Experimental determination of Si, Mg, and Ca isotope fractionation during enstatite melt evaporation

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Abstract
Evaporation of silicate materials from Earth or its precursors may be important in shaping their primordial compositions represented by undifferentiated meteorites, e.g., enstatite chondrites; however, the conditions under which evaporation occurs and the extent of evaporation-induced elemental and isotope fractionation remain uncertain. Here, we experimentally determine the volatility and isotope fractionation of Si, Mg, Ca, Nb, and Ta during enstatite melt evaporation at 2423–2623 K using a High-temperature Conical Nozzle Levitator. Homogenous glasses are recovered after experiments, then we use EPMA and LA-ICP-MS to measure the elemental compositions, MC-ICP-MS to measure the Si and Mg isotopes, and TIMS to measure the Ca isotopes. Our results show that the evaporation rates of Si are larger than Mg and the mean vapor/melt isotope fractionation factors ($\alpha = R_{\text{vapor}}/R_{\text{melt}}$; $R$=isotope ratio) are 0.99585±0.00002 for $^{29}\text{Si}/^{28}\text{Si}$ and 0.98942±0.00130 for $^{25}\text{Mg}/^{24}\text{Mg}$. However, neither evaporative loss of Ca, Nb, and Ta nor Ca isotope fractionation was observed within analytical errors. In conjunction with previous studies, we find that in an evaporation experiment the saturation degree (partial vapor pressure/equilibrium vapor pressure) of Si ($S_\text{Si}$) is larger than $S_{\text{Mg}}$ when Si is more volatile than Mg, and vice versa. If the Mg/Ca and Si/Ca ratios and isotopes in the bulk silicate Earth are attributed to the evaporation of enstatite chondrite-like precursors, evaporation temperatures > 5000 K and $S_\text{Si} < S_{\text{Mg}}$ are required.

Keywords: Enstatite, planetary evaporation, high-temperature experiments, isotopic fractionation, Earth’s composition

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Introduction

The chemical composition of the bulk silicate Earth (BSE) provides tight constraints on the nature of Earth’s building blocks, and Earth’s formation and evolution processes. The BSE and enstatite chondrites (EC) share nearly identical mass-independent stable isotopes of various elements such as O, Cr, and Ti, and therefore it has been proposed that Earth’s main building blocks are EC-like materials (Warren 2011; Dauphas 2017). However, this hypothesis has been challenged by the fact that the isotope compositions of Si and Mg in the BSE are heavier than those observed in ECs (Fitoussi and Bourdon 2012; Hin et al. 2017). Such discrepancies in Si and Mg isotopes were attributed to the processes producing mass-dependent isotopic fractionation, such as the incorporation of Si in Earth’s core to explain the BSE’s heavy Si isotopes because of the preferential partitioning of light Si isotopes into metallic phases (Shahar et al. 2009). However, this requires Si in Earth’s core (~12 wt.%) in excess of that permitted by geophysical constraints (Badro et al. 2014) or unrealistically low core–mantle equilibration temperatures (~1500 K) (Fitoussi and Bourdon 2012). The required ~12% Si in the core could potentially be reduced if we consider the Si isotope heterogeneity in the mantle predicted by first-principles calculations, which suggest that the lower mantle (and hence the BSE) might have lighter Si isotopes compared to the upper mantle (Huang et al. 2014). However, core-formation cannot explain the BSE’s heavy Mg isotopes due to the lithophile nature of Mg (Du et al. 2017).

Evaporation of molten planetesimals resulting from the decay of short-lived nuclides or accretionary collision (Tonks & Melosh, 1993; Young et al., 2019), which will be referred to as “post-nebular evaporation” hereafter (O’Neill and Palme 2008), may cause mass-dependent Si and Mg isotopic fractionation and explain the BSE’s heavy Si and Mg isotopes. Pringle et al. (2014) argued that planetesimal evaporation may explain the heavy Si isotopes in angrites (volatile-depleted mafic igneous meteorites from an early formed asteroid), and a series of melt–vapor equilibration events during collisional accretion may explain the BSE’s heavy Mg isotopes (Hin et al. 2017). Young et al. (2019) evaluated the near-equilibrium isotopic fractionation during planetesimal evaporation, and suggested that the BSE’s Mg and Si isotopes may result from losing ~12% Mg and ~15% Si. However, both the Hin and Young models, if using EC-like precursors, cannot explain the BSE’s Mg/Ca and Si/Ca ratios due to insufficient Si or Mg loss. Moreover, whether the use of the equilibrium isotopic fractionation factors (α) approximated to reduced partition function ratios of gaseous species and forsterite in
these previous models affects the conclusions remains uncertain.

To investigate whether post-nebular evaporation can explain the Mg/Ca and Si/Ca ratios and isotopes in the BSE, the $\alpha$ of Si, Mg, and Ca during evaporation of silicate melts of relevant compositions must be determined. Most previous studies focus on evaporation at nebular-like conditions (Davis et al. 1990; Richter et al. 2002, 2007; Mendybaev et al. 2013, 2017, 2021), where the surrounding gas pressure is low ($<10^{-4}$ bar). However, post-nebular evaporation likely occurs at dynamic gas environments with high surrounding gas pressures and temperatures due to planetary collisions (Visscher and Fegley 2013) or high oxygen fugacities (Sossi et al. 2019), which may result in different isotopic fractionations. For example, Badro et al. (2021) found that the $\alpha$ of Si and Mg in their 1-atm levitation evaporation experiments are larger than those in the vacuum experiments even though they performed their experiments with the same CAI-like composition at the same temperature (1873 K). To better understand the isotopic fractionation of Si, Mg, and Ca during post-nebular evaporation, here we experimentally measure the $\alpha$ of Si, Mg, and Ca during enstatite melt evaporation at 2423–2623 K. We then evaluate whether post-nebular evaporation can explain the Mg/Ca and Si/Ca ratios and isotopes in the BSE.

**Methods**

**High-temperature experiments**

We synthesized a silicate (~2 g) with enstatite composition and used it as an analog of the silicate part of EC. Pure MgO, SiO$_2$, and CaCO$_3$ powders (>99.995%) in enstatite stoichiometry, doped with trace amounts of Nb and Ta, were mixed in an agate mortar for ~1 hour and then melted in a Pt crucible in a muffle furnace. The sample was heated at 1973 K in air for 1 hour and quenched by dropping the Pt crucible into cold water. The recovered silicate was white due to the formation of micro-sized crystals during quench (Figures 1a-c). The recovered silicate was broken into small pieces using a hammer. Some pieces were cut and polished into beads of ~3mm diameter for subsequent evaporation experiments (Figure 1a), and the other pieces were randomly picked for EPMA and LA–ICP–MS analyses to obtain the chemical compositions. The random pieces of synthetic silicate contained $63.26\pm1.22$ wt.% SiO$_2$, $35.19\pm1.12$ wt.% MgO, $1.27\pm0.18$ wt.% CaO, $84\pm7$ ppm Nb, and $204\pm16$ ppm Ta (Table 1; ±2σ).

The evaporation experiments were conducted by using a High-temperature Conical Nozzle Levitator at Materials Development, Inc. This method avoids chemical
contamination from capsule material or wire loops at high temperatures, and provides conditions that achieve evaporation from free surfaces in a controlled-gaseous environment (Tangeman et al., 2001). Silicate beads of ~3 mm diameter were levitated in an argon gas flow of ~600 SCCM through a 1 mm diameter nozzle, with gas advective velocity ≈13 m/s. The argon gas was in 99.999% purity, containing ~1 ppm O₂, ~5 ppm N₂, and ~2 ppm H₂O+CO+CO₂ in volume. The samples were heated within 5 seconds to the target temperatures of 2423, 2523, and 2623 K by using a partially focused CO₂ laser (10.6 µm wavelength, model i401, Synrad, Inc.). The sample surface temperature was measured by using an optical pyrometer (Chino model IRC, Chino Works America), and the temperature fluctuation was ~50 K and occasionally over 100 K in a few experiments (supplementary Figure S1). The experiments were quenched by shutting off the laser after running 2–9 mins. The effect of temperature fluctuation on the run duration at the target temperature was estimated using the procedure of Ni et al. (2021) (supplementary Text S1). The sample was weighed before and after the experiment to calculate the sample mass loss fraction. In our laser-heated experiments, the sample mass loss fraction should not exceed 0.5% at heating up stage (~5 s), given an average mass loss rate of ~0.1% per second at 2623 K, as calculated by assuming a linear relationship between the total mass loss fraction and the run duration. Therefore, the chemical fractionation during the heating up stage is negligible and not considered in subsequent discussions.

**Analytical techniques**

The recovered samples were homogeneous glasses (Figures 1d-e and Figure S2). One half of the sample was prepared for major and trace element analyses using EPMA and LA-ICP-MS, respectively, and the other half prepared for Si, Mg, and Ca isotopic analyses.

Major element compositions of all samples were analyzed with a JEOL JXA-8230 EPMA equipped with five wavelength-dispersive spectrometers (WDS). The samples were coated with a thin conductive carbon film (20 nm) before analysis. Operating conditions for quantitative WDS analyses involved an accelerating voltage of 15 kV, a beam current of 10 nA, and a 10 µm spot size. The peak counting time was 10 s for Si, Mg, and Ca, and the background counting time was 5 s on the high- and low-energy background positions. Olivine (Si, Mg) and Diopside (Ca) are used as the standards. As for the line scanning, an accelerating voltage of 15 kV, a beam current of 50 nA, and a 2 µm spot size were used. The dwell time of every spot is 1 s.
The Nb and Ta concentrations in the starting enstatite glass and the evaporated silicate glasses were measured by using an Agilent 7900 Quadrupole ICP-MS coupled to a Photon Machines Analyte HE 193-nm ArF Excimer Laser Ablation system (Li, 2018). Helium was applied as a carrier gas. Argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP. Reference material NIST 610 was used as external standard. The Si contents in the samples measured by EPMA were used as internal standard. Analytical uncertainties for the trace elements are within 5% relative.

The Si and Mg isotopes of the sample glasses were measured using MC-ICP-MS (Neptune Plus from Thermo-Fisher Scientific) at Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China. Chemical purification for measuring Si isotopes was processed following the method modified from (Georg et al. 2006). The sample powder was mixed with high purity NaOH and then was fused in a silver crucible at 993 K for 10 mins to produce a water-soluble metastable silicate. The fusion cake was then fully dissolved with ultra-pure water (18.2 MΩ·cm) and HNO₃ was added to attain a sample solution of 1% HNO₃ (v/v) for column chemistry. The sample solution (containing ~30 μg Si) was purified through 2 mL of cation exchange resin (AG50W-X12, 200–400 mesh, Bio-Rad, USA) that had been cleaned with 3 mol/L HNO₃, 6 mol/L HNO₃, 6 mol/L HCl, and 6 mL ultra-pure water in sequence. Silicon was collected from the column right after 1 mL sample solution of 1% HNO₃ was loaded and then eluted with 6 mL ultra-pure water (Yu et al. 2018).

Chemical purification for measuring Mg isotopes was processed following the method of An et al. (2014). A mixture of concentrated HF–HNO₃ (~3:1, v/v) was used for digestion. After the initial digestion and evaporation to dryness, samples were treated with aqua regia and dried again. Samples were then refluxed with concentrated HNO₃ to remove residual fluorides and finally dissolved in 1 mL 2 N HNO₃ before column chemistry (An et al. 2014). Mg purification was performed through 2 mL of Bio-Rad AG50W-X12 (200–400 mesh) cation resin. Before the start of every chemical separation procedure, the resin was pre-cleaned with 4 mL 4 N HNO₃ + 0.5 N HF and ultra-pure water alternatively three times, and then conditioned with 3 mL 2 N HNO₃ twice. 5 mL 2N HNO₃ + 0.5N HF and 6 mL 1 N HNO₃ was loaded to elute the interferential elements. Magnesium was then collected right after 22 mL 1 N HNO₃ was eluted.

Both Si and Mg isotopes were analyzed using MC-ICP-MS. A quartz dual cyclonic-spray chamber and a PFA microflow nebulizer (Elemental Scientific Inc., U.S.A.)
with an uptake rate of ~50 μL/min were used for sample introduction. The three stable isotopes of Si and Mg were collected by Faraday cup L3 (28Si and 24Mg), C (29Si and 25Mg), and H3 (30Si and 26Mg). A block of analysis consisted of 60 cycles of data with an integration time of 2.097 s per cycle. A single analysis is corresponded to 1 bracket using the sample-standard bracketing method, while an analytical session consisted of 3 repeated runs of the same solution. An on-peak baseline was measured with 30 cycles and 1 s integration time per cycle. Instrument operating conditions are described in supplementary Table S1.

The analyses of Ca isotopes were performed using thermal ionization mass spectrometry (TIMS, Thermo Triton) at State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. An aliquot containing ~30 μg of Ca was mixed with 42Ca - 43Ca double-spike solution (40Ca/42Ca ≈ 7) before purification. The samples were then dried down and re-dissolved in 50 μL of 1.6 N HCl for the column chemistry. Calcium purification was performed using 1 mL of Bio-Rad AG MP-50 cation resin. Samples were loaded to preconditioned (with 5 mL of 1.6 N HCl) resin, then matrices were eluted with 16.95 mL of 1.6 N HCl, and Ca was collected with 27 mL of 1.6 N HCl (Liu et al. 2017). After the Ca-bearing solution was evaporated to dryness, it was treated with concentrated HNO3 several times and finally re-dissolved it with 10 μL 10% v/v HNO3 for TIMS analysis (Liu et al. 2017). About 3 μg purified Ca isotopes were loaded as calcium nitrate onto a 99.995% Ta filament. The measurement of calcium began when the intensity of the 40Ca signal reached 15 V, and each run consisted of 8 blocks and 26 cycles. Instrumental fractionation was corrected using the 42Ca - 43Ca double spike technique using an offline iterative routine with an exponential law, similar to the method of Heuser et al. (2002). The details of purification procedures and instrumental running conditions are described by Liu et al. (2017) and Wu et al. (2020).

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

$$\delta J^{1} E (\text{‰}) = \left( \frac{\left( \frac{^j E}{^i E} \right)_{\text{sample}}}{\left( \frac{^j E}{^i E} \right)_{\text{standard}}} - 1 \right) \times 1000$$ (1)

where j and i are the heavy and light atomic number of element E, respectively. The standards for Si, Mg, and Ca isotopes are NBS-28, DSM-3, and SRM915a, respectively. We routinely measured the isotopic compositions of other standards, BHVO-2, BCR-2, SRM915a, and Seawater. Our obtained data ($\delta^{29}\text{Si}_{\text{BHVO-2}} = -0.162\pm0.020\text{‰}, \delta^{25}\text{Mg}_{\text{BCR-2}} = -0.108\pm0.012\text{‰}, \delta^{44}\text{Ca}_{\text{SRM915a}} = 0.01\pm0.10\text{‰}, \delta^{44}\text{Ca}_{\text{Seawater}} = 1.88\pm0.15\text{‰}$) are in good agreement with literature values.
agreement with the suggested values \( \text{http://georem.mpch-mainz.gwdg.de} \). No mass-independent fractionation was found for Si or Mg isotopes (Figure S3) as for Ca isotopes (Zhang et al. 2014).

### Results

#### Elemental loss fraction and fractionation

The chemical compositions and sample mass loss fraction of the recovered samples are summarized in Table 1. The SiO\(_2\) contents of the samples (45.30–57.53 wt.%) decrease with increasing the sample mass loss fraction. Much faster evaporation of Si compared to that of other elements results in an increase of the MgO and CaO contents (40.37–52.59 wt.% and 1.32–2.22 wt.%, respectively), as well as the Nb and Ta contents (102–127 ppm and 251–324 ppm, respectively) with increasing the fraction of sample lost.

Estimation of the elemental loss fractions requires knowing the composition of starting silicate beads. The compositions measured from random pieces of synthetic starting silicate here were used as the representative of starting composition since we did not measure the compositions of the silicate beads used in our experiments. In order to check the representative of the measured compositions, the CaO contents of the starting silicate beads were estimated by mass balance given its refractory nature. Figure 2a shows that CaO contents of the starting silicate beads are different, but with an average value identical to the CaO content we measured for the bulk starting silicate (1.27±0.18 wt.%), suggesting that the randomly-picked pieces could reasonably represent the silicate beads used in our experiments despite minor heterogeneities. The SiO\(_2\) and MgO contents of the starting silicate beads should also within the ranges of measured SiO\(_2\) (63.26±1.22 wt.%) and MgO (35.19±1.12 wt.%) contents of bulk starting silicate as well as CaO, although they could not be estimated in similar way due to the evaporation loss.

There are two methods to calculate the molar loss fraction \( f \) of an element: 1) by mass balance or 2) by the approach of normalization to a refractory element (e.g., Ca) and the starting material as done in previous studies (Richter et al. 2007; Mendybaev et al. 2013). We used both methods to calculate the \( f_{\text{Si}} \) and \( f_{\text{Mg}} \). The former method is readily to apply given the total mass loss of the sample and its SiO\(_2\) and MgO contents before and after experiment (Table 1). However, the latter method is not suitable to our experiments due to the large uncertainties of starting CaO content (1.27±0.18 wt.%). In
the latter method, \( f_{\text{Mg}} \) could be calculated via \( 1 - (\text{MgO/CaO})_{\text{norm}} \), where \( (\text{MgO/CaO})_{\text{norm}} \) refers to MgO/CaO ratio of the sample divided by MgO/CaO ratio of the starting materials, and \( f_{\text{Si}} \) is calculated in the same way. However, if calculating \( (\text{MgO/CaO})_{\text{norm}} \) using the CaO content of the bulk starting silicate, our samples M04, M07, and M09 all produce \( (\text{MgO/CaO})_{\text{norm}} \) values larger than one and consequently negative \( f_{\text{Mg}} \) values (Figure 2b), which should not be possible for evaporation experiments. We noticed that our bulk starting silicate is not homogeneous in CaO (Figure 2a) probably due to the formation of microcrystals during the synthesis (Figure 1c). Therefore, the calculated \( f_{\text{Mg}} \) of these three experiments could be seriously affected by the heterogeneity of CaO in the bulk starting silicate. For this reason, the \( f \) values calculated by mass balance (Figure 2c; Table 1) will be used in below discussions.

Plotting \( f_{\text{Si}} \) and \( f_{\text{Mg}} \) as a function of the sample mass loss fraction, Figure 3a shows that up to \( \sim 60\% \) Si was evaporated, whereas Mg exhibited significant evaporation only when \( \sim 20\% \) sample mass (or \( \sim 30\% \) Si) was evaporated. Limited Mg was evaporated at the early stage of evaporation leading to the produced vapor depleted in Mg relative to Si, which is consistent with previous theoretical results on enstatite melt (Xiao and Stixrude 2018). These results also indicate that the evaporation rate of Si is larger than Mg, i.e., Si is more volatile than Mg in our experiments. Our results also demonstrate that Ca, Nb, and Ta were not evaporated within analytical uncertainty (Figure S4). The refractory nature of Ca is consistent with the thermodynamical predictions (Ivanova et al., 2021) and previous evaporation experiments (e.g., Richter et al., 2007; Mendybaev et al., 2013; 2021), which showed that Ca evaporates only after Si and Mg are exhausted. In addition, the refractory nature of Nb and Ta is in accordance with their high 50% condensation temperature (Wood et al. 2019), suggesting that evaporation may not cause Nb and Ta fractionation nor the subchondritic Nb/Ta ratio in the BSE (Münker et al. 2003, 2017).

Isotopic fractionation

As shown in Figure 3b, both the bulk starting silicate-normalized \( \delta^{29}\text{Si}_{\text{norm}} \) (\( \sim 1-3.5\% \)) and \( \delta^{25}\text{Mg}_{\text{norm}} \) (\( \sim 0.1-1.2\% \)) increase with increasing sample mass loss fraction. However, initially Si was lost faster than Mg, and \( \delta^{29}\text{Si}_{\text{norm}} \) was larger than \( \delta^{25}\text{Mg}_{\text{norm}} \). Enrichment of the residual melt in MgO results in faster evaporation of Mg and thus faster increase of \( \delta^{25}\text{Mg}_{\text{norm}} \) after \( \sim 20\% \) sample mass was lost. These results indicate that light Mg and Si isotopes partitioned preferentially into the vapor during evaporation, consistent with theoretical expectations and earlier experimental works.
did not show any systematic variation because Ca was not evaporated when the Si and Mg remained in the silicate melt (Richter et al. 2007; Mendybaev et al. 2013, 2021; Ivanova et al. 2021). Our results of Ca are different from, but not contradictory with, previous experiments on synthetic CaTiO$_3$ perovskite at conditions of $\sim$10$^{-6}$ Torr and $\sim$2273 K, which showed that up to $\sim$90% Ca was evaporated and the measured $\delta^{44}$Ca$_{\text{norm}}$ was up to $\sim$100‰, with vapor/melt $\alpha^{(44}\text{Ca}/^{40}\text{Ca}) = 0.9562\pm0.0040$ (Zhang et al. 2014).

To quantify the Si and Mg isotopic fractionation induced by evaporation, we assume a Rayleigh distillation to describe the isotopic fractionation. Because in our experiments, the vapor escaped constantly with the argon flow and the recovered samples were chemically homogenous (Figure S2), indicating that diffusion in the melt was sufficiently fast relative to the evaporation rate. According to the Rayleigh distillation, we have:

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

(2)

where $R_{j/i}$ and $R_{j/i,0}$ are the ratio between the heavy isotope j and light isotope i in the residual silicate and starting silicate, respectively. The $f_i$ is the molar loss fraction of i - after evaporation and $i/j\alpha_{\text{exp}}$ is the mean isotopic fractionation factor between vapor and melt. The $f^{28}\text{Si}$ and $f^{25}\text{Mg}$ could be determined by combining the molar loss fraction and measured isotopes of Si and Mg in the samples. Taking the natural logarithm for both sides of Eq. (2), we obtained:

$$\ln(R_{j/i}/R_{j/i,0}) = (i/j\alpha_{\text{exp}} - 1)\ln(1 - f_i)$$

(3)

Linear correlations between $\ln(R_{j/i}/R_{j/i,0})$ and $\ln(1 - f_i)$ were observed for Si and Mg isotopes (Figure 4), justifying the assumption of a Rayleigh distillation. The values of $i/j\alpha_{\text{exp}}$ in Eq. (3) can be derived from slopes of linear regressions of the experimental data. Limited temperature dependence of $\alpha_{\text{exp}}$ was found in our experiments, yielding a mean $\alpha_{\text{exp}}$ of 0.99585$\pm$0.00002 for $^{28}\text{Si}/^{28}\text{Si}$ and 0.98942$\pm$0.00130 for $^{25}\text{Mg}/^{24}\text{Mg}$ (Figure 4).

The experimentally obtained vapor–melt isotopic fractionation is net isotopic fractionation ($\Delta_{\text{net}}$) and its relationship with equilibrium isotopic fractionation ($\Delta_{\text{eq}}$) and kinetic isotopic fractionation ($\Delta_{\text{kin}}$) can be expressed as (Dauphas et al. 2015):

$$\Delta_{\text{net}} = \Delta_{\text{eq}} + (1-S)\Delta_{\text{kin}}$$

(4)

In Eq. (4), $\Delta$ is related to $\alpha$ through $\Delta = 1000\times(\alpha-1)$, and $S$ is the saturation degree of evaporation, which is defined as $S = P_i/P_{i,\text{sat}}$, where $P_i$ and $P_{i,\text{sat}}$ refer to the partial vapor pressure and equilibrium vapor pressure of i at the evaporation conditions, respectively, and $0 < S \leq 1$. The $\Delta_{\text{eq}}$ is a function of $1/T^2$ (Bigeleisen and Mayer 1947; Urey 1947) and
would be too small to be measured by experiments at very high temperatures, which is thus usually estimated from the ratio of reduced partition function between gaseous species and melts. Since reduced partition function for Si in silicate melt is still lacking, we approximated it with crystalline enstatite (Javoy et al. 2012) because of its similar chemical composition to our enstatite melt, which yielded $\Delta_{\text{eq}}(^{29}\text{Si}) = -2.140 \times 10^6 / T^2$. We used the result of gas-enstatite melt calculated by Luo et al. (2018) for Mg isotopes, yielding $\Delta_{\text{eq}}(^{25}\text{Mg}) = -0.8772 \times 10^6 / T^2$. The $\Delta_{\text{kin}}$ during evaporation can be calculated by assuming the rate of gaseous species at the evaporating surface following a Maxwell-Boltzmann distribution (Richter et al. 2002):

$$\frac{1}{\delta} \Delta_{\text{kin}} (\%o) = -1000 \times \left[ 1 - \varepsilon_i / \varepsilon_j (m_i / m_j)^{0.5} \right]$$  \hspace{1cm} (5)

where $\varepsilon_i, \varepsilon_j$ denote evaporation coefficients, and $m_i, m_j$ denote the mass of i, j species in the vapor. Assuming that $\varepsilon$ is mass-independent, the theoretical kinetic fractionation $\Delta_{\text{kin}}(^{29}\text{Si})$ and $\Delta_{\text{kin}}(^{25}\text{Mg})$ are $-11.174\%o$ and $-19.419\%o$, respectively, when SiO and Mg are the dominant species in the vapor (De Maria et al. 1971; Shornikov and Yakovlev 2015; Costa et al. 2017). Using the $\Delta_{\text{eq}}$ and $\Delta_{\text{kin}}$ for $^{29}\text{Si}$ and $^{25}\text{Mg}$ in these previous studies, we calculated the $S$ values in our experiments, which yielded $S_{\text{Si}} = 0.662 \pm 0.002$ and $S_{\text{Mg}} = 0.459 \pm 0.068$.

**Discussion**

**Factors controlling Si and Mg isotopic fractionation**

The $\Delta_{\text{net}}$ is controlled by both temperature and $S$ as shown in Eq. (4). However, the temperature effect could be limited at non-equilibrium conditions because the $\Delta_{\text{eq}}$ at high-temperature is much closer to zero. This explains that the obtained $\alpha_{\text{exp}}$ for $^{29}\text{Si}/^{28}\text{Si}$ or $^{25}\text{Mg}/^{24}\text{Mg}$ are temperature-independent in our experiments (Figure 4). At non-equilibrium conditions, the $S$ value could significantly affect $\Delta_{\text{net}}$ for $^{29}\text{Si}$ and $^{25}\text{Mg}$.

For comparison, the $S$ values obtained in previous experiments are summarized in Table S2 and plotted in Figure 5a. The first-order observation is that the $S$ values obtained at vacuum or near-vacuum conditions ($\sim 10^{-9}$–$10^{-4}$ bar) are smaller than those obtained in levitation experiments, which may be determined by the mechanism how vapor escapes from the melt surface. In vacuum or near-vacuum experiments, the gaseous species escape through diffusion triggered by a self-generated composition gradient in the surrounding gas (Richter et al. 2002). The velocity of argon flow in our experiments was $\sim 13 \text{ m/s}$. Using a typical diameter of 3 mm of our samples, we determined a Reynolds number of 390 and Pécel number of 15–22 (Text S2), which indicates the vapor flow in
our experiments was laminar and the dominant mechanism for gaseous species escaping from the melt surface was advection (Sossi et al. 2019; Badro et al. 2021). In the levitation experiments, a gaseous boundary layer could form around the melt sphere and suppress an instant escape of the vapor, which makes $S$ values in the levitation experiments larger than those in the vacuum or near-vacuum experiments (Ni et al., 2021; Sossi et al., 2020; Young et al., 2022).

Figure 5a also shows that although $S_{\text{Si}}$ is larger than $S_{\text{Mg}}$ in our experiments, that $S_{\text{Si}} < S_{\text{Mg}}$ is also observed in previous experiments. We find that the relative volatility of Si and Mg may determine $S_{\text{Si}} < S_{\text{Mg}}$ or $S_{\text{Si}} > S_{\text{Mg}}$. As the $S_{\text{Si}}$ and $S_{\text{Mg}}$ in Figure 5 were derived from a series of experiments, we used the $(\text{Mg}/\text{Si})_{\text{max}}/(\text{Mg}/\text{Si})_{\text{ini}}$ ratio to approximately represent the relative volatility of Si and Mg during evaporation, where $(\text{Mg}/\text{Si})_{\text{max}}$ refers to the Mg/Si ratio in the recovered sample with a maximum mass loss fraction from a series of experiments, and $(\text{Mg}/\text{Si})_{\text{ini}}$ refers to the Mg/Si ratio in the starting silicate. Figure 5b shows that the $(1-S_{\text{Mg}})/(1-S_{\text{Si}})$ and $(\text{Mg}/\text{Si})_{\text{max}}/(\text{Mg}/\text{Si})_{\text{ini}}$ are strongly correlated ($R^2 = 0.81$), and that $S_{\text{Si}}$ is larger than $S_{\text{Mg}}$ when Si is more volatile than Mg, and vice versa. To explain these observations, we used the Hertz-Knudsen equation to describe the evaporation flux of Mg and Si, and the relationship of $S_{\text{Si}}$ and $S_{\text{Mg}}$ could be written as:

$$
\frac{1-S_{\text{Mg}}}{1-S_{\text{Si}}} = \frac{\varepsilon_{\text{SiO}} \gamma_{\text{SiO}} K_{\text{Si}}/M_{\text{Mg}}}{\varepsilon_{\text{Mg}} \gamma_{\text{MgO}} K_{\text{Mg}}/M_{\text{SiO}}} \times \frac{\ln(1-f_{\text{Mg}})}{\ln(1-f_{\text{Si}})}
$$

(6)

where $K_{\text{Si}}$ and $K_{\text{Mg}}$ are the equilibrium constant of the reactions that describe the evaporation of MgO and SiO$_2$ from the silicate melt as gaseous Mg and SiO in the vapor; $\gamma_{\text{MgO}}$ and $\gamma_{\text{SiO}}$ are the activity coefficients of MgO and SiO$_2$ in the silicate melt; $M_{\text{Mg}}$ and $M_{\text{SiO}}$ are the molar mass of gaseous Mg and SiO in the vapor. A detailed deduction of Eq. (6) is provided in supplementary Text S3. Eq. (6) shows that the $(1-S_{\text{Mg}})/(1-S_{\text{Si}})$ is a function of $\varepsilon_{\text{SiO}} \gamma_{\text{SiO}} K_{\text{Si}}/M_{\text{Mg}}$, and $\ln(1-f_{\text{Mg}})/\ln(1-f_{\text{Si}})$. If the evaporation coefficient and the equilibrium constant are constant in an experiment at a given temperature (e.g., Badro et al., 2021), the $(1-S_{\text{Mg}})/(1-S_{\text{Si}})$ is a function of $\gamma_{\text{SiO}}/\gamma_{\text{MgO}}$ and $\ln(1-f_{\text{Mg}})/\ln(1-f_{\text{Si}})$. For melt evaporation at given conditions, the increase in the volatility of MgO relative to that of SiO$_2$ are usually accompanied by an increase in $\gamma_{\text{MgO}}/\gamma_{\text{SiO}}$ (Richter et al., 2007; Badro et al., 2021) and an increase in $f_{\text{Mg}}$ relative to $f_{\text{Si}}$. Therefore, the $(1-S_{\text{Mg}})/(1-S_{\text{Si}})$ must decrease with increasing the volatility of MgO relative to that of SiO$_2$, qualitatively consistent with our observations shown in Figure 5b. Our experiments also show an increase in $\gamma_{\text{MgO}}/\gamma_{\text{SiO}}$ as the evaporation proceeded.
Lu et al.: Evaporation of Si-Mg-Ca in enstatite melt

(Figure S5), consistent with the increased volatility of MgO relative to that of SiO$_2$ (Richter et al. 2002, 2007). Accordingly, the silicate melt composition could play an important role in controlling the relative volatility of SiO$_2$ and MgO and $S_{Si}$ and $S_{Mg}$. However, it should be noted that “volatility” is more an empirical statement than a strict definition in thermodynamic or kinetic, and the relative volatility of SiO$_2$ and MgO during evaporation may be a multi-function of not only silicate melt composition but also parameters such as pressure, the quantitative effects of which require future studies.

**Implications**

The Si and Mg isotopic differences between the BSE, CI chondrites, and EC ($\Delta^{29}\text{Si}_{BSE-chondrite}$; $\Delta^{25}\text{Mg}_{BSE-chondrite}$) are $0.100 \pm 0.022\%$ for $\Delta^{29}\text{Si}_{BSE-CI}$, $(0.160-0.190) \pm 0.032\%$ for $\Delta^{29}\text{Si}_{BSE-EC}$, $0.011 \pm 0.011\%$ for $\Delta^{25}\text{Mg}_{BSE-CI}$, and $(0.011-0.013) \pm 0.009\%$ for $\Delta^{25}\text{Mg}_{BSE-EC}$ (Savage and Mynier 2013; Zambardi et al. 2013; Hin et al. 2017). If both $\Delta^{29}\text{Si}_{BSE-chondrite}$ and $\Delta^{25}\text{Mg}_{BSE-chondrite}$ result only from post-nebular evaporation, the evaporation-induced Si and Mg isotopic fractionation ($\Delta^{29}\text{Si}_{evap}$ and $\Delta^{25}\text{Mg}_{evap}$) must satisfy:

$$\Delta^{29}\text{Si}_{evap} = \Delta^{29}\text{Si}_{BSE-chondrite} \quad (7)$$

and

$$\Delta^{25}\text{Mg}_{evap} = \Delta^{25}\text{Mg}_{BSE-chondrite} \quad (8)$$

Since evaporation generally occurs in an open system (Nie and Dauphas 2019), the $\Delta^{29}\text{Si}_{evap}$ and $\Delta^{25}\text{Mg}_{evap}$ can be estimated by using the Rayleigh distillation model:

$$\Delta^{29}\text{Si}_{evap} = \Delta_{net}^{(29}\text{Si}) \ln (1-f_{Si}) \quad (9)$$

and

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

In Eqs. (9) and (10), the evaporative $f_{Si}$ and $f_{Mg}$ and the $\Delta_{net}^{(29}\text{Si})$ and $\Delta_{net}^{(25}\text{Mg})$ must be known to obtain $\Delta^{29}\text{Si}_{evap}$ and $\Delta^{25}\text{Mg}_{evap}$. To calculate $f_{Si}$ and $f_{Mg}$ for Earth, we assume that Earth’s precursor bodies have Mg/Ca and Si/Ca ratios identical to those of CI chondrites or EC, and the sub-chondritic Mg/Ca and Si/Ca ratios in the BSE result solely from post-nebular evaporative loss of Si and Mg because Ca is highly refractory as stated above. For instance, the $f_{Si}$ for using a CI-like precursor was calculated as $f_{Si} = [1 - (\text{Si/Ca})_{BSE}/(\text{Si/Ca})_{CI}]$. To calculate $\Delta_{net}^{(29}\text{Si})$ and $\Delta_{net}^{(25}\text{Mg})$ for Earth, we used different temperatures (to obtain $\Delta_{eq}$) and $S$ values in Eq. (4).

Figures 6a-b show the calculated $\Delta^{29}\text{Si}_{evap}$ and $\Delta^{25}\text{Mg}_{evap}$ as a function of
temperature and $S$ with fixed $f_{Si}$ and $f_{Mg}$ for different chondritic precursors. We can see from Figures 6a-b that increasing evaporation temperature and $S$ could effectively decrease $\Delta^{29}\text{Si}_{\text{evap}}$ and $\Delta^{25}\text{Mg}_{\text{evap}}$. Figure 6a shows that to explain the observed $\Delta^{29}\text{Si}_{\text{BSE-chondrite}}$, it requires evaporation temperatures of 3000–7000 K and 0.980 ≤ $S_{\text{Si}}$ ≤ 1. However, Figure 6b shows that to explain the observed $\Delta^{25}\text{Mg}_{\text{BSE-chondrite}}$, it requires evaporation temperatures of 4000–7000 K and 0.998 ≤ $S_{\text{Mg}}$ ≤ 1. Particularly, if Earth’s precursor bodies have EC-like composition as suggested by the Ca isotopes and many other mass-independent isotopic anomalies (Warren 2011; Dauphas 2017; Huang and Jacobsen 2017), evaporation temperatures > 5000 K are required to explain the observed $\Delta^{25}\text{Mg}_{\text{BSE-EC}}$ (Figure 6b). Therefore, evaporation temperatures > 5000 K are needed to explain both $\Delta^{25}\text{Mg}_{\text{BSE-EC}}$ and $\Delta^{29}\text{Si}_{\text{BSE-EC}}$. In order to further constrain the range of $S_{\text{Si}}$/S$_{\text{Mg}}$ that are required to explain both $\Delta^{25}\text{Mg}_{\text{BSE-EC}}$ and $\Delta^{29}\text{Si}_{\text{BSE-EC}}$, we additionally modeled the $\Delta^{25}\text{Mg}_{\text{evap}}$/ $\Delta^{29}\text{Si}_{\text{evap}}$ as a function of $S_{\text{Si}}$/S$_{\text{Mg}}$ at 5000–7000 K and $S_{\text{Mg}}$ of 0.998–1. Figures 6c-d show that to explain the observed $\Delta^{25}\text{Mg}_{\text{BSE-EC}}$/$\Delta^{29}\text{Si}_{\text{BSE-EC}}$, the $S_{\text{Si}}$/S$_{\text{Mg}}$ must be smaller than 1 at the evaporation temperatures of 5000–7000 K. The required high evaporation temperatures are relevant to planetary collisions (Canup 2012).

The above results demonstrate that post-nebular evaporation occurring at temperatures > 5000 K and $S_{\text{Si}}$/S$_{\text{Mg}}$ < 1 can explain the Mg/Ca and Si/Ca ratios and isotopes in the BSE, if EC-like materials are Earth’s main building blocks. It is worth pointing out that if we use $\Delta_{eq}^{29}\text{Si}$ derived from the gas-crystalline forsterite system, as used in Hin et al. (2017) and Young et al. (2019), the $S_{\text{Si}}$ value and temperature required to explain the BSE’s Si isotopes will increase by 0.002 and ~150 K, respectively. However, the use of $\Delta_{eq}^{25}\text{Mg}$ derived from the gas-crystalline forsterite system would not change $S_{\text{Mg}}$ or the evaporation temperature required to explain the BSE’s Mg isotopes because the $\Delta_{eq}^{25}\text{Mg}$ obtained from the gas-crystalline forsterite and the gas-enstatite melt systems are nearly the same, with a difference of only 0.0014‰ at 3000 K (Luo et al. 2018). In addition, in our model the isotopic fractionation factor and relative volatility of Si and Mg were assumed to be constant during the evaporation. However, they may be determined by not only the silicate melt composition but also the vapor pressure and the presence of volatiles. Also note that 5000 K is far outside our experiment temperatures and the thermodynamics of the melt under these conditions are highly uncertain. Future experiments that simulate actual conditions of planetary evaporation are needed to better understand its role in shaping Earth’s chemical compositions.
Our evaporation model provides a potential solution to the non-chondritic Mg/Ca and Si/Ca ratios and isotopes in the BSE, as those in recent studies (Hin et al. 2017; Young et al. 2019). Previous studies show that in the early solar system, Si isotopic fractionation between gaseous SiO and forsterite at nebular conditions may explain the variations in Si isotopes among Earth and other planetary bodies (Dauphas et al. 2015), which was further substantiated by Fe isotopes (Sossi et al. 2016). However, Mg does not show considerable isotope fractionation at the same process because limited amounts of initial Mg would be in the gas when forsterite was fully condensed (Dauphas et al. 2015); thus, a post-nebular process is still required. Recently, it was also suggested that Earth's Si, Mg, and Ca isotopes could be inherited from the accreted materials via pebble accretion without the need of evaporative fractionation, as supported by the identical mass-dependent Ca, Mg, and Si isotopes between Earth and chondrules in CV (Olsen et al. 2016; Amsellem et al. 2017; Kadlag et al. 2021). However, the mass-independent isotopes are distinct between Earth and chondrules of carbonaceous chondrites, but nearly the same between Earth and chondrules of EC (Schneider et al. 2020).

Our model implies that if Earth's Si and Mg isotope compositions are attributed alone to the evaporation of EC-like precursors, the evaporation temperatures may be over 5000 K. Such high temperatures imply that moderately and highly volatile elements must be completely lost during evaporation. In this case, Earth's additional accretion of materials with limited evaporative loss of volatiles or without volatile loss are required to explain Earth's volatile budget (Li et al. 2022), as supported by the K and S isotopes, and the volatile element depletion pattern in the BSE (Braukmüller et al. 2019; Li 2021; Tian et al. 2021; Wang et al. 2021).

Acknowledgments

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Figure captions

**Figure 1.** Images of the samples. (a) A typical silicate bead prepared for levitation evaporation experiment (left) and a transparent recovered sample (right). (b) Backscattered electron (BSE) image of the starting silicate. (c) A closer-view of the starting silicate, showing presence of micro-crystals probably formed during quench. (d) BSE image of a recovered sample (run M05). (e) A closer-view of a selected region in image d to show the homogeneity in structure and composition. The circular spots in images b and d are laser pits of LA–ICP–MS analysis.

**Figure 2.** (a) The CaO contents in the starting silicate beads estimated by mass balance for recovered samples M01 to M09. (b) The Si and Mg loss fraction calculated by normalization approach. Note that the (MgO/CaO)\textsubscript{norm}, for example, is the MgO/CaO ratio of a recovered sample normalized to that of the bulk starting silicate, i.e., (MgO/CaO)\textsubscript{norm} = (MgO/CaO)\textsubscript{sample} / (MgO/CaO)\textsubscript{starting}. (c) The Si and Mg loss fraction calculated by mass balance approach.

**Figure 3.** The Si and Mg molar loss fraction (a) and isotopes (b) of recovered samples as a function of the sample mass loss fraction. Note that the isotopes of the recovered samples were normalized to those of the bulk starting silicate, e.g., δ\textsubscript{29}Si\textsubscript{norm} = δ\textsubscript{29}Si\textsubscript{sample} – δ\textsubscript{29}Si\textsubscript{starting}. Also note that the variation of δ\textsubscript{29}Si\textsubscript{norm} and δ\textsubscript{25}Mg\textsubscript{norm} are coupled with the Si and Mg molar loss fraction, respectively.

**Figure 4.** The correlation between 1000×ln(R\textsubscript{j/i}/R\textsubscript{j/i,0}) and –ln(1–f) for Si (a) and Mg (b) isotopes in our experiments (red lines). The experimental results at 1873 K in Badro et al. (2021) are plotted for comparison. The isotopic fractionation factors are obtained by linear fitting not forced to go through (0,0) with errors in 2σ. The calculated kinetic and equilibrium isotopic fractionation factors of Si and Mg at 2623 K are also plotted for comparison (see main text for detailed calculations).

**Figure 5.** (a) Comparisons of \( S\textsubscript{Si} \) (open symbols) and \( S\textsubscript{Mg} \) (solid symbols) determined in our experiments and previous experiments. Vacuum or near-vacuum experiments and levitation experiments are separated by the dash line. The experimental temperature is color-coded. (b) Correlation between the \( (1–S\textsubscript{Mg})/(1–S\textsubscript{Si}) \) and \( (Mg/Si)\text{max}/(Mg/Si)\text{ini} \) with \( R^2 = 0.80 \). Note that \( S\textsubscript{Si} \) is larger than \( S\textsubscript{Mg} \) when Si is more volatile than Mg, and vice versa.
The symbols in b are the same as those in a, and the abbreviated references are: B21 (Badro et al. 2021), D90 (Davis et al. 1990), W01 (Wang et al. 2001), R07 (Richter et al. 2007), K09 (Knight et al. 2009), M13 (Mendybaev et al. 2013), M17 (Mendybaev et al. 2017), M21 (Mendybaev et al. 2021).

**Figure 6.** Diagrams constrain the conditions of post-nebular evaporation that could explain the differences in Mg/Ca and Si/Ca ratios and isotopes between the BSE and chondrites. *(a-b)* The evaporation-induced isotopic fractionation ($\Delta^{29}\text{Si}_{\text{evap}}$ and $\Delta^{25}\text{Mg}_{\text{evap}}$) as a function of temperature and $S$. *(c-d)* The evaporation-induced isotopic fractionation of $^{25}\text{Mg}$ and $^{29}\text{Si}$ ($\Delta^{25}\text{Mg}_{\text{evap}}/\Delta^{29}\text{Si}_{\text{evap}}$) as a function of $S_{\text{Mg}}$, $S_{\text{Si}}/S_{\text{Mg}}$, and temperature. Note that the $f_{\text{Mg}}$ and $f_{\text{Si}}$ used in the above modelling are fixed at the values determined from the difference in Mg/Ca and Si/Ca ratios of the BSE from those of chondrites (see main text for details). Plots *(a-b)* show that to explain the $\Delta^{29}\text{Si}_{\text{BSE-EC}}$, it requires evaporation temperatures of 3000–7000 K, whereas to explain the $\Delta^{25}\text{Mg}_{\text{BSE-EC}}$, it requires evaporation temperatures of 5000–7000 K; plots *(c-d)* show that to explain the $\Delta^{25}\text{Mg}_{\text{BSE-EC}}/\Delta^{29}\text{Si}_{\text{BSE-EC}}$, the $S_{\text{Si}}/S_{\text{Mg}}$ must be smaller than 1. If the core/mantle Si isotope fractionation is considered, as indicated by the line arrow in plot *(a)*, the observed $\Delta^{29}\text{Si}_{\text{BSE-chondrite}}$ would be smaller. CI = CI chondrite; EC = enstatite chondrite (EH, EL). See the main text for more details.
References cited


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Table 1. Elemental and isotopic compositions of the starting silicate and sample glasses.

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<th>M08</th>
<th>M09</th>
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<th>BCR-2*</th>
<th>SRM</th>
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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 with the suggested values from the GeoReM database (http://georem.mpch-mainz.gwdg.de); c. The mass loss fractions (f) are calculate by mass balance via  

$$ f_i = \frac{(M_{i0} - M_{i,t})}{M_{i0}} $$

where $M_{i0}$ and $M_{i,t}$ are the starting mass and recovered mass of element $i$ that could be readily obtained by $C_{i0} M_{sample,0}$ and $C_{i,t} M_{sample,t}$ respectively. The $C_{i0}$ 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 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 negligible. Hence, the molar loss fractions could be considered equal to the mass loss fractions.
Starting CaO (wt.%) calculated by mass balance

Bulk starting silicate

\[ \text{Si loss fraction (\%)} \text{ calculated by } (\text{SiO}_2/\text{CaO})_{\text{norm}} \]

\[ \text{Mg loss fraction (\%)} \text{ calculated by } (\text{MgO}/\text{CaO})_{\text{norm}} \]

(a) Starting CaO (wt.%) 

(b) Mg loss fraction (%)

(c) Si loss fraction (%)

\[ \text{Si loss fraction (\%)} \text{ calculated by mass balance} \]

\[ \text{Mg loss fraction (\%)} \text{ calculated by mass balance} \]
\[ 1000 \times \ln \left( \frac{R_{j/i}}{R_{j/i,0}} \right) - \ln(1 - f_{28Si}) \]

\( a_{\text{kin}} = 0.98883 \)

\( a_{\text{eq}} = 0.99964 \) (2623 K)

\( a_{\exp} = 0.99585 \pm 0.00002 \)

\( a_{\exp} = 0.99700 \pm 0.00045 \)

\[ 1000 \times \ln \left( \frac{R_{j/i}}{R_{j/i,0}} \right) - \ln(1 - f_{24Mg}) \]

\( a_{\text{eq}} = 0.99987 \) (2623 K)

\( a_{\text{kin}} = 0.9798 \)

\( a_{\exp} = 0.99500 \pm 0.00054 \)

\( a_{\exp} = 0.98942 \pm 0.00130 \)

(a) ... (b) Badro et al., 2021 (1873 K)
This study

Vacuum or near-vacuum

$T$ (K)

$S_{\text{Si}}$ $S_{\text{Mg}}$

(1 - $S_{\text{Mg}}$) / (1 - $S_{\text{Si}}$)

$S_{\text{Si}} > S_{\text{Mg}}$
$S_{\text{Si}} < S_{\text{Mg}}$

$R^2 = 0.80$

Volatility:

Si < Mg
Si > Mg
Observed $\Delta^{29}\text{Si}$:

- $S_{\text{Si}} = 0.980$
- $S_{\text{Si}} = 1$

Observed $\Delta^{25}\text{Mg}$:

- $S_{\text{Mg}} = 0.998$
- $S_{\text{Mg}} = 1$

(a) $S_{\text{Si}} / S_{\text{Mg}}$
(b) $S_{\text{Si}} / S_{\text{Mg}}$
(c) $S_{\text{Si}} / S_{\text{Mg}}$
(d) $S_{\text{Si}} / S_{\text{Mg}}$