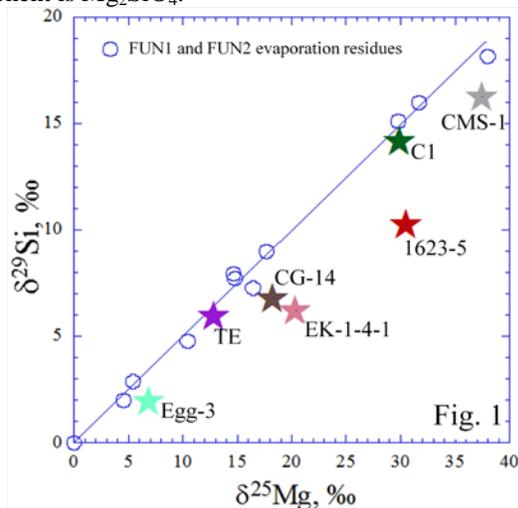


EVOLUTION OF CHEMICAL AND ISOTOPIC COMPOSITIONS OF FUN CAIS: EXPERIMENTAL MODELLING. R. A. Mendybaev¹, F. M. Richter¹, C. D. Williams², A. V. Fedkin¹ and M. Wadhwa². ¹University of Chicago, Chicago, IL 60637, USA (ramendyb@uchicago.edu); ²Arizona State University, Tempe, AZ 85287, USA.

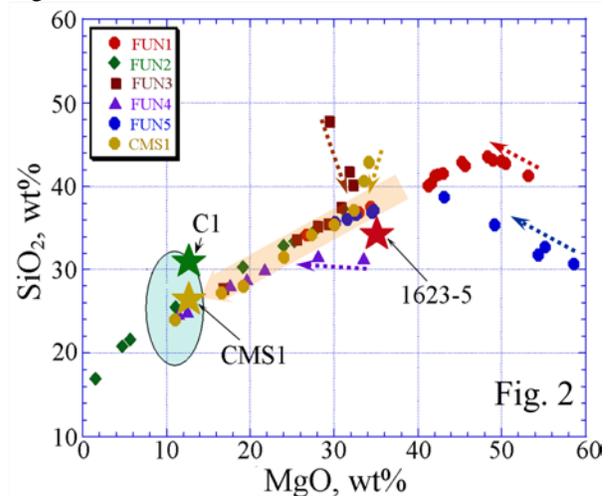
Introduction: Extremely large mass-dependent fractionations of Si, Mg and O isotopes in FUN (Fractionation and Unidentified Nuclear) CAIs suggest that their precursors lost significant amount of matter by evaporation. Our earlier experiments [1] using FUN1 and FUN2 forsterite-rich melts showed that not only do the evaporation trajectories of FUN1 and FUN2 pass close to the chemical composition of C1 and Vig1623-5 FUN CAIs respectively, but also that the isotopic compositions of Mg, Si and O of the evaporation residues are close to the measured values in natural FUN CAIs (Fig. 1). Fig. 1 also shows that enrichment in ²⁹Si of both FUN1 and FUN2 evaporation residues is about half that of ²⁵Mg as expected if the evaporating component is Mg₂SiO₄.



Here we report results of our new evaporation experiments in which SiO₂-rich or MgO-rich (relative to forsterite) CMAS liquids were evaporated at the same conditions as in the earlier work. The goal of the experiments was to check how chemical and isotopic compositions of such melts would evolve during evaporation. We will demonstrate that after initially predominant loss of SiO₂ (in case of SiO₂-rich melts) or MgO (in case of MgO-rich melts), the residual melts become forsteritic in composition with evaporation trajectories converging to the ones observed earlier for FUN1 and FUN2 melts. This along with the fact that isotopic composition of the evaporation residues are close to those in FUN CAIs allows us to conclude that bulk chemical composition of natural FUN inclusions should be on or close to the trend defined by the evaporation residues.

Experimental: All six compositions were evaporated in the same vacuum furnace at 1900°C and total pressure ~10⁻⁶ torr (see [1] for the experimental details). Texture and chemical composition of the evaporation residues were studied using the JEOL JSM-5800LV SEM equipped with an Oxford Link ISIS-300 energy-dispersive microanalytical system. The magnesium and silicon isotopic composition of CMS1 and FUN5 evaporation residues were measured using a Photon Machines Analyte 193 excimer laser ablation system connected to a ThermoFinnigan Neptune multicollector ICPMS. The laser beam diameter was from 37 to 96 μm depending on the Si and Mg concentration [2].

Results and Discussion: Fig. 2 shows evaporation trajectories for all six melt compositions in MgO-SiO₂ space. Compositions of the natural CMS-1, C1 and Vig1623-5 FUN CAIs are shown as stars.



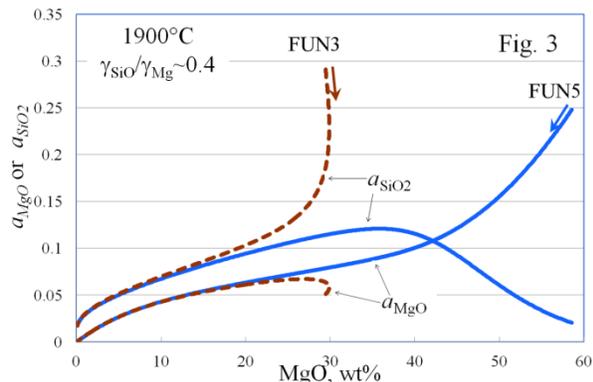
Note that evaporation of Si-rich melts (CMS1 and FUN3 starting compositions) starts with much faster evaporation of Si over Mg, and that the MgO wt% in the residual melt could even increase (as in case of FUN 3) although MgO is also evaporating. After this initial stage of evaporation the trajectories of FUN3 and CMS1 join the trend established by the FUN1 and FUN2 evaporation residues. When a Mg-rich melt, such as FUN5, evaporates, it first lose Mg faster than Si until the residual melt becomes forsteritic and then follow the same trend as FUN1 and FUN2. Fig. 2 clearly illustrate that evaporation trajectories of the melts, regardless of their starting composition, eventually converge to a single trend (shown as a wide light

brown arrow). Also note that natural FUN CAIs with measured bulk chemical composition (C1, CMS-1 and Vig1623-5) plot on or very close to a “converged trend” established in our experiments.

Experimental evaporation trajectories shown in Fig. 2 can be fit by the calculated ones using thermodynamic model of Grossman et al. [3] and assuming that $\gamma_{\text{SiO}}/\gamma_{\text{Mg}} \sim 0.4$ in

$$\frac{J_{\text{Si}}}{J_{\text{Mg}}} = \frac{\gamma_{\text{SiO}} P_{\text{SiO}}}{\gamma_{\text{Mg}} P_{\text{Mg}}} \sqrt{\frac{m_{\text{Mg}}}{m_{\text{SiO}}}},$$

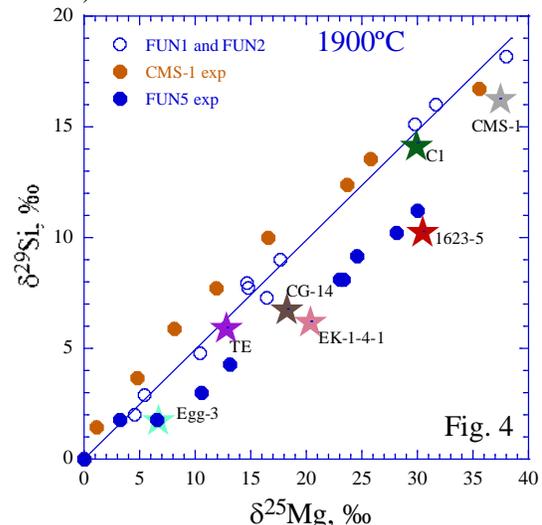
where $J_{\text{Si}}/J_{\text{Mg}}$ is the ratio of the molar fluxes of silicon and magnesium, $\gamma_{\text{SiO}}/\gamma_{\text{Mg}}$ is the ratio of the evaporation coefficients of $\text{SiO}_{(\text{g})}$ and $\text{Mg}_{(\text{g})}$, P_i is the equilibrium vapor pressures of SiO and Mg over the melt at given temperature, and m_i is the molecular weight of the evaporating $\text{Mg}_{(\text{g})}$ and $\text{SiO}_{(\text{g})}$. The ratio of $\gamma_{\text{SiO}}/\gamma_{\text{Mg}}=1$ was found by Richter et al. [4] to fit their experimental data on evaporation of Type B CAI-like melt.



It is activities of the MgO and SiO_2 in a melt that control equilibrium vapor pressures of the evaporating $\text{SiO}_{(\text{g})}$ and $\text{Mg}_{(\text{g})}$, and thus evolution of melt composition during evaporation under high vacuum conditions. Fig. 3 shows the trends in the activities of MgO and SiO_2 in the FUN3 and FUN5 melts as a function of MgO content in the melt. Two stages can be distinguished in Fig. 3: 1) fast drop in a_{SiO_2} for FUN3 at ~30% MgO and in a_{MgO} for FUN5 as MgO content in the melt decreases from ~58% to ~43% wt%; and 2) slow decrease in a_{MgO} and a_{SiO_2} at lower values of wt% MgO in the residual melts. The range of MgO values in Fig. 3 is close to the range of values of the experimental residues in Fig. 2. Note that a_{MgO} and a_{SiO_2} curves for FUN3 and FUN5 melts eventually converge at ~20 wt% (for a_{SiO_2}) and ~25 wt% MgO (for a_{MgO}), which explains why at the late stages of evaporation of FUN3 and FUN 5 melts they evolve along very similar trajectories.

Fig. 4 is similar to Fig. 1, but now includes Mg and Si isotopic trajectories for MgO -rich (FUN5) and SiO_2 -rich (CMS1) melts. It shows that most of FUN5 residues plot below but parallel to the solid line estab-

lished by FUN1 and FUN2 residues, while CMS1 residues plot above the line. The FUN5 isotopic trajectory can be explained by the initially higher evaporation rates of magnesium compared to silicon which will result in a higher degree of isotopic fractionation of Mg compared to Si . This causes the isotopic fractionation trajectory to be below the solid line. As the FUN5 residual melt becomes more forsteritic, further evaporation would fractionate Mg by 2‰ amu^{-1} per 1‰ amu^{-1} of fractionation of Si isotopes causing the points to plot parallel to the line in Fig. 4. In case of Si -rich CMS1 melt, initially Si evaporates faster than Mg , which will bring the CMS1 isotopic trajectory above the solid line. Note that two most evaporated FUN5 residues (32 and 35 wt% MgO) are chemically and isotopically very close to the Vig1623-5 FUN CAI. It also appears that isotopic compositions of EK1-4-1, CG-14 and Egg-3 FUN CAIs could be better explained by evaporation of MgO -rich precursors (like FUN5) rather than being forsteritic in composition (like FUN1 and FUN2).



Conclusions: 1) Evaporation trajectories in MgO - SiO_2 space of all six Mg - and Si -rich melts studied converge to a single trend (Fig. 2) after a sufficient amount of evaporation has taken place. 2) The bulk chemical composition of natural FUN CAIs with highly fractionated Mg and Si isotopes indicating significant degree of evaporation should plot on this “converged trend”. 3) The large enrichments in heavy Si and Mg isotopes of natural FUN CAIs can be explained by evaporation of forsterite-rich or forsterite+ MgO -rich precursors (Fig. 4).

References: [1] Mendybaev R. A. et al. (2013) *GCA*, 123, 368–384. [2] Williams C. D. et al. (2014) *LPSC 45* (this meeting). [3] Grossman L. et al. (2000) *GCA*, 64, 2879–2894. [4] Richter F. M. et al. (2002) *GCA*, 66, 521–540.