

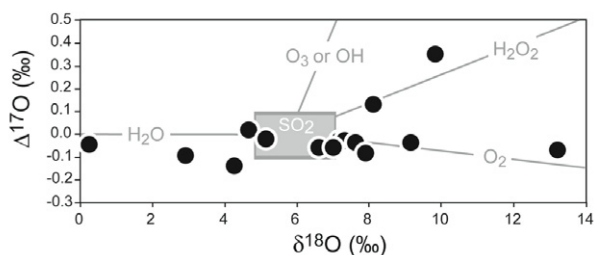
Multi-isotope (^{17}O , ^{18}O , ^{34}S) study of volcanic sulfate from modern tropospheric eruptions

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New high-precision measurements of O and S isotopic compositions of sulfate extracted from ash collected during or immediately after 20th–21st centuries tropospheric eruptions demonstrate significant ranges with respect to SO_4 concentration (350 to 7500ppm), $\delta^{18}\text{O}$ (0.2 to 13.2‰), $\Delta^{17}\text{O}$ (-0.14‰ to 0.35‰), and $\delta^{34}\text{S}$ (3.9 to 10.5‰), earlier study demonstrated $\Delta^{33}\text{S}=0‰$. Differences up to $\pm 2‰$ in S-isotopes composition from the initial magmatic SO_2 reflect efficient oxidation and Rayleigh distillation processes in the volcanic plume itself. The differences in O-isotopes composition reflect differences in tropospheric oxidation pathways of volcanic SO_2 , which can be correlated to oxidation processes in the plume and climate/weather condition during eruptions. Humid conditions above the volcano during the eruption promoted heterogeneous oxidation in aqueous phase via mass-independent H_2O_2 or O_3 . However, this oxidation pathway seems unrealistic to explain our samples showing the highest $\delta^{18}\text{O}$ and the lowest $\Delta^{17}\text{O}$. Samples with moderate $\delta^{18}\text{O}$ and the highest $\Delta^{17}\text{O}$, underwent oxidation via H_2O_2 rather than O_3 , which would lead to unrealistically high $\Delta^{17}\text{O}$ for moderate $\delta^{18}\text{O}$. However, in a relatively dry troposphere above the volcano during eruption, homogeneous oxidation via OH, H_2O and O_2 was prominent. In such a case, to explain the composition difference between volcanic sulfate and the initial volcanic SO_2 , OH radicals supply less than 2%, while H_2O and O_2 have both the largest contribution, between 40 and 60% each.



Experimental element partitioning between silicate and carbonatite melts and evidence for liquid immiscibility

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Silicate-carbonatite liquid immiscibility is one of three proposed origins of carbonatites. A suitable tool to test the liquid immiscibility hypothesis is trace element partitioning between conjugate melt pairs occurring in volcanoes erupting both silicate and carbonatite magmas.

The strategy of this study is to experimentally obtain liquid immiscibility, segregate the coexisting liquids by centrifuging and determine element partition coefficients for highly sodic and highly potassic carbonatite-silicate melt systems. These partition coefficients are then applied to test whether liquid immiscibility was the process forming kamafugite-carbonatite pairs. In comparison with the only existing previous centrifuge study [1], we study close-to-natural systems and determine ≥ 40 element partition coefficients. The investigated sodic system is from Lee & Wyllie [2], the potassic system simulates the Italian intra-appenninic kamafugite-carbonatite suite. Kamafugites are highly silica undersaturated, have extreme K_2O contents and $\text{K}_2\text{O}/\text{Na}_2\text{O} > 5$, crystallizing phlogopite, olivine, leucite, melilite, and also kalsilite. They are associated with carbonatites, which at some localities carry mantle xenoliths indicating that they originate from depths > 45 km.

Immiscible carbonatite-silicate melts devoid of crystals are produced at 1 GPa, 1230 °C and 1.7 GPa, 1220 °C for the sodic and ultrapotassic systems, respectively. The trace element spiked starting materials were first equilibrated in static experiments, reloaded in a single stage piston cylinder mounted on a centrifuge [3], and rerun at identical P-T conditions at 700 g for 3–5 hours to physically separate the liquids. LA-ICPMS analyses were performed on two centrifuged experiments representing the two systems. First results indicate that most partition coefficients do not deviate within 0.8 log-unit from unity except for HFSE and HREE, which partition into the silicate melt in the sodic system.

[1] Veksler *et al.* (1998) *J. Pet.* **39**, 2095–2104. [2] Lee & Wyllie (1997) *CMP* **127**, 1–16. [3] Schmidt *et al.* (2006) *Science* **312**, 1646–1650.