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Dissolved selenium speciation and species-specific isotopic compositions derived from weathering mine wastes

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Dissolved selenium (Se) exists in multiple oxidation states (–2 to +6) and as diverse inorganic and organic species. While biogeochemical processes including redox transformations, mineral-fluid interactions, and biological uptake induce significant Se isotope fractionation, species-specific Se isotopic signatures and fractionation patterns remain poorly quantified. We are developing a pragmatic methodology to quantify inorganic (selenite, selenate, selenide) and methylated (methaneseleninic and -selenonic acid) Se at ppb levels, and to determine species-specific isotopic signatures in Se-enriched samples.

Our approach uses mixed-mode liquid chromatography to effectively isolate both organic and inorganic Se solutes using anion-exchange and reversed-phase separation simultaneously, as well as tailored TQ-ICP-MS detection for isotope (semi)quantification, eliminating major isobaric interferences using collision/reaction cells. On-column isotope fractionation of individual Se species during chromatography was significant but effectively accounted for by quantitative species separation (99.9999%) and fraction collection prior to isotope analysis. Selenium isotopic signatures of chemical standards were determined for individual Se species and revealed consistently light $\delta^{82/76}$Se signatures relative to reference standard NIST-3149.

The methodology was subsequently applied to Se-rich (up to 100 ppb) leachates from mine waste rock stockpiles from a Canadian mining industry partner. In these samples, the majority of Se existed as selenite, with minor (<20%) contributions of selenate and methane seleninic acid, as well as small concentrations of other unidentified organic Se species. Overall, organic Se species showed significantly more negative $\delta^{82/76}$Se isotopic signatures than inorganic Se species. Isotope mass-balance calculations show that the species-specific Se isotopic composition was in >90% agreement with bulk sample Se isotope compositions, however, reliable delta ratio determination could only be achieved for samples with sufficient concentrations of individual Se species and/or high recovery of bulk Se content: many samples contained <1 ppb organic Se, insufficient for reliable isotope quantification.

This work presents a practical alternative method to determine Se isotopic signatures in enriched, circumneutral mine waste leachate samples. By extension, our work may also help elucidate the biogeochemical cycling of Se in a variety of other industrial and environmental settings.