1 **Experimental determination of Si, Mg, and Ca isotope fractionation during**

2 **enstatite melt evaporation**

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12 **Abstract**

13 Evaporation of silicate materials from Earth or its precursors may be important in

14 shaping their primordial compositions represented by undifferentiated meteorites, e.g.,

15 enstatite chondrites; however, the conditions under which evaporation occurs and the

16 extent of evaporation-induced elemental and isotope fractionation remain uncertain.

17 Here, we experimentally determine the volatility and isotope fractionation of Si, Mg, Ca,

18 Nb, and Ta during enstatite melt evaporation at 2423–2623 K using a High-temperature

19 Conical Nozzle Levitator. Homogenous glasses are recovered after experiments, then we

20 use EPMA and LA-ICP-MS to measure the elemental compositions, MC-ICP-MS to

21 measure the Si and Mg isotopes, and TIMS to measure the Ca isotopes. Our results show

22 that the evaporation rates of Si are larger than Mg and the mean vapor/melt isotope

23 fractionation factors (α=R_{vapor}/R_{melt}; R=isotope ratio) are 0.99585±0.00002 for ^{29}Si/^{28}Si

24 and 0.98942±0.00130 for ^{25}Mg/^{24}Mg. However, neither evaporative loss of Ca, Nb, and

25 Ta nor Ca isotope fractionation was observed within analytical errors. In conjunction

26 with previous studies, we find that in an evaporation experiment the saturation degree

27 (partial vapor pressure/equilibrium vapor pressure) of Si (S_{Si}) is larger than S_{Mg} when Si

28 is more volatile than Mg, and vice versa. If the Mg/Ca and Si/Ca ratios and isotopes in

29 the bulk silicate Earth are attributed to the evaporation of enstatite chondrite-like

30 precursors, evaporation temperatures > 5000 K and S_{Si} < S_{Mg} are required.

31

32 **Keywords:** Enstatite, planetary evaporation, high-temperature experiments, isotopic

33 fractionation, Earth's composition

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Introduction

36

37   The chemical composition of the bulk silicate Earth (BSE) provides tight constraints

38   on the nature of Earth's building blocks, and Earth's formation and evolution processes.

39   The BSE and enstatite chondrites (EC) share nearly identical mass-independent stable

40   isotopes of various elements such as O, Cr, and Ti, and therefore it has been proposed

41   that Earth's main building blocks are EC-like materials (Warren 2011; Dauphas 2017).

42   However, this hypothesis has been challenged by the fact that the isotope compositions

43   of Si and Mg in the BSE are heavier than those observed in ECs (Fitoussi and Bourdon

44   2012; Hin et al. 2017). Such discrepancies in Si and Mg isotopes were attributed to the

45   processes producing mass-dependent isotopic fractionation, such as the incorporation

46   of Si in Earth's core to explain the BSE's heavy Si isotopes because of the preferential

47   partitioning of light Si isotopes into metallic phases (Shahar et al. 2009). However, this

48   requires Si in Earth's core (~12 wt.%) in excess of that permitted by geophysical

49   constraints (Badro et al. 2014) or unrealistically low core–mantle equilibration

50   temperatures (~1500 K) (Fitoussi and Bourdon 2012). The required ~12% Si in the

51   core could potentially be reduced if we consider the Si isotope heterogeneity in the

52   mantle predicted by first-principles calculations, which suggest that the lower mantle

53   (and hence the BSE) might have lighter Si isotopes compared to the upper mantle

54   (Huang et al. 2014). However, core-formation cannot explain the BSE's heavy Mg

55   isotopes due to the lithophile nature of Mg (Du et al. 2017).

56   Evaporation of molten planetesimals resulting from the decay of short-lived

57   nuclides or accretionary collision (Tonks & Melosh, 1993; Young et al., 2019), which will

58   be referred to as "post-nebular evaporation" hereafter (O'Neill and Palme 2008), may

59   cause mass-dependent Si and Mg isotopic fractionation and explain the BSE's heavy Si

60   and Mg isotopes. Pringle et al. (2014) argued that planetesimal evaporation may explain

61   the heavy Si isotopes in angrites (volatiles-depleted mafic igneous meteorites from an

62   early formed asteroid), and a series of melt–vapor equilibration events during

63   collisional accretion may explain the BSE's heavy Mg isotopes (Hin et al. 2017). Young et

64   al. (2019) evaluated the near-equilibrium isotopic fractionation during planetesimal

65   evaporation, and suggested that the BSE's Mg and Si isotopes may result from losing

66   ~12% Mg and ~15% Si. However, both the Hin and Young models, if using EC-like

67   precursors, cannot explain the BSE's Mg/Ca and Si/Ca ratios due to insufficient Si or Mg

68   loss. Moreover, whether the use of the equilibrium isotopic fractionation factors (α)

69   approximated to reduced partition function ratios of gaseous species and forsterite in

70 these previous models affects the conclusions remains uncertain.

71 To investigate whether post-nebular evaporation can explain the Mg/Ca and Si/Ca

72 ratios and isotopes in the BSE, the α of Si, Mg, and Ca during evaporation of silicate melts

73 of relevant compositions must be determined. Most previous studies focus on

74 evaporation at nebular-like conditions (Davis et al. 1990; Richter et al. 2002, 2007;

75 Mendybaev et al. 2013, 2017, 2021), where the surrounding gas pressure is low (<10⁻⁴

76 bar). However, post-nebular evaporation likely occurs at dynamic gas environments

77 with high surrounding gas pressures and temperatures due to planetary collisions

78 (Visscher and Fegley 2013) or high oxygen fugacities (Sossi et al. 2019), which may

79 result in different isotopic fractionations. For example, Badro et al. (2021) found that the

80 α of Si and Mg in their 1-atm levitation evaporation experiments are larger than those in

81 the vacuum experiments even though they performed their experiments with the same

82 CAI-like composition at the same temperature (1873 K). To better understand the

83 isotopic fractionation of Si, Mg, and Ca during post-nebular evaporation, here we

84 experimentally measure the α of Si, Mg, and Ca during enstatite melt evaporation at

85 2423–2623 K. We then evaluate whether post-nebular evaporation can explain the

86 Mg/Ca and Si/Ca ratios and isotopes in the BSE.

87

88 **Methods**

89 **High-temperature experiments**

90 We synthesized a silicate (~2 g) with enstatite composition and used it as an analog

91 of the silicate part of EC. Pure MgO, SiO₂, and CaCO₃ powders (>99.995%) in enstatite

92 stoichiometry, doped with trace amounts of Nb and Ta, were mixed in an agate mortar

93 for ~1 hour and then melted in a Pt crucible in a muffle furnace. The sample was heated

94 at 1973 K in air for 1 hour and quenched by dropping the Pt crucible into cold water.

95 The recovered silicate was white due to the formation of micro-sized crystals during

96 quench (Figures 1a-c). The recovered silicate was broken into small pieces using a

97 hammer. Some pieces were cut and polished into beads of ~3mm diameter for

98 subsequent evaporation experiments (Figure 1a), and the other pieces were randomly

99 picked for EPMA and LA–ICP–MS analyses to obtain the chemical compositions. The

100 random pieces of synthetic silicate contained 63.26±1.22 wt.% SiO₂, 35.19±1.12 wt.%

101 MgO, 1.27±0.18 wt.% CaO, 84±7 ppm Nb, and 204±16 ppm Ta (Table 1; ±2σ).

102 The evaporation experiments were conducted by using a High-temperature Conical

103 Nozzle Levitator at Materials Development, Inc. This method avoids chemical

104   contamination from capsule material or wire loops at high temperatures, and provides

105   conditions that achieve evaporation from free surfaces in a controlled-gaseous

106   environment (Tangeman et al., 2001). Silicate beads of ~3 mm diameter were levitated

107   in an argon gas flow of ~600 SCCM through a 1 mm diameter nozzle, with gas advective

108   velocity ≈13 m/s. The argon gas was in 99.999% purity, containing ~1 ppm O_2, ~5 ppm

109   N_2, and ~2 ppm $H_2O+CO+CO_2$ in volume. The samples were heated within 5 seconds to

110   the target temperatures of 2423, 2523, and 2623 K by using a partially focused CO_2 laser

111   (10.6 µm wavelength, model i401, Synrad, Inc.). The sample surface temperature was

112   measured by using an optical pyrometer (Chino model IRC, Chino Works America), and

113   the temperature fluctuation was ~50 K and occasionally over 100 K in a few

114   experiments (supplementary Figure S1). The experiments were quenched by shutting

115   off the laser after running 2–9 mins. The effect of temperature fluctuation on the run

116   duration at the target temperature was estimated using the procedure of Ni et al. (2021)

117   (supplementary Text S1). The sample was weighed before and after the experiment to

118   calculate the sample mass loss fraction. In our laser-heated experiments, the sample

119   mass loss fraction should not exceed 0.5% at heating up stage (~5 s), given an average

120   mass loss rate of ~0.1% per second at 2623 K, as calculated by assuming a linear

121   relationship between the total mass loss fraction and the run duration. Therefore, the

122   chemical fractionation during the heating up stage is negligible and not considered in

123   subsequent discussions.

124   **Analytical techniques**

125   The recovered samples were homogeneous glasses (Figures 1d-e and Figure S2).

126   One half of the sample was prepared for major and trace element analyses using EPMA

127   and LA-ICP-MS, respectively, and the other half prepared for Si, Mg, and Ca isotopic

128   analyses.

129   Major element compositions of all samples were analyzed with a JEOL JXA-8230

130   EPMA equipped with five wavelength-dispersive spectrometers (WDS). The samples

131   were coated with a thin conductive carbon film (20 nm) before analysis. Operating

132   conditions for quantitative WDS analyses involved an accelerating voltage of 15 kV, a

133   beam current of 10 nA, and a 10 µm spot size. The peak counting time was 10 s for Si,

134   Mg, and Ca, and the background counting time was 5 s on the high- and low-energy

135   background positions. Olivine (Si, Mg) and Diopside (Ca) are used as the standards. As

136   for the line scanning, an accelerating voltage of 15 kV, a beam current of 50 nA, and a 2

137   µm spot size were used. The dwell time of every spot is 1s.

138   The Nb and Ta concentrations in the starting enstatite glass and the evaporated

139   silicate glasses were measured by using an Agilent 7900 Quadrupole ICP-MS coupled to

140   a Photon Machines Analyte HE 193-nm ArF Excimer Laser Ablation system (Li, 2018).

141   Helium was applied as a carrier gas. Argon was used as the make-up gas and mixed with

142   the carrier gas via a T-connector before entering the ICP. Reference material NIST 610

143   was used as external standard. The Si contents in the samples measured by EPMA were

144   used as internal standard. Analytical uncertainties for the trace elements are within 5%

145   relative.

146   The Si and Mg isotopes of the sample glasses were measured using MC-ICP-MS

147   (Neptune Plus from Thermo-Fisher Scientific) at Key Laboratory of Crust-Mantle

148   Materials and Environments, University of Science and Technology of China. Chemical

149   purification for measuring Si isotopes was processed following the method modified

150   from (Georg et al. 2006). The sample powder was mixed with high purity NaOH and

151   then was fused in a silver crucible at 993 K for 10 mins to produce a water-soluble

152   metastable silicate. The fusion cake was then fully dissolved with ultra-pure water (18.2

153    $M\Omega\cdot cm$) and HNO_3 was added to attain a sample solution of 1% HNO_3 (v/v) for column

154   chemistry. The sample solution (containing ~30 μg Si) was purified through 2 mL of

155   cation exchange resin (AG50W-X12, 200–400 mesh, Bio-Rad, USA) that had been

156   cleaned with 3 mol/L HNO_3, 6 mol/L HNO_3, 6 mol/L HCl, and 6 mL ultra-pure water in

157   sequence. Silicon was collected from the column right after 1 mL sample solution of 1%

158   HNO_3 was loaded and then eluted with 6 mL ultra-pure water (Yu et al. 2018).

159   Chemical purification for measuring Mg isotopes was processed following the

160   method of An et al. (2014). A mixture of concentrated $HF–HNO_3$ (~3:1, v/v) was used for

161   digestion. After the initial digestion and evaporation to dryness, samples were treated

162   with aqua regia and dried again. Samples were then refluxed with concentrated HNO_3 to

163   remove residual fluorides and finally dissolved in 1 mL 2 N HNO_3 before column

164   chemistry (An et al. 2014). Mg purification was performed through 2 mL of Bio-Rad

165   AG50W-X12 (200–400 mesh) cation resin. Before the start of every chemical separation

166   procedure, the resin was pre-cleaned with 4 mL 4 N HNO_3 + 0.5 N HF and ultra-pure

167   water alternatively three times, and then conditioned with 3 mL 2 N HNO_3 twice. 5 mL

168   2N HNO_3 + 0.5N HF and 6 mL1 N HNO_3 was loaded to elute the interferential elements.

169   Magnesium was then collected right after 22 mL 1 N HNO_3 was eluted.

170   Both Si and Mg isotopes were analyzed using MC-ICP-MS. A quartz dual

171   cyclonic-spray chamber and a PFA microflow nebulizer (Elemental Scientific Inc., U.S.A.)

172   with an uptake rate of ~50 μL/min were used for sample introduction. The three stable

173   isotopes of Si and Mg were collected by Faraday cup L3 (^{28}Si and ^{24}Mg), C (^{29}Si and ^{25}Mg),

174   and H3 (^{30}Si and ^{26}Mg). A block of analysis consisted of 60 cycles of data with an

175   integration time of 2.097 s per cycle. A single analysis is corresponded to 1 bracket using

176   the sample-standard bracketing method, while an analytical session consisted of 3

177   repeated runs of the same solution. An on-peak baseline was measured with 30 cycles

178   and 1 s integration time per cycle. Instrument operating conditions are described in

179   supplementary Table S1.

180   The analyses of Ca isotopes were performed using thermal ionization mass

181   spectrometry (TIMS, Thermo Triton) at State Key Laboratory of Isotope Geochemistry,

182   Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. An aliquot

183   containing ~30 μg of Ca was mixed with ^{42}Ca - ^{43}Ca double-spike solution (^{40}Ca/^{42}Ca ≈ 7)

184   before purification. The samples were then dried down and re-dissolved in 50 μL of 1.6

185   N HCl for the column chemistry. Calcium purification was performed using 1 mL of

186   Bio-Rad AG MP-50 cation resin. Samples were loaded to preconditioned (with 5 mL of

187   1.6 N HCl) resin, then matrices were eluted with 16.95 mL of 1.6 N HCl, and Ca was

188   collected with 27 mL of 1.6 N HCl (Liu et al. 2017). After the Ca-bearing solution was

189   evaporated to dryness, it was treated with concentrated HNO_3 several times and finally

190   re-dissolved it with 10 μL 10% v/v HNO_3 for TIMS analysis (Liu et al. 2017). About 3 μg

191   purified Ca isotopes were loaded as calcium nitrate onto a 99.995% Ta filament. The

192   measurement of calcium began when the intensity of the ^{40}Ca signal reached 15 V, and

193   each run consisted of 8 blocks and 26 cycles. Instrumental fractionation was corrected

194   using the ^{42}Ca – ^{43}Ca double spike technique using an offline iterative routine with an

195   exponential law, similar to the method of Heuser et al. (2002). The details of purification

196   procedures and instrumental running conditions are described by Liu et al. (2017) and

197   Wu et al. (2020).

198   The Si, Mg, and Ca isotopes are expressed in the standard δ-notation in per mil

199   relative to the standard:

$$\delta^j E\ (\text{‰}) = \left[\left(\frac{^jE}{^iE} \right)_{sample} \Big/ \left(\frac{^jE}{^iE} \right)_{standard} - 1 \right] \times 1000 \qquad (1)$$

201   where j and i are the heavy and light atomic number of element E, respectively. The

202   standards for Si, Mg, and Ca isotopes are NBS-28, DSM-3, and SRM915a, respectively. We

203   routinely measured the isotopic compositions of other standards, BHVO-2, BCR-2,

204   SRM915a, and Seawater. Our obtained data (δ^{29}Si$_{BHVO-2}$ = −0.162±0.020‰, δ^{25}Mg$_{BCR-2}$ =

205   −0.108±0.012‰, δ^{44}Ca$_{SRM915a}$ = 0.01±0.10‰, δ^{44}Ca$_{seawater}$ = 1.88±0.15‰) are in good

206   agreement with the suggested values (http://georem.mpch-mainz.gwdg.de). No

207   mass-independent fractionation was found for Si or Mg isotopes (Figure S3) as for Ca

208   isotopes (Zhang et al. 2014).

209

210   **Results**

211   **Elemental loss fraction and fractionation**

212   The chemical compositions and sample mass loss fraction of the recovered samples

213   are summarized in Table 1. The SiO_2 contents of the samples (45.30–57.53 wt.%)

214   decrease with increasing the sample mass loss fraction. Much faster evaporation of Si

215   compared to that of other elements results in an increase of the MgO and CaO contents

216   (40.37–52.59 wt.% and 1.32–2.22 wt.%, respectively), as well as the Nb and Ta contents

217   (102–127 ppm and 251–324 ppm, respectively) with increasing the fraction of sample

218   lost.

219   Estimation of the elemental loss fractions requires knowing the composition of

220   starting silicate beads. The compositions measured from random pieces of synthetic

221   starting silicate here were used as the representative of starting composition since we

222   did not measure the compositions of the silicate beads used in our experiments. In order

223   to check the representative of the measured compositions, the CaO contents of the

224   starting silicate beads were estimated by mass balance given its refractory nature.

225   Figure 2a shows that CaO contents of the starting silicate beads are different, but with

226   an average value identical to the CaO content we measured for the bulk starting silicate

227   (1.27±0.18 wt.%), suggesting that the randomly-picked pieces could reasonably

228   represent the silicate beads used in our experiments despite minor heterogeneities. The

229   SiO_2 and MgO contents of the starting silicate beads should also within the ranges of

230   measured SiO_2 (63.26±1.22 wt.%) and MgO (35.19±1.12 wt.%) contents of bulk starting

231   silicate as well as CaO, although they could not be estimated in similar way due to the

232   evaporation loss.

233   There are two methods to calculate the molar loss fraction (f) of an element: 1) by

234   mass balance or 2) by the approach of normalization to a refractory element (e.g., Ca)

235   and the starting material as done in previous studies (Richter et al. 2007; Mendybaev et

236   al. 2013). We used both methods to calculate the f_{Si} and f_{Mg}. The former method is

237   readily to apply given the total mass loss of the sample and its SiO_2 and MgO contents

238   before and after experiment (Table 1). However, the latter method is not suitable to our

239   experiments due to the large uncertainties of starting CaO content (1.27±0.18 wt.%). In

240 the latter method, f_{Mg} could be calculated via $1 - (MgO/CaO)_{norm}$, where $(MgO/CaO)_{norm}$

241 refers to MgO/CaO ratio of the sample divided by MgO/CaO ratio of the starting

242 materials, and f_{Si} is calculated in the same way. However, if calculating $(MgO/CaO)_{norm}$

243 using the CaO content of the bulk starting silicate, our samples M04, M07, and M09 all

244 produce $(MgO/CaO)_{norm}$ values larger than one and consequently negative f_{Mg} values

245 (Figure 2b), which should not be possible for evaporation experiments. We noticed that

246 our bulk starting silicate is not homogeneous in CaO (Figure 2a) probably due to the

247 formation of microcrystals during the synthesis (Figure 1c). Therefore, the calculated f_{Mg}

248 of these three experiments could be seriously affected by the heterogeneity of CaO in the

249 bulk starting silicate. For this reason, the f values calculated by mass balance (Figure 2c;

250 Table 1) will be used in below discussions.

251 Plotting f_{Si} and f_{Mg} as a function of the sample mass loss fraction, Figure 3a shows

252 that up to ~60% Si was evaporated, whereas Mg exhibited significant evaporation only

253 when ~20% sample mass (or ~30% Si) was evaporated. Limited Mg was evaporated at

254 the early stage of evaporation leading to the produced vapor depleted in Mg relative to

255 Si, which is consistent with previous theoretical results on enstatite melt (Xiao and

256 Stixrude 2018). These results also indicate that the evaporation rate of Si is larger than

257 Mg, *i.e.,* Si is more volatile than Mg in our experiments. Our results also demonstrate that

258 Ca, Nb, and Ta were not evaporated within analytical uncertainty (Figure S4). The

259 refractory nature of Ca is consistent with the thermodynamical predictions (Ivanova et

260 al., 2021) and previous evaporation experiments (e.g., Richter et al., 2007; Mendybaev et

261 al., 2013; 2021), which showed that Ca evaporates only after Si and Mg are exhausted. In

262 addition, the refractory nature of Nb and Ta is in accordance with their high 50%

263 condensation temperature (Wood et al. 2019), suggesting that evaporation may not

264 cause Nb and Ta fractionation nor the subchondritic Nb/Ta ratio in the BSE (Münker et

265 al. 2003, 2017).

Isotopic fractionation

267 As shown in Figure 3b, both the bulk starting silicate-normalized $\delta^{29}Si_{norm}$ (~1–

268 3.5‰) and $\delta^{25}Mg_{norm}$ (~0.1–1.2‰) increase with increasing sample mass loss fraction.

269 However, initially Si was lost faster than Mg, and $\delta^{29}Si_{norm}$ was larger than $\delta^{25}Mg_{norm}$.

270 Enrichment of the residual melt in MgO results in faster evaporation of Mg and thus

271 faster increase of $\delta^{25}Mg_{norm}$ after ~20% sample mass was lost. These results indicate

272 that light Mg and Si isotopes partitioned preferentially into the vapor during

273 evaporation, consistent with theoretical expectations and earlier experimental works

274   (e.g., Richter et al., 2002, 2007; Mendybaev et al., 2021; Badro et al., 2021). The $\delta^{44}Ca_{norm}$

275   did not show any systematic variation because Ca was not evaporated when the Si and

276   Mg remained in the silicate melt (Richter et al. 2007; Mendybaev et al. 2013, 2021;

277   Ivanova et al. 2021). Our results of Ca are different from, but not contradictory with,

278   previous experiments on synthetic $CaTiO_3$ perovskite at conditions of $\sim 10^{-6}$ Torr and

279   ~ 2273 K, which showed that up to $\sim 90\%$ Ca was evaporated and the measured

280    $\delta^{44}Ca_{norm}$ was up to $\sim 100\%$, with vapor/melt $\alpha(^{44}Ca/^{40}Ca) = 0.9562 \pm 0.0040$ (Zhang et

281   al. 2014).

282   To quantify the Si and Mg isotopic fractionation induced by evaporation, we assume

283   a Rayleigh distillation to describe the isotopic fractionation. Because in our experiments,

284   the vapor escaped constantly with the argon flow and the recovered samples were

285   chemically homogenous (Figure S2), indicating that diffusion in the melt was sufficiently

286   fast relative to the evaporation rate. According to the Rayleigh distillation, we have:

287    $$R_{j/i}/R_{j/i,0} = (1 - f_i)^{^{j/i}\alpha_{exp}-1} \tag{2}$$

288   where $R_{j/i}$ and $R_{j/i,0}$ are the ratio between the heavy isotope j and light isotope i in the

289   residual silicate and starting silicate, respectively. The f_i is the molar loss fraction of i -

290   after evaporation and $^{j/i}\alpha_{exp}$ is the mean isotopic fractionation factor between vapor and

291   melt. The $f^{28}Si$ and $f^{24}Mg$ could be determined by combining the molar loss fraction and

292   measured isotopes of Si and Mg in the samples. Taking the natural logarithm for both

293   sides of Eq. (2), we obtained:

294    $$\ln(R_{j/i}/R_{j/i,0}) = (^{j/i}\alpha_{exp} - 1)\ln(1 - f_i) \tag{3}.$$

295   Linear correlations between $\ln(R_{j/i}/R_{j/i,0})$ and $\ln(1 - f_i)$ were observed for Si and Mg

296   isotopes (Figure 4), justifying the assumption of a Rayleigh distillation. The values of

297    $^{j/i}\alpha_{exp}$ in Eq. (3) can be derived from slopes of linear regressions of the experimental data.

298   Limited temperature dependence of α_{exp} was found in our experiments, yielding a mean

299   α_{exp} of 0.99585 ± 0.00002 for $^{29}Si/^{28}Si$ and 0.98942 ± 0.00130 for $^{25}Mg/^{24}Mg$ (Figure 4).

300   The experimentally obtained vapor–melt isotope fractionation is net isotopic

301   fractionation (Δ_{net}) and its relationship with equilibrium isotope fractionation (Δ_{eq}) and

302   kinetic isotope fractionation (Δ_{kin}) can be expressed as (Dauphas et al. 2015):

303    $$\Delta_{net} = \Delta_{eq} + (1-S)\,\Delta_{kin} \tag{4}.$$

304   In Eq. (4), Δ is related to α through $\Delta = 1000 \times (\alpha-1)$, and S is the saturation degree of

305   evaporation, which is defined as $S = P_i/P_{i,sat}$, where P_i and $P_{i,sat}$ refer to the partial vapor

306   pressure and equilibrium vapor pressure of i at the evaporation conditions, respectively,

307   and $0 < S \leq 1$. The Δ_{eq} is a function of $1/T^2$ (Bigeleisen and Mayer 1947; Urey 1947) and

308 would be too small to be measured by experiments at very high temperatures, which is

309 thus usually estimated from the ratio of reduced partition function between gaseous

310 species and melts. Since reduced partition function for Si in silicate melt is still lacking,

311 we approximated it with crystalline enstatite (Javoy et al. 2012) because of its similar

312 chemical composition to our enstatite melt, which yielded $\Delta_{eq}(^{29}Si) = -2.140 \times 10^6/T^2$. We

313 used the result of gas-enstatite melt calculated by Luo et al. (2018) for Mg isotopes,

314 yielding $\Delta_{eq}(^{25}Mg) = -0.8772 \times 10^6/T^2$. The Δ_{kin} during evaporation can be calculated by

315 assuming the rate of gaseous species at the evaporating surface following a

316 Maxwell-Boltzmann distribution (Richter et al. 2002):

$$^{j/i}\Delta_{kin} (‰) = -1000 \times [1 - \varepsilon_j / \varepsilon_i (m_i/m_j)^{0.5}] \tag{5}$$

318 where ε_i, ε_j denote evaporation coefficients, and m_i, m_j denote the mass of i, j species in

319 the vapor. Assuming that ε is mass-independent, the theoretical kinetic fractionation

320 $\Delta_{kin}(^{29}Si)$ and $\Delta_{kin}(^{25}Mg)$ are $-11.174‰$ and $-19.419‰$, respectively, when SiO and Mg

321 are the dominant species in the vapor (De Maria et al. 1971; Shornikov and Yakovlev

322 2015; Costa et al. 2017). Using the Δ_{eq} and Δ_{kin} for ^{29}Si and ^{25}Mg in these previous studies,

323 we calculated the S values in our experiments, which yielded $S_{Si} = 0.662 \pm 0.002$ and $S_{Mg} =$

324 0.459 ± 0.068.

325

326 **Discussion**

327 **Factors controlling Si and Mg isotopic fractionation**

328 The Δ_{net} is controlled by both temperature and S as shown in Eq. (4). However, the

329 temperature effect could be limited at non-equilibrium conditions because the Δ_{eq} at

330 high-temperature is much closer to zero. This explains that the obtained α_{exp} for $^{29}Si/^{28}Si$

331 or $^{25}Mg/^{24}Mg$ are temperature-independent in our experiments (Figure 4). At

332 non-equilibrium conditions, the S value could significantly affect Δ_{net} for ^{29}Si and ^{25}Mg.

333 For comparison, the S values obtained in previous experiments are summarized in Table

334 S2 and plotted in Figure 5a. The first-order observation is that the S values obtained at

335 vacuum or near-vacuum conditions ($\sim 10^{-9}-10^{-4}$ bar) are smaller than those obtained in

336 levitation experiments, which may be determined by the mechanism how vapor escapes

337 from the melt surface. In vacuum or near-vacuum experiments, the gaseous species

338 escape through diffusion triggered by a self-generated composition gradient in the

339 surrounding gas (Richter et al. 2002). The velocity of argon flow in our experiments was

340 ~ 13 m/s. Using a typical diameter of 3 mm of our samples, we determined a Reynolds

341 number of 390 and Péclet number of 15–22 (Text S2), which indicates the vapor flow in

342 our experiments was laminar and the dominant mechanism for gaseous species

343 escaping from the melt surface was advection (Sossi et al. 2019; Badro et al. 2021). In

344 the levitation experiments, a gaseous boundary layer could form around the melt sphere

345 and suppress an instant escape of the vapor, which makes S values in the levitation

346 experiments larger than those in the vacuum or near-vacuum experiments (Ni et al.,

347 2021; Sossi et al., 2020; Young et al., 2022).

348   Figure 5a also shows that although S_{Si} is larger than S_{Mg} in our experiments, that S_{Si}

349 $< S_{Mg}$ is also observed in previous experiments. We find that the relative volatility of Si

350 and Mg may determine $S_{Si} < S_{Mg}$ or $S_{Si} > S_{Mg}$. As the S_{Si} and S_{Mg} in Figure 5 were derived

351 from a series of experiments, we used the $(Mg/Si)_{max}/(Mg/Si)_{ini}$ ratio to approximately

352 represent the relative volatility of Si and Mg during evaporation, where $(Mg/Si)_{max}$ refers

353 to the Mg/Si ratio in the recovered sample with a maximum mass loss fraction from a

354 series of experiments, and $(Mg/Si)_{ini}$ refers to the Mg/Si ratio in the starting silicate.

355 Figure 5b shows that the $(1-S_{Mg})/(1-S_{Si})$ and $(Mg/Si)_{max}/(Mg/Si)_{ini}$ are strongly

356 correlated ($R^2 = 0.81$), and that S_{Si} is larger than S_{Mg} when Si is more volatile than Mg,

357 and vice versa. To explain these observations, we used the Hertz-Knudsen equation to

358 describe the evaporation flux of Mg and Si, and the relationship of S_{Si} and S_{Mg} could be

359 written as:

$$360 \qquad \frac{1-S_{Mg}}{1-S_{Si}} = \frac{\varepsilon_{SiO}\,\gamma_{SiO2}\,K_{Si}\sqrt{M_{Mg}}}{\varepsilon_{Mg}\,\gamma_{MgO}\,K_{Mg}\sqrt{M_{SiO}}} \times \frac{\ln(1-f_{Mg})}{\ln(1-f_{Si})} \qquad (6)$$

361 where K_{Si} and K_{Mg} are the equilibrium constant of the reactions that describe the

362 evaporation of MgO and SiO_2 from the silicate melt as gaseous Mg and SiO in the vapor;

363 γ_{MgO} and γ_{SiO2} are the activity coefficients of MgO and SiO_2 in the silicate melt; M_{Mg} and

364 M_{SiO} are the molar mass of gaseous Mg and SiO in the vapor. A detailed deduction of Eq.

365 (6) is provided in supplementary Text S3. Eq. (6) shows that the $(1-S_{Mg})/(1-S_{Si})$ is a

366 function of $\frac{\varepsilon_{SiO}\,\gamma_{SiO2}\,K_{Si}\sqrt{M_{Mg}}}{\varepsilon_{Mg}\,\gamma_{MgO}\,K_{Mg}\sqrt{M_{SiO}}}$ and $\ln(1-f_{Mg})/\ln(1-f_{Si})$. If the evaporation coefficient and

367 the equilibrium constant are constant in an experiment at a given temperature (e.g.,

368 Badro et al., 2021), the $(1-S_{Mg})/(1-S_{Si})$ is a function of the $\gamma_{SiO2}/\gamma_{MgO}$ and

369 $\ln(1-f_{Mg})/\ln(1-f_{Si})$. For melt evaporation at given conditions, the increase in the

370 volatility of MgO relative to that of SiO_2 are usually accompanied by an increase in

371 $\gamma_{MgO}/\gamma_{SiO2}$ (Richter et al., 2007; Badro et al., 2021) and an increase in f_{Mg} relative to f_{Si}.

372 Therefore, the $(1-S_{Mg})/(1-S_{Si})$ must decrease with increasing the volatility of MgO

373 relative to that of SiO_2, qualitatively consistent with our observations shown in Figure

374 5b. Our experiments also show an increase in $\gamma_{MgO}/\gamma_{SiO2}$ as the evaporation proceeded

375 (Figure S5), consistent with the increased volatility of MgO relative to that of SiO_2

376 (Richter et al. 2002, 2007). Accordingly, the silicate melt composition could play an

377 important role in controlling the relative volatility of SiO_2 and MgO and S_{Si} and S_{Mg}.

378 However, it should be noted that "volatility" is more an empirical statement than a strict

379 definition in thermodynamic or kinetic, and the relative volatility of SiO_2 and MgO

380 during evaporation may be a multi-function of not only silicate melt composition but

381 also parameters such as pressure, the quantitative effects of which require future

382 studies.

383

384 **Implications**

385 The Si and Mg isotopic differences between the BSE, CI chondrites, and EC ($\Delta^{29}Si_{BSE-}$

386 $_{chondrite}$; $\Delta^{25}Mg_{BSE-chondrite}$) are 0.100 ± 0.022‰ for $\Delta^{29}Si_{BSE-CI}$, (0.160~0.190) ± 0.032‰

387 for $\Delta^{29}Si_{BSE-EC}$, 0.011 ± 0.011‰ for $\Delta^{25}Mg_{BSE-CI}$, and (0.011~0.013) ± 0.009‰ for

388 $\Delta^{25}Mg_{BSE-EC}$ (Savage and Moynier 2013; Zambardi et al. 2013; Hin et al. 2017). If both

389 $\Delta^{29}Si_{BSE-chondrite}$ and $\Delta^{25}Mg_{BSE-chondrite}$ result only from post-nebular evaporation, the

390 evaporation-induced Si and Mg isotopic fractionation ($\Delta^{29}Si_{evap}$ and $\Delta^{25}Mg_{evap}$) must

391 satisfy:

$$\Delta^{29}Si_{evap} = \Delta^{29}Si_{BSE-chondrite} \tag{7}$$

393 and

$$\Delta^{25}Mg_{evap} = \Delta^{25}Mg_{BSE-chondrite} \tag{8}$$

395 Since evaporation generally occurs in an open system (Nie and Dauphas 2019), the

396 $\Delta^{29}Si_{evap}$ and $\Delta^{25}Mg_{evap}$ can be estimated by using the Rayleigh distillation model:

$$\Delta^{29}Si_{evap} = \Delta_{net} (^{29}Si) \ln (1-f_{Si}) \tag{9}$$

398 and

$$\Delta^{25}Mg_{evap} = \Delta_{net} (^{25}Mg) \ln (1-f_{Mg}) \tag{10}.$$

400 In Eqs. (9) and (10), the evaporative f_{Si} and f_{Mg} and the $\Delta_{net}(^{29}Si)$ and $\Delta_{net}(^{25}Mg)$ must be

401 known to obtain $\Delta^{29}Si_{evap}$ and $\Delta^{25}Mg_{evap}$. To calculate f_{Si} and f_{Mg} for Earth, we assume that

402 Earth's precursor bodies have Mg/Ca and Si/Ca ratios identical to those of CI chondrites

403 or EC, and the sub-chondritic Mg/Ca and Si/Ca ratios in the BSE result solely from

404 post-nebular evaporative loss of Si and Mg because Ca is highly refractory as stated

405 above. For instance, the f_{Si} for using a CI-like precursor was calculated as f_{Si} = [1 −

406 $(Si/Ca)_{BSE}/(Si/Ca)_{CI}$]. To calculate $\Delta_{net}(^{29}Si)$ and $\Delta_{net}(^{25}Mg)$ for Earth, we used different

407 temperatures (to obtain Δ_{eq}) and S values in Eq. (4).

408 Figures 6a-b show the calculated $\Delta^{29}Si_{evap}$ and $\Delta^{25}Mg_{evap}$ as a function of

409   temperature and S with fixed f_{Si} and f_{Mg} for different chondritic precursors. We can see

410   from Figures 6a-b that increasing evaporation temperature and S could effectively

411   decrease $\Delta^{29}Si_{evap}$ and $\Delta^{25}Mg_{evap}$. Figure 6a shows that to explain the observed $\Delta^{29}Si_{BSE-}$

412    $_{chondrite}$, it requires evaporation temperatures of 3000–7000 K and $0.980 \leq S_{Si} \leq 1$.

413   However, Figure 6b shows that to explain the observed $\Delta^{25}Mg_{BSE-chondrite}$, it requires

414   evaporation temperatures of 4000–7000 K and $0.998 \leq S_{Mg} \leq 1$. Particularly, if Earth's

415   precursor bodies have EC-like composition as suggested by the Ca isotopes and many

416   other mass-independent isotopic anomalies (Warren 2011; Dauphas 2017; Huang and

417   Jacobsen 2017), evaporation temperatures > 5000 K are required to explain the

418   observed $\Delta^{25}Mg_{BSE-EC}$ (Figure 6b). Therefore, evaporation temperatures > 5000 K are

419   needed to explain both $\Delta^{25}Mg_{BSE-EC}$ and $\Delta^{29}Si_{BSE-EC}$. In order to further constrain the

420   range of S_{Si}/S_{Mg} that are required to explain both $\Delta^{25}Mg_{BSE-EC}$ and $\Delta^{29}Si_{BSE-EC}$, we

421   additionally modeled the $\Delta^{25}Mg_{evap}/\Delta^{29}Si_{evap}$ as a function of S_{Si}/S_{Mg} at 5000–7000 K and

422   S_{Mg} of 0.998–1. Figures 6c-d show that to explain the observed $\Delta^{25}Mg_{BSE-EC}/\Delta^{29}Si_{BSE-EC}$,

423   the S_{Si}/S_{Mg} must be smaller than 1 at the evaporation temperatures of 5000–7000 K. The

424   required high evaporation temperatures are relevant to planetary collisions (Canup

425   2012).

426   The above results demonstrate that post-nebular evaporation occurring at

427   temperatures > 5000 K and $S_{Si}/S_{Mg} < 1$ can explain the Mg/Ca and Si/Ca ratios and

428   isotopes in the BSE, if EC-like materials are Earth's main building blocks. It is worth

429   pointing out that if we use $\Delta_{eq}(^{29}Si)$ derived from the gas-crystalline forsterite system, as

430   used in Hin et al. (2017) and Young et al. (2019), the S_{Si} value and temperature required

431   to explain the BSE's Si isotopes will increase by 0.002 and ~150 K, respectively. However,

432   the use of $\Delta_{eq}(^{25}Mg)$ derived from the gas-crystalline forsterite system would not change

433   S_{Mg} or the evaporation temperature required to explain the BSE's Mg isotopes because

434   the $\Delta_{eq}(^{25}Mg)$ obtained from the gas-crystalline forsterite and the gas-enstatite melt

435   systems are nearly the same, with a difference of only 0.0014‰ at 3000 K (Luo et al.

436   2018). In addition, in our model the isotopic fractionation factor and relative volatility of

437   Si and Mg were assumed to be constant during the evaporation. However, they may be

438   determined by not only the silicate melt composition but also the vapor pressure and

439   the presence of volatiles. Also note that 5000 K is far outside our experiment

440   temperatures and the thermodynamics of the melt under these conditions are highly

441   uncertain. Future experiments that simulate actual conditions of planetary evaporation

442   are needed to better understand its role in shaping Earth's chemical compositions.

443   Our evaporation model provides a potential solution to the non-chondritic Mg/Ca

444   and Si/Ca ratios and isotopes in the BSE, as those in recent studies (Hin et al. 2017;

445   Young et al. 2019). Previous studies show that in the early solar system, Si isotopic

446   fractionation between gaseous SiO and forsterite at nebular conditions may explain the

447   variations in Si isotopes among Earth and other planetary bodies (Dauphas et al. 2015),

448   which was further substantiated by Fe isotopes (Sossi et al. 2016). However, Mg does

449   not show considerable isotope fractionation at the same process because limited

450   amounts of initial Mg would be in the gas when forsterite was fully condensed (Dauphas

451   et al. 2015); thus, a post-nebular process is still required. Recently, it was also suggested

452   that Earth's Si, Mg, and Ca isotopes could be inherited from the accreted materials via

453   pebble accretion without the need of evaporative fractionation, as supported by the

454   identical mass-dependent Ca, Mg, and Si isotopes between Earth and chondrules in CV

455   (Olsen et al. 2016; Amsellem et al. 2017; Kadlag et al. 2021). However, the

456   mass-independent isotopes are distinct between Earth and chondrules of carbonaceous

457   chondrites, but nearly the same between Earth and chondrules of EC (Schneider et al.

458   2020).

459   Our model implies that if Earth's Si and Mg isotope compositions are attributed

460   alone to the evaporation of EC-like precursors, the evaporation temperatures may be

461   over 5000 K. Such high temperatures imply that moderately and highly volatile elements

462   must be completely lost during evaporation. In this case, Earth's additional accretion of

463   materials with limited evaporative loss of volatiles or without volatile loss are required

464   to explain Earth's volatile budget (Li et al. 2022), as supported by the K and S isotopes,

465   and the volatile element depletion pattern in the BSE (Braukmüller et al. 2019; Li 2021;

466   Tian et al. 2021; Wang et al. 2021).

467

475   **Figure captions**

476   **Figure 1.** Images of the samples. **(a)** A typical silicate bead prepared for levitation

477   evaporation experiment (left) and a transparent recovered sample (right). **(b)**

478   Backscattered electron (BSE) image of the starting silicate. **(c)** A closer-view of the

479   starting silicate, showing presence of micro-crystals probably formed during quench. **(d)**

480   BSE image of a recovered sample (run M05). **(e)** A closer-view of a selected region in

481   image **d** to show the homogeneity in structure and composition. The circular spots in

482   images **b** and **d** are laser pits of LA–ICP–MS analysis.

483

484   **Figure 2. (a)** The CaO contents in the starting silicate beads estimated by mass balance

485   for recovered samples M01 to M09. **(b)** The Si and Mg loss fraction calculated by

486   normalization approach. Note that the $(MgO/CaO)_{norm}$, for example, is the MgO/CaO

487   ratio of a recovered sample normalized to that of the bulk starting silicate, *i.e.*,

488     $(MgO/CaO)_{norm} = (MgO/CaO)_{sample} / (MgO/CaO)_{starting}$. **(c)** The Si and Mg loss fraction

489   calculated by mass balance approach.

490

491   **Figure 3.** The Si and Mg molar loss fraction **(a)** and isotopes **(b)** of recovered samples as

492   a function of the sample mass loss fraction. Note that the isotopes of the recovered

493   samples were normalized to those of the bulk starting silicate, e.g., $\delta^{29}Si_{norm} = \delta^{29}Si_{sample}$

494     $- \delta^{29}Si_{starting}$. Also note that the variation of $\delta^{29}Si_{norm}$ and $\delta^{25}Mg_{norm}$ are coupled with the

495   Si and Mg molar loss fraction, respectively.

496

497   **Figure 4.** The correlation between $1000 \times \ln(R_{j/i}/R_{j/i,0})$ and $-\ln(1-f)$ for Si **(a)** and Mg **(b)**

498   isotopes in our experiments (red lines). The experimental results at 1873 K in Badro et

499   al. (2021) are plotted for comparison. The isotopic fractionation factors are obtained by

500   linear fitting not forced to go through (0,0) with errors in 2σ. The calculated kinetic and

501   equilibrium isotopic fractionation factors of Si and Mg at 2623 K are also plotted for

502   comparison (see main text for detailed calculations).

503

504   **Figure 5. (a)** Comparisons of S_{Si} (open symbols) and S_{Mg} (solid symbols) determined in

505   our experiments and previous experiments. Vacuum or near-vacuum experiments and

506   levitation experiments are separated by the dash line. The experimental temperature is

507   color-coded. **(b)** Correlation between the $(1-S_{Mg})/(1-S_{Si})$ and $(Mg/Si)_{max}/(Mg/Si)_{ini}$ with

508     $R^2 = 0.80$. Note that S_{Si} is larger than S_{Mg} when Si is more volatile than Mg, and vice versa.

509   The symbols in **b** are the same as those in **a**, and the abbreviated references are: B21

510   (Badro et al. 2021), D90 (Davis et al. 1990), W01 (Wang et al. 2001), R07 (Richter et al.

511   2007), K09 (Knight et al. 2009), M13 (Mendybaev et al. 2013), M17 (Mendybaev et al.

512   2017), M21 (Mendybaev et al. 2021).

513

514   **Figure 6.** Diagrams constrain the conditions of post-nebular evaporation that could

515   explain the differences in Mg/Ca and Si/Ca ratios and isotopes between the BSE and

516   chondrites. **(a-b)** The evaporation-induced isotopic fractionation ($\Delta^{29}Si_{evap}$ and $\Delta^{25}Mg_{evap}$)

517   as a function of temperature and S. **(c-d)** The evaporation-induced isotopic fractionation

518   of ^{25}Mg and ^{29}Si ($\Delta^{25}Mg_{evap}/\Delta^{29}Si_{evap}$) as a function of S_{Mg}, S_{Si}/S_{Mg}, and temperature. Note

519   that the f_{Mg} and f_{Si} used in the above modelling are fixed at the values determined from

520   the difference in Mg/Ca and Si/Ca ratios of the BSE from those of chondrites (see main

521   text for details). Plots **a-b** show that to explain the $\Delta^{29}Si_{BSE-EC}$, it requires evaporation

522   temperatures of 3000–7000 K, whereas to explain the $\Delta^{25}Mg_{BSE-EC}$, it requires

523   evaporation temperatures of 5000–7000 K; plots **c-d** show that to explain the

524    $\Delta^{25}Mg_{BSE-EC}/\Delta^{29}Si_{BSE-EC}$, the S_{Si}/S_{Mg} must be smaller than 1. If the core/mantle Si isotope

525   fractionation is considered, as indicated by the line arrow in plot **a**, the observed

526    $\Delta^{29}Si_{BSE-chondrite}$ would be smaller. CI = CI chondrite; EC = enstatite chondrite (EH, EL).

527   See the main text for more details.

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711

712 **Table 1.** Elemental and isotopic[a] compositions of the starting silicate and sample glasses.

Run No.	Starting	M01	M02	M03	M04	M05	M06	M07	M08	M09	BHVO-2[b]	BCR-2[b]	SRM	Seawater[b]
Temperature (K)		2623	2623	2623	2523	2523	2523	2423	2423	2423				
Laser-on duration (s)		120	300	420	120	300	540	300	420	540				
Final diameter (mm)		3.20	2.80	2.83	3.39	3.11	2.92	3.23	3.02	3.07				
Starting mass (mg)		57.3	55.3	60.2	62.5	62.8	55.4	59.9	62.6	52.7				
Final mass (mg)		44.9	35	36.2	53.4	47.7	37.3	52.4	44.4	42.1				
Sample mass loss fraction		21.6	36.7	39.9	14.6	24	32.7	12.5	29.1	20.1				
Si molar loss fraction (%)[c]		33.5	53.7	57.0	23.0	36.4	48.3	20.4	44.1	32.2				
2σ		1.4	1.0	1.0	1.6	1.3	1.1	1.7	1.1	1.4				
Mg molar loss fraction (%)		1.0	7.5	10.2	1.3	1.5	5.1	-0.4	3.7	0.2				
2σ		3.3	3.0	2.9	3.3	3.2	3.1	3.4	3.2	3.3				
Ca molar loss fraction (%)		-1.2	-6.6	-5.1	3.1	-4.1	-4.4	9.1	-4.4	3.8				
2σ		15.2	15.6	15.2	14.3	15.2	15.1	13.2	15.0	14.2				
SiO_2 (wt.%)	63.26	53.62	46.32	45.30	57.07	52.97	48.55	57.53	49.91	53.68				
2σ	1.22	0.48	0.38	0.54	0.50	0.42	0.44	0.56	0.30	0.46				
MgO (wt.%)	35.19	44.44	51.40	52.59	40.69	45.63	49.72	40.37	47.80	43.97				
2σ	1.12	0.38	0.32	0.38	0.40	0.30	0.40	0.46	0.36	0.38				
CaO (wt.%)	1.27	1.64	2.14	2.22	1.44	1.74	1.97	1.32	1.87	1.53				
2σ	0.18	0.08	0.08	0.06	0.06	0.06	0.06	0.04	0.04	0.06				
Nb (ppm)	84	102	124	127					113					
2σ	7	4	3	3					3					
Ta (ppm)	204	251	307	324					287					
2σ	16	11	14	17					6					
$\delta^{29}Si$ (‰)	-0.036	1.648	3.199	3.459	1.070	1.985	2.757	0.894	2.169	1.509	-0.162			
2σ	0.032	0.017	0.025	0.036	0.023	0.014	0.027	0.045	0.074	0.067	0.020			
$\delta^{30}Si$ (‰)	-0.122	3.202	6.223	6.715	2.125	3.895	5.416	1.748	4.270	2.954	-0.313			
2σ	0.042	0.031	0.033	0.044	0.014	0.063	0.038	0.044	0.047	0.025	0.031			
$\delta^{25}Mg$ (‰)	-0.892	-0.666	0.054	0.304	-0.770	-0.593	-0.248	-0.799	-0.508	-0.676		-0.108	-0.108	
2σ	0.023	0.027	0.015	0.026	0.005	0.026	0.017	0.003	0.012	0.025		0.012	0.012	
$\delta^{26}Mg$ (‰)	-1.699	-1.280	0.105	0.602	-1.498	-1.171	-0.480	-1.523	-0.969	-1.314		-0.189	-0.189	
2σ	0.056	0.048	0.006	0.032	0.008	0.041	0.030	0.017	0.015	0.041		0.032	0.032	
$\delta^{44}Ca$ (‰)	1.498	1.547	1.647	1.570	1.557	1.537	1.680	1.560	1.570	1.450			0.010	1.883
2σ	0.043	0.066	0.096	0.043	0.052	0.052	0.082	0.107	0.114	0.059			0.100	0.154

713 Note: **a.** The standards for Si, Mg, and Ca isotope are NBS-28, DSM-3, and SRM915a, respectively; **b.** Measured values for these standards are in good agreements
714 with the suggested values from the GeoReM database (http://georem.mpch-mainz.gwdg.de); **c.** The mass loss fractions (f_i) are calculate by mass balance via $f_i =$
715 $(M_{i,0}-M_{i,t})/M_{i,0}$, where $M_{i,0}$ and $M_{i,t}$ are the starting mass and recovered mass of element i that could be readily obtained by $C_{i,0} \times M_{sample,0}$ and $C_{i,t} \times M_{sample,t}$, respectively.
716 The $C_{i,0}$ and $C_{i,t}$ are the starting and recovered content of element i, and the $M_{sample,0}$ and $M_{sample,t}$ are the starting and recovered mass of the sample listed above. Note
717 that although the average molar mass of i of the sample would change after experiment due to the evaporation-induced isotopic fractionation, such minor change is
718 negligible. Hence, the molar loss fractions could be considered equal to the mass loss fractions.

a

5 mm

b

1 mm

c

5 μm

d

1 mm

e

50 μm

(a), (b) Legend: **2423 K** **2523 K** **2623 K** **Badro et al., 2021 (1873 K)**

Panel (a): y-axis $1000 \times \ln\left(R_{j/i}/R_{j/i,0}\right)$, x-axis $-\ln(1-f^{28}\mathrm{Si})$

$\alpha_{kin} = 0.98883$

$\alpha_{exp} = 0.99585 \pm 0.00002$

$\alpha_{exp} = 0.99700 \pm 0.00045$

$\alpha_{eq} = 0.99964$ (2623 K)

Panel (b): y-axis $1000 \times \ln\left(R_{j/i}/R_{j/i,0}\right)$, x-axis $-\ln(1-f^{24}\mathrm{Mg})$

$\alpha_{kin} = 0.97980$

$\alpha_{exp} = 0.98942 \pm 0.00130$

$\alpha_{exp} = 0.99500 \pm 0.00054$

$\alpha_{eq} = 0.99987$ (2623 K)