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The sulfate capacity of silicate melts at atmospheric pressure

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Sulfur dissolves in silicate melts at atmospheric pressure and low oxygen fugacities (fO_2) as sulfide (S^{2-}), but as sulfate (S^{6+} or SO_4^{2-}) at higher fO_2 (e.g., [1]). The solubility of S^{2-} in silicate melts is described by the reaction $\frac{1}{2} S_2 + O^{2-}(\text{melt}) = \frac{1}{2} O_2 + S^{2-}(\text{melt})$, leading to the definition of the "Sulfide Capacity", CS^{2-}, of the melt as $CS^{2-} = [S^{2-}](fO_2)^{1/2}(fS_2)^{-1/2}$, where $[S^{2-}]$ is the concentration of S^{2-} in the melt, and is a function of melt composition, temperature and pressure [1]. This theoretical relationship has been validated by experiment over a wide range of silicate melt compositions, e.g., [2]. It was proposed by [1] that the solubility of S as SO_4^{2-} can be described by an analogous reaction: $S_2 + 3/2\ O_2 + O^{2-}(\text{melt}) = SO_4^{2-}(\text{melt})$, defining the "Sulfate Capacity" as $CSO_4^{2-} = [SO_4^{2-}](fS_2)^{-1/2}(fO_2)^{-3/2}$.

We measured CSO_4^{2-} in nearly 50 silicate melt compositions, quenched from 1100 to 1500°C after equilibration in a gas-mixing furnace, using SO_2 and O_2 mixtures to control fO_2 and fS_2 in the high fO_2 regime where the concentrations of S^{2-} in the melts are effectively zero. Sulfur contents in the recovered glasses were measured by electron microprobe. Selected compositions were used to verify whether the S contents varied as $(fS_2)^{1/2}(fO_2)^{3/2}$. All were found to do so within experimental uncertainty, confirming the validity of the sulfate solution mechanism, while also implying that the amount of sulfite (S^{4+} or SO_3^{2-}) dissolved in silicate melts is negligible at atmospheric pressure. CSO_4^{2-} varies strongly with the melt composition, increasing with CaO, Na_2O and K_2O, but not with MgO or FeO_{tot}; hence the compositional dependence of CSO_4^{2-} is very different from that of CS^{2-}, which depends mainly on FeO contents in natural-composition melts [2]. CSO_4^{2-} decreases markedly with increasing temperature, much more so than C_{S2-}. The ratio of sulfate to sulfide in silicate melts is given by $[SO_4^{2-}]/[S^{2-}] = (CSO_4^{2-}/\ CS^{2-})(fO_2)^2$. Hence sulfate is favoured over sulfide by high CaO, Na_2O and K_2O, and low FeO, and by decreasing temperature at constant fO_2.

[1] Fincham, C.J.B., & Richardson, F.D. (1954) Proc. Royal Soc. London. Series A. Math. Phys. Sciences, 223, 40-62.

[2] O'Neill, H. St.C., & Mavrogenes, J.A. (2002). J. Petrol., 43, 1049-1087.