

Energetic property of magma degassing: a thermodynamic model

Shigeru Yamashita

Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori 682-0193, Japan (e-mail: shigeru@misasa.okayama-u.ac.jp)

Knowledge of the latent heat of water dissolution in silicate melts is of importance for understanding the energetic property of magma degassing. I present here a thermodynamically based model for computing the latent heat of water dissolution in rhyolite melt. Fundamental assumption in the model developed here is that hydrous rhyolite melt can be treated as the system H₂O molecules (melt) – OH groups (melt) – O (melt), and that these three quasi-chemical components mixes ideally. The melt –water vapor equilibrium is expressed by the following two reactions: H₂O (vapor) = H₂O molecule (melt) (heterogeneous reaction) and H₂O molecule (melt) + O (melt) = 2 OH (melt) (homogeneous reaction). Yamashita (1999) found that under the same assumption, all previously published solubility data for water in rhyolite melts are reproduced over a wide range of temperature from ~700 to 1200 degree C at pressure to 100 MPa. His non-linear multiple regression for the solubility dataset converged upon the standard enthalpy of heterogeneous reaction = -25.3 ± 4.8 kJ / mol water at (1bar, T), the standard enthalpy of homogeneous reaction = 25.8 ± 11.8 kJ / mol water at (P, T), and the standard entropy of homogeneous reaction = 6.0 ± 8.7 J / mol water per K at (P, T). In this study, these optimum parameters were used to estimate the latent heat of water dissolution in rhyolite melts along the water solubility surface. The results demonstrate that at pressure between ~20 MPa and 0.1 MPa, the latent heat of water dissolution monotonously decreases with decreasing water content (hence with decreasing H₂O vapor pressure), where the absolute value is negative (Fig. 1). This monotonous decrease arises from a great change in the enthalpic contribution of homogeneous reaction to the latent heat of water dissolution; the fraction of water that has been converted to OH groups by homogeneous reaction approaches unity as water content decreases, which thereby yields the maximum enthalpic contribution of homogeneous reaction. As homogeneous reaction is endothermic (as is indicated by positive sign of the standard enthalpy), whereas heterogeneous reaction is exothermic, the latent heat of water dissolution decreases as water content in the melt decreases. At pressure above ~20 MPa, a cancellation of these two enthalpic contributions occurs. The latent heat of water dissolution roughly levels out over the pressure range ~20 MPa to 100 MPa as a result of this cancellation (Fig. 1). The latent heat of water dissolution estimated at 850 degree C is approximately -7 kJ / mol water at 20 MPa, and practically zero at 0.1 MPa. Although standard error of estimation is large (up to ± 6 kJ), the present results help in evaluating the energetic property of magma degassing under geologically relevant conditions. A numerical calculation for the conservation of energy in a rising water-saturated rhyolite magma (that is, when the exsolved H₂O is sustained in the melt as vapor bubbles) suggests that at pressures below 100 MP, the latent heat of water dissolution causes a temperature drop of only <10 degree C (Fig. 2).

References:

- Burnham C.W. & Davis N.F. (1974). *Amer. J. Sci.* 274, 902-940.
- Holloway J.R. (1977). In: Fraser D.G. (ed.) *Thermodynamics of Geology*, pp161-181.
- Lange R.A. & Navrotsky A. (1992). *Contrib. Mineral. Petrol.* 110, 311-320.
- Ochs F.A. & Lange R.A. (1997). *Contrib. Mineral. Petrol.* 129, 155-165.
- Sahagian D.L. & Proussevitch A.A. (1996). *J. Volcanol. Geotherm. Res.* 74, 19-38.
- Yamashita S. (1999). *J. Petrol.* 40, 1497-1507.

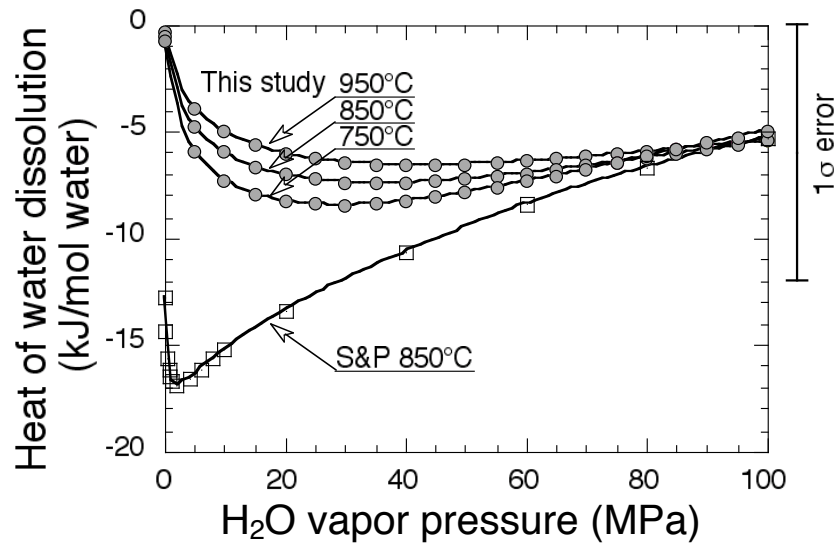


Figure 1. Latent heat of water dissolution in rhyolite melts modeled along the water solubility surface. Data labeled by S&P represent earlier thermodynamic model proposed for albite melt by Sahagian and Proussevitch (1996). The absolute values of the latent heat of water dissolution by the S&P model are substantially greater than those obtained by the present model at relatively low pressure. Such a large discrepancy probably stems from that the S&P model depends on the Burnham and Davis (1974)'s activity-temperature relation for water dissolved in albite melt, which needs to be revised at pressure below 200 MPa (Yamashita, 1999).

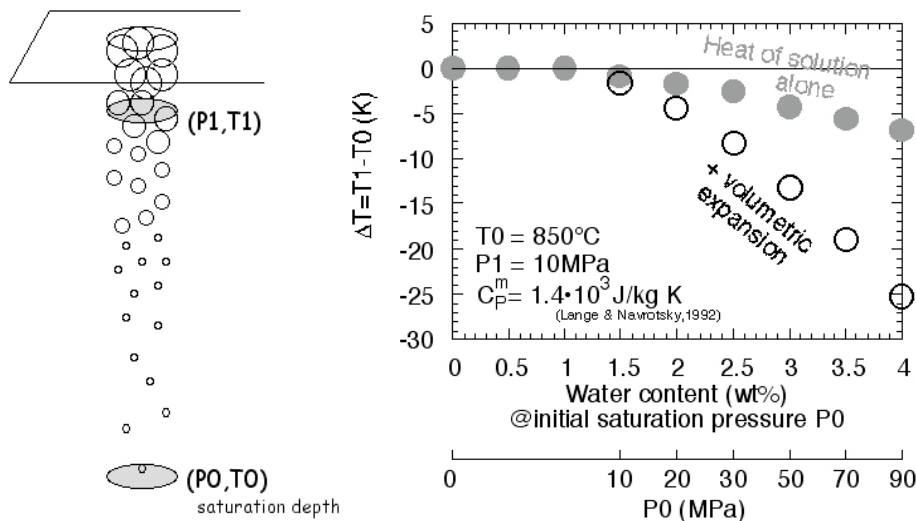


Figure 2. Energetic conservation for degassing in a rising water-saturated rhyolite magma as a function of initial water content of the melt. The energy conservation equation was numerically integrated from the initial water saturation depth to the magma fragmentation depth based on the latent heat of water dissolution in rhyolite melt (this study), the heat capacity of rhyolite melt (Lange & Navrotsky, 1992) and available equation of state (hydrous rhyolite melt, Ochs & Lange, 1997; H₂O vapor, Holloway, 1977).