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Chalcophile elements on collision course: S and Se isotope ratio measurements using the Sapphire Dual Path MC-ICP-MS with Collision/Reaction Cell

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Chalcophile elements and their isotope ratios provide insights into a wide range of terrestrial processes from mantle fractionation to hydrothermal alteration and enable environmental and biogeochemical tracing. In this study, we will present isotope ratio data for S and Se measured on a Nu Sapphire Dual Path MC-ICP-MS with Collision/Reaction Cell to remove isobaric interferences.

Plasma-based S isotope measurements suffer from several isobaric interferences such as $^{16}O_2^+$ on $^{32}S^+$, $^{16}O^{17}O^+$ on $^{33}S^+$, $^{16}O^{18}O^+$ on $^{34}S^+$, and $^{18}O_2^+$ on $^{36}S^+$. For Se, numerous Ar-based (Ar dimers, $^{40}Ar^{37}Cl$) and Kr interferences affect all Se isotopes and have limited the exploration of this isotopic system thus far. While O, Ar, and Kr-based interferences can be well-supressed using He-H_2 gas mixtures, both isotopic systems are prone to forming SH and SeH that will limit the accuracy of isotope ratio measurements. Thus, for both systems, a variety of reaction gases will be evaluated including He-H_2 and He-SF_6 gas mixtures as well as N_2.

Preliminary results using He-H_2 as reaction gas for Se reveal efficient Ar-Ar and Kr interference removal but significant SeH formation rates (~ 3%). After correction for SeH based on in-run measurements of $^{78}SeH^+$ relative to $^{78}Se^+$, Se isotope ratios in wet plasma using a self-aspirating nebuliser are well reproducible with a short-term repeatability of, e.g., $2\sigma_S$ SD < 35 ppm for $^{80}Se/^{78}Se$, $2\sigma_S$ SD < 45 ppm for $^{76}Se/^{78}Se$, or $2\sigma_S$ SD < 40 ppm for $^{77}Se/^{78}Se$ (with s = sample). Individual measurement errors are between 10-40 ppm (2 σ_S SE) for the different major Se isotope ratios. Isotope fractionation is thereby demonstrable mass-dependent with linear regression slopes of 1.994-1.997 (R^2 = 0.999) for ln($^{82}Se/^{78}Se$) vs. ln ($^{80}Se/^{78}Se$) over two analytical sessions.