

## Sulfur isotope variation in arc basalts revealed by secondary ionization mass spectrometry: Measurements of melt inclusions

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Understanding sulfur recycling in arcs is hampered by poor constraints on initial  $\delta^{34}\text{S}$  of undegassed mafic magmas. We measured sulfur isotope ratios in mafic melt inclusions by (SIMS) from three arc volcanoes, Galunggung, and Krakatau in Indonesia, and Augustine volcano, in Alaska. These data provide a novel view of the variability of initial S isotope ratios in mafic arc magmas.

Melt inclusions obtained from a 1982-1983 Galunggung basaltic bomb yield  $\delta^{34}\text{S}$  values ranging from -2.8‰ to 9.6‰ with 1950 - 990 ppm S. A few inclusions have mantle  $\delta^{34}\text{S}$  between -0.8‰ and 1.9‰, 1950 - 1710 ppm S and 0.25 to 0.30 wt.% H<sub>2</sub>O. Melt inclusions in lapilli from a 1982 scoria fall sample yield much higher dissolved H<sub>2</sub>O of 3.70 wt.% (by FTIR) and  $\delta^{34}\text{S}$  values from -2.8‰ to 7.6 ‰ with S concentrations of 330 to 1410 ppm.

Pre-1883 basaltic scoria from Krakatau volcano yield melt inclusions with 1.8 - 4.1 wt.% dissolved H<sub>2</sub>O, 79 - 1017 ppm CO<sub>2</sub>, and 620-2400 ppm S. SIMS measurements yield  $\delta^{34}\text{S}$  values ranging from 1.6‰ to 8.7‰ and no correlation with S.

A Pleistocene basaltic pyroclastic deposit from Augustine volcano contains basaltic melt inclusions with high dissolved volatiles, 8.0 wt.% H<sub>2</sub>O, 6900 ppm S and 3950 ppm Cl. SIMS measurements yield  $\delta^{34}\text{S}$  values of 9.6‰ to 17.2‰ for inclusions with 2624 to 4650 ppm S. Extreme volatile enrichment, and elevated  $\delta^{34}\text{S}$  values indicate a <sup>34</sup>S-enriched component in the magma source region.

Sulfur (XANES) spectra obtained from Galunggung, Krakatau and Augustine melt inclusions yields prominent peaks at 2482 eV indicating SO<sub>4</sub> as the dominant form of dissolved sulfur. Iron XANES spectra from these melt inclusions are currently being evaluated for Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios.

## Ar diffusion in basaltic glass and implications for thermochronology in oceanic ridge settings

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Down-temperature extrapolation of laboratory argon diffusion data to conditions relevant to shallow crustal settings is the major uncertainty in modeling natural diffusion properties. For example, in the case of basaltic glass, anomalous behavior related to the glass transition renders diffusion data collected above 600°C irrelevant to crustal conditions prevalent for the uppermost portion of oceanic crust. Our results indicate that measurements made as low as 400°C may be affected. We have used a halogen light-based image furnace to measure the diffusion of reactor-induced argon (<sup>37</sup>Ar, <sup>39</sup>Ar) in vacuum-fused Kilauea basaltic glass at temperatures between 100-300°C. Sized fractions of raw crushed glass and sized fractions of air-abraded particles derived from the crushed material. Five different nominal size fractions of basaltic glass were analyzed (mean sieve diameters of ~850, 325, 170, 80, and 40 μm respectively). Size and shape distributions were digitally imaged. The calculated sphericity, symmetry, and convexity of the abraded size fractions approached values for spherical grains. Less ideal behavior and wider variation in these parameters was observed for the untreated crushed material. The image furnace-based diffusion experiments produced reproducible and self-consistent results between 100-300°C for all air-abraded size fractions. The activation energy (73.6 ± 0.6 kJ/mol) and frequency factor (1.8 ± 0.2 × 10<sup>-13</sup> m<sup>2</sup>/s) yield bulk closure temperatures that range from 13 to 354 °C for diffusive length scales of 0.001 to 1 cm and cooling rates of 1-100°C/m. y. The results indicate that basaltic glass is less retentive with respect to Ar diffusion than previous studies had indicated. Only rapidly cooled, cm-scale unaltered glass formed near spreading ridges appears capable of recording the time of basalt eruption during the formation of new oceanic crust. Results from naturally crushed but untreated glass fragments yielded similar Ar diffusivities but lower activation energies that we interpret in terms of non-ideality of particle geometry. Above 300°C, we reproducibly detected non-linear Arrhenius behavior that may forecast the higher temperature glass transition.