

THE EFFECT OF SAMPLE SIZE ON EXPERIMENTAL EVAPORATION OF TYPE B CAIs. R.A. Mendybaev¹, A.M. Davis^{1,2}, and F.M. Richter¹. ¹Department of the Geophysical Sciences, ²Enrico Fermi Institute, University of Chicago, Chicago, IL 60637 (ramendyb@midway.uchicago.edu)

Introduction: Ca-Al-rich inclusions (CAIs) from CV3 chondrites are often found to be enriched in the heavy isotopes of Si and Mg (e.g., [1]), which is usually interpreted as resulting from the partial evaporation of the more volatile components of the CAIs during a high temperature, partially molten stage. Because of this, evaporation of Ca-Al-rich melts as well as high temperature minerals and mineral assemblages have been extensively studied experimentally (e.g., [2-7]). In the case of Type B CAI-like melts, evaporation in vacuum and in H₂ results in losses of Si and Mg relative to the much less volatile Al and Ca, and also enrichment of the evaporation residues in the heavy isotopes of Mg. This enrichment follows a Rayleigh fractionation curve (i.e., $R/R_0 = f^{(\alpha-1)}$, where R is the isotopic ratio, initially R_0 , f is the fraction of the evaporating species remaining in the residue, and α is the gas-melt isotopic fractionation factor). However, the Mg isotope fractionation factor found in experiments is noticeably closer to one ($\alpha=0.989$ and 0.987 in vacuum and $P_{H_2} \sim 2 \times 10^{-4}$ bar, respectively) than the theoretically expected value ($\alpha = \sqrt{24/25} = 0.980$). Similar departures from the theoretically expected fractionation were observed for evaporation of forsterite [3, 6]. This discrepancy between the measured and the theoretically expected fractionation could be due to diffusion not being sufficiently fast to maintain homogeneity of the melt during evaporation. A more likely explanation is recondensation which will occur whenever the pressure of the evaporating species at the evaporating surface becomes a significant fraction of the saturation vapor pressure. When this is the case, the evaporation rate and fractionation factors measured in samples evaporated in a system with finite conductance should vary with sample size and temperature. This is because at finite conductance the pressure in the vicinity of the sample should be proportional to the total flux, which increases in proportion to the sample surface area at fixed temperature, and with temperature at fixed surface area. Richter et al. [7] reported on experiments showing that the Mg isotopic fractionation of residues from experiments on CAI-like liquids evaporated in a special low-pressure hydrogen furnace ($T=1500^\circ\text{C}$, $P_{H_2} \sim 2 \times 10^{-4}$ bar) involved a kinetic fractionation with $\alpha=0.987$, independent of sample size. That seemed to cast some doubt on the idea that the departures from the theoretical fractionation factor were due to either recondensation or to chemical and isotopic inhomogeneity of the evaporating sample due to insufficiently

fast diffusion. Here we present the results of a larger set of experiments aimed at determining the effect, if any, of sample size and temperature on the evaporation rate and isotopic fractionation of Type B CAI-like liquids in vacuum.

Experimental methods: The experiments were conducted in a high-vacuum ($P \leq 10^{-6}$ torr) furnace at 1800° , 1700° and 1600°C . As a starting material we used B133-glass (12.0 wt% MgO, 46.1 wt% SiO₂, 19.4 wt% Al₂O₃ and 25.5 wt% CaO) suspended on Ir-wire loops of 1.0, 2.5, 3.3 and 6.0 mm in diameter. The initial surface area of these samples varied from about 3.5 to 85 mm². Details of the furnace configuration and sample preparation procedure are given in [4]. We used a JEOL JSM-5800LV scanning electron microscope with an Oxford/Link ISIS-300 x-ray microanalysis system to determine the chemical composition of the starting materials and run products, and a modified AEI IM-20 ion microprobe to measure Mg isotopic composition.

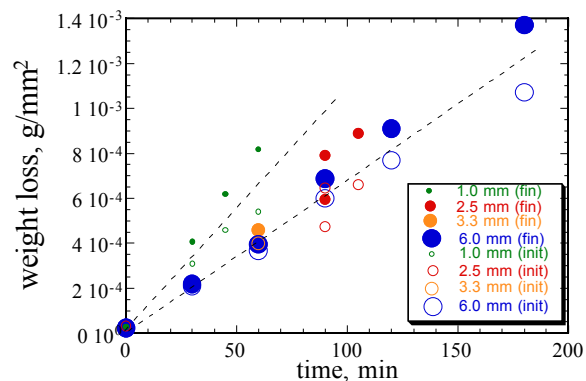


Fig. 1. Weight loss of B-133R samples at 1800°C normalized to the initial (open symbols) and final (closed symbols) surface area. Sample size refers to the diameter.

Results and discussion: Fig. 1 shows weight loss normalized by the initial and final surface area of the experimental charges. Comparing the composition of the evaporation residues to the starting composition shows that the weight loss is caused by loss of Mg and Si, not Ca or Al. The rate of weight loss from the 2.5, 3.3 and 6.0 mm diameter samples evaporated at 1800°C are not resolvable different from each other. The average for these samples is $(6.8 \pm 0.8) \times 10^{-6}$ g/mm²/min. The rate of mass loss from the 1.0 mm diameter samples is about 50% higher, averaging $(1.1 \pm 0.2) \times 10^{-5}$ g/mm²/min. Smaller samples are ex-

pected to have larger evaporation rates if recondensation is playing a significant role, but the dependence should be linear as a function of sample surface area, and thus the similarity of evaporation rate among the other samples ranging in area from $\sim 15 \text{ mm}^2$ to $\sim 80 \text{ mm}^2$ (see Fig. 2) would seem to argue against recondensation being important for these larger samples where the effects should be most obvious. We also note that the smaller the sample size, the larger the potential error in our ability to determine the surface area. It is quite possible that we are systematically underestimating the actual evaporating surface area of the 1.0 mm samples if the melt wets and covers the entire surface of the Ir wire loop.

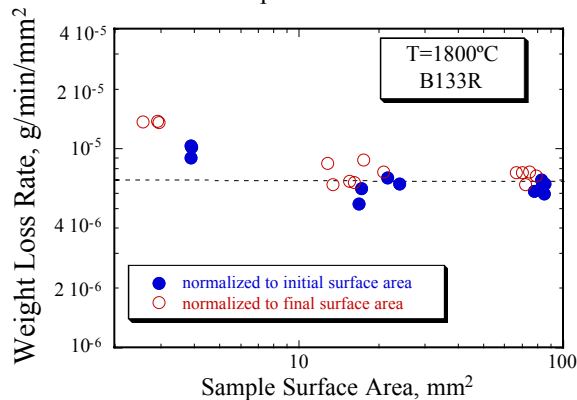


Fig. 2. Weight loss rate vs. sample surface area.

An alternative to using surface area to change the net evaporation rate is to vary the temperature at which the evaporation takes place. Experiments run at different temperatures also allow us to determine the apparent activation energy of evaporation of CAI-like melts. The weight loss rates of 1.0 mm samples evaporated at 1800°C, 1700°C and 1600°C are $\sim 1.1 \times 10^{-5}$, $\sim 2 \times 10^{-6}$ and $\sim 3 \times 10^{-7} \text{ g/mm}^2/\text{min}$, respectively, which corresponds to an apparent activation energy of evaporation $E_a = 580 \text{ kJ/mole}$, which is close to the value of $628 \pm 16 \text{ kJ/mole}$ reported for evaporation of single crystal forsterite [4] and is indistinguishable from $584 \pm 28 \text{ kJ/mole}$ calculated from the results on evaporation of polycrystalline forsterite [3].

Ion microprobe measurements confirm what has been seen several times before, that evaporation of molten samples produces residues enriched in the heavy isotopes of the evaporating species. Fig. 3 shows that regardless of sample size, the Mg isotopic fractionations of the evaporation residues from our experiments form a linear trend in a plot of $\ln(R/R_0)$ vs. $-\ln f$ where R/R_0 is the $^{25}\text{Mg}/^{24}\text{Mg}$ ratio measured in the residue divided by that of the starting composition and f is the fraction Mg remaining. Rayleigh fractionation produces a linear trend with slope $1-\alpha$. The linear trend of the data in Fig. 3 can be reasonably well

fit by a fractionation factor of $\alpha=0.987$ with no apparent distinction as to sample size. Our results, both in terms of the magnitude of the fractionation factor and its lack of dependence on sample size, are very similar to those of Richter et al. [7] for residues from experiments run at $P_{\text{H}_2} \sim 2 \times 10^{-4} \text{ bar}$ and 1500°C. If significant recondensation takes place during evaporation experiments of CAI-like liquids one would expect the fractionation factor to vary systematically with sample size and approach the theoretically expected value for fractionation of ^{24}Mg from ^{25}Mg ($\alpha=0.980$) as sample size approaches zero. Fig. 3 shows no evidence of such a trend, from which we conclude that recondensation is not the reason the kinetic fractionation factor for Mg isotopes during evaporation as measured by us in two different furnaces and under different conditions is not the commonly expected value.

We are starting to take seriously the possibility that departures from the theoretically expected fractionation of isotopes by evaporation may not be experimental artifacts, and may in fact be the behavior even when the ideal conditions assumed in theory are realized.

References: [1] Clayton et al. (1988) *Phil. Trans. Roy. Soc. Lon.* A325, 483-501. [2] Davis A.M. et al. (1990) *Nature*, **347**, 655-658. [3] Hashimoto A. (1990) *Nature*, **347**, 53-55. [4] Wang J. (1994) Ph.D. thesis, University of Chicago. [5] Nagahara H. and Ozawa K. (1996) *GCA*, **60**, 1445-1459. [6] Tsuchiyama A. et al. (1999) *GCA*, **63**, 2451-2466. [7] Richter F.M. (2002) *GCA*, in press.

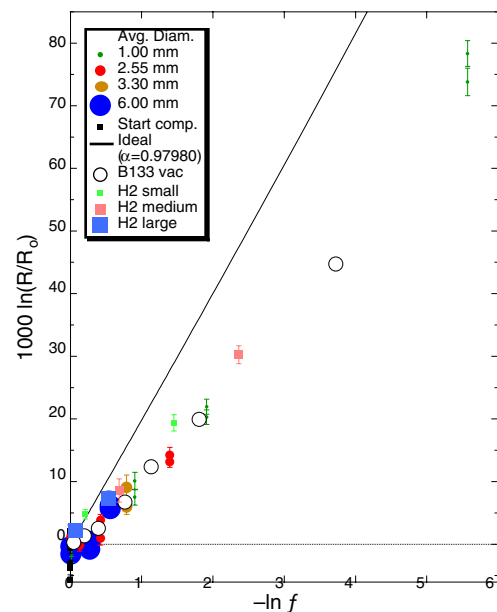


Fig. 3. Mg isotopic fractionation vs. fraction Mg remaining.