

## MAGNESIUM ISOTOPIC FRACTIONATION DURING EVAPORATION OF CAI-LIKE MELTS IN LOW-PRESSURE HYDROGEN GAS AND IN VACUUM: SIMILARITIES AND DIFFERENCES.

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**Introduction:** The coarse-grained igneous texture of Type B and compact Type A CAIs suggest that their precursors have experienced high-temperature melting event followed by slow cooling. The melting also resulted in evaporation of moderately volatile elements as indicated by their enrichments in heavy Mg and Si isotopes of up to several ‰ in “normal” CAIs, and up to ~40‰ in  $\delta^{25}\text{Mg}$  and ~15‰ in  $\delta^{29}\text{Si}$  in highly fractionated FUN and Type F CAIs (e.g., [1–2]). The observed isotopic fractionations have been successfully reproduced in vacuum evaporation experiments (e.g., [3–7]). However, it remains unclear if vacuum experiments adequately describe the evaporation process under low-pressure hydrogen conditions of solar nebula. It is known that evaporation kinetics in  $\text{H}_2$ -rich gas is much faster than in vacuum (e.g., [4]), but very little is known about the effects on isotopic fractionations. By measuring Mg isotopic composition of evaporation residues from a limited set of experiments at  $P_{\text{H}_2}=2\times 10^{-4}$  bar and 1500°C using the old AEI IM-20 ion microprobe at the University of Chicago, it was shown [4] that the obtained Mg isotopic fractionation factor  $\alpha_{25,24}=0.98689\pm 0.00071$  is different from the often-assumed  $\alpha_{25,24}=\sqrt{24/25}=0.97980$  and closer to the ones from vacuum experiments. The values of  $\alpha_{25,24}$  for vacuum evaporation have been since significantly improved by use of modern analytical instruments [5–7], but no new experiments have been conducted in low-pressure  $\text{H}_2$  gas.

The purpose of this work was to produce new data on evaporation of CAI-like melts in low-pressure  $\text{H}_2$  gas and compare the chemical and isotopic fractionation trends with those from vacuum experiments. The results of the study on evaporation kinetics are reported in a companion abstract by Kamibayashi et al. [8]. Here we discuss if evaporation under such different conditions affects the isotopic fractionation of Mg.

**Experimental:** As a starting material in the experiments we used CAI4B2 composition, close to those of non-FUN forsterite-bearing CAIs. As there is no measurable chemical and isotopic fractionation in runs a few minutes long at 1600°C in vacuum [5], we considered CAI4B2-1 (see Table) as starting material. Low-pressure  $\text{H}_2$  evaporation experiments were conducted at

Hokkaido University. After premelting in 1 atm air the samples were heated in vacuum at 1600°C for 5 minutes followed by continued heating at 1600°C and  $P_{\text{H}_2}=2\times 10^{-4}$  bar (see [8] for details). Vacuum experiments were conducted at the University of Chicago using the same protocol as in [5–7].

Texture and chemical composition of the evaporation residues was studied with a TESCAN LYRA3 FIB/FESEM equipped with an Oxford AZtec x-ray microanalysis system. We used the solution technique to measure Mg isotopic composition with a Nu Plasma II [9].

**Results and Discussion:** Chemical composition of the evaporation residues and their isotopic composition of Mg (relative to DSM3) are shown in the Table below. Despite faster evaporation of Mg and Si (by ~40×) at  $P_{\text{H}_2}=2\times 10^{-4}$  bar compared to in vacuum, their evaporation trajectories remain the same as illustrated in Fig. 1.

Sample	time, min	MgO wt%	SiO <sub>2</sub> wt%	Al <sub>2</sub> O <sub>3</sub> wt%	CaO wt%	$\delta^{25}\text{Mg}$ ‰	$\delta^{26}\text{Mg}$ ‰
<i>low P<sub>H2</sub> experiments</i>							
CAI4B2-2	3	15.37	35.17	27.62	21.85	-0.97	-1.90
CAI4B2-16	10	14.66	33.54	28.90	22.90	0.04	0.06
CAI4B2-12	20	12.62	31.44	30.99	24.96	2.76	5.42
CAI4B2-3	30	3.24	22.15	42.32	32.28	19.70	38.89
CAI4B2-14	35	9.42	28.89	34.16	27.53	7.18	14.09
CAI4B2-10	45	5.54	25.35	38.06	31.06	15.12	29.81
CAI4B2-4	60	0.02	0.73	63.03	36.22		
<i>vacuum experiments</i>							
CAI4B2-1	5	15.71	36.58	26.52	21.19	-1.66	-3.21
CAI4B2-25	300	14.35	34.00	27.92	23.72		
CAI4B2-22	600	12.76	32.13	30.01	25.10		
CAI4B2-21	1200	7.87	27.92	35.47	28.74		
CAI4B2-23	1700	4.02	23.75	40.1	32.13		
CAI4B2-20	1800	0.09	9.40	50.6	39.90		
CAI4B2-24	2100	3.40	22.89	41.27	32.44		
CAI4B2-18	2400	0.00	13.59	48.01	38.40		
CAI4B2-19	3300	0.08	9.89	49.65	40.38		

Figure 2 shows Mg isotopic composition of CAI4B2 residues, expressed as  $1000\times \ln(R/R_0)$ , where R is  $^{24}\text{Mg}/^{25}\text{Mg}$  in a sample and  $R_0$  is their ratio in the starting material, versus a fraction of  $^{24}\text{Mg}$  remaining in the residues, expressed as  $\ln(f^{24}\text{Mg})$ . Figure 2 shows that all samples evaporated at  $2\times 10^{-4}$  bar  $\text{H}_2$ , except for CAI4B2-10, plot on a line with slope of  $11.825\pm 0.0931$  which results in Mg isotopic fractionation factors  $\alpha_{25,24}=0.98818\pm 0.00009$  exactly the same as  $\alpha_{25,24}=0.98822\pm 0.00010$  for CAIB melt evaporated at 1600°C in vacuum [5]. CAI4B2-10 appears as an intergrowth of elongated crystals of gehlenitic melilite (Åk~10), that most likely were crystallized during the run, and glass (Fig. 1b in [8]), while all other samples were quenched

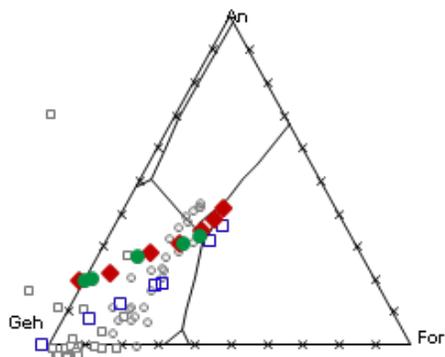


Fig. 1. Evaporation trajectories of CAI4B2 at  $2 \times 10^{-4}$  bar  $H_2$  (red diamonds) and in vacuum experiments (green circles) at  $1600^\circ\text{C}$  and  $1900^\circ\text{C}$  (open blue squares) [10]. Small grey symbols show compositions of Type B and Type A CAIs.

to clear glasses. It seems possible that some isotopic fractionation could have occurred between the crystalline melilite and the still-evaporating melt during the run which affected the bulk Mg isotopic composition. Therefore, we believe that CAI4B2-10 should not be considered in calculations of the best fit line in Fig. 2.

Figure 3 shows Mg isotopic composition of CAI4B2 residues from low-pressure hydrogen experiments expressed in  $\delta'$  notation such that  $\delta^{25}\text{Mg}' = 1000 \times \ln(\delta^{25}\text{Mg}/1000 + 1)$  and similarly for  $\delta^{26}\text{Mg}'$ . All experimental residues plot on a well defined line with slope  $\beta = 0.51123 \pm 0.00060$  (2std) which is the same as 0.511 of the exponential fractionation line and clearly off the power law (0.501), linear (0.5), ideal Rayleigh (0.516) and equilibrium (0.521) fractionation lines. The value of  $0.51123 \pm 0.00060$  is different from  $0.51279 \pm 0.00058$  [11] obtained from vacuum evaporation experiments with CAIB [5] and FUN [6] melts Mg isotopic composition of which was measured using a Micromass Isoprobe MC-ICPMS. The reason for such differences in fractionation laws is not yet clear. We should note that Mg isotopic composition of FUN2 residues from  $1700^\circ\text{C}$  vacuum experiments [12] measured with Nu Plasma MC-ICPMS resulted in fractionation law  $0.51234 \pm 0.00084$  which is the same, within the errors, as  $0.51123 \pm 0.00060$  obtained from our low-pressure  $H_2$  experiments.

**Conclusion:** By comparing chemical and isotopic compositions of evaporation residues from  $1600^\circ\text{C}$  experiments in low-pressure  $H_2$  gas and in vacuum, we conclude: 1) Despite the much faster evaporation of Mg and Si at  $2 \times 10^{-4}$  bar  $H_2$  than in vacuum, their chemical evaporation trajectories remain the same; 2) Evaporation of CAI-like melts in  $P_{H_2} = 2 \times 10^{-4}$  bar and in vacuum does not affect Mg isotopic fractionation ( $\alpha_{25,24} = 0.98818 \pm 0.00009$  at  $1600^\circ\text{C}$ ); 3) Mg isotopic fractionation in low-pressure  $H_2$  evaporation experiments

( $0.51123 \pm 0.00060$ ) follows the exponential law (0.511).

The results presented here for evaporation in  $P_{H_2} = 2 \times 10^{-4}$  bars show that chemical and isotopic fractionation is very much the same as in vacuum. Thus previous interpretations of the isotopic fractionation of natural CAIs based on the vacuum experiments remain correct and do not require revisions. One does need to keep in mind that the presence of hydrogen does significantly increase the rate of evaporation [8].

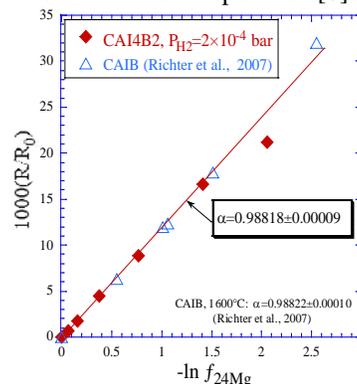


Fig. 2. Mg isotopic compositions of CAI4B2 residues from low-pressure  $H_2$  experiments (red diamonds) vs. fraction of  $^{24}\text{Mg}$  remaining in residues relative to CAI4B2-1 ( $\delta^{25}\text{Mg} = 0$ ,  $f^{24}\text{Mg} = 1$ ). CAIB vacuum experiments at  $1600^\circ\text{C}$  [5] are shown as open triangles.

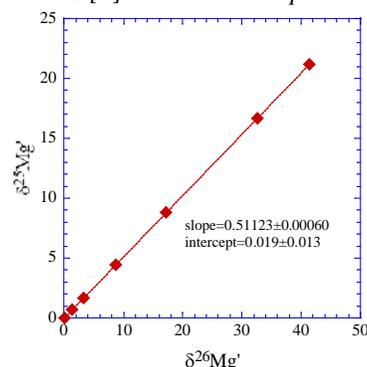


Fig. 3. Mg isotopic composition of residues normalized to CAI4B2-1 ( $\delta^{25,26}\text{Mg} = 0$ ) in the experiments at  $2 \times 10^{-4}$  bar  $H_2$  expressed in  $\delta'$  notation.

**References:** [1] Grossman L. et al. (2000) *GCA*, 64, 2879–2894. [2] Williams C. D. et al. (2017) *GCA*, 201, 25–48. [3] Davis A. M. et al. (1990) *Nature*, 347, 655–658; [4] Richter F. M. et al. (2002) *GCA*, 66, 521–540; [5] Richter F. M. et al. (2007) *GCA* 71, 5544–5564; [6] Mendybaev R. A. et al. (2013) *GCA*, 123, 368–384; [7] Mendybaev R. A. et al. (2017) *GCA*, 201, 49–64; [8] Kamibayashi M. et al. (2018) *LPSC 49<sup>th</sup>* (this volume); [9] Teng F.-Z. et al. (2010) *GCA*, 74, 4150–4166; [10] Mendybaev R. A. and Richter F. M. (2016) *LPSC 47<sup>th</sup>*, Abstract #2929; [11] Davis A. M. et al. (2015) *GCA*, 158, 245–261; [12] Mendybaev R. A. et al. (2013) *LPSC 44<sup>th</sup>*, Abstract #3017.