

Compositional dependence of sulfur speciation in Terrestrial and Martian magmas

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The capacity of magmas to transport sulfur from mantle to crust strongly influences a planet's surface chemistry. Sulfur is perhaps exceptional among the elements in the diversity of its chemical speciation, exhibiting four redox species at geologically relevant conditions: sulfide (2-), elemental sulfur (0), sulfite (4+) and sulphate (6+). Furthermore, the solubility of sulfur in a magma (and hence the magma's capacity for delivering mantle-derived sulfur to the crust) depends critically on its oxidation state. Our aim with this experimental study was to quantitatively determine the chemical speciation of sulfur within several common magmas, as a function of oxygen fugacity (fO_2).

We have performed a series of experiments on six sulfur-bearing silicate melts, which together represent a broad range of naturally occurring compositions: two putative Martian basalts, two terrestrial MORBs (one primitive, one evolved), an andesite, and a dacite. These melts were equilibrated together (at one-atmosphere pressure, 1300°C) with various CO-CO₂-SO₂ gas mixtures, which imposed a range of fO_2 s. This range spanned -2 to +1.6 log units (relative to the Quartz-Fayalite-Magnetite or QFM buffer), and the step-size was 0.25 log units. The quenched glasses were analyzed by X-ray Absorption Spectroscopy (specifically XANES) at the Diamond synchrotron (UK), and the spectra obtained were used to determine the species of sulfur present in each glass. The chemical composition of each glass (including their sulfur contents) was characterized by electron-probe microanalysis.

Despite the generally low concentrations of sulfur in our glasses (never exceeding 0.24 wt%), we have clearly resolved the crossover between reduced (S²⁻) and oxidized (S⁶⁺) species for three of our basalts. The other three melts yielded more noisy XANES spectra, and as a result their redox crossovers are visible, but less clearly resolved. For every melt composition, the redox crossover is a continuous (though fairly sharp) function of fO_2 : our spectra confirm the coexistence of sulfide and sulfate species in each of the melts at their crossover positions. Curiously, the positions and widths of the crossovers are not the same for each melt, revealing a compositional control on sulfur speciation. Our Martian basalts have the crossover centered on QFM+0.25, with a width of slightly less than 2 log units. Our terrestrial MORBs are similar, although the Primitive MORB shows some evidence for partial oxidation at lower fO_2 . The andesite crossover occurs \sim 0.5 log units lower than the basalts (QFM-0.25), and has a similar width. The position of the dacite crossover is unconstrained, but our spectra conclusively show its width to be extremely large: \sim 3 log units.

We interpret these compositional effects on redox chemistry as arising from contrasting sulphur activities in the different silicate melts, due to interactions with specific elements present. Iron is probably the strongest candidate for influencing sulphur activity. At a given fO_2 , our glasses' sulfur concentrations (where measurable) correlate positively with their FeO contents as predicted by O'Neill and Mavrogenes (2002). This is suggestive of an Fe-S interaction which stabilizes reduced sulphur in iron-rich melts, and is consistent with the early oxidation of our andesite, dacite and Primitive MORB, which contain significantly less Fe than the other three basalts.