Mass spectrometric effects on 'clumped isotopes' calibration

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Carbonate 'clumped isotopes' thermometry is based on a Δ_{47}-temperature relationship that was obtained using calcite formed at known temperatures and verified using biogenic carbonates, all analysed on one mass spectrometer. Wider spread of 'clumped isotopes' measurements requires strict examination of its applicability to other analysis conditions.

Decomposition-recombination reactions of CO_2 within the ion source promote random distribution of isotopes among all isotopologues, thus modifying Δ_{47} without affecting $\delta^{13}C$ and $\delta^{18}O$. We observed persistent deviations from the nominal Δ_{47} values of NBS-19 and cylinder CO_2, indicating randomization of 5% of the CO_2 molecules. A scaling factor of 0.95 was thus applied, resulting in an offset of up to 0.005‰ from previously determined Δ_{47} in speleothem samples.

$CaCO_3$ precipitated inorganically at a temperature range of 26–40°C resulted in Δ_{47}=0.617–0.545‰, and a correlation of $\Delta_{47}=56808/T^2-0.026$. Scaling the data by 0.95 resulted in Δ_{47} values that were within 0.004‰ of the original 'clumped isotopes' thermometer, thus providing a confirmation of the original calibration using a different set of carbonate materials and independent sample preparation and analysis.

The observed offsets are small and easily overlooked, as they are within the analytical errors of one analysis. However, they are significant compared to the desired precision (obtained through replicates) and are likely to vary among mass spectrometers. Thorough standardization is required to account for these effects, highlighting the need to develop standard materials before a wide spread application of 'clumped isotope' thermometry.

Mobility of lithophile trace elements during the late magmatic stage in the felsic Gawler Range Volcanics, South Australia

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The Mesoproterozoic (ca. 1.6 Ga) Gawler Range Volcanics (GRV) and the coeval Hiltaba Suite Granite form a silicic large igneous province (10^5 km^3) emplaced in an intracontinental setting in the Gawler Craton, South Australia [1, 2]. The world-class Cu-Au-U Olympic Dam deposit is both spatially and temporally associated with the province. The hydrothermally altered rocks hosting the Olympic Dam deposit are associated with high REE contents (La+Ce = 0.5 wt%) and fluorine-bearing phases are ubiquitous [3].

The transition between magmatic and hydrothermal stages is considered to be crucial for the formation of ore deposits and the exsolution of an aqueous fluid has been proven to be an effective way of sequestering metals from the magma [e.g. 4]. However, lithophile elements are considered to be immobile in aqueous solutions and need to be complexed to be transported. The GRV-Hiltaba Suite province offers the opportunity to study a F- and lithophile element-rich system and establish possible relations with the mentioned deposit.

We report the occurrence of lithophile trace element (REE+Y, HFSE)-bearing accessory minerals (zircon, fluorite, Nb-bearing Ti oxide, REE-fluoro-carbonate) inside cavities (amygdales, micromiaroles, lithophysal vugs, ≤ 2 mm in size) in the GRV. These minerals can account for most of the content of lithophile trace elements in these rocks. Textures and the association with non-magmatic phases (e.g. epidote) suggest that these minerals crystallised from a fluid. Melt inclusion analysis suggests the magma as a possible source of F (F ≤ 1.3 wt%).

We hypothesise that, due to a high solubility of accessory minerals, trace elements and F were concentrated in the melt by fractional crystallisation. Upon saturation, they could have been extracted by an exsolving F-bearing fluid. Trace element-bearing accessory phases could have then crystallised from such a fluid.

[1] Blissett (1993) *Geol. Sur. SA Bull.* **1**, 107-124. [2] Allen *et al.* (2008) *JVGR* **172**, 132-147. [3] Cross *et al.* (1993) *Geol. Sur. SA Bull.* **1**, 132-139. [4] Davidson & Kamenetsky (2007) *Chem. Geol.* **237**, 372-383.