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Sulfur speciation in magmatic silicate melts from mantle sources to eruptive degassing

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The solubility of sulfur in silicate melts in equilibrium with a gas phase at ambient pressure has been experimentally measured as a function of temperature under both reduced (sulfur as S^{2-}) and oxidized (sulfur as S^{6+} or SO_4^{2-}) conditions for a wide range of melt compositions of geological relevance. The results can be systematized using thermodynamic models for the sulfide and sulfate capacities of the silicate melts (C_S^{2-} and C_S^{6+}), based on a two-sublattice treatment of the melts (i.e., cation and anion sublattices). Combining the two models gives the range of oxygen fugacities over which the speciation of S in the melts changes from predominantly S^{2-} to predominantly S^{6+}, at ambient pressure. The results show that the mid-point of the transition, where $S^{6+}/S^{2-} = 1$, is calculated to occur at $Fe^{3+}/\sum Fe = 0.16$ for a synthetic parental mid-ocean ridge basalt composition at 1230ºC, with $Fe^{3+}/\sum Fe$ increasing slightly with decreasing temperature. The models may also be combined with further experimental data from the literature at both ambient and super-ambient pressures, to determine the maximum solubilities of sulfur in silicate melts coexisting with FeS-rich sulfide (the Sulfide Content at Sulfide Saturation or SCSS) or with $CaSO_4$ (the Sulfate Content at Anhydrite Saturation or StCAS). The resulting models are not well constrained as regards the effects of pressure and H_2O contents. To address these issues, new experiments have been done in the piston-cylinder apparatus, in which haplobasaltic melt compositions were brought into equilibrium with both FeS-rich matte and anhydrite simultaneously, at 1200 to 1500ºC and 0.5 to 4 GPa. The quenched glasses were analysed by electron microprobe, and both $S^{6+}/\sum S$ and $Fe^{3+}/\sum Fe$ measured by XANES spectroscopy. The results show a limited range of $S^{6+}/\sum S$ (0.6 to 0.8) at near constant $Fe^{3+}/\sum Fe$ (0.17 ± 0.015), but with very large total S contents that are difficult to reconcile with extrapolations from ambient-pressure models. The discrepancy suggests additional S species other than just S^{6+} and S^{2-} may be present at intermediate redox states at high pressure, although this is not evident from the XANES spectra.