

Effect of sulphur and oxygen fugacity on vapour-saturation pressure calculations

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Dissolved H₂O and CO₂ concentrations in silicate glass are often used to calculate the entrapment pressure of a melt inclusion, eruption pressure of matrix glass, and composition of a vapour bubble in a melt inclusion. Currently available programs to calculate the pressure of vapour-saturation ($P_{\text{sat}}^{\text{v}}$) and coexisting vapour composition from measured concentrations of dissolved volatiles in melts/glasses (e.g., VolatileCalc, MagmaSat, VESICAL, etc.) assume the vapour contains only H₂O and CO₂, neglecting the role of sulphur- and other hydrogen- and carbon-bearing species in the vapour. We have developed a thermodynamic model where the melt contains H₂O_{mol}, OH⁻, CO_{2,mol}, CO₃²⁻, S²⁻, and SO₄²⁻; and the vapour contains O₂, H₂, H₂O, CO, CO₂, CH₄, S₂, SO₂, H₂S, and OCS. The pressure at which the sum of the partial pressures of all the vapour species equals the total pressure is $P_{\text{sat}}^{\text{v}}$, and the vapour composition is given by the partial pressures of the vapour species. The fugacities of CO₂ (f_{CO_2}) and H₂O ($f_{\text{H}_2\text{O}}$) are calculated from dissolved H₂O_{mol} and CO₃²⁻ concentrations using known solubility functions. We use the concepts of sulphide and sulphate capacity which, given f_{O_2} (e.g., from Fe³⁺/Fe²⁺ or S⁶⁺/S²⁻) and the total dissolved sulphur (S_{T}), are used to solve for f_{S_2} . Given these fugacities (f_{CO_2} , $f_{\text{H}_2\text{O}}$, f_{O_2} , and f_{S_2}), we calculate f_{H_2} , f_{CO} , f_{SO_2} , f_{CH_4} , $f_{\text{H}_2\text{S}}$, and f_{OCS} as a function of total pressure. Fugacities of all vapour species are converted to partial pressures and mole fractions (i.e., vapour composition) at a given pressure using fugacity coefficient functions. For the same dissolved H₂O and CO₂ in the melt: (1) Including additional vapour species increases calculated $P_{\text{sat}}^{\text{v}}$ – hence, previous estimates of $P_{\text{sat}}^{\text{v}}$ represent minima. This also applies to our results as we have not included Cl, F, N, etc. -bearing species, but their contributions to total pressure are typically smaller than S-bearing species. And (2) decreasing melt f_{O_2} increases the calculated $P_{\text{sat}}^{\text{v}}$ because the proportion of species such as H₂ and CO increases in the vapour. Additionally, we show how bounds on f_{O_2} are obtained by comparing S_{T} to the sulphide content at sulphide saturation and/or sulphate content at anhydrite saturation.