

EVAPORATION KINETICS OF CAI-LIKE MELTS IN LOW-PRESSURE HYDROGEN GAS AND IN VACUUM: SIMILARITIES AND DIFFERENCES. M. Kamibayashi¹, R. A. Mendybaev^{2,3}, F. M. Richter^{2,3} and S. Tachibana^{1,4}. ¹Department of Natural History Sciences, Hokkaido University, Sapporo 060-0810, Japan (michiru@ep.sci.hokudai.ac.jp); ²Department of the Geophysical Sciences, ³Center for Cosmochemistry, University of Chicago, Chicago, IL 60637, USA; ⁴UTokyo Organization for Planetary and Space Science (UTOPS), University of Tokyo, Tokyo 113-0033, Japan.

Introduction: Coarse-grained igneous texture and strong enrichments in heavy magnesium, silicon and oxygen isotopes observed in some calcium-, aluminum-rich inclusions (CAIs) indicate that the CAI precursors have experienced highly energetic heating events that resulted in their melting and evaporation of moderately volatile elements and their associated isotopic fractionations. Extensive laboratory study have been conducted to reproduce chemical and isotopic signatures of the CAIs by evaporating CAI-like melts at high temperatures in vacuum (e.g., [1–5]). Despite the fact that the experiments successfully reproduce the major chemical and isotopic features of “normal” and FUN CAIs, an important concern was whether vacuum experiments adequately describe evaporation of CAI-like melts under low-pressure hydrogen conditions of the solar nebula. Richter et al. [2] evaporated CAI-like melt at 1500°C and $P_{H_2}=2\times 10^{-4}$ bar and showed that evaporation kinetics of Si and Mg is ~100 times faster than expected in vacuum. No direct comparison with vacuum experiments has been made due to very slow evaporation rates at 1500°C in vacuum. Here for the first time we report the results of the study on evaporation kinetics of Mg and Si from the same CAI-like melt that was evaporated at the same temperature (1600°C) in vacuum ($<10^{-7}$ bar) and in low-pressure H_2 gas (1.6×10^{-4} bar). Isotopic fractionation of Mg and Si in these evaporation experiments are reported in a companion abstract by Mendybaev et al. [6].

Experimental: As a starting material we used a composition (15.7 wt% MgO, 36.6 wt% SiO₂, 26.5 wt% Al₂O₃, 21.2 wt% CaO, labeled as CAI4B2) close to those of non-FUN forsterite-bearing CAIs of [7].

Low-pressure hydrogen experiments were conducted at Hokkaido University using premelted (at 1550°C in air) samples on a 0.25 mm diameter Ir-wire loop. The furnace with a sample was evacuated to better than 10^{-9} bar, preheated at 500°C for ~1 hr and after pressure in the chamber decreased below 10^{-9} bar, the sample was heated to 1600°C at ~20°C/min. After 5 min at 1600°C in vacuum, H_2 gas was introduced into the furnace at controlled flow rate such that pressure in the chamber was kept constant at 1.6×10^{-4} bar. After heating for a predetermined time period the sample was quenched by turning power off.

Vacuum evaporation experiments were conducted

at the University of Chicago using the same experimental protocol as in [2–5].

Weight and surface geometry of the samples were measured before and after each experiment. Texture and chemical composition of the evaporation residues were studied using a TESCAN LYRA3 FIB/FESEM with an Oxford AZtec x-ray microanalysis system.

Results: Run durations, chemical composition of the evaporation residues and the calculated evaporation rates of Mg and Si are presented in the table below.

Sample	time min	MgO wt%	SiO ₂ wt%	Al ₂ O ₃ wt%	CaO wt%	Mg lost mole %	Si lost mole %	J_{Mg} mol cm ⁻² s ⁻¹	J_{Si} mol cm ⁻² s ⁻¹
<i>low P_{H2} experiments</i>									
B2-1	0	15.71	36.58	26.52	21.19	0.2			
B2-2	3	15.37	35.17	27.62	21.85	4.6	6.3	9.7E-08	2.0E-07
B2-16	10	14.66	33.54	28.90	22.90	13.6	15.1	1.2E-07	2.1E-07
B2-12	20	12.62	31.44	30.99	24.96	31.2	26.4	1.3E-07	1.8E-7
B2-3	30	3.24	22.15	42.32	32.28	86.5	68.4	2.0E-07	2.2E-07
B2-14	35	9.42	28.89	34.16	27.53	52.9	38.0	1.4E-07	1.6E-07
B2-10	45	5.54	25.35	38.06	31.06	75.7	52.3	1.6E-07	1.7E-07
B2-4	60	0.02	0.73	63.03	36.22	99.9	99.1	1.3E-07	1.9E-07
<i>vacuum experiments</i>									
B2-25	300	14.35	34.00	27.92	23.72	16.0	14.5	3.7E-09	5.2E-09
B2-22	600	12.76	32.13	30.01	25.10	29.2	23.4	3.7E-09	4.6E-09
B2-21	1200	7.87	27.92	35.47	28.74	63.2	44.0	3.6E-09	3.9E-09
B2-23	1700	4.02	23.75	40.1	32.13	83.1	57.0	4.1E-09	4.4E-09
B2-20	1800	0.09	9.40	50.6	39.90	99.7	86.6	3.9E-09	5.4E-09
B2-24	2100	3.40	22.89	41.27	32.44	85.9	59.2	3.7E-09	4.0E-09
B2-18	2400	0.00	13.59	48.01	38.40	100.0	79.2	3.2E-09	3.9E-09

The typical textures of run products are shown in Fig. 1: most evaporation residues appear as clear glasses (Fig. 1a) except for the most evaporated samples that quenched into intergrowth of åkermanitic melilite plus glass (Fig. 1b) or into CaAl₂O₄ (Fig. 1c).

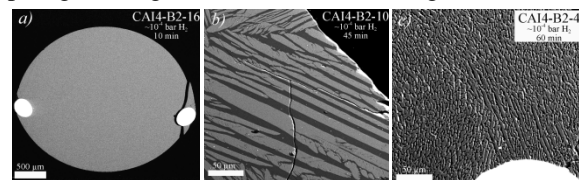


Fig. 1. Typical textures of CAI4B2 residues: a) clear glass CAI4B2-16; b) CAI4B2-10 quenched into intergrowth of åkermanitic melilite (light) plus glass (dark); c) CAI4B2-4 quenched into CaAl₂O₄.

Evaporation fluxes of Mg and Si were obtained by taking into account the initial and final weights and surface areas of a sample calculated assuming that molten droplets are spheroids with axis equal to a diameter of Ir-wire loop and to a thickness of the droplet. Corrections for size of the droplets at 1600°C were made using density-composition-temperature relationships of [8].

The table shows that Si in low-pressure H_2 experiments at 1600°C evaporate by ~35% faster than Mg:

$J_{Mg} \sim 1.4 \times 10^{-7}$ and $J_{Si} \sim 1.9 \times 10^{-7}$ moles/cm²/s. Evaporation rates of Si and Mg in vacuum experiments ($J_{Mg} \sim 3.8 \times 10^{-9}$ and $J_{Si} \sim 4.6 \times 10^{-9}$ moles/cm²/s) are about 40 times slower than in vacuum. Figure 2 shows that despite different evaporation rates of Si and Mg under the different conditions, their evaporation trajectories are the same. Compositions of most evaporation residues (excluding the most evaporated sample with MgO < 0.1 wt%) in Fig. 2 plot along a line with the same slope of ~ 1.4 .

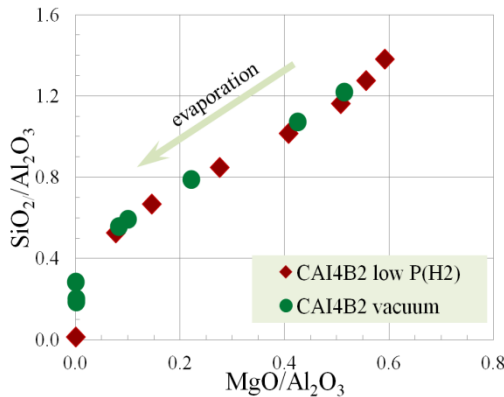


Fig. 2. Evaporation trajectories of CAI4B2 in low-pressure H₂ and in vacuum experiments at 1600°C.

Discussion: Figure 3 compares evaporation rates of Mg and Si from CAI4B2 melt in vacuum and in low-pressure H₂ at 1600°C with those of previous works with CAI-like melts [2-3]. The Figure shows that for all compositions studied (except for BCAI melt evaporated at P_{H2} = 2 × 10⁻⁴ bar at 1500°C [2]) Si evaporates somewhat faster than Mg. The reason for faster evaporation of Mg compared to Si from BCAI melt most likely is due to melt composition: starting BCAI melt is forsteritic, while all other melts are anorthitic or melilitic in composition.

Vacuum evaporation rate of Mg determined in this study is slightly higher than that for CAIB melt at 1600°C [3], but are in good agreement with extrapolation from higher temperatures [3].

The evaporation rates of Mg and Si at 1600°C in low-pressure H₂ (1.6 × 10⁻⁴ bar) are ~ 40 times larger than those in vacuum, while those at 1500°C and 1.8 × 10⁻⁴ bar were calculated to be ~ 100 times larger than in vacuum [2]. Mg evaporation rate measured in our experiments is consistent with the extrapolated value from [2], which calculated the evaporation rates of Mg from CAI-like melt at 1500–1300°C when the evaporation coefficient of ~ 0.07 was adapted. The evaporation coefficient of ~ 0.07 is also consistent with those reported in vacuum experiments [2, 3].

The difference in evaporation rates in vacuum and in low-pressure hydrogen can be explained by the increase in the equilibrium vapor pressures of Mg and Si

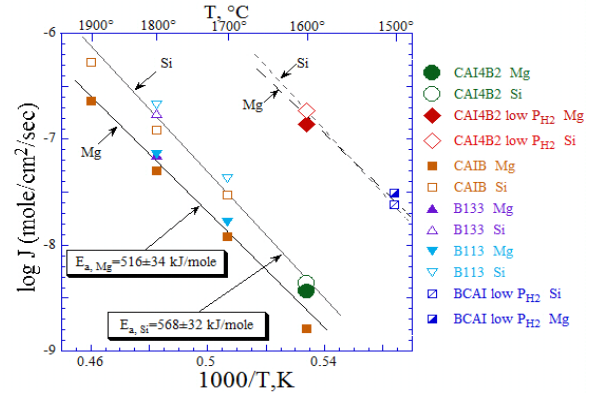


Fig. 3. Evaporation rates of Mg (closed symbols) and Si (open symbols): CAI4B2 – this work; CAIB – from [3]; B133, B113, BCAI – from [2].

when H₂ is present. While hydrogen promotes much faster evaporation of Mg and Si from CAI-like melts, it does not change the evaporation trajectory.

Using all available data on evaporation rates of Mg and Si from CAI-like melts (Fig. 3), we determined activation energies $E_{a,Mg} = 516 \pm 34$ kJ/mole and $E_{a,Si} = 568 \pm 32$ kJ/mole for vacuum evaporation. These activation energies also fit experimentally determined evaporation rates at P_{H2} $\sim 2 \times 10^{-4}$ bar at 1500°C and 1600°C (dashed lines in Fig. 3).

Conclusions: 1) Evaporation at 1600°C in low pressure H₂ (1.6 × 10⁻⁴ bar) is faster than in vacuum, as expected; 2) chemical evaporation trends in low-pressure H₂ and in vacuum are the same; 3) the evaporation rates of Mg and Si from molten CAI-like liquids can be expressed as $J_i = J_{0i} e^{-E_{RT}}$ with, in case of vacuum evaporation, $J_{0Mg} = 6.0 \times 10^5$ mol/cm²/s, $J_{0Si} = 3.4 \times 10^7$ mol/cm²/s and activation energies of 516 ± 34 kJ/mol for Mg and 568 ± 32 kJ/mol for Si. To model evaporation under more realistic solar nebula pressure of P_{H2} $\sim 2 \times 10^{-4}$ bar, $J_{0Mg} = 3.5 \times 10^7$ mol/cm²/s and $J_{0Si} = 1.3 \times 10^9$ mol/cm²/s should be used. For other compositions and other hydrogen pressures the values of J_{0i} are proportional to their vapor pressure that can be calculated by thermodynamic modeling as described in [9].

References: [1] Davis A. M. et al. (1990) *Nature*, 347, 655–658; [2] Richter F. M. et al. (2002) *GCA*, 66, 521–540; [3] Richter F. M. et al. (2007) *GCA*, 71, 5544–5564; [4] Mendybaev R. A. et al. (2013) *LPSC 44th*, Abstract #3017; [5] Mendybaev R. A. et al. (2017) *GCA*, 201, 49–64; [6] Mendybaev R. A. et al. (2018) *LPSC 49th* (this volume); [7] Bullock E. S. et al (2012) *Meteoritics*, 47, 2128–2147; [8] Lange R. A. and Carmichael I. S. (1987) *GCA*, 51, 2931–2946; [9] Grossman L. et al. (2000) *GCA*, 64, 2879–2894.