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The Development of Reference Material and Calibration Curves for Hydrogen and Oxygen Isotope Analysis of Tourmaline by Secondary Ion Mass Spectrometry (SIMS)

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Hydrogen (H) and oxygen (O) stable isotopes are used to trace fluid sources, as well as metals and contaminants in the environment and Earth's subsurface. In particular, the isotopic composition of tourmaline has been used to establish formation processes for critical metal deposits. Tourmaline-supergroup minerals provide the unique opportunity to quantify both H and O isotope ratios from the same grain using *in-situ* analytical techniques (*e.g.* SIMS). Tourmaline's chemical diversity and common zoning render it a difficult mineral to analyze with a high degree of accuracy, yet its formation in a wide range of geological environments situates it as an important petrogenetic indicator. Large differences in the chemical composition of a mineral are problematic during SIMS analysis, as instrumental mass fractionation (IMF) often varies with the chemical composition of the analyte. Therefore, the development of calibration curves based on tourmalines with varying chemical composition is necessary for accurate analysis by SIMS. Tourmaline samples were evaluated for homogeneity with respect to elemental composition (electron microprobe analysis), bulk isotope composition (gas source mass spectrometry), and *in-situ* isotope composition (SIMS). Six reference materials for H and O isotope analysis using a CAMECA 7f SIMS instrument were developed. Spot-to-spot reproducibility for these tourmalines was between 4-5‰ and 0.6-1.0‰ for hydrogen and oxygen isotopes, respectively. A strong correlation was found between IMF and several elements (B, Si, Ca, Fe, and Fe#), however the Fe content has the greatest effect on IMF. Two calibration curves were developed for the correction of H and O isotope ratios as measured by SIMS using reference tourmalines with varying Fe content (0.00 to 14.00 wt.% Fe). We present the first calibration curve used to correct for the fractionation of H isotope ratios in tourmaline measured by SIMS. We also suggest that tourmaline-supergroup minerals require a suite of at least three reference tourmalines with a range of Fe content, to ensure accurate and precise H and O analysis by SIMS. A single reference tourmaline may be used only if the unknown and reference tourmalines have the same Fe content.