Thermal and chemical evolution in the early Solar System as recorded by FUN CAIs: Part II – Laboratory evaporation of potential CMS-1 precursor material

Ruslan A. Mendybaev a,b,* Curtis D. Williams c,1, Michael J. Spicuzza d, Frank M. Richter a,b, John W. Valley d, Alexei V. Fedkin a,b, Meenakshi Wadhwa c

a Department of the Geophysical Sciences, University of Chicago, Chicago, IL 60637, United States
b Chicago Center for Cosmochemistry, University of Chicago, Chicago, IL 60637, United States
c School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, United States
d Department of Geoscience, University of Wisconsin, Madison, WI 53706, United States

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Abstract

We present the results of laboratory experiments in which a forsterite-rich melt estimated to be a potential precursor of Allende CMS-1 FUN CAI was evaporated into vacuum for different lengths of time at 1900 °C. The evaporation of this melt resulted in residues that define trajectories in chemical as well as magnesium, silicon and oxygen isotopic composition space and come very close to the measured properties of CMS-1. The isotopic composition of the evaporation residues was also used to determine the kinetic isotopic fractionation factors $a_{2,1}$ (vapor-melt) defined as the ratio of isotopes 2 and 1 of a given element in the evaporating gas divided by their ratio in the evaporating source for evaporation of magnesium ($a_{25,24}$ for $^{25}\text{Mg}/^{24}\text{Mg}$), silicon ($a_{29,28}$ for $^{29}\text{Si}/^{28}\text{Si}$) and oxygen ($a_{18,16}$ for $^{18}\text{O}/^{16}\text{O}$) from the forsterite-rich melt at 1900 °C. The values of $a_{25,24} = 0.98383 \pm 0.00033$ and $a_{29,28} = 0.99010 \pm 0.00038$ are essentially independent of change in the melt composition as evaporation proceeds. In contrast, $a_{18,16}$ changes from $0.9815 \pm 0.0016$ to $0.9911$ when the residual melt composition changes from forsteritic to melilitic. Using the determined values of $a_{25,24}$ and $a_{29,28}$ and present-day bulk chemical composition of the CMS-1, the composition of the precursor of the inclusion was estimated to be close to the clinopyroxene + spinel + forsterite assemblage condensed from a solar composition gas. The correspondence between the chemical composition and isotopic fractionation of experimental evaporation residues and the present-day bulk chemical and isotopic compositions of CMS-1 is evidence that evaporation played a major role in the chemical evolution of CMS-1.

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1. INTRODUCTION

Calcium-, aluminum-rich inclusions (CAIs) are the oldest known materials to have formed in the Solar System (e.g., Lugmair and Shukolyukov, 2001; Amelin et al., 2002, 2010; Bouvier and Wadhwa, 2010; Connelly et al., 2012). The most extensively studied CAIs are coarsely-grained Type B inclusions composed mainly of melilit, spinel, fassaite and anorthite, and Compact Type A (CTA).
inclusions composed mainly of melilite (>60 vol%), spinel, perovskite and often Ti-rich fassaite (e.g., Grossman, 1975, 1980; Simon et al., 1999; MacPherson, 2007). All Type B CAIs and majority of CTAs are believed have been formed by crystallization of partially molten droplets, and the coarse-grained texture of the Type B CAIs has been reproduced in laboratory dynamic crystallization experiments (e.g., Stolper and Paque, 1986; Beckett et al., 1990; Mendybaev et al., 2006) when partially molten droplets were cooled from ~1450 °C at less than 50 °C per hour. Typical Type B and CTA CAIs are characterized by well resolved mass-dependent fractionations of magnesium, silicon and oxygen isotopes (e.g., δ26Mg up to 11‰ relative to Burma spinel and δ28Si up to 5‰ relative to NBS-28 quartz; see Grossman et al., 2000, 2008 and references therein) which are attributed to a Rayleigh-type distillation. The correlated mass-dependent fractionations of silicon and magnesium isotopes have been also found in laboratory experiments in which CAI-like melts were evaporated in low-pressure conditions (Richter et al., 2002, 2007; Knight et al., 2009; Mendybaev et al., 2013a).

Most FUN CAIs (CAIs with Fractionation and Unidentified Nuclear effects, Wasserburg et al., 1977) are similar to isotopically “normal” (non-FUN) CAIs in terms of their bulk chemical and mineral compositions (see Clayton et al., 1984; Davis et al., 1991; Krot et al., 2014; Williams et al., 2017 and references therein). However, in contrast to normal CAIs, the classical FUN CAIs display little or no excess of radiogenic 26Mg, and are characterized by large mass-dependent isotopic fractionation of magnesium and silicon (δ26Mg up to ~40‰ and δ28Si up to ~15‰), distinct oxygen isotopic composition of their high-temperature minerals, and mass-independent isotopic anomalies of unknown origin in a number of elements. Some of these CAIs are characterized by large kinetic mass-dependent isotope fractionation effects and lack mass-independent anomalies (“F” or FUN-like CAIs, such as TE; e.g., Clayton et al., 1984), while other CAIs have large nuclear anomalies without significant kinetic isotope fractionation (“UN” CAIs, e.g., Ireland, 1988). Mass-dependent fractionation of magnesium, silicon and oxygen isotopes observed in CAIs are usually associated with their evaporation under low-pressure conditions that results in faster evaporation of lighter isotopes and thus enrichments of the evaporation residues in heavy isotopes (e.g., Esat et al., 1986; Davis et al., 1990; Ireland et al., 1992; Wang et al., 2001; Richter et al., 2002, 2007; Richter, 2004; Yamada et al., 2006; Knight et al., 2009). Recent experiments by Mendybaev et al. (2010, 2013a,b) showed that evaporation of a MgO- and SiO2-rich melt in vacuum results in the evaporation residues with chemical and isotopic compositions of magnesium, silicon and oxygen close to the levels measured in FUN (and FUN-like) CAIs.

On a three-oxygen isotope diagram (Fig. 1) the oxygen isotopic compositions of FUN and FUN-like CAIs is distinctly different from that of “normal” CAIs and plot to the right of the CCAM (Carbonaceous Chondrite Anhydrous Mineral) mixing line with slope ~1 defined by minerals in the “normal” CAIs (Clayton et al., 1977). The isotopic composition of spinel, forsterite and often pyroxene in the FUN CAIs fall along a mass-fractionation line (FUN FL) with slope ~1/2 that is parallel to the mass-dependent terrestrial fractionation line (TFL) but significantly displaced with typical Δ17O ~−24‰, although some FUNs, such as TE, are less 16O-rich with Δ17O up to ~16.4‰ (e.g., Krot et al., 2010, 2014). The oxygen isotopic compositions of mineral grains along FUN FL are believed to reflect the crystallization sequence of minerals from an evaporating melt. The degree of mass-dependent oxygen isotopic fractionation due to evaporation, as estimated from the difference between the δ18O and δ17O of the most fractionated spinel grain (δ18O = −15.4‰ and δ17O = −32.2‰, Williams et al., 2017) along the FUN FL and the δ18O and δ17O values at the intersection of the FUN FL and CCAM lines (δ18O = −48‰ and δ17O = −49‰). We use the values of Δ17O ~ 3‰ as our best estimates of oxygen isotopic fractionation caused by evaporation.

Fig. 1. Oxygen isotopic composition of individual minerals in Allende FUN CAI CMS-1 (Williams et al., 2017). The degree of mass-dependent oxygen isotopic fractionation due to evaporation (shown as dashed lines) was estimated from the difference between the δ18O and δ17O of the most fractionated spinel grain (δ18O = −15.4‰ and δ17O = −32.2‰, Williams et al., 2017) along the FUN FL and the δ18O and δ17O values at the intersection of the FUN FL and CCAM lines (δ18O = −48‰ and δ17O = −49‰). We use the values of Δ17O ~ 3‰ as our best estimates of oxygen isotopic fractionation caused by evaporation.
rounded cavities filled with matrix material. CMS-1 has an igneous texture and is composed of 39% melilitite, 30% Ti-Al-rich pyroxene, 24% spinel with minor amounts of hibonite and perovskite along its margins. Chemically it consists of 34.8 wt% Al₂O₃, 25.4 wt% SiO₂, 23.9 wt% CaO, 11.9 wt% MgO, 1.4 wt% FeO, 1.1 wt% TiO₂ and small amounts of Na₂O, K₂O, Cr₂O₃, and Cl₂O (Williams et al., 2017).

with the melt, molar mass of the gas species vapor pressures in equilibrium with the condensed phase, and temperature. The relative evaporation rates of magnesium and silicon and oxygen isotopes by evaporation we report the results of a new set of laboratory evaporation experiments in which a melt with an estimated CMS-1 precursor composition was evaporated to varying degrees in a high vacuum furnace. The resulting evaporation residues will be referred to as the FUNC residues. Their bulk chemical composition as well as their chemical and isotopic compositions were measured and compared to those of CMS-1.

2. SOME THEORETICAL ASPECTS OF VACUUM EVAPORATION

It was shown (e.g., Richter et al., 2002, 2007) that laboratory evaporation of silicate melts in vacuum can be successfully described by the standard Hertz-Knudsen formulation (see Hirth and Pound, 1963):

\[
J_i = \sum_{j=1}^{n} n_j \gamma_{ij} P_j \frac{1}{\sqrt{2 \pi m_j R T}}
\]

where \( J_i \) is the net evaporative flux (in moles per unit area per time) of a component \( i \) (element or isotope), \( n_j \) is the number of atoms of \( j \) in the \( j \)th gas species containing \( i \), \( \gamma_{ij} \) is the evaporation coefficient for the \( j \)th gas species, and \( P_j \) is the saturation vapor pressure of \( j \). \( m_j \) is the molar mass of the gas species \( j \) that would be in equilibrium with the melt, \( R \) is the gas constant, and \( T \) is the absolute temperature. In case of magnesium and silicon evaporating from silicate melts, the equilibrium gas is predominantly Mg(g) and SiO(g) as was determined experimentally (e.g., Nichols et al., 1995), and Eq. (1) can be simplified as:

\[
J_{Mg} = \frac{\gamma_{Mg} P_{Mg}}{\sqrt{2 \pi m_{Mg} R T}}
\]

and

\[
J_{SiO} = \frac{\gamma_{SiO} P_{SiO}}{\sqrt{2 \pi m_{SiO} R T}}
\]

where \( J_{Mg} \) and \( J_{SiO} \) are the evaporative fluxes of magnesium and silicon, \( \gamma_{Mg} \) and \( \gamma_{SiO} \) are the empirical evaporation coefficients of Mg(g) and SiO(g), \( P_{Mg} \) and \( P_{SiO} \) are their vapor pressures in equilibrium with the condensed phase, \( m_{Mg} \) and \( m_{SiO} \) are their masses, and \( T \) is the absolute temperature. The relative evaporative rates of magnesium and silicon can be calculated using the relationship:

\[
J_{SiO} = \frac{\gamma_{SiO} P_{SiO}}{\gamma_{Mg} P_{Mg}} \sqrt{\frac{m_{Mg}}{m_{SiO}}}
\]

if the evaporation coefficients and equilibrium vapor pressures are known. The evaporation coefficients need to be determined experimentally as they cannot be calculated theoretically, and it was found that the values of \( \gamma_{Mg} \) and \( \gamma_{SiO} \) determined from vacuum evaporation experiments using silicate melts (e.g., Richter et al., 2007; Knight et al., 2009; Mendybaev et al., 2013a,b) are quite different from unity although the reason of such deviations remains unknown. Equilibrium speciation and vapor pressures of the evaporating gases can be measured experimentally using Knudsen cell techniques (e.g., Nichols et al., 1995), but we do not measure them in our experiments and use thermodynamic calculations to estimate the relevant vapor pressures.

Eq. (1) also describes the kinetic fractionation of isotopes in vacuum. Similarly to Eq. (4), the ratio of the fluxes of isotopes 1 and 2 of a given element \( i \) can be expressed as:

\[
\frac{J_{i2}}{J_{i1}} = \frac{\gamma_{i2} P_{i2}}{\gamma_{i1} P_{i1}} \sqrt{\frac{m_{i1}}{m_{i2}}}
\]

again assuming that the element \( i \) evaporates predominantly as a single gas species; \( R_{i1} \) is the atomic ratio of isotopes 2 and 1 in the evaporating source. The ratio of the isotopic fluxes \( J_{i2}/J_{i1} \) in the evaporating gas to the atomic ratio \( R_{i2,1} \) defines the isotopic fractionation factor \( \alpha_{i2,1} \)

\[
\alpha_{i2,1} = \left( \frac{\gamma_{i2}}{\gamma_{i1}} \right) \sqrt{\frac{m_{i1}}{m_{i2}}}
\]

When the fractionation factor \( \alpha_{i2,1} \) is unchanging as evaporation proceeds the isotopic composition of the evaporation residues evolve via Rayleigh fractionation (e.g., Esat, 1984; Davis et al., 1990, 2015; Richter et al., 2002, 2007; Richter, 2004) given as:

\[
R_{i2,1} = R_0 \alpha_{i2,1}^{f_i-1}
\]

or

\[
\ln(R_{i2,1}/R_0) = (\alpha_{i2,1} - 1) \ln f_i
\]

where \( R_{i2,1} \) is the ratio of isotopes 2 and 1 of a given chemical element \( i \) in the evaporation residue, \( R_0 \) is their isotopic ratio in the starting material prior to evaporation, \( f_i \) is the fraction of the isotope 1 remaining in the residue after evaporation.

The Rayleigh fractionation relationships given above will be used here to calculate the chemical and isotopic fractionations during vacuum evaporation of the FUNC forsteritic melt.

3. EXPERIMENTAL TECHNIQUE

3.1. Starting materials and experimental procedure

The starting material containing 37.9 wt% MgO, 11.6 wt% Al₂O₃, 42.9 wt% SiO₂, and 7.6 wt% CaO was evaporated in vacuum (<10⁻⁵ bars) at 1900 °C. The composition, selected as a potential precursor of CMS-1, was obtained by adding MgO and SiO₂ to the reported bulk composition of the inclusion (Williams et al., 2017) in such amounts that when sufficiently evaporated this material would be expected to produce fractionations in Mg and Si isotopes close to \( \delta^{28}\text{Si} = 15.54 \)
Here we assumed that evaporation of the CMS-1 precursor (FUNC melt) would fractionate magnesium and silicon isotopes the same way (i.e., the isotopic fractionation factors will remain the same) as was determined from evaporation experiments with forsteritic FUN1 and FUN2 melts (Mendybaev et al., 2013a) with significantly different bulk chemical compositions than the FUNC melt. The mixture of MgO (Alfa Aesar, 99.998%), SiO2 (Aldrich98, >99.95%), Al2O3 (Alfa Aesar98, 99.99%), and CaCO3 (Alfa Aesar98, 99.99%) was homogenized in the Retsch® MM200 oscillating mill using a 5 ml agate jar and two 7 mm agate balls. The vacuum evaporation was run in a high-temperature high-vacuum furnace at the University of Chicago (see Hashimoto, 1990 for the furnace details). After the sample was placed into the furnace at room temperature, it was pumped down to about 10⁻⁶ bars, and the temperature was then raised to 1400 °C at 20 °C/min and held at this temperature for about 20 min to allow the degas. Once the furnace temperature reached 1900 °C, it was pumped down to about 10⁻⁶ bars, and the temperature was then raised to 1900 °C at 20 °C/min and held at this temperature for about 20 min to allow the degas. Once the furnace pressure had dropped to ~10⁻⁹ bars, the temperature was raised to 1900 °C at 40 °C/min and the sample allowed to evaporate for a predetermined amount of time (from 0 to 55 min). An experiment was ended by cutting the power to the heating elements (see Mendybaev et al., 2013a for the details). The evaporation residue was removed from a cold furnace and broken into several pieces for separate chemical and isotopic analysis. The experiment (FUNC-5 in Tables 1 and 2) in which the sample was quenched immediately after the furnace temperature reached 1900 °C (i.e., run duration at 1900 °C is zero minutes) is referred as a “zero-time” run.

3.2. Analytical techniques

3.2.1. Chemical composition of evaporation residues

The texture and chemical composition of theFUNC evaporation residues were studied using a JEOL JSM-5800LV scanning electron microscope equipped with an Oxford/Link ISIS-300 energy-dispersive X-ray (EDX) microanalysis system at the University of Chicago. The working conditions involved a 15 keV accelerating voltage and a 0.4 nA beam current with natural and synthetic materials used as calibration standards. The chemical composition of the samples was determined either by averaging at least 20 spots analyzed across the sample (for the residues that quenched to glass) or by averaging the results of scanning 15–20 areas of ~250 × 200 microns in dimension for the residues that quenched to intergrowth of forsterite and glass.

3.2.2. Magnesium and silicon isotopic analyses

Isotopic composition of magnesium and silicon of the FUNC evaporation residues was measured using a Photon Machine Analyte 193 laser ablation system connected to a ThermoFinnigan Neptune MC-ICPMS (multicollector inductively coupled plasma mass spectrometer) at the Arizona State University (see accompanying paper by Williams et al. for details). Magnesium isotopes (24Mg, 25Mg and 26Mg as well as 27Al) were measured simultaneously during one session; silicon isotopes (28Si, 29Si and 30Si) were also measured simultaneously but in a separate analytical session. All isotopic measurements were conducted in high-resolution mode using 100 to 275 μm diameter spot sizes depending on the magnesium and silicon concentrations of the sample. The measurements consisted of approximately 320 s of data acquisition per spot with forty 8 s integrations. Individual samples were bracketed by a synthetic B133R-10 glass with a bulk composition similar to that of a typical Type B CAI (Richter et al., 2007; Janney et al., 2011). The magnesium isotopic composition of B133R-10 relative to DSM3 is δ²⁵Mg = -1.77 ± 0.16‰ and δ²⁶Mg = -3.51 ± 0.28‰ and that of silicon relative to NBS-28 is δ²⁸Si = 0.00 ± 0.15‰ and δ³⁰Si = -0.01 ± 0.11‰. The details of the analytical procedure including the matrix effect corrections are given in Janney et al. (2011).

3.2.3. Oxygen isotopic analyses

Oxygen isotopic composition of the FUNC samples was measured at the University of Wisconsin-Madison by laser fluorination of 1.5–2.9 mg chips. Oxygen produced by laser heating in a BrF5 atmosphere was carefully purified by passing the released gas through a number of traps, converted to CO2 on hot graphite, and analyzed for 18O and 16O with a Finnigan MAT 251 mass spectrometer. All measurements were made in one session. During the measurements, the δ16O values of unknowns were adjusted down by 0.22‰ based on the average of six analyses of the UWG-2 garnet standard (δ16O = 5.80‰ vs. VSMOW) that bracket unknown analyzes during the same session. The details of the analytical method and data standardization were described by Valley et al. (1995) and by Spicuzza et al. (2007). The correlation between δ16O and δ18O values in FUN1 and FUN2 evaporation residues (δ17O = 0.15 × δ18O) reported previously by Mendybaev et al. (2010, 2013a) was used to calculate δ17O values for the FUNC residues.

4. RESULTS

The textures of the quenched samples are very similar to those of the FUN1 and FUN2 evaporation residues (Fig. 3 of Mendybaev et al., 2013a). The least evaporated samples FUNC-5 and FUNC-10 (Table 1) are composed of very fine grained intergrowths of forsterite and glass; the more evaporated samples (FUNC-1, -9, and -3) have a barred olivine texture similar to those in chondrules; and the most evaporated sample FUNC-6 appears as a clear homogeneous glass. The fact that the experimental temperature...
Table 1

<table>
<thead>
<tr>
<th>Sample Run</th>
<th>Initial</th>
<th>Final</th>
<th>Weight change, loss, %</th>
<th>MgO ±2</th>
<th>Al₂O₃ ±2</th>
<th>SiO₂ ±2</th>
<th>CaO ±2</th>
<th>MgO/Al₂O₃</th>
<th>SiO₂/MgO</th>
<th>Al₂O₃/MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>FUNC</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0 ±0.1</td>
<td>11.6</td>
<td>42.9</td>
<td>42.9</td>
<td>7.6</td>
<td>1.2</td>
<td>2.6</td>
<td>1.0</td>
</tr>
<tr>
<td>B133R-10</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0 ±0.1</td>
<td>11.6</td>
<td>42.9</td>
<td>42.9</td>
<td>7.6</td>
<td>1.2</td>
<td>2.6</td>
<td>1.0</td>
</tr>
<tr>
<td>FUNC-5</td>
<td>1.2</td>
<td>1.2</td>
<td>0.9 ±0.1</td>
<td>11.6</td>
<td>42.9</td>
<td>42.9</td>
<td>7.6</td>
<td>1.2</td>
<td>2.6</td>
<td>1.0</td>
</tr>
<tr>
<td>FUNC-10</td>
<td>1.2</td>
<td>1.2</td>
<td>0.9 ±0.1</td>
<td>11.6</td>
<td>42.9</td>
<td>42.9</td>
<td>7.6</td>
<td>1.2</td>
<td>2.6</td>
<td>1.0</td>
</tr>
<tr>
<td>FUNC-15</td>
<td>1.2</td>
<td>1.2</td>
<td>0.9 ±0.1</td>
<td>11.6</td>
<td>42.9</td>
<td>42.9</td>
<td>7.6</td>
<td>1.2</td>
<td>2.6</td>
<td>1.0</td>
</tr>
<tr>
<td>FUNC-20</td>
<td>1.2</td>
<td>1.2</td>
<td>0.9 ±0.1</td>
<td>11.6</td>
<td>42.9</td>
<td>42.9</td>
<td>7.6</td>
<td>1.2</td>
<td>2.6</td>
<td>1.0</td>
</tr>
<tr>
<td>FUNC-25</td>
<td>1.2</td>
<td>1.2</td>
<td>0.9 ±0.1</td>
<td>11.6</td>
<td>42.9</td>
<td>42.9</td>
<td>7.6</td>
<td>1.2</td>
<td>2.6</td>
<td>1.0</td>
</tr>
<tr>
<td>FUNC-30</td>
<td>1.2</td>
<td>1.2</td>
<td>0.9 ±0.1</td>
<td>11.6</td>
<td>42.9</td>
<td>42.9</td>
<td>7.6</td>
<td>1.2</td>
<td>2.6</td>
<td>1.0</td>
</tr>
<tr>
<td>FUNC-35</td>
<td>1.2</td>
<td>1.2</td>
<td>0.9 ±0.1</td>
<td>11.6</td>
<td>42.9</td>
<td>42.9</td>
<td>7.6</td>
<td>1.2</td>
<td>2.6</td>
<td>1.0</td>
</tr>
<tr>
<td>FUNC-40</td>
<td>1.2</td>
<td>1.2</td>
<td>0.9 ±0.1</td>
<td>11.6</td>
<td>42.9</td>
<td>42.9</td>
<td>7.6</td>
<td>1.2</td>
<td>2.6</td>
<td>1.0</td>
</tr>
<tr>
<td>FUNC-45</td>
<td>1.2</td>
<td>1.2</td>
<td>0.9 ±0.1</td>
<td>11.6</td>
<td>42.9</td>
<td>42.9</td>
<td>7.6</td>
<td>1.2</td>
<td>2.6</td>
<td>1.0</td>
</tr>
<tr>
<td>FUNC-50</td>
<td>1.2</td>
<td>1.2</td>
<td>0.9 ±0.1</td>
<td>11.6</td>
<td>42.9</td>
<td>42.9</td>
<td>7.6</td>
<td>1.2</td>
<td>2.6</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The isotopic compositions of the starting FUNC material and evaporation residues are given in Table 1. Run durations listed in the Table are times during which samples were evaporated at 1900 °C. About 5% weight loss occurred even in the zero-time experiment as also indicated by lower SiO₂/Al₂O₃ and MgO/Al₂O₃ ratios in the FUNC-5 compared to the FUNC starting material. To compensate for the chemical and isotopic fractionations during the ramping up of the furnace temperature to 1900 °C, we used the zero-time run residue as the effective starting composition. Table 2 shows the degree of the evaporation expressed as fractions of magnesium (f_{24Mg}) and silicon (f_{28Si}) and oxygen (f_{16O}) remaining in the evaporated residues and also the associated isotopic fractionations relative to that of the zero-time run. Because aluminum is very refractory and does not evaporate during the experiments, the values of f_{24Mg} were calculated as (MgO/Al₂O₃)_{residue}/(MgO/Al₂O₃)_{zero-time} run with corrections for contribution of ²⁵Mg and ²⁶Mg (1.1% for the most evaporated sample FUNC-6). The f_{28Si} and f_{16O} were calculated in the same way.

Fig. 2 shows the evaporation trajectory from the FUNC experiments in the anorthite – gehlenite – forsterite ternary diagram. The figure shows that as evaporation proceeds the composition of the evaporation residues (shown as filled circles) evolves from the forsterite stability field to the melilitte stability field. Because CaO and Al₂O₃ do not evaporate from the melt at the conditions of the experiments, the plot of weight percents of SiO₂ versus MgO can be used to fully characterize the evaporation trajectory. The trajectory in SiO₂-MgO space is shown in Fig. 3. Figs. 2 and 3 also show evaporation trajectories of the FUN1 (open circles) and FUN2 (open diamonds) melts from Mendybaev et al. (2013a) evaporated at the same conditions and the bulk composition of CMS-1 CAI (FUNC shown as a star) normalized to 100% of CaO + MgO + Al₂O₃ + SiO₂ (24.95 wt% CaO, 12.42 wt% MgO, 36.22 wt% Al₂O₃, 26.41 wt% SiO₂). The thin curve fitting the experimental residues in Fig. 3 is an evaporation trajectory of the FUNC melt calculated the same way as described by Grossman et al. (2000) with the ratio of evaporation coefficients of Mg (γ_{Mg}) and Si (γ_{Si}) used in Eq. (4) is equal to 2.1 (see Section 4.1 for details). The composition of the gas phase in equilibrium with the melt along the calculated trajectory is shown in Fig. 4 which illustrates that the major magnesium and silicon bearing species above the FUC melt are Mg₂SiO₄ and SiO₂ as was also determined experimentally (e.g.,
Table 2
Fractions of magnesium, silicon and oxygen remaining in the FUNC evaporation residues and their isotopic compositions normalized to the zero-time residue.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run duration, f</th>
<th>$^{26}$Mg_{t=0} ±2</th>
<th>$^{25}$Mg_{t=0} ±2</th>
<th>$^{30}$Si_{t=0} ±2</th>
<th>$^{29}$Si_{t=0} ±2</th>
<th>$^{18}$O_{t=0} ±2</th>
<th>$^{17}$O_{t=0} ±2</th>
</tr>
</thead>
<tbody>
<tr>
<td>FUNC-5</td>
<td>0</td>
<td>1.000 ±0</td>
<td>0.0</td>
<td>0.6</td>
<td>0.0</td>
<td>0.3</td>
<td>1.000 ±0</td>
</tr>
<tr>
<td>FUNC-10</td>
<td>15</td>
<td>0.78 ±0</td>
<td>3.6</td>
<td>1.5</td>
<td>1.0</td>
<td>0.8</td>
<td>0.669 ±3</td>
</tr>
<tr>
<td>FUNC-3</td>
<td>30</td>
<td>0.51 ±0</td>
<td>9.9</td>
<td>2.5</td>
<td>1.0</td>
<td>0.5</td>
<td>0.518 ±3</td>
</tr>
<tr>
<td>FUNC-9</td>
<td>60</td>
<td>0.30 ±0</td>
<td>14.4</td>
<td>3.2</td>
<td>1.0</td>
<td>0.3</td>
<td>0.318 ±3</td>
</tr>
<tr>
<td>FUNC-3</td>
<td>45</td>
<td>0.20 ±0</td>
<td>23.4</td>
<td>5.7</td>
<td>1.0</td>
<td>0.2</td>
<td>0.206 ±3</td>
</tr>
<tr>
<td>FUNC-4</td>
<td>60</td>
<td>0.13 ±0</td>
<td>34.2</td>
<td>7.9</td>
<td>1.0</td>
<td>0.1</td>
<td>0.128 ±3</td>
</tr>
</tbody>
</table>

The magnesium, silicon and oxygen isotopic compositions of the FUNC evaporation residues expressed in the delta notation defined as

$$\delta^\text{Mg} = 1000 \times \left( \frac{\text{Me}_{\text{sample}}}{\text{Me}_{\text{standard}}} - 1 \right)$$

and

$$\delta^\text{Si} = 1000 \times \left( \frac{\text{Si}_{\text{sample}}}{\text{Si}_{\text{standard}}} - 1 \right),$$

for magnesium and silicon, for example, are listed in Table 1 relative to the starting materials. We found that isotopically all FUNC residues are uniform without any spatial variations in their Mg and Si isotopic compositions. As was noted above, to compensate for the isotopic fractionations during the ramping up the furnace temperature to 1900 °C, the isotopic compositions of the run products were normalized to the zero-time residue (sample FUNC-5; all in permil) are shown as the star. Oxygen isotopic composition of Nichols et al., 1995).

Figs. 2 and 3 illustrate that: 1) the evaporation of the silica-rich FUNC melt starts with faster evaporation of silicon compared to magnesium very much like what was observed in experiments of Richter et al. (2002, 2007) evaporating Type B CAI-like melt in vacuum, and opposite to what was observed in our experiments using the magnesia-rich FUN1 melt (Mendybaev et al., 2013a) in which magnesium initially evaporated faster than silicon; 2) after this initial evaporation step that lasted for ~15 min at 1900 °C, the evaporation trajectory of the FUNC melt converges with that of the FUN1 and FUN2 melts; 3) the evaporation trajectory of the FUNC melt passes very close to the composition of CMS-1 and it takes less than an hour to produce residues (FUNC-4 and FUNC-6, see Table 1) with chemical and isotopic compositions close to CMS-1; 4) the experimental evaporation trajectory of the FUNC melt can be nicely fit by a trajectory calculated using $\gamma_{\text{Mg}/\text{SiO}} = 2.1$. This ratio is different from $\gamma_{\text{Mg}/\text{SiO}} = 0.74$ used by Richter et al. (2007) to fit experimental data on the evaporation of a Type B CAI-like melt at 1600 °C and $\gamma_{\text{Mg}/\text{SiO}} = 1.0$ to fit experimental data at 1800 °C and 1900 °C. The difference in $\gamma_{\text{Mg}/\text{SiO}}$ of melt trajectories in the melilitic stability field reported by Richter et al. (2007) and those of melts in the forsterite stability field reported here are a clear indication that $\gamma_{\text{Mg}/\text{SiO}}$ depends not only on temperature but also on the composition of the starting materials evaporated. The change in the value of $\gamma_{\text{Mg}/\text{SiO}}$ from 2.1 to 1.0 as melt composition changes from forsteritic to melilitic explains the departure of the most evaporated experimental residue in Figs. 2 and 3 from the evaporation trajectory calculated using $\gamma_{\text{Mg}/\text{SiO}} = 2.1$.

4.2. Magnesium, silicon and oxygen isotopic compositions of the FUNC evaporation residues

The magnesium, silicon and oxygen isotopic compositions of the FUNC evaporation residues expressed in the delta notation defined as

$$\delta^\text{Mg} = 1000 \times \left( \frac{\text{Mg}_{\text{Me}}}{\text{Mg}_{\text{standard}}} - 1 \right)$$

and

$$\delta^\text{Si} = 1000 \times \left( \frac{\text{Si}_{\text{Si}}}{\text{Si}_{\text{standard}}} - 1 \right),$$

for magnesium and silicon, for example, are listed in Table 1 relative to the starting materials. We found that isotopically all FUNC residues are uniform without any spatial variations in their Mg and Si isotopic compositions. As was noted above, to compensate for the isotopic fractionations during the ramping up the furnace temperature to 1900 °C, the isotopic compositions of the run products were normalized to the zero-time residue (sample FUNC-5; $\delta^{26}$Si±0, $\delta^{25}$Mg±0, $\delta^{24}$Mg±0) and listed in Table 2 as $\delta^{26}$Mg_{t=0}, $\delta^{25}$Mg_{t=0}, $\delta^{24}$Mg_{t=0}, $\delta^{29}$Si_{t=0}, $\delta^{28}$Si_{t=0}, $\delta^{17}$O_{t=0} and $\delta^{18}$O_{t=0}. Relationships between $\delta^{29}$Si_{t=0} and $\delta^{28}$Mg_{t=0} and $\delta^{17}$O_{t=0} and $\delta^{25}$Mg_{t=0} in the FUNC residues (all in permil) are shown in Fig. 5 along with the measured average silicon and magnesium isotopic compositions of CMS-1 ($\delta^{28}$Mg = 32.72 ± 0.50‰, $\delta^{28}$Si = 15.54 ± 0.27‰; Williams et al., 2017) shown as the star. Oxygen isotopic composition of...
CMS-1 shown in Fig. 5 is our estimate of isotopic fractionation due to evaporation ($\Delta^{18}O \sim 32\%$) obtained by the extent of the change in $\delta^{18}O$ along that portion of the isotopic fractionations that fall along the slope 1/2 line defined by the spinel grains (see Fig. 1 for details). Fig. 5 shows that the isotopic composition of CMS-1 plots on or very close to the dashed curves which are the best fits through the FUNC experimental residues, and is within few permil of the fractionation in the most evaporated FUNC-6 residue ($\delta^{25}Mg_{t=0} = 35.0 \pm 0.3\%e$, $\delta^{29}Si_{t=0} = 16.6 \pm 0.1\%e$, and $\delta^{18}O_{t=0} = 29.1 \pm 0.1\%e$). The initially faster enrichments in heavy $^{28}Si$ relative to $^{25}Mg$ reflect the initially faster evaporation of silicon relative to magnesium seen in Figs. 2 and 3. Because under low vacuum conditions the SiO is expected to be the major evaporating gas containing oxygen (Fig. 4), one would also expect the initial faster enrichment of $^{28}O$ over $^{25}Mg$, which is also seen in Fig. 5. The fact that the $\delta^{29}Si$, $\delta^{25}Mg$ and $\delta^{18}O$ of CMS-1 are very close to the isotopic trajectories in $\delta^{29}Si$-$\delta^{25}Mg$ and $\delta^{18}O-$ $\delta^{29}Si$ space of the FUNC evaporation residues is strong evidence that isotopic composition of CMS-1 reflects the effect of evaporation in the same way as in our laboratory experiments.

### 4.3. Kinetic isotope fractionation factor for silicon, magnesium, and oxygen

When a silicate melt evaporates in vacuum, mass-dependent isotopic fractionation takes place due to a faster evaporation of lighter isotopes of a given element relative to heavy ones. As a measure of the isotopic fractionation we will use the kinetic isotopic fractionation factor $x_{2,1}$ defined as the ratio of isotopes 2 and 1 of element i in the evaporating gas divided by their ratio in the evaporating source melt (see Eqs. (6) and (7) in Section 2). It has often been assumed that the value of $x_{2,1}$ is equal to the inverse square root of the ratio of masses of evaporating isotopes, which in the case of $^{25}Mg$ and $^{24}Mg$, for example, would result in $x_{25,24} = \sqrt{24/25} = 0.97980$. It has been shown, however, that the experimentally measured values of $x_{2,1}$, at least in the case of vacuum evaporation of silicon, magnesium and oxygen from silicate melts (e.g., Davis et al., 1990; Wang et al., 2001; Richter et al., 2002, 2007; Knight et al., 2009; Mendybaev et al., 2013a), are significantly different from the theoretically expected values. In this section we use our experimental data on magnesium, silicon and oxygen isotopic fractionation during evaporation of FUNC forsterite-rich melt to determine the kinetic fractionations factors and compare them with those from our previous experiments.

Our estimate of the chemical composition of the starting FUNC melt that when sufficiently evaporated would result in a residue that is close chemically and isotopically to the CMS-1 FUN CAI, was made using Eq. (6) with values for the kinetic isotopic fractionation factors of $x_{25,24} = 0.98372 \pm 0.00041$ and $x_{29,24} = 0.9899 \pm 0.0004$ (Mendybaev et al., 2013a) between $^{25}Mg$ and $^{24}Mg$ and between $^{28}Si$ and $^{29}Si$, respectively, during evaporation of FUN1 and FUN2 melts in vacuum at 1900 °C. The assumption that $x_{25,24}$ and $x_{29,24}$ for the FUNC melt would be close to those for the FUN1 and FUN2 forsteritic residues was based on
iment as the effective initial composition in Eq. (6). For topic composition of the sample from the zero-time experiment, MgO, the next most abundant silicon- and magnesium-bearing species over the evaporating FUNC melt while the partial pressures of SiO<sub>2</sub> and oxygen-bearing species is SiO(g) while O<sub>2</sub>(g) and O(g) are less abundant by a factor of >50. The most abundant oxygen-bearing species, are lower by a factor of 50. The most abundant oxygen-bearing species is SiO(g) while O<sub>2</sub>(g) and O(g) are less abundant by a factor of 2 to 4. As silicon and magnesium evaporate, the residual FUNC melt becomes enriched in the refractory calcium and aluminum resulting in decrease of partial pressures of silicon- and magnesium-bearing species and increase of that of calcium- and aluminum-bearing species.

our finding that despite significant difference in the starting bulk chemical compositions of FUN1 and FUN2 the values of \(x_{25,24}\) and \(x_{29,28}\) were the same. We can now test this assumption using the results of the FUNC evaporation experiments listed in Table 2 to determine the values of \(x_{25,24}\) and \(x_{29,28}\), and also \(x_{18,16}\) for \(^{18}\)O/\(^{16}\)O.

As mentioned above we can use the elemental and isotopic composition of the sample from the zero-time experiment as the effective initial composition in Eq. (6). For \(^{25}\)Mg/\(^{24}\)Mg the fractionation, Eq. (7) can be rewritten as

\[
\ln(R/R_0) = (x_{25,24} - 1) \ln(f_{24Mg})
\]

where \(R = \text{^{25}Mg/}^{24}\text{Mg}\) of the evaporation residue, \(R_0 = \text{^{25}Mg/}^{24}\text{Mg}\) in the zero-time run sample FUNC-5, \(x_{25,24}\) is the kinetic fractionation factor for \(^{25}\)Mg/\(^{24}\)Mg, and \(f_{24Mg}\) is the fraction of the \(^{24}\)Mg remaining in the residue. According to Eq. (8) if the kinetic isotope fractionation due to evaporation is a Rayleigh process, then \(\ln(R/R_0)\) of a set of evaporation residues should be a linear function of \(\ln(f_{24Mg})\) with a slope corresponding to \(x_{25,24} - 1\).

This not only provides a way to accurately determine the value of \(x_{25,24}\) that fits the entire data set, but also serves to test and validate the key assumption that the process is indeed Rayleigh fractionation (e.g., Davis et al., 2015).

The same approach outlined above was used to determine the isotopic fractionation factors \(x_{29,28}\) for the fractionation of \(^{29}\)Si relative to \(^{28}\)Si and \(x_{18,16}\) for the fractionation of \(^{18}\)O relative to \(^{16}\)O.

Fig. 6 shows the magnesium isotopic composition of the FUNC evaporation residues given in Table 2 expressed as 1000*ln(\(R/R_0\)) versus fraction of \(^{25}\)Mgg remaining in the residue expressed as −ln(\(f_{24Mg}\)). The magnesium isotopic data of the residues, when plotted in this way, fall along a line with slope \(x_{25,24} - 1\) corresponding to \(x_{25,24} = 0.98383 ± 0.00033\), which within error is the same as \(x_{25,24} = 0.98372 ± 0.00041\) for the FUN1 and FUN2 forsterite-rich residues (Mendybaev et al., 2013a) and 0.98417 ± 0.00039 determined by Davis et al. (1990) for molten Mg<sub>2</sub>SiO<sub>4</sub>, but different from \(x_{25,24} = 0.98607 ± 0.00016\) determined for Type B CAI-like melt (Richter et al., 2007). Most importantly, the experimentally obtained values of \(x_{25,24}\) are distinctly different from \(x_{25,24} = \sqrt{24/25} = 0.97980\).

Fig. 7 is the same as Fig. 6 but for silicon isotopes. Similar to the magnesium data, the silicon isotopic compositions plot along a line with slope corresponding to \(x_{29,28} = 0.99010 ± 0.00038\) which is effectively the same as \(x_{29,28} = 0.9899 ± 0.0004\) determined for FUN1 and FUN2 evaporated in vacuum at 1900 °C (Mendybaev et al., 2013a) and \(x_{29,28} = 0.98985 ± 0.00044\) with no resolvable variations with temperature for Type B CAI-like melt (Knight et al., 2009). The experimentally obtained values...
of $x_{29.28}$ are close to, but resolvably different, from $x_{29.28} = \sqrt{m_{29} \gamma_{Mg}/m_{28} \gamma_{Si}} \approx 44/45 = 0.98883$.

Fig. 8 shows that when the measured oxygen isotopic composition data for the FUNC residues are plotted in the same way as was done for the magnesium and silicon data, they fall along two distinct trends. The evaporation residues with bulk composition in forsterite stability field define a line with the slope corresponding to $x_{18,16} = 0.9815 \pm 0.0016$ which is effectively the same as for evaporation residues from molten Mg$_2$SiO$_4$ ($x_{18,16} = 0.9805 \pm 0.0003$; Davis et al., 1990), a solar composition melt ($x_{18,16} = 0.9797 \pm 0.0030$ at 2000 °C and 0.9795 \pm 0.00010 at 1800 °C calculated from the data of Wang et al., 2001), and the FUN1 and FUN2 residues ($x_{18,16} = 0.9786 \pm 0.0015$, Mendybaev et al., 2010, 2013a).

The two most evaporated FUNC residues with bulk composition in the forsterite field plot along a line with the slope corresponding to $x_{18,16} \approx 0.9911$, which is close to $x_{18,16} \approx 0.9916$ for the most evaporated FUN2 residues with composition in the forsterite field (Mendybaev et al., 2010, 2013a).

5. DISCUSSION

A major goal of this study was to test by laboratory experiments if vacuum evaporation of an appropriately chosen the MgO- and SiO$_2$-rich melt could result in a residue with the chemical and isotopic compositions close to those of the natural CMS-1 FUN CAI, and if so, whether such a potential precursor of CMS-1 could be a condensate from a solar composition gas.

5.1. Chemical and isotopic composition of FUNC evaporation residues and CMS-1 FUN CAI

Two major processes that operate during evaporation of a melt in vacuum are: (1) evaporation from the melt/gas interface, and (2) supply of material from the inner parts of the molten droplet to the melt/gas interface by diffusion. The facts that all FUNC evaporation residues, including those quenched into forsterite + glass, are chemically and isotopically homogeneous (within the uncertainties) suggest that cation diffusion in the molten FUNC droplets at 1900 °C is fast compared to evaporation of Mg and Si from the surface of the melt and thus cannot be the rate-limiting step. Below we will discuss the results on evaporation of magnesium and silicon from the surface of FUNC melt.

5.1.1. Chemical composition

The evaporation of magnesium and silicon from silicate melts is expected to be dominated by the reactions:

\[
\text{MgO}_{(melt)} \rightarrow \text{Mg}_{(g)} + 0.5\text{O}_{2(g)} \quad (9) \\
\text{SiO}_2_{(melt)} \rightarrow \text{SiO}_{(g)} + 0.5\text{O}_{2(g)} \quad (10)
\]

Eqs. (2) and (3) indicate that the evaporation rates of magnesium and silicon, $J_{Mg}$ and $J_{SiO}$, are proportional to the vapor pressure of their dominating gas species $P_{Mg}$ and $P_{SiO}$ in equilibrium with the condensed phase (Fig. 4) and to the empirical evaporation coefficient $\gamma_{Mg}$ and $\gamma_{SiO}$.
the residual melt. As a result, during evaporation of any SiO$_2$- and MgO-rich melt the ratio $\alpha_{SiO_2}/\alpha_{MgO}$ is expected to settle around some value which will remain constant as evaporation proceeds. Fig. 9 illustrates this behavior during evaporation of the FUNC melt at 1900 °C; the activities of SiO$_2$ and MgO in an evolving melt were calculated the same way as used by Grossman et al. (2008) but with $\gamma_{SiO_2}/\gamma_{Mg}=2.1$ which was the value used in Fig. 3 to fit the composition of the experimental FUNC residues. Comparing Figs. 3 and 9 one can see that the observed evaporation trajectory from vacuum experiments follows the thermodynamically expected pattern: evaporation starts with faster loss of SiO$_2$ relative to MgO, followed by essentially a linear trend with slope close to $-0.5$ on the SiO$_2$–MgO diagram (Fig. 3). The linear part of the trend in Fig. 3 converges with those of FUN1 and FUN2. The same convergence was observed in all our experiments when MgO- and/or SiO$_2$-rich forsteritic melts were evaporated at the same conditions (Mendybaev et al., 2014). As the FUNC melt continues to evaporate, the composition of the residual melts becomes melilitic as illustrated in Fig. 2, and thus spinel, melilite and pyroxene observed in CMS-1 are expected to crystallize from this evolved melt as it cools.

5.1.2. Isotopic composition

The faster initial evaporation of SiO$_2$ over MgO from the FUNC melt in vacuum discussed above causes an initially higher degree of fractionation of silicon and oxygen isotopes (silicon evaporates mostly as SiO(g), see Fig. 4) compared to magnesium as reflected in the shape of $\delta^{28}$Si$_{t=0}$ and $\delta^{18}$O$_{t=0}$ vs. $\delta^{25}$Mg$_{t=0}$ curves in Fig. 5. We should note, however, that the initially faster losses of silicon and oxygen compared to magnesium from the FUNC melt does affect their isotopic fractionation factors: Figs. 6–8 show that all experimental residues with composition within the forsterite stability field plot along a single line with $x_{25,24} = 0.98383 \pm 0.00033$, $x_{29,28} = 0.99010 \pm 0.00038$ and $x_{18,16} = 0.9815 \pm 0.0016$. This, along with the fact that the experimentally obtained value of $x_{25,24}$, $x_{29,28}$ and $x_{18,16}$ for FUNC are within error the same as for forsteritic FUN1, FUN2 and Mg$_2$SiO$_4$ melts, suggests that the kinetic isotopic fractionation factor is independent of chemical composition of melts in the forsterite field. On the other hand, the above value of $x_{25,24}$ is significantly different from $x_{25,24} = 0.98607 \pm 0.00016$ determined by Richter et al. (2007) for the melilitic Type B CAI-like melt and $x_{25,24} = 0.98567 \pm 0.00046$ obtained by Mendybaev et al. (2013a) for the most evaporated (i.e., melilitic) FUN2 experimental residues. Similar changes in the isotopic fractionation factor were observed for oxygen isotopes: from $x_{18,16} = 0.9815 \pm 0.0016$ for melts in the forsterite field to $x_{18,16} \sim 0.9911$ for the FUNC residues in the melilitic field and from $x_{18,16} = 0.9786 \pm 0.0015$ to $x_{18,16} \sim 0.9916$ for the FUN2 residue compositions within the forsterite field and melilitic field, respectively. The fractionation factors for silicon isotopes were found to be the same both for forsteritic and melilitic melts: $x_{25,24} = 0.99010 \pm 0.00038$ within the whole range of compositions for the FUNC melt (Fig. 7) which is the same as $x_{29,28} = 0.9899 \pm 0.0004$ determined for FUN1 and FUN2 melt (Mendybaev et al., 2013a) and $x_{29,28} = 0.98985 \pm 0.00044$ for the melilitic Type B CAI-like melt (Knight et al., 2009). The reason why the
isotopic fractionation factors depend on melt composition for some elements but not for others remains unclear. It might be the result of changes in the melt structure as it evolves from forsteritic (SiO\textsubscript{2}\textsuperscript{2-} network structure) to mellite (Si\textsubscript{2}O\textsubscript{5}\textsuperscript{2-} network structure) with associated polymerization of SiO\textsubscript{2} monomers into Si\textsubscript{2}O\textsubscript{5}\textsuperscript{2-} dimers resulting in release of free oxygen (see Mysen et al., 1982 and references therein). The fact that there are no abrupt changes in the equilibrium speciation of the gas phase above the evaporating melt (Fig. 4) eliminates the gas phase being responsible for the changes in the isotopic fractionation factors.

As it was also noted earlier, the experimentally determined values of the isotopic fractionation factors shown in Figs. 6–8 are distinctly different from values calculated as the inverse square root of the ratio of mass of the isotopes. Lack of resolvable dependence of $\delta^{25,24}$ on sample size found in experiments when the mellite Type B CAI-like droplets 1–6 mm in size were evaporated in vacuum (Richter et al., 2007) and in low-pressure $H_{2}$ furnace (Parsad et al., 2000) along with theoretical arguments, allowed Richter et al. (2007) to make a persuasive case that the reason for the observed departure of the experimental fractionation factors from the inverse square root value was not the result of recondensation in the experiments. The implication is that the departure is due to the evaporation coefficients themselves being mass-dependent (i.e. $\gamma_{1,1}/\gamma_{1,2} \neq 1$).

Fig. 10 shows the oxygen isotopic composition of individual minerals in CMS-1 CAI and in the FUNC evaporation residues. Because only $\delta^{18}O$ of the FUNC residues was measured, the $\delta^{17}O$ values were calculated from the correlation between $\delta^{18}O$ and $\delta^{17}O$ measured previously in FUN1 and FUN2 evaporation residues ($\delta^{17}O = 0.515 \times \delta^{18}O$, Mendybaev et al., 2010, 2013a). We also assumed that the starting FUNC melt and precursor of CMS-1 had oxygen isotopic composition $\delta^{17}O = -49\%e$ and $\delta^{18}O = -48\%e$ (the values at the intersection of CCAM and FUN fractionation lines). Fig. 10 shows that not only the FUNC oxygen isotopic composition evolves along the same FUN FL as the range of the oxygen isotopic compositions measured. This again strongly indicates that evaporation played a major role during formation and evolution of FUN (and FUN-like) CAIs and is responsible for their enrichments in heavy isotopes.

5.2. Chemical composition of the precursor of CMS-1

The vacuum evaporation of the FUNC melt for 55 min at 1900 °C resulted in a residue (FUNC-6) with chemical and magnesium, silicon, and oxygen isotope compositions close to that of CMS-1. This suggests that our initial choice of the possible precursor of CMS-1 was quite reasonable and thus its composition should be close to that of the zero-time FUNC-5 residue: 34.1 wt% MgO, 13.9 wt% Al\textsubscript{2}O\textsubscript{3}, 42.9 wt% SiO\textsubscript{2} and 9.1 wt% of CaO.

The precursor composition of CMS-1 can also be calculated using Eq. (6) to determine the amounts of MgO and SiO\textsubscript{2} evaporated given the isotopic composition of magnesium and silicon in CMS-1 and the experimentally determined values of $\delta^{25,24}$ and $\delta^{29,28}$ (Figs. 6 and 7). This amount of evaporated magnesium and silicon is then added back to the present-day bulk composition of the inclusion to give an estimate of its precursor. Using the values of $\delta^{25}Mg = 32.72 \pm 0.50\%e$ and $\delta^{29}Si = 15.54 \pm 0.27\%e$ for CMS-1 CAI (Williams et al., 2017) and fractionation factors $\varepsilon_{25,24} = 0.98383 \pm 0.00033$ for $^{25}Mg/^{24}Mg$ and $\varepsilon_{29,28} = 0.99010 \pm 0.00038$ for $^{29}Si/^{28}Si$, the estimates of the fraction of original magnesium and silicon remaining in the inclusion calculated using relationship (6) and taking into account abundance ratios of magnesium (Catanzaro et al., 1966) and silicon (Coplen et al., 2002) isotopes would be $f^{29,28}_{Mg} \sim 0.128$ to 0.148 and $f^{29,28}_{Si} \sim 0.193$ to 0.229. These estimated values also take into account uncertainties both in the measured isotopic fractionations in CMS-1 CAI and in the experimentally determined fractionation factors $\varepsilon_{25,24}$ and $\varepsilon_{29,28}$. Thus the CMS-1 precursor composition can be estimated by adding back $\sim$85 to 87% of lost magnesium and $\sim$77 to 81% of lost silicon to the present-day bulk composition of the inclusion normalized to 100% of MgO + CaO + Al\textsubscript{2}O\textsubscript{3} + SiO\textsubscript{2} (24.95 wt% CaO, 12.42 wt% MgO, 36.22 wt% Al\textsubscript{2}O\textsubscript{3}, 26.41 wt% SiO\textsubscript{2} and renormalizing again to 100% and is shown in Fig. 11 as a cloud of open circles with composition ranging from $\sim$29 to 36 wt % MgO and $\sim$41.0 to 49 wt% SiO\textsubscript{2} (CaO/Al\textsubscript{2}O\textsubscript{3} = 0.69). The range of the estimated CMS-1 precursor composition is somewhat SiO\textsubscript{2}-rich compared to the equilibrium assembly of clinopyroxene + spinel + forsterite which in a solar composition gas is stable from $\sim$1260 K to 1290 K at $P_{H_{2}} = 10^{-5}$ bars (from $\sim$18 to 45 wt% MgO in Fig. 11) and from $\sim$1370 K to 1415 K at $P_{H_{2}} = 10^{-7}$ bars (from...
~26.5 to 46.5 wt% MgO in Fig. 11). It should be mentioned that increasing MgO content of the present-day composition of CMS-1 CAI by 3 wt% and lowering SiO2 content by 3 wt% would shift the cloud of CMS-1 precursors to the right by 6.5 wt% along x-axis and down by 6 wt% along y-axis, and onto the calculated solar gas condensation curve. There are various reasons why the measured present-day bulk composition of CMS-1 FUN CAI might be uncertain by as much as several wt%. First, the reported bulk chemical composition of CMS-1 FUN CAI is based on analyses of one section which might not reflect the average bulk composition of the inclusion. Furthermore, the reported CaO/Al2O3 ratio of CMS-1 (0.69) is significantly lower than the solar ratio of 0.792, which could mean that the reported composition does not represent the inclusion as a whole, or that the precursor of CSM-1 was not a direct condensate from an exact solar composition gas but rather is an aggregate of early Solar System condensates mixed in different proportions.

Regardless of whether CMS-1 precursor was or was not a direct condensate from a solar composition gas, its isotopic compositions clearly indicate that the precursor has experienced a relatively short but energetic thermal processing (such as shock heating) under low-pressure conditions in the solar nebula which caused its melting and evaporation of substantial amounts of magnesium, silicon, and oxygen (Richter et al., 2006). Given that the CMS-1 precursor was undoubtedly very forsterite-rich, a sufficient degree of melting at above the solidus of ~1300 °C (Osborn et al., 1969; our calculated liquidus temperature is 1532 °C which is close to that of Osborn and Gee, 1969) will be required to produce significant amount of melt to allow such massive volatilization and isotopic fractionation. In order to produce the observed enrichments in heavy magnesium and silicon isotopes of the order of δ25Mg ~ 30–40‰ and δ29Si = 15–20‰ by evaporation in a solar gas at P(H2) = 10−4 bar, it would take only a few minutes if precursor material had evaporated at 1900 °C and not much more than about an hour if evaporated at 1600 °C (see Richter et al., 2002, 2007; Mendybaev et al., 2013b for the effect of P(H2) and temperature on the evaporation rates of silicate melts). We should note that evaporation of magnesium and silicon from the CMS-1 precursor would lower the liquids of the residual melt such that in a solar nebula environment the droplet will remain molten as it cools and will continue to evaporate at temperatures significantly less than 1600 °C.

5.3. Laboratory evaporation experiments and natural FUN CAIs

Figs. 3 and 5 illustrate that a simple isothermal evaporation in vacuum at 1900 °C of the FUNC starting material results in a residue trajectory that passes very close to Allende FUN CAI CMS-1 by simultaneously fitting its reported chemical and isotopic composition. To the best of our knowledge, the only FUN CAIs other than the
one studied here for which the bulk chemical and silicon, magnesium and oxygen isotopic compositions have been reported are Allende C1 and Vigarano 1623-5 (see Mendybaev et al., 2013a). Despite this lack of reported bulk chemical composition for other FUN (and FUN-like) CAIs, we can still test whether the correlations between the various isotopic fractionations in these CAIs are comparable to those of the experimental evaporation residues. Fig. 12 compares the relationships between $\delta^{29}$Si versus $\delta^{25}$Mg and $\delta^{18}$O versus $\delta^{25}$Mg in FUN (and FUN-like) CAIs for which the relevant data have been reported (Clayton et al., 1984, 1988; Brigham, 1990; Davis et al., 1991; Thrane et al., 2008; Williams et al., 2017) with that from the FUNC, FUN1, and FUN2 evaporation residues with composition within the forsterite stability field (Fig. 2). The solid lines are best fits to the $\delta^{29}$Si versus $\delta^{25}$Mg data and for the $\delta^{18}$O versus $\delta^{25}$Mg data from FUN1 and FUN2 experiments (Mendybaev et al., 2013a). The dotted lines are the best fits of the FUNC data. The dashed line in (b) is an extrapolation of the $\delta^{18}$O-$\delta^{25}$Mg correlation line of the FUN1 and FUN2 data.

Fig. 12. Relationships between $\delta^{29}$Si and $\delta^{25}$Mg (a) and $\delta^{18}$O and $\delta^{25}$Mg (b) in FUN CAIs (shown as stars). $\delta^{29}$Mg and $\delta^{28}$Si values in panel (a) are from Clayton et al. (1988), Brigham (1990) and Davis et al. (1991). The $\delta^{18}$O values in panel (b) are our estimates of the oxygen isotopic fractionation caused by evaporation using data of Davis et al. (2000), Krot et al. (2014), and Williams et al. (2017). Also shown are data for the FUNC (solid circles), FUN1 (open squares) and FUN2 (open diamonds) evaporation residues with composition within the forsterite stability field (Fig. 2). The solid lines are best fits to the $\delta^{29}$Si versus $\delta^{25}$Mg data and for the $\delta^{18}$O versus $\delta^{25}$Mg data from FUN1 and FUN2 experiments (Mendybaev et al., 2013a). The dotted lines are the best fits of the FUNC data. The dashed line in (b) is an extrapolation of the $\delta^{18}$O-$\delta^{25}$Mg correlation line of the FUN1 and FUN2 data.

6. CONCLUSIONS

The chemical and isotopic compositions of experimental residues produced by evaporation of a silicon-
magnesium-rich melt at 1900 °C in vacuum together with the properties of CMS-1 FUN CAIs allow us to conclude:

(1) Evaporation of the forsteritic FUNC melt in a simple one-stage heating process in vacuum at 1900 °C for less than an hour resulted in a residue with bulk chemical and isotopic compositions very close to that of Allende FUN CAI CMS-1. If the evaporation had taken place in a low-pressure hydrogen-dominated solar nebula gas, it would have taken only a few minutes at 1900 °C and less than an hour at 1700 °C to evaporate ~80% of silicon and ~85% of magnesium from a precursor material to produce enrichments in heavy silicon and magnesium isotopes to the levels comparable to what is measured in CMS-1 ($^{28}\text{Si} = 15.5 \pm 0.27\%e$ and $^{26}\text{Mg} = 32.7 \pm 0.50\%e$). These very short timescales suggest that the precursor of CMS-1 experienced very energetic (>1700 °C) short duration event(s) that resulted in at least partial melting and significant evaporation of silicon, magnesium and oxygen.

(2) The experimentally determined kinetic isotopic fractionation factors $x_{25.24} = 0.98383 \pm 0.00033$, $x_{29.28} = 0.99010 \pm 0.00038$ and $x_{18,16} = 0.9815 \pm 0.00016$ for the forsterite-rich FUNC melt are within error the same as reported previously for FUN1 and FUN2 forsterite-rich melts. As residual melt enters the melilite stability field, $x_{18,16}$ changes to ~0.9911 which is close to that of the most evaporated FUN2 melt reported by Mendybaev et al. (2013a).

(3) Using the present-day bulk chemical and isotopic compositions of CMS-1 of Williams et al. (2017) and the experimentally determined values for $x_{25.24}$ and $x_{29.28}$, we estimated that the CMS-1 precursor was a forsterite-rich object containing ~29 to 36 wt % MgO and ~41.0 to 49 wt% SiO$_2$ which is close to but somewhat more silica-rich than the clinopyroxene + spinel + forsterite assembly that is stable in a solar composition gas at 1370–1410 K at P$_{H_2}$ = 10$^{-3}$ bars and 1260–1290 K at P$_{H_2}$ = 10$^{-5}$ bars. These temperatures are significantly lower than that required to melt the CMS-1 precursor (solidus ~1300 °C, liquidus 1532 °C) to a very high degree such that evaporation of silicon and magnesium from such melt would result in the isotopic fractionations measured in the CMS-1 CAI.

REFERENCES


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