Calorimetry of liquids in the system Na$_2$O-Fe$_2$O$_3$-SiO$_2$

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ABSTRACT

Transposed-temperature, drop-calorimetry measurements were performed in the systems Na$_2$SiO$_3$-Fe$_2$O$_3$-SiO$_2$ and Na$_2$SiO$_3$-NaFeSi$_2$O$_6$ at 1373 K to investigate thermodynamic properties of Fe$^{3+}$-bearing silicate liquids. The results confirm previously measured enthalpy of Na$_2$SiO$_3$ and SiO$_2$ melts. No significant heats of mixing were observed in the Na$_2$SiO$_3$-SiO$_2$ liquids or in peralkaline liquids in the system Na$_2$SiO$_3$-Fe$_2$O$_3$. The enthalpy of mixing of peralkaline liquids in the system Na$_2$SiO$_3$-Fe$_2$O$_3$-SiO$_2$ was less than the standard deviation of drop calorimetry (approx. ±10 kJ/mol). From calorimetric data of Na$_2$SiO$_3$-Fe$_2$O$_3$ liquids extrapolated to hematite composition and published heat capacity, the enthalpy of fusion of hematite is estimated to be 83.3 ± 10.5 kJ/mol at 1373 K and 133.4 ± 10.5 kJ/mol at its melting point 1895 K. The Fe$^{3+}$/Fe$^{2+}$ ratio of the liquid was estimated from thermodynamic calculations using the fusion enthalpy of hematite and published data of FeO and O$_2$, and reproduced measured Fe$^{3+}$/Fe$^{2+}$ ratios in natural silicate liquids and in CaO-Al$_2$O$_3$-Fe$_2$O$_3$-SiO$_2$ liquids. No significant heats of mixing were observed in the Na$_2$SiO$_3$-NaFeSi$_2$O$_6$ liquids. The enthalpy of formation of NaFeSi$_2$O$_6$ (acmite) at 1bar and 298 K calculated from calorimetric data is –2546.9 ± 17 kJ/mol. The enthalpy and entropy of fusion of acmite are estimated to be 70.5 ± 9.4 kJ/mol and 51.3 ± 6.8 J/K-mol, respectively, at metastable congruent melting point, 1373 K. The entropy of fusion of acmite is similar to that of NaAlSi$_2$O$_6$ (jadeite), indicating that Fe$^{3+}$ and Al$^{3+}$ have analogous structural roles in pyroxene melts.

INTRODUCTION

To formulate phase equilibria and element partitioning in silicate systems, many studies have attempted to calibrate the thermodynamic mixing properties of silicate liquid based on the published phase-equilibrium data and known thermodynamic properties of solid and liquid phases (e.g., Berman and Brown 1984; Ghiorso and Sack 1995; Holland and Powell 2001; Andersson et al. 2002). In those analyses, heats of fusion of end-member components are fundamental thermodynamic quantities to calculate enthalpy and entropy of liquids. Direct calorimetric measurements of multicomponent silicate liquids (Navrotsky et al. 1989; Tarina et al. 1994; DeYoreo et al. 1995; Sugawara and Akaogi 2003a) not only provide heats of fusion of solids and heats of mixing of liquids independent of phase equilibrium data, but also give insight into the physicochemical meaning of excess enthalpy of silicate liquids (Navrotsky 1997). Therefore, calorimetric measurements of silicate liquids are essential for quantitative and precise understanding of igneous processes.

The Fe contents and Fe$^{3+}$/Fe$^{2+}$ ratios of magmas affect their structural roles in pyroxene melts.

The oxygen fugacity of terrestrial magmas range between –3 to +5 log $f_{o_2}$ unit with respect to NNO [$\Delta$NNO = log $f_{o_2}$(sample)–log $f_{o_2}$(Ni-NiO buffer)] (Carmichael and Ghiorso 1990). Their liquid included much Fe$^{3+}$ as well as Fe$^{2+}$. For example, experimental results by Kress and Carmichael (1988) indicated that the Fe$_2$O$_3$ content of natural silicate liquid containing 11.1 wt% total FeO (MORB composition) is only 0.69 wt% at $\Delta$NNO = –3, whereas at $\Delta$NNO = +3.5, the Fe$_2$O$_3$ content increases to 7.18 wt%. The Fe$_2$O$_3$ is an important major component of magmatic liquids, however, direct enthalpy measurements for Fe$^{3+}$-bearing silicate liquids have not been performed. The reason for this lack of data is the experimental difficulty in carrying out high-temperature drop calorimetry for Fe-bearing silicate liquids. Although the Fe$^{3+}$/Fe$^{2+}$ ratio of silicate liquid increases with increasing oxygen fugacity, 10–50 wt% of the total Fe in liquids of natural composition and in the system CaO-Al$_2$O$_3$-FeO-SiO$_2$ (CAFS) still remains as FeO in air (Kilinc et al. 1983; Kress and Carmichael 1988, 1991). In calorimetric measurements for such liquids, starting compositions will be required in which the Fe$_2$O$_3$ and FeO contents are adjusted to an equilibrium Fe$^{3+}$/Fe$^{2+}$ ratio in a liquid state at given temperature, oxygen fugacity, and liquid composition. Furthermore, because calorimetric measurements...