoupled and $^{187}Os$ was concentrated in domains within the crystals, indicating mobility of $^{187}Os$ in molybdenite (Scherstén and Stein, unpublished data). Heterogeneity of $^{187}Os/^{187}Re$ ratios is a challenge that has been overcome by some workers in that accurate Re-Os ages may be obtained by taking a whole-grain or whole-rock approach in preparing molybdenite separates; ages are verified using several different mineral separates derived from the sample (Stein et al. 1998a). Laser ablation ICP-MS may be a useful tool to better understand mobility of Re and $^{187}Os$ within molybdenite.

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