A method for controlling alkali-metal oxide activities in one-atmosphere experiments and its application to measuring the relative activity coefficients of NaO$_{0.5}$ in silicate melts

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ABSTRACT

The activity of alkali metal oxides can be controlled in one-atmosphere wire-loop experiments at high temperature by suspending a crucible containing alkali silicate melt beneath the samples. The method has been applied to measuring the activity coefficient of NaO$_{0.5}$ in a series of CMAS-NaO$_{0.5}$ melts relative to that in the anorthite-diopside eutectic composition at 1400 °C, using a reservoir of NaO$_{0.5}$-SiO$_2$. The results show that this relative activity coefficient decreases strongly with SiO$_2$, increases with CaO and MgO, but is insensitive to AlO$_{1.5}$. This latter behavior is inconsistent with “quasi-crystalline” models of melt thermodynamics that hypothesize Na-Al species.

INTRODUCTION

A well-known problem afflicting high-temperature experiments at atmospheric pressure or under vacuum is loss of alkalis by volatilization (e.g., Donaldson et al. 1975; Donaldson 1979; Corrigan and Gibb 1979; Appora et al. 2003). In extreme cases of high temperatures, low $f_{O_2}$, small sample sizes, and long run times, the alkali elements may be lost almost entirely from the experimental charge (e.g., O’Neill and Mavrogenes 2002). The wire-loop method of suspending samples is particularly vulnerable to alkali loss (Donaldson et al. 1975), but such loss is also observed in stirred-crucible experiments (Ertel et al. 1997). Yet it is often also observed that intended alkali-free compositions become contaminated in one-atmosphere experiments from alkalis lost from previous experiments in the same furnace. Furthermore, alkalis often seem to exchange between wire-loop samples run adjacent to each other; for example, Appora et al. (2003, p. 465) reported that “glasses with initially different Na contents approach a common major-element composition (in some cases including increases of Na-poor glasses loaded adjacent to Na-rich glasses) over the course of an experiment, suggesting that Na is not only lost but also exchanged between adjacent melt drops.” In fact, the Na exchange between samples in an experiment appears to be quite remarkably quantitative, as the example shown in Figure 1 from my own work demonstrates.

Here I discuss a method of controlling alkali metal oxide activities in one-atmosphere experiments based on these observations. I have recently used the method to investigate the effects of NaO$_{0.5}$ on the solubilities of S in silicate melts at low $f_{O_2}$, extending previous work reported in O’Neill and Mavrogenes (2002), and on the activity coefficients of Ni and Co in CMAS-NaO$_{0.5}$ melts, extending the previous work on CaO-MgO-AlO$_{1.5}$-SiO$_2$ (CMAS) melts reported in O’Neill and Eggins (2002). These new results will be presented elsewhere; here, I showcase the method by reporting a preliminary investigation on how the activity coefficients of NaO$_{0.5}$ in silicate melts ($\gamma_{NaO_{0.5}}$) vary in the system CMAS at 1400 °C. Of particular interest is testing the hypothesis widely adopted in the geological literature that the thermodynamics of silicate melts can be modelled appropriately using components that reflect the stoichiometries of the crystals in equilibrium with the melts between their solidi and liquidi (the “quasi-crystalline” model; Hess 1977; Burnham 1981; Ghiorso and Sack 1995; Holland and Powell 2001). Alkali metals occur in common rock-forming minerals coupled with Al (e.g., for Na, some common components are NaAlSiO$_4$ in nepheline, NaAlSi$_2$O$_6$ in feldspar, and NaAl$_2$Si$_2$O$_6$ in clinopyroxene), which, in the quasi-crystalline hypothesis, implies Na-Al interactions in the melts. Thermodynamically, the formation of a complex between components in a silicate melt causes negative departures from ideal mixing (e.g., Navrotsky 1995; Hess 1995), hence the hypothetical Na-Al interactions should result in a decrease in the activity coefficient of NaO$_{0.5}$ as the Al$_{0.5}$ content in the melt increases, if the relative mole fractions of other components are held constant. This is readily tested with the method described here.

EXPERIMENTAL STRATEGY

The method has the virtue of being very simple and easy to implement. Typically, samples in one-atmosphere gas-mixing experiments are attached to wire loops (e.g., Donaldson et al. 1975); in my laboratory, the loops are then suspended, several at a time, from a “chandelier” made of thick Pt wire, as described in O’Neill and Mavrogenes (2002) and O’Neill and Eggins (2002). The control of NaO$_{0.5}$ activity is achieved by hanging an open Pt crucible containing a suitable composition on the join NaO$_{0.5}$-SiO$_2$ a few centimeters beneath the “chandelier.” Obviously any alkali oxide-silica mixture can be used as required (KO$_{0.5}$-SiO$_2$, NaO$_{0.5}$-KO$_{0.5}$-SiO$_2$, etc.). The crucible contains 5 to 10 g of melt, thus providing a reservoir of the alkali oxide that is 10$^2$ to 10$^3$ times that in the samples (which typically weigh <100 mg each). Alkali evaporates from the surface of the crucible [NaO$_{0.5}$ (reservoir) $\rightarrow$ Na(g) + 1/4 O$_2$], bathing the samples in alkali vapor, which dissolves in the samples [Na(g) + 1/4 O$_2$ $\rightarrow$ NaO$_{0.5}$ (sample)]. As implied by the data in Figure 1, the alkali loss out of the hot zone of the furnace is slow, and a time series...