Investigating diffusive fractionation of volatiles in Hawaiian lava fountains

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Kīlauea's 2018 lower East Rift Zone eruption included the first long-lived lava fountaining in Hawaii since the 1980s. The combination of fountaining, modern gas measurement techniques, and the relative accessibility of the eruption site allowed for unprecedented study of syn-eruptive degassing processes. Our dataset comprises measurements of gas chemistry by open-path Fourier Transform Infrared (FTIR) spectroscopy and UAS (uncrewed aircraft system)-borne multi-GAS sensors, and of glass chemistry of melt embayments in phenocrysts in fountain tephra by electron microprobe analysis. Our multimethod measurements identified discrepancies between measured and expected gas ratios, which we suggest are due to kinetic effects related to different volatile diffusivities in magma.

Studies of Kīlauea's gas emissions have long indicated the existence of a multi-stage degassing process in which magmas release CO_2 -rich gas during ascent, after which they re-equilibrate to shallow storage conditions. Upon later eruption of the CO_2 -depleted magma at the summit or rift zone, the associated gases are SO_2 -rich, with a remarkably stable CO_2/SO_2 molar ratio of ~0.2–0.3. During the 2018 eruption, UAS multi-GAS-derived CO_2/SO_2 ratios for the bulk fountain plume were consistent with this expected low CO_2/SO_2 .

However, FTIR measurements of CO₂/SO₂ were somewhat higher (≤ 0.8) for the main 2018 lava flow, and higher still (~ 1) for gases measured at the Ahu'ailā'au fountain base. FTIR-measured SO₂/HCl ratios also differ between lava flow (≥ 50) and fountain (≤ 50) gases. This too contrasts with the understanding that shallower degassing of S-depleted melt is associated with lower S/Cl ratios.

Melt embayments in tephra sample phenocrysts exhibit gradients of decreasing sulfur content towards vesicles; such gradients are not seen for faster-diffusing chlorine. This suggests that discrepancies between gas chemistry observations may be explained by diffusive fractionation of volatiles in the fast-rising magma feeding the lava fountains. We conclude that comparatively slow sulfur diffusion likely led to disequilibrium degassing in the fountain, resulting in the unexpectedly high fountain CO_2/SO_2 and low fountain SO_2/HCl ratios. We evaluate this hypothesis by considering modeled diffusion timescales, magma ascent rate, and lava fountain height.

Our findings highlight the utility of integrating multiple datasets to probe the dynamic degassing processes associated