

**CHEMICAL AND ISOTOPIC FRACTIONATIONS DURING EVAPORATION OF CAI-LIKE MELTS.**

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**Introduction:** Formation and pre-accretional thermal processing of Ca-, Al-rich inclusions (CAIs) - the oldest rocks of the solar system - remain a major unsolved problem in cosmochemistry. Laboratory experiments and theoretical modeling are required to understand the major processes that resulted in formation of CAIs and quantitatively interpret the observations (e.g., texture, mineralogy, chemical and isotopic compositions). The coarse-grained igneous texture of Type B and compact Type A CAIs suggests that their precursors have experienced a high-temperature melting event followed by slow cooling. If such melting occurred under low-pressure conditions, such as in solar nebula, the expected evaporation of chemical elements would cause the depletion of CAI precursors in Mg and Si, as well as enrichment in their heavy isotopes. Evaporation of CAI-like melts was extensively studied in vacuum experiments (e.g., [1–5]). Recently a CAI-like melt was also evaporated under low-pressure H<sub>2</sub> conditions [6, 7]. The main outcomes from these experiments will be reviewed, and the remaining questions that still need to be answered will be pointed out.

**Results and Discussion:** The evaporation of CAI-like melts starts with faster evaporation either Mg or Si (depending on melt composition) followed by their loss at about the same rate. Experiments at P<sub>H<sub>2</sub></sub>=2×10<sup>-4</sup> bar showed that H<sub>2</sub> only affects evaporation rate (~40 times faster than in vacuum at 1600°C) [6], but not evaporation trajectory (i.e., the chemical composition changes the same way). Using the measured evaporation rates, the evaporation coefficients  $\gamma_{Mg}$  and  $\gamma_{Si}$  in Hertz-Knudsen equation were found to be ~0.2 at 1900°C and ~0.07 at 1600°C for both Mg and Si. The obtained  $\gamma$ 's are close to those measured for solid material (~0.05 to 0.1; e.g., [8–9]) and significantly less than  $\gamma$ 's ~1 for molten SiO<sub>2</sub> [10] and Al<sub>2</sub>O<sub>3</sub> [11]. The possibility that  $\gamma$ 's in CMAS melt might be 5–10 times lower than in pure molten oxides needs to be checked experimentally.

The evaporation of CMAS melts under low-pressure conditions results in large mass-dependent isotopic fractionations up to the levels observed in FUN and Type F CAIs (e.g., 39‰ in  $\delta^{25}Mg$  and 16‰ in  $\delta^{29}Si$  in Allende FUN CAI CMC-1 [12]. When evaporated at low-pressure H<sub>2</sub>, Mg isotopes fractionate the same way as in vacuum (Si fractionation needs to be confirmed) [7]. To reconstruct CAI precursor composition using the present day chemical and isotopic composition of a CAI, the isotopic fractionation factor (shows how much Mg or Si should evaporate to produce a certain degree of isotopic fractionation) needs to be known. The fractionation factors,  $\alpha_{25,24}$  for <sup>25</sup>Mg relative to <sup>24</sup>Mg, or  $\alpha_{29,28}$  for <sup>29</sup>Si relative to <sup>28</sup>Si, can be determined by measuring chemical and Mg and Si isotopic compositions of the evaporation residues. We found that the Mg isotopic fractionation factor depends on melt composition:  $\alpha_{25,24} = 0.9838 \pm 0.0003$  for forsteritic [4, 5] and  $\alpha_{25,24} = 0.9861 \pm 0.0002$  for melilitic [3, 4] melts at 1900°C, which are significantly different from  $\alpha_{25,24} = \sqrt{24/25} = 0.97980$  expected if Mg evaporates as Mg<sub>(g)</sub>. Si isotopic fractionation factor was found to be independent of melt composition with  $\alpha_{29,28} = 0.9899 \pm 0.0004$  regardless of temperature [4, 5, 13]. The value of  $\alpha_{29,28}$  is resolvably different from  $\alpha_{29,28} = \sqrt{44/45} = 0.98883$  expected if Si evaporates as SiO<sub>(g)</sub>. The reason for such deviations of  $\alpha_{25,24}$  and  $\alpha_{29,28}$  from the experimentally obtained values is not clear, but most likely it is related to the speciation of the gas phase at the melt/gas interface under non-equilibrium conditions.

**Future experiments:** Evaporation of Type B CAI-like melts under low-pressures but cooling conditions to see the effect of mineral crystallization from a still-evaporating melt on isotopic composition of minerals or isotopic zoning within a mineral. To address the thermal history of CAIs depleted in Mg and Si but showing no isotopic fractionations, the pressure effect (10<sup>-3</sup> – 10<sup>-1</sup> bars) on the isotopic fractionation will need to be checked.

**References:** [1] Floss C. et al. (1996) *Geochim. Cosmochim. Acta* 60:1975–1997. [2] Wang J. et al. (2001) *Geochim. Cosmochim. Acta* 65:479–494. [3] Richter F. M. et al. (2007) *Geochim. Cosmochim. Acta* 71:5544–5564. [4] Mendybaev R. A. et al. (2013) *Geochim. Cosmochim. Acta* 123:368–384. [5] Mendybaev R. A. et al. (2017) *Geochim. Cosmochim. Acta* 201:49–64. [6] Kamibayashi M. et al. (2018) *LPS XLIX*, Abstract #2432. [7] Mendybaev et al. (2018) *LPS XLIX*, Abstract #2580. [8] Pound G. M. (1972) *J. Phys. Chem. Ref. Data*. 1:135–146. [9] Jacobson N. et al. (2017) *J. Eur. Ceram. Soc.* 37:2245–2252. [10] Shornikov S. I. et al. (1999) *Rus.J. Gener. Chem.* 69:197–206. [11] Burns R. P. (1966) *J. Chem. Phys.* 44:3307–3319. [12] Williams C. D. et al. (2017) *Geochim. Cosmochim. Acta* 201:25–48. [13] Knight et al. (2009) *Geochim. Cosmochim. Acta* 73:6390–6401.