

Sulphur Isotopes: An important geochemical tracer in fluid-melt system?

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Sulphur is a major volatile in magmatic systems and preferably partitions into the fluid phase upon decompression in a fluid-melt system [1]. Considering the dependence of sulphur isotope fractionation on sulphur speciation [2] sulphur isotopes could become an important geochemical tracer e.g. for fluxes across subduction zones. However, experimental data on sulphur isotope fractionation between fluid and melt is scarce and no data exists for geologically relevant melt compositions. Recent advances in *in situ* sulphur isotopes analyses using secondary ion mass spectroscopy (SIMS) enable determinations of the isotopic composition in silicate glasses with low sulphur content (<300 ppm S; [3]) and thus experimental investigations of the sulphur isotope fractionation between melt and (aqueous) fluid upon degassing. We conducted isothermal decompression experiments in internally heated pressure vessels (IHPV) using volatile-bearing (~6 wt% H₂O, 140 to 2700 ppm S, 0 to 1000 ppm Cl) dacitic andesites as starting material, synthesised in IHPV at 1030°C, ~500 MPa and $\log(fO_2) = \text{QFM}+0.8$ to $\text{QFM}+4$ (QFM: quartz-magnetite-fayalite buffer). The decompression experiments were carried out at 1030°C and fO_2 ranging from $\text{QFM}+0.8$ to $\text{QFM}+4$. Pressure was released continuously from ~400 MPa to 150, 100 or 70 MPa with rates (r) ranging from 0.001 to 0.2 MPa/s. The samples were either rapidly quenched after decompression or further annealed for various times (t_A) at final conditions (1 to 72 h) before quenching. The S and H₂O concentrations in the melt before and after decompression were measured by electron microprobe and IR-spectroscopy, respectively. The isotopic composition of S ($\delta^{34}\text{S}_{\text{melt}}$) was determined by SIMS. The gas-melt isotopic fractionation factor (α_{g-m}) for closed-system degassing was calculated according to Holloway and Blank [4] utilizing mass balance.

SIMS analyses reveal that α_{g-m} remains almost constant over a wide range of r and t_A . Results show that at ~90% degassing of S, $\delta^{34}\text{S}_{\text{melt}}$ increases significantly by ~2‰ at $>\text{QFM}+3$ ($\alpha_{g-m} \approx 0.9981$; S-speciation in the melt $\text{S}^{6+}/(\text{S}^{6+}+\text{S}^{2-}) \approx 1.00$ [5]) relative to initial melt and decreases by ~4‰ at $\text{QFM}+1.1$ ($\alpha_{g-m} \approx 1.0040$; $\text{S}^{6+}/(\text{S}^{6+}+\text{S}^{2-}) \approx 0.56$ [5]). These trends are in accordance with observations in arc magmas [6] but exceed the expected isotopic fractionation estimated using the available theoretical and experimental data from the 80's [7].

First decompression experiments conducted at higher temperatures (1100°C and 1150°C) in Pt or AuPd capsules indicate that α_{g-m} decreases (0.9981 to 0.9961) with increasing T (1030 – 1150°C) under oxidizing conditions ($\geq\text{QFM}+2$). The preliminary data provides first insights on the temperature dependence of fluid-melt S-isotope fractionation in oxidized geologically relevant systems at high $p - T$ conditions. Further experiments are planned to verify our results and possibly to establish S-isotopes as a powerful geochemical tracer in magmatic fluid-melt systems.

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