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Chemical-Thermodynamic Explorations on the Dissolution of Water in Magma: Breaking of the Ideal Mixing Model and Estimations of Temperature Change with Decompression-Induced Vesiculation

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論 文 名　：　Chemical-Thermodynamic Explorations on the Dissolution of Water in Magma: Breaking of the Ideal Mixing Model and Estimations of Temperature Change with Decompression-Induced Vesiculation
(マグマにおける水の溶解に関する化学熱力学的考察:理想混合モデルの破れと減圧発泡に伴う温度変化の見積り)

区　　分　：　甲

論 文 内 容 の 要 旨

Since water solubility in magmas (silicate melts) is a very fundamental and important piece of information in volcanology, it has been investigated extensively from both experimental and theoretical perspectives. Nevertheless, there has been no consensus on the consistency between experimentally determined water solubility values and those estimated through a chemical thermodynamics-based theoretical equation. In this study, I explicitly revisit this traditional problem and consider how the consistency should be established between experimental and theoretical values for the partial molar volume and heat of dissolution of water, which characterize the pressure- and temperature-dependence of water solubility, respectively.

The partial molar volume of water in silicate melt has been often estimated through an indirect way in which an experimentally determined water solubility in silicate melt is substituted into a theoretical equation derived from chemical thermodynamics. However, it has been also often reported that the values estimated in such a way significantly deviated from the value estimated through a direct method such as density measurement of quenched glass. In this study, I attributed this paradox to the assumption of the ideal mixing of bridging oxygen (O) of silicate and water (molecular water H_2O_m and hydroxyl groups OH), i.e., neglecting non-ideality, in the theoretical equation of water solubility used in the past. Therefore, I showed that the assumption of the ideal mixing is broken by a simple calculation, and by applying the asymmetric regular solution model for the three components mentioned above, I found that strong positive non-ideality appears when H2Om enters an environment with high O content.

Next, by using the above results to describe the equilibrium constant for the first dissolution reaction of water into melt (r1: H_2O_m (vapor) ⇔ H_2O_m (in melt)) and substituting it into the theoretical equation, I calculated the enthalpy change (i.e., the heat of dissolution of water into melt) for r1 in a wide range of temperatures and pressures. As a result, the heat of dissolution for r1 is about −20 kJ/mol regardless of the temperature and pressure, indicating that it is an exothermic reaction. By adding the heat of dissolution for the second reaction (r2: H_2O_m (in melt) + Si-O-Si ⇔ 2 Si-OH, endothermic), the heat of dissolution for the entire dissolution reaction can also be calculated over a wide temperature and pressure range. The results show a

shift toward endothermic at higher temperatures and toward exothermic at lower temperatures and higher pressures, but the magnitude of the shift is highly dependent on the previously estimated value of the heat of dissolution for r2, which varies depending on the method of measurement of the speciation of H_2O_m and OH.

Furthermore, based on these values, I numerically calculated the temperature change of hydrous rhyolitic melt with decompression-induced water vesiculation ascending a volcanic conduit, assuming it is the equilibrium degassing in a closed system. The results showed that the effects of the heat of exsolution of water from melt and the mechanical work of bubble expansion contributed to warming and cooling the system, respectively, and the sum of them resulted in slight cooling due to the relation of their magnitudes.

In the future, by combining the results of this study with the effect of latent heat of crystallization of magma and solving them simultaneously, it may be possible to construct a new conduit flow model with an enhanced material science aspect that incorporates temperature changes due to vesiculation and crystallization in magma.