Improved matrix correction of $\delta^{18}O$ analysis by SIMS for pyralspite and Cr-pyrope garnets

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Stable isotope analysis of complex solid-solution minerals by SIMS requires a large suite of matching standards. There is no theoretical basis for extrapolating SIMS bias based on cation composition thus samples are generally calibrated by isostructural standards. For oxygen isotope analysis of pyralspite garnets, a proposed matrix correction based on grossular (Ca) component (X_{Grs}) [1] has been generally accepted [2–4]. However, in recent SIMS sessions we noticed significant dispersion (>0.5‰) in the low-Ca, near end-member, pyralspite garnets such as pyrope (Mg), almandine (Fe^{2+}) and spessartine (Mn). Corrections for these components using a linear fit and/or a single component cannot explain the observed dispersions of low-Ca pyralspite garnets [3–5].

In this test study, pyralspite and grossular garnets are calibrated with three binaries (Ca–Mg, Mn–Mg and Fe^{2+}–Mg) instead of only X_{Grs}. Each calibration curve was fitted by a quadratic equation with three standards. A single pyrope standard was common to all calibrations and thus a total of 7 standards were used for calibrations. This correction scheme was evaluated using the measured offset of corrected $\delta^{18}O$ vs. $\delta^{18}O_{True}$ value (measured by laser-fluorination, gas-source-MS) for 27 published [1] and 22 new garnet standards. Biases are session specific. For session on 6/24/2014, the value of 2 standard deviations (2SD) of the residual after Ca correction was 0.81‰. Finally, after the Mn and Fe^{2+} corrections were performed, the 2SD of the final residual was 0.33‰, better than the residual if we apply only the X_{Grs} correction [1] (0.75‰). In addition, we analyzed 6 new Cr-pyrope garnet standards [6] to evaluate the effect of Cr on the matrix correction which has not previously been studied. The calibration curve for Cr-pyrope garnets reveals that the bias derived from Cr concentration is ~ 1.1‰ at 13.4 wt.% Cr_2O_3.

[1] Page *et al*. (2010) *Chem. Geol*. **270,** 9–19. [2] Raimondo *et al*. (2012) *J. Metamorph. Geol*. **30,** 255–280. [3] Ickert & Stern (2013) *Geostand. Geoanalytical Res*. **37,** 429–448. [4] Martin *et al*. (2014) *Chem. Geol*. **374-375,** 25–36. [5] Vielzeuf et al. (2005) *Chem. Geol*. **223,** 208–226. [6] Howarth et al. (2014) *Lithos* **184-187**, 209–224.