

MASS-DEPENDENT Mg AND Si ISOTOPIC FRACTIONATION OF ALLENDE FUN CAI CMS-1: IMPLICATIONS FOR THERMAL AND CHEMICAL EVOLUTION OF THE EARLY SOLAR SYSTEM.

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Introduction: Many calcium-aluminum-rich inclusions (CAIs) solidified from melt droplets early in the Solar System's history. Experimental studies [1-6] demonstrate that melting of potential precursor materials of CAIs would be accompanied by evaporative loss of moderately refractory elements such as silicon and magnesium and the enrichment of their heavy isotopes in the residual melt and its crystallization products according to the Rayleigh law:

$$R/R_0 = f^{(\alpha-1)} \quad (1)$$

R is the ratio of the heavy to light isotope in the evaporation residue, R_0 is the initial ratio, f is the fraction of the parent element remaining in the residue and α is the kinetic isotope fractionation factor.

Fractional loss of silicon and magnesium from CAI precursors due to Rayleigh processes is thought to be the cause of the Type A and B CAIs being enriched in the heavy isotopes of silicon and magnesium and the deviations of their observed bulk compositions from those predicted by equilibrium condensation models [7]. FUN (Fractionation and Unidentified Nuclear effects) CAIs also display correlated mass-dependent isotopic variations in silicon and magnesium, however, the degree of fractionation is much larger than those typically observed in most Type A and Type B CAIs (e.g., [8-10]). The large, mass-dependent fractionation observed in FUN CAIs, in conjunction with parameters derived from laboratory experiments [1-6], suggests that a very large fraction (up to 90% in the case of magnesium) of these elements was lost from the original precursor material during partial and/or complete melting.

Recently, we reported on the silicon, magnesium and oxygen isotopic composition of a new FUN CAI from Allende (designated CMS-1) [11,12]. CMS-1 is characterized by large mass-dependent fractionation of silicon ($\delta^{29}\text{Si} \sim 16.3$), magnesium ($\delta^{25}\text{Mg} \sim 37.5$) and oxygen ($\delta^{18}\text{O} \sim 16.0$). Here we report additional *in situ* magnesium isotopic data for the primary phases (spinel, melilite, fassaite) that comprise CMS-1. Furthermore, a new set of vacuum experiments were performed in which a plausible precursor for CMS-1 was melted and evaporated to varying degrees. The experimental results were then compared to the bulk chemi-

cal and isotopic composition of CMS-1 to further constrain its thermal and chemical evolution.

Experimental and Analytical Techniques: Evaporation experiments were conducted in a vacuum furnace at 1900°C following the methods of [7]. Starting materials (37.9% MgO, 11.6% Al₂O₃, 42.9% SiO₂, 7.6% CaO) were placed in a cold furnace which was then evacuated to $\sim 10^{-6}$ torr and the temperature increased to 1900°C. The sample was allowed to evaporate at this temperature for a preset period of time and then cooled at several hundred degrees per minute.

The magnesium isotopic composition of evaporation experiments were measured using a Photon Machines Analyte 193 excimer laser ablation system connected to a ThermoFinnigan Neptune multicollector inductively coupled plasma mass spectrometer. Laser ablation measurements employed spot analyses with diameters ranging from 37 to 96 μm depending on the Si and Mg concentration of the experimental run product. Relatively short 4 ns laser pulses of 7 mJ energy were used.

Additional magnesium isotopic measurements were performed on the primary phases of CMS-1 using the Cameca IMS-1280 ion microprobe at the University of Wisconsin following the methods of [13]. Magnesium isotopic data were collected using a primary 5-8 nA O⁻ beam defocused to approximately 15 μm . Four Faraday cups enabled simultaneous measurements of ²⁴Mg, ²⁵Mg, ²⁶Mg and ²⁷Al.

Results and Discussion: Allende FUN CAI CMS-1 is an irregularly shaped compact Type A inclusion. Its primary mineralogy consists of Ti-Al-rich pyroxene, melilite, abundant inclusions of spinel, and a spinel-rich outer rim. Ti-Al-rich pyroxene ranges in TiO₂ content from 3.8 to 12.6 wt.%, while the åkermanite content of melilite varies between 17.9 and 48.0 mole %. The interior spinel is nearly pure MgAl₂O₄, while many spinel in the outer rim have FeO contents greater than 16.0 wt.%.

Silicon and magnesium isotopic composition of CMS-1, as previously determined by laser ablation [11], define relatively restricted ranges ($\delta^{29}\text{Si} = 16.3 \pm 0.5 \text{ amu}^{-1}$, $\delta^{25}\text{Mg} = 37.5 \pm 2.5 \text{ amu}^{-1}$). These values likely represent compositional mixtures of the three primary phases given the size and depths of laser

spots used, and also likely approximate the bulk silicon and magnesium isotopic composition of CMS-1.

The magnesium isotopic composition of melilite, as determined with the ion microprobe, varies between 30.71 and 36.60 ‰ amu⁻¹, while that of pyroxene ranges from 32.75 to 35.20 ‰ amu⁻¹. Interior spinel typically displays magnesium isotopic compositions identical to the phases enclosing them (either melilite or pyroxene). For instance, the magnesium isotopic composition of spinel enclosed by melilite varies between 30.98 and 33.75 ‰ amu⁻¹, while that of spinel enclosed by pyroxene ranges from 33.63 to 37.48 ‰ amu⁻¹. FeO-rich spinel located in the outer rim display the heaviest magnesium isotopic compositions with values in excess of 39 ‰ amu⁻¹.

The bulk composition of CMS-1 is typical of Compact Type A CAIs and an equivalent melt would have the predicted crystallization sequence spinel – melilite – pyroxene, which is consistent with the texture, mineralogy, and oxygen isotopic composition of this inclusion. The earliest-crystallizing melilite is characterized by a magnesium isotopic composition in excess of 30 ‰ amu⁻¹. This observation implies that CMS-1 had already undergone a large degree of mass-dependent fractionation, and thereby lost the majority of its moderately refractory elements through evaporation, prior to the onset of fractional crystallization.

The magnesium isotopic compositions of interior spinel are similar to their host phases implying that the magnesium isotopic composition of interior spinel continued to re-equilibrate with the melt until poikilolithically enclosed by either melilite or pyroxene. FeO-rich spinel in the outer rim of CMS-1 displays the largest degree of mass-dependent fractionation suggesting these spinel maintained equilibrium with the continually evolving melt until complete crystallization of the inclusion. This may indicate that evaporative loss and mass-dependent fractionation of magnesium continued throughout the crystallization sequence of CMS-1.

Evaporation experiments on the estimated CMS-1 precursor material resulted in large degrees of evaporative loss and isotopic fractionation of both silicon and magnesium. The experimental residues define an isotopic fractionation factor (α) of 0.98972 ± 0.00061 and 0.98318 ± 0.00061 for silicon ($\alpha^{29}\text{Si}$) and magnesium ($\alpha^{25}\text{Mg}$), respectively (Fig. 1), derived from the linearized form of Eq. 1:

$$\ln(R/R_0) = -(1-\alpha) \ln(f) \quad (2)$$

These fractionation factors are similar to those derived from previously studied melts of CMAS composition (e.g., [3]). When the evaporation residues are compared to the bulk composition estimated for CMS-1 (plotted in Fig. 2), these kinetic fractionation factors can be used to estimate the amount of silicon and mag-

nesium lost from the system and predict the precursor composition for CMS-1 (Fig. 2).

The isotopic fractionation of the most evaporated residue is almost identical to that measured in CMS-1. The kinetic fractionation factors and the measured mass-dependent fractionation of silicon and magnesium in CMS-1 suggest that greater than 80% of silicon and magnesium were lost from its precursor material through evaporative processes. Adding silicon and magnesium back to estimates of the current bulk composition of CMS-1 using these data results in a precursor composition similar to that expected to condense from a gas of Solar composition [7].

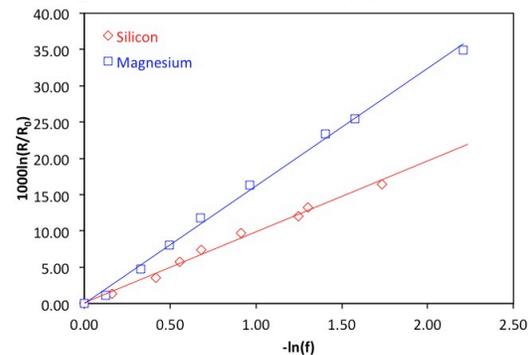


Figure 1 Rayleigh plot showing mass-dependent fractionation of silicon and magnesium as a function of the fraction of each element remaining in the residues from evaporation experiments using starting material of CMS-1's estimated precursor composition. Slope of the best fit line is equivalent to $1-\alpha/1000$.

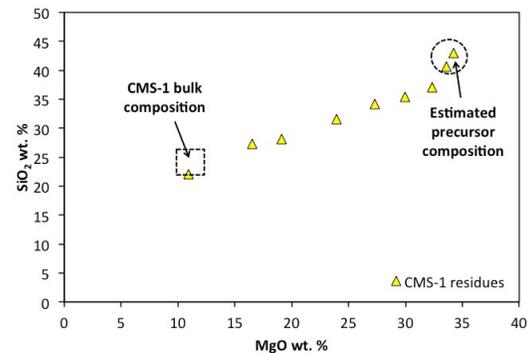


Figure 2 The composition of evaporation residues (filled triangles), predicted precursor composition (open circle), and bulk composition of CMS-1 (square) shown in SiO₂-MgO space. Note the close correspondence between the chemical fractionation of CMS-1 and that of the most evaporated residue.

References: [1] Davis A. M. et al. (1990) *Nature*, 347, 655-658. [2] Knight K. B. et al. (2009) *GCA*, 73, 6390-6401. [3] Mendybaev R. A. et al. (2013) *GCA*, 123, 368-384. [4] Richter F. M. et al. (2002) *GCA*, 66, 521-540. [5] Richter F. M. et al. (2007) *GCA*, 71, 5544-5564. [6] Wang J. et al. (2001) *GCA*, 65, 479-494. [7] Grossman L. et al. (2000) *GCA*, 64, 2879-2894. [8] Clayton R. N. and Mayeda T. K. (1977) *GRL*, 4 295-298. [9] Clayton R. N. et al. (1978) *LPSCVIII*, 1267-1278. [10] Wasserburg G. J. et al. (1977) *GRL*, 4 299-302. [11] Williams C. D. et al. (2013) *LPSC XXXVIII*, #2435. [12] Williams C. D. et al. (2012) *76th MetSoc*, #5102. [13] Kita N. et al. (2012) *GCA*, 86, 37-51.