The effects of oxygen fugacity on sulfur diffusion in dacite melts

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Sulfur is the third most abundant volatile species in magmas. One of the key questions in understanding the global S cycle is the S excess problem [1] which is linked to the presence of an exsolved volatile phase in magma reservoirs and intimately related to volatile diffusion [2]. Sulfur diffusion in silicate melts is a function of pressure, temperature and composition (including water content). Existing S diffusion data reveal large scatter ([2] for compilation) potentially due to the poorly established effects of oxidation state on S diffusion.

In silicate melts with oxygen fugacities corresponding to two log units above FMQ, S is mostly present as sulfate (SO_4^{2-}) whereas at values below FMQ it mostly occurs as sulfide (S^{2-}) [3]. The contrasting oxidation states result in a rather large range of possible (effective) ionic radii ranging from 1.84 Å for the reduced to 2.50 Å for the oxidized species ([4] and refs. therein). It is, therefore, expected that S diffusion is sensitive to varying oxygen fugacities. However, the published data do not show any significant systematic difference in diffusivities over a relatively large fO_2 range.

In order to explore this issue, we investigated S diffusion in natural dacitic melts under different oxygen fugacity conditions. The experiments were conducted with a hydrothermal, rapid-quench, cold seal pressure vessel under hydrous condition (4.5 wt. % H_2O) at 200 MPa in the temperature range between 950°C to 1100°C. Oxygen fugacity was varied between fairly reducing (FMQ -0.8) and more oxidizing conditions (FMQ +2.5). On the base of diffusion profiles measured by electron microprobe, we established two Arrhenian equations revealing one order of magnitude higher S diffusivity at reducing conditions compared to those determined at more oxidizing conditions. This study demonstrates for the first time that oxygen fugacity has a significant effect on S diffusivity.

[1] Shinohara (2008) *Rev. Geophys.* **46**, 1-31. [2] Behrens & Stelling (2011) *Rev. Mineral. Geochem.* **73**, 79-111. [3] Jugo (2009) *Geology* **37**, 415-418. [4] Baker & Rutherford (1996) *Contrib. Mineral. Petrol.* **123**, 335-344.