

Additional insight into natural $^{185}\text{Re}/^{187}\text{Re}$ of various materials

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Following the preliminary work of Zimmerman et al [1] and the impressive results of Miller et al [2], additional investigation into the natural $^{185}\text{Re}/^{187}\text{Re}$ isotopic ratio supports the notion that variability of the ratio may exist in different geological samples and Re-bearing materials.

Four molybdenite samples, including NIST RM 8599 [3], and AIRIE's Re standard solution (RR-4, prepared from potassium perrhenate), were analyzed for their Re isotopic composition (IC) in triplicate. All samples showed elevated Re IC relative to the "true" value of 0.5974 [4]. The analyses followed standard Re-Os procedures except sample Re was liberated with concentrated HNO_3 in open glass beakers rather than Carius tubes. Anion exchange Re separation followed conversion of the solution to HCl form. Single bead Re clean-up resulted in notable NTIMS signal improvement.

NTIMS multi-collector faraday cup measurements are ruled out as causing elevated ICs as RR-4 loaded directly onto outgassed Pt filaments yields the expected ratio (0.59735 ± 0.00044 1σ stdev, $n=6$). Excluding two outliers, the mean $^{185}\text{Re}/^{187}\text{Re}$ is 0.5989 ± 0.0014 1σ stdev ($n=16$). Interestingly, every sample's IC was above 0.5974 yet there are no systematic correlations between IC and material type or molybdenite geologic setting.

Summarizing the Re IC of the analyzed samples relative to the true value of 0.5974 is difficult because of analytical concerns. The molybdenites selected (save RM 8599) have geologically unusual low Re concentrations between 1ppm and 50ppb. Column chemistry was hampered by extreme Mo:Re and low total Re. RM 8599 and RR-4 amounts were selected to best match the low Re molybdenites. As such, NTIMS signals for all samples were less than ideal. It is therefore difficult to determine whether the elevated Re ICs are analytically robust or biased by anomalous column chemistry and weak signals. Additional analyses using high Re molybdenites along with matching 8599 and RR-4 are in progress to test for biases resulting from low total Re.

[1] Zimmerman *et al.* (2011) *Min. Mag.* **75**, 2287. [2] Miller *et al.* (2009) *J. Anal. Atom. Spect.* **24**, 1069-1078. [3] Markey *et al.* (2007) *Chem. Geol.* **244**, 74-87. [4] Gramlich *et al* (1973) *J. Res. Nat. Bur. Stand.* **77**, 691-698.

Release of engineered nanomaterials from flexible thin-film photovoltaic cells

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Organic photovoltaic solar cells (OPVs) are a promising renewable energy technology. In consideration of the anticipated forthcoming large-scale production, the environmental impact of OPVs should be benchmarked to commercially available thin film technologies such as CuInGaSe cells (CIGS). Whereas most research focusses on performance of photovoltaics, little is known on the environmental fate and effect of their constituents such as engineered nanomaterials after their life cycle. CIGS rely on hazardous metal(oids) such as Cu, In, Ga, Se, Mo and Cd. However, also OPV – although based on light-absorbing organic molecules – contain metals such as Al, In, and Ag, some of which applied in nanoparticulate form.

For the first time, this study investigates the leaching behavior of engineered inorganic nanomaterials present in OPV and CIGS. Leaching scenarios investigated under environmentally relevant conditions, like exposition to acidic rain and mechanical stress, were carried out for long term. Metal concentrations were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). This allowed the calculation of the predicted environmental concentrations for different scenarios, which were set in relation to corresponding WHO water limits. Furthermore, models for the observed leaching kinetics of the most relevant metals were determined. Eventually, all released inorganic components were investigated by time-resolved ICP-MS in order to distinguish between dissolved and nanoparticulate states. Our results show that after four months, OPV do not pose any risk to the environment regarding their engineered inorganic nanomaterial content, even under most conservative scenarios. On the other hand, high amounts of Mo, Se and Cd were leaching from CIGS. Under the constraints of this study, these would exceed drinking water limits many times.