

The making of drop calorimeter for measurement of heats of mixing of magmatic liquids

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Introduction

Enthalpy of silicate liquid is one of the fundamental physical properties for thermodynamic formulation of phase equilibria, element partitioning and element diffusion in magmatic systems. For a given temperature and composition, the enthalpy of liquid can be calculated from enthalpy of fusion of minerals and heat capacity and heats of mixing of liquids. The enthalpy of fusion of minerals and heat capacity of molten minerals has reported for two decades. In contrast, the heats of mixing and excess heat capacities of multicomponent silicate liquids are still poorly understood.

It is reported that the heats of mixing of pseudobinary silicate liquids are generally within ± 30 kJ/mol and mostly ± 5 - ± 10 kJ/mol (Sugawara, 2005b). Although the heats of mixing are only the size of 3-10% of enthalpies of fusion, those can affect liquidus temperatures of minerals by as much as ± 100 K (Sugawara and Akaogi, 2003; Sugawara, 2005a). The knowledges of compositional dependence of the heats of mixing also give insight into the understanding of structure and speciation of magmatic liquids (Navrotsky, 1995). Therefore, calorimetric measurements of the heats of mixing of silicate liquids are essential for quantitative and precise understanding of igneous processes.

Purpose of this study

Because of large errors in enthalpies by transposed-temperature drop calorimetry (± 15 kJ/mol; Sugawara and Akaogi, 2004) and compositional limit in differential scanning calorimetry (Sugawara and Akaogi, 2003), it is difficult to measure the small heats of mixing of liquids for wide ranges of composition by direct calorimetric measurements. The heats of mixing can also be determined by a combination of solution calorimetry of glass and drop calorimetry of liquid. This indirect technique can provides precise data of small excess enthalpy of liquid within ± 10 kJ/mol (Sugawara, 2005b).

The purposes of this study are to measure (1) excess heat capacities of silicate liquids (in the system Sa-Di, Ab-Fo and Jd-Di), (2) fictive temperatures of drop-quenched silicate liquids and (3) heat capacities of Fe²⁺-bearing silicate liquids (the system Di-Fa-An-Ab and Fo-Fa-Di-An-Ab-Sa) by drop calorimetry, and finally to determine the heats of mixing of magmatic silicate liquids as a function of temperature and composition based on a combination of the data by the drop calorimetry and the solution calorimetry.

The making of drop calorimeter

The author made the drop calorimeter to perform above measurements. The upper part of the calorimeter is a LaCrO₃ furnace, which can heat up to 2080 K. The lower part is a detector of an ice calorimeter made from pyrex vessels and copper block with fins for radiation. Calorimeter well and gates to prevent transfer of heat from furnace to the calorimeter are made of aluminum alloy. All metallic parts were formed by a lathe and a milling machine. The measurements are made by the drop of molten sample in an ice calorimeter under the argon or CO/CO₂ gas flow. The calorimeter apparatus and experimental technique are basically identical to those described by Richet et al. (1982). The first experimental data by this calorimeter will be reported in session.