Tourmaline reference materials for the *in situ* determination of lithium isotope composition

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We have investigated four widely available natural tourmaline samples [1, 2] with the goal of characterizing a suite of reference materials for the *in situ* determination of lithium isotope ratios. These four materials span a wide range in both major element compositions and lithium concentrations and form a good foundation for the calibration of δ^7Li determinations for microanalytical methods. Our SIMS homogeneity testing document that three of these materials have constant ^{7}Li/^{6}Li compositions at our sub-10 ng sampling mass. Data from the fourth material suggest a possible variation of up to 2.5 ‰ in isotope ratio between fragments of the single crystal, although this observation needs further confirmation. The absolute δ^7Li values of the four materials were determined independently by solution MC-ICP-MS analyses conducted in two laboratories. Absolute Li concentrations have been estimated for all four materials using SIMS in conjunction with data from the literature, revealing that the Li concentrations in this suite of materials span a range in excess of three orders of magnitude. Furthermore, we tested for the presence of any SIMS chemical matrix effect by means of a ^{7}Li/^{6}Li intercomparison between the various RMs in conjunction with the results from the wet chemical investigation. Finally, we discuss some of the analytical considerations that can impact the quality of SIMS δ^7Li determinations.

[1] Dyar *et a*l. (2001) *Geostandards Newsletter* **25/2**, 441-463.
[2] Tonarini *et al.* (2003) *Geostandards Newsletter* **27/1**, 21-39.

Equilibrium mercury isotope fractionation between dissolved Hg(II) species and thiol-bound Hg

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Stable Hg isotope ratios provide a new tool to trace Hg sources and transformations in the environment. The fate and mobility of Hg is strongly influenced by sorption to organic matter. Thiols (-SH) are the dominant Hg-binding groups in natural organic matter. Here, we report experimental and computational results on equilibrium Hg isotope fractionation between dissolved Hg(II) species and thiol-bound Hg.

Hg(II) chloride and nitrate solutions were equilibrated (24h, dark) in parallel batches with varying amounts of resin with thiol-functional groups (Amberlite GT-73) resulting in different fractions of thiol-bound and free Hg. Dissolved Hg(II) was separated from Hg on resin by filtration, before thiol-bound Hg was desorbed with HCl/BrCl. Both fractions were analyzed for Hg by CV-AFS and Hg isotope ratios by CV-MC-ICPMS using standard-bracketing and Tl mass bias correction (2SD of δ^{202}Hg $\leq$0.08‰). All Hg isotopes were measured simultaneously to study potential mass-independent fractionation (MIF) of odd Hg isotopes. Theoretical equilibrium Hg isotope effects by mass-dependent (MDF) and nuclear-volume (NVF) fractionation were calculated for all Hg isotopes and 14 relevant Hg(II) species.

The experimental data revealed that thiol-bound Hg was enriched in light Hg isotopes by 0.55‰ and 0.62‰ (δ^{202}Hg) relative to $HgCl_2$ and $Hg(OH)_2$, respectively. No significant MIF was measured. Calculated MDF (0.14‰ and 0.49‰), and NVF (0.43‰ and 0.17‰) of $Hg(SMe)_2$ relative to $HgCl_2$ and $Hg(OH)_2$, respectively, were in excellent agreement with the experimental data indicating that a combination of MDF and NVF is responsible for the observed Hg isotope effects. In contrast to previous work, no significant MIF due to NVF was predicted from the calculations in line with the experimental data. Our results indicate that (i) significant equilibrium Hg isotope fractionation may occur in nature without redox transition, and (ii) nuclear-volume fractionation must be considered in addition to classic mass-dependent fractionation to explain Hg isotope variations.