

THERMODYNAMICS AND EVAPORATION KINETICS OF CAI-LIKE MELTS. R. A. Mendybaev¹, S. I. Shornikov², N. S. Jacobson³ and B. Kowalski³, ¹University of Chicago, Chicago, IL 60637 (ramendyb@uchicago.edu), ²Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow 119991, ³NASA Glenn Research Center, Cleveland, OH 44135.

Introduction: Coarse-grained igneous textures of Ca-, Al-rich inclusions (CAIs) suggest that precursors of such CAIs have experienced high-temperature melting events. Melting under the low-pressure conditions of the solar nebula would result in evaporation of moderately volatile elements and thus in chemical and mass-dependent isotopic fractionations that are recorded in CAIs. High-temperature vacuum evaporation experiments conducted in our lab (e.g., [1–4]) have reproduced the major chemical and isotopic features of natural CAIs and large experimental dataset is now available. Recently it was shown that evaporation of a CAI-like melt at 2×10^{-5} and 2×10^{-4} bars of H_2 [5–7] only affects evaporation kinetics of Mg and Si, while chemical evaporation trajectories and isotopic fractionations remain the same as in vacuum experiments. The results imply that the extensive experimental database from vacuum experiments can be safely used to model evaporation of CAI precursors in low-pressure H_2 gas of solar nebula.

The next logical step is to develop an accurate thermodynamic model to quantitatively describe the evaporation process of any composition melt, including chondrule-like, at given P - T conditions. Several such attempts have been already made using Berman's CMAS model or its combination with the MELTS code [8–10]. The evaporation process can be described by the Hertz-Knudsen equation. The chemical evolution of a CAI-like CMAS (CaO-MgO- Al_2O_3 - SiO_2) melt during evaporation at a given temperature is controlled by relative evaporative fluxes of moderately volatile Mg and Si (refractory Ca and Al remain in the melt until near-complete evaporation of Mg and Si or crystallization of refractory phases):

$$\frac{J_{SiO}}{J_{Mg}} = \frac{\gamma_{SiO} P_{SiO}}{\gamma_{Mg} P_{Mg}} \sqrt{\frac{m_{Mg}}{m_{SiO}}}, \quad (1)$$

where J_i , γ_i , P_i and m_i are the evaporative flux, evaporation coefficient, equilibrium vapor pressure over the melt and molar mass of i , respectively. Thus to model the evaporation process thermodynamically, γ_i and thermodynamic activities of melt components a_i (to calculate P_i) must be known. It is clear that the calculated values of a_i strongly depend on choice of thermochemical data and their treatment by the model used in calculations. The accuracy of the models can be tested by comparing the calculated a_i s with the experimentally measured ones. However, no such measurements are available for CAI-like compositions.

At this point, the way to test an accuracy of thermodynamic models in predicting chemical evaporation trajectories is to compare the results of calculations with experimentally obtained ones. Below we provide the results of such testing. We also report our preliminary results for experimentally determined γ_{Si} for molten SiO_2 .

Results: Figure 1a (from [1]) shows that when CMAS model [11] is used to model evaporation of Type B CAI-like (CAIB) melilitic melt, a strong temperature effect on chemical evaporation profiles (lines) is expected when $\gamma_{Mg}/\gamma_{Si} = 0.74$ is used in calculations. On the contrary, a very weak temperature effect was observed in experiments (symbols). To fit experimental profiles, different γ_{Mg} and γ_{Si} at different temperatures are required: $\gamma_{Mg} = 0.18$ and $\gamma_{Si} = 0.16$ at $1900^\circ C$, $\gamma_{Mg} = \gamma_{Si} \sim 0.13$ at $1800^\circ C$, and $\gamma_{Mg} = 0.06$ and $\gamma_{Si} = 0.07$ at $1600^\circ C$ [1]. In the case of forsteritic melts, $\gamma_{Si}/\gamma_{Mg} \sim 2.1$ at $1900^\circ C$ was used to fit the experimental data [4]. The cause of variations of γ_i s remains unclear.

We recently started testing the thermodynamic model of Shornikov [12] which is based on the theory of ideal associated solutions (IAS) and uses experimental data on activities of melt components in CaO-MgO-FeO- Al_2O_3 - TiO_2 - SiO_2 system directly determined by Knudsen effusion mass spectrometry. Figure 1b shows the calculated evaporation profiles for the same CAIB melt. In accord with experiments the model predicts a weak temperature effect on evaporation, although the calculated profiles plot slightly above (within 5 wt% SiO_2) the experimental ones ($\gamma_{Si}/\gamma_{Mg} = 1$ was assumed in the calculations). Figure 2 compares evaporation trajectories for different composition melts and illustrates that calculated trajectories reproduce experimental ones for CAI4 and 5aN melts, but plot systematically above the experimental ones for CAIB and CMS1 melts, again assuming $\gamma_{Si}/\gamma_{Mg} = 1$.

Evaporation coefficients of Mg and Si are unknowns in Eqn. (1), along with a_i s, required to describe evaporation process thermodynamically. The method of determining γ_i s by fitting experimental profiles works only if thermodynamic properties of a melt are accurately known. This normally is the case for metals and simple oxide melts (e.g., molten SiO_2 or Al_2O_3). However, it might not work for silicate melts with poorly constrained a_i 's. This implies that γ_{SiO} and γ_{Mg} obtained by fitting the experimental data are not true evaporation coefficients, and as a such the values cannot be used to model evaporation of different composition melts.

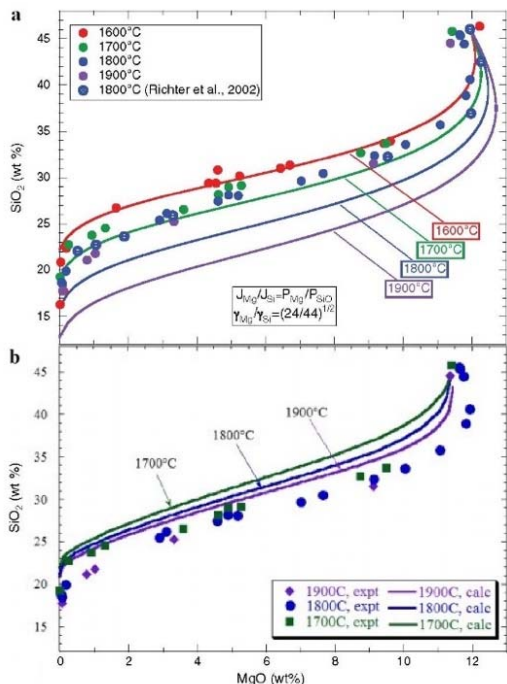


Fig. 1. Experimental (symbols) and calculated (lines) evaporation profiles for Type B CAI-like melt at different temperatures: (a) calculated using [11] with $\gamma_{\text{Mg}}/\gamma_{\text{SiO}_2} = 0.74$ (from [1]); (b) calculated using [12] with $\gamma_{\text{Mg}} = \gamma_{\text{SiO}_2} = 1$.

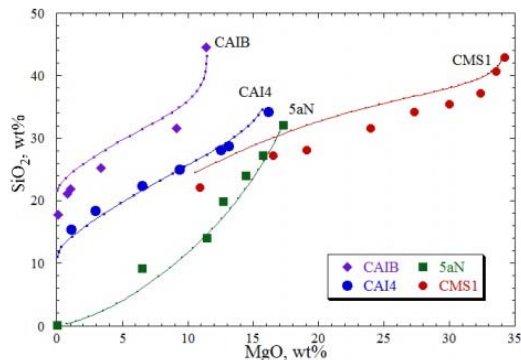


Fig. 2. Experimental and thermodynamically calculated evaporation profiles for different composition melts at 1900°C. $\gamma_{\text{Mg}} = \gamma_{\text{SiO}_2} = 1$ was used in the calculations.

The proper way of determining true evaporation coefficients is by comparing free-surface (Langmuir) and equilibrium (Knudsen) evaporation fluxes: $\gamma_i = J_{i,\text{free}} / J_{i,\text{eq}}$. To determine $J_{i,\text{free}}$ and $J_{i,\text{eq}}$ we used vacuum thermogravimetric apparatus (TGA) at NASA Glenn Research Center (see [13] for details of the apparatus). As a starting material in Langmuir experiments we used SiO_2 powder (99.995 % pure) with 1 wt% of ultrafine-grained Ir metal that was loaded onto 2.5 mm diameter Ir-wire loop; an Ir cell with 1 mm diameter orifice loaded with pure SiO_2 or $\text{SiO}_2 + 1$ wt% Ir was used to measure the equilibrium flux. The experiments were con-

ducted at 1800°C in a high-temperature vacuum furnace at total pressure of 5×10^{-6} torr or less; temperature was controlled by W5Re/W26Re thermocouple located next to the sample or sample assembly; weight of the assembly was monitored by a recording microbalance every 6 sec. The result of a typical TGA experiment using the loop technique is shown in Fig. 3. The figure shows linear weight loss of SiO_2 with time with evaporation rate of $0.3 \text{ mg/mm}^2\text{-hr}$. When SiO_2 loaded into Ir-cell was evaporated under the same conditions, the weight loss with time was also linear, but the measured evaporation rate was $6.8 \text{ mg/mm}^2\text{-hr}$. The measured $J_{i,\text{free}}$ and $J_{i,\text{eq}}$ results in $\gamma_{\text{Si}} \sim 0.04$ which is close to the values obtained for crystalline SiO_2 ([13] and references therein).

Future work: To test possible effects of melt structure on evaporation coefficient of SiO_2 , we will conduct the same experiments using molten gehlenite and anorthite. After determining γ_{Si} for Mg-free silicate melts, we will evaporate several CMAS melts to determine γ_{Mg} . We will also experimentally measure activities of components in the same silicate melt. Experimentally measured γ_{iS} and a_{iS} will be used to test and optimize available thermodynamic models of evaporation of CAI-like CMAS melts.

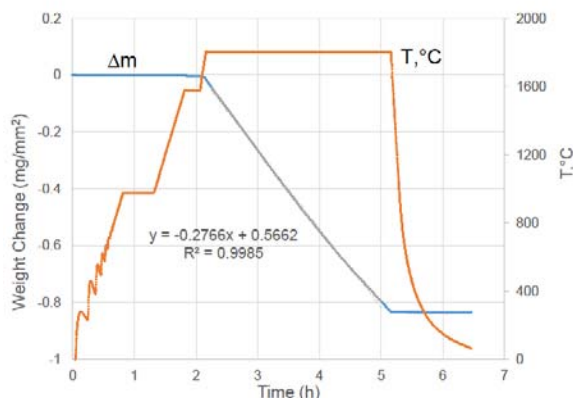


Fig. 3. Weight loss of SiO_2 (blue) and temperature schedule (orange) in a typical free-surface TGA run.

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