Heat of water dissolution in rhyolite melt

Shigeru Yamashita[1]

[1] ISEI, Misasa

http://www.misasa.okayama-u.ac.jp/~shigeru/shigeru.html

Knowledge of the heat of water dissolution in silicate melts is of importance for understanding the energetic properties of vesiculation in a rising magma. I present here a thermodynamically based model for computing the 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 H_2O molecules (melt)-OH groups (melt)-O (melt), and that these three quasi-chemical components mixes ideally. The melt-water vapor equilibrium is then expressed by the following two reactions: H_2O (vapor) = H_2O molecule (melt) (heterogeneous reaction) and H_2O 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 well 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 kJ / mol water at (1bar, T), the standard enthalpy of homogeneous reaction = 25.8 kJ / mol water at (P, T), and the standard entropy of homogeneous reaction = 6.0 J / mol water per K at (P, T). I use these optimum parameters to estimate the heat of water dissolution in rhyolite melts along the water solubility surface.

At H_2O vapor pressure between ~20 MPa and 0.1 MPa, the heat of water dissolution monotonously decreases with decreasing water content (hence with decreasing H_2O vapor pressure), where the absolute value is negative. This monotonous decrease arises from a great change in the enthalpic contribution of homogeneous reaction to the 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 heat of water dissolution rapidly decreases as water content in the melt decreases. At H_2O vapor pressure above ~20 MPa, a cancellation of the changes in these two enthalpic contributions occur. The heat of water dissolution roughly levels out over the pressure range ~20 MPa to 100 MPa as a result of this cancellation.

The heat of water dissolution estimated at 850 degree C is approximately -7 kJ / mol water at 20 MPa of H_2O vapor pressure, 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 properties of vesiculation in a rising rhyolite magma. A numerical simulation suggests that at pressures below 100 MPa (the pressure range important to magma degassing), the heat of water dissolution causes a temperature drop of less than 10 degree C.