Supplementary Material: Appendix D

At equilibrium there is equality of chemical potentials (μ) between H_2O dissolved in the melt (m) and exsolved as a vapor (v)

$$\mu^m_{H_2O} = \mu^v_{H_2O} \qquad (D1)$$

The corresponding free energy balance for this equilibrium is

$$0 = \Delta G^o_{(T,P)} + RT\, ln\frac{f^v_{H_2O}}{a^m_{H_2O}} \qquad (D2)$$

where $\Delta G^o_{(T,P)}$ is the standard state free energy change for the equilibrium represented by Eq. D1, f^v_{H2O} is the fugacity of H_2O vapour, and a^m_{H2O} is the activity of H_2O in the melt. Expansion of Eq. D2 in terms of standard state values of enthalpy ($\Delta H^o_{(T,P)}$) and entropy ($\Delta S^o_{(T,P)}$) yields:

$$0 = \Delta H^o_{(T,P)} - T\Delta S^o_{(T,P)} + RT\, ln\frac{f^v_{H_2O}}{a^m_{H_2O}} \qquad (D3)$$

The activity of H_2O in the melt can be approximated as the square of H_2O content measured, assuming all H_2O is speciated as OH at low pressure, low concentrations and high temperatures. This assumption is corroborated by Silver and Stolper (1988), Ihinger et al. (1999) and Zhang et al. (2007) and coincides with previous H_2O solubility models (Nicholls, 1980; Burnham 1994; Sahagian and Proussevitch 1996). Thus,

$$a^m_{H_2O} = [x_{H_2O}]^2 \qquad (D4)$$

The fugacity of H_2O vapour is the fugacity for H_2O in the vapour at the experimental conditions ratioed to the standard state conditions: a pure ideal gas at atmospheric pressure (i.e. 101325 Pa). Assuming that the bubbles in our experiments contain pure H_2O fluid at the model internal bubble pressure (cf. Table 3):

$$f^v_{H2O} = \frac{P_{H2O}}{101325} = \frac{101828}{101325} \cong 1 \qquad (D5)$$

Substituting these values in to equation D3 yields

$$0 = \Delta H^o_{(T,P)} - T\Delta S^o_{(T,P)} + RT\, ln\frac{1}{[x_{H_2O}]^2} \qquad (D6)$$

The corresponding equilibrium constant (K_1) is

$$K_1 = \frac{1}{[x_{H_2O}]^2} = [x_{H_2O}]^{-2} = exp^{\frac{-\Delta H^o}{RT}} exp^{\frac{\Delta S^o}{R}} \qquad (D7)$$

This can be rearranged to form the Arrhenian equation:

$$ln\ x_{H_2O} = \frac{\Delta H^o}{2RT} + \frac{-\Delta S^o}{2R} \qquad \text{(D8)}$$

where slope (m) and intercept (b) are:

$$m = \frac{\Delta H^o}{2R} \qquad \text{(D9)}$$

$$b = \frac{-\Delta S^o}{2R} \qquad \text{(D10)}$$

We obtained estimates for ΔH^o and ΔS^o from fitting Eq. D8 to our experimental data over the temperature range 900 to 1050°C (cf. Fig. 6a).

References

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