

27 **Abstract**

28 **How and when Earth's volatile content was established is controversial with**
29 **several mechanisms postulated, including planetesimal evaporation, core**
30 **formation, and the late delivery of undifferentiated chondrite-like materials. The**
31 **isotopes of volatile elements such as sulfur can be fractionated during planetary**
32 **accretion and differentiation, and thus are potential tracers of these processes.**
33 **Using first-principles calculations, we examine sulfur isotope fractionation during**
34 **core formation and planetesimal evaporation. We find no measurable sulfur**
35 **isotope fractionation between silicate and metallic melts at core-forming**
36 **conditions, indicating that the observed light sulfur isotope composition of the**
37 **bulk silicate Earth relative to chondrites cannot be explained by metal-silicate**
38 **fractionation. Our thermodynamic calculations show that sulfur evaporates**
39 **mostly as H₂S during planetesimal evaporation when nebular H₂ is present. The**
40 **observed bulk Earth sulfur isotope signature and abundance can be reproduced**
41 **by the evaporative loss of about 90% sulfur mainly as H₂S from molten**
42 **planetesimals before nebular H₂ is dissipated. The heavy sulfur isotope**
43 **composition of the Moon relative to the Earth is consistent with evaporative sulfur**
44 **loss under 94-98% saturation condition during the Moon-forming giant impact.**
45 **In summary, volatile evaporation from molten planetesimals prior to Earth's**
46 **formation likely played a key role in establishing Earth's volatile element content.**

47

48 Understanding the accretion history of Earth's volatile elements, such as sulfur (S),
49 carbon (C), hydrogen (H) and nitrogen (N), is of profound importance for
50 understanding planetary formation, evolution, and habitability. Earth formed
51 from protoplanetary embryos with chemical compositions assumed to be similar to
52 undifferentiated chondrites¹. Compared with the solar composition and primitive
53 chondrites, the bulk silicate Earth (BSE) has a similar refractory lithophile element
54 abundance pattern but is strongly depleted in volatile elements². Different
55 interpretations have been proposed to explain this strong volatile element depletion. For

56 instance, the depletion pattern could be explained qualitatively by the late accretion of
57 10-20% of a volatile-rich body to a volatile-depleted proto-Earth³. Partial melting and
58 vaporization on bodies heated by the decay of short-lived nuclei⁴, such as ²⁶Al, may
59 have caused extensive volatile loss in the protoplanetary embryos that formed Earth^{5,6}.
60 Depletion of some siderophile (iron-loving) elements, such as S, may also be associated
61 with core-mantle differentiation⁷⁻⁹ and/or the Hadean sulfide segregation into the core¹⁰.
62 However, a recent study¹¹ argued that the volatile depletion in the BSE was inherited
63 from a carbonaceous chondrite-like source, suggesting that exotic addition of materials
64 or vaporization from Earth's precursors are not strictly required.

65 The abundance of volatiles and their isotopic compositions are commonly used to
66 distinguish between different mechanisms for establishing a volatile depleted
67 mantle. Sulfur, selenium (Se), and tellurium (Te) are highly siderophile elements with
68 similar and relatively low 50% condensation temperatures in a solar nebula
69 composition gas¹². Measurements of S, Se, and Te abundances in mantle peridotites
70 suggest that a volatile-rich late veneer of carbonaceous-chondrite-like material is
71 required to explain the relative ratios of S, Se and Te in the BSE¹³, but it is debated
72 whether peridotites preserve primitive mantle signatures¹⁴. The BSE has an average
73 stable S isotope composition (expressed as $\delta^{34}\text{S} = [({}^{34}\text{S}/{}^{32}\text{S})_{\text{sample}}/({}^{34}\text{S}/{}^{32}\text{S})_{\text{CDT}} - 1] \times 1000 \text{ ‰}$
74 and CDT is Canyon Diablo Troilite) of $-1.40 \pm 0.50\text{‰}$ (1SD)^{15,16}, which is significantly
75 lower than the average chondritic values¹⁷⁻¹⁹ (Fig. 1). Labidi et al.^{15,16} argued that core-
76 mantle differentiation^{7,8}, rather than a late veneer, was responsible for the sub-
77 chondritic $\delta^{34}\text{S}$ of the BSE. Equilibrium S isotope fractionation factors at core-forming
78 conditions are required to test this hypothesis, however, to date such data are not well
79 constrained. Published experiments²⁰ on S isotope fractionation between metal and
80 silicate melt have been performed only at $< 2 \text{ GPa}$ and $< 2000 \text{ K}$, whereas the pressure
81 and temperature (P - T) for Earth's core formation are expected to be much higher²¹. Both
82 experimental and theoretical studies²²⁻²⁴ demonstrate that the structure of silicate melts
83 changes dramatically with pressure, indicating that metal-silicate S isotopic
84 fractionation measured at low pressure cannot be directly applied to high-pressure core

85 formation²⁰.

86 As a volatile element, S would have undergone significant vaporization during
87 Earth's accretion like other moderately volatile elements⁵ such as Bi, Sn, Pb, and Zn.
88 Previous studies have investigated S isotope fractionation during evaporation from
89 troilite²⁵, and Mg and Si isotope fractionation during planetesimal evaporation^{6,26}, but
90 the effect of evaporation on S isotopes from planetesimals is unexplored. Whether the
91 sub-chondritic $\delta^{34}\text{S}$ of the BSE is related to S loss during early vaporization from Earth's
92 precursor bodies fundamentally impacts our understanding of the volatile depletion in
93 the BSE.

94 **Structural properties of sulfur in melts**

95 Here we present first-principles calculations that constrain the equilibrium S
96 isotope fractionation between silicate and metallic melts, and between the vapor phase
97 and silicate melt. We first conducted first-principles molecular dynamics (FPMD)
98 simulations based on density functional theory (DFT) (see Methods) to obtain the
99 structures of S-bearing silicate and metallic melts at 4-105 GPa and 3000 K. The
100 structural information of S shows a large difference under relatively reducing and
101 oxidizing conditions. Under relatively oxidizing conditions ($\text{Mg}_{32}\text{Si}_{32}\text{O}_{96}\text{SO}_2$), S is
102 directly bonded to O to form sulfate with a short S-O distance of ~ 1.5 Å (Extended
103 Data Fig. 1). In contrast, S is bonded to Fe, Mg and/or Si in $\text{Mg}_{32}\text{Si}_{32}\text{O}_{95}\text{S}$ and
104 $\text{Mg}_{41}\text{Ca}_2\text{Fe}_5\text{Si}_{32}\text{Al}_4\text{O}_{117}\text{S}$ melts (Extended Data Fig. 2), which correspond to relatively
105 reducing conditions. In Fe_{97}S_3 and $\text{Fe}_{87}\text{Ni}_4\text{Si}_{10}\text{O}_2\text{C}_2\text{S}_3$ melts, S is dominantly bonded to
106 Fe and/or Ni with a S-Fe/Ni distance of ~ 2.1 Å (Extended Data Fig. 3 and 4).

107 The average force constants $\langle F \rangle$ of S in silicate and metallic melts (Extended
108 Data Fig. 5 and Supplementary Table 1) were estimated using the small displacement
109 method based on the harmonic approximation (see Methods and supporting materials).
110 The $\langle F \rangle$ values of S are dominated by structural properties such as bond lengths. For
111 instance, the $\langle F \rangle$ of S in the $\text{Mg}_{32}\text{Si}_{32}\text{O}_{96}\text{SO}_2$ melt is much larger than those in
112 $\text{Mg}_{32}\text{Si}_{32}\text{O}_{95}\text{S}$, $\text{Mg}_{41}\text{Ca}_2\text{Fe}_5\text{Si}_{32}\text{Al}_4\text{O}_{117}\text{S}$, $\text{Fe}_{87}\text{Ni}_4\text{Si}_{10}\text{O}_2\text{C}_2\text{S}_3$, and Fe_{97}S_3 melts, which

113 can be explained by the much shorter S-O distance in $\text{Mg}_{32}\text{Si}_{32}\text{O}_{96}\text{SO}_2$ than the S-
114 Mg/Fe/Si/Ni distances in melts under relatively reducing conditions. In contrast, the
115 $\langle F \rangle$ of S in reducing silicate melts ($\text{Mg}_{32}\text{Si}_{32}\text{O}_{95}\text{S}$ and $\text{Fe}_{87}\text{Ni}_4\text{Si}_{10}\text{O}_2\text{C}_2\text{S}_3$) are slightly
116 larger than those in metallic melts (Fe_{97}S_3 and $\text{Fe}_{87}\text{Ni}_4\text{Si}_{10}\text{O}_2\text{C}_2\text{S}_3$), although this
117 difference becomes somewhat greater at > 80 GPa. Both silicate and metallic melts
118 become substantially more packed with increasing compression and hence, their S force
119 constants increase significantly with pressure. Compared with $\text{Mg}_{32}\text{Si}_{32}\text{O}_{95}\text{S}$ and Fe_{97}S_3
120 melts, the $\langle F \rangle$ of S in $\text{Mg}_{41}\text{Ca}_2\text{Fe}_5\text{Si}_{32}\text{Al}_4\text{O}_{117}\text{S}$ and $\text{Fe}_{87}\text{Ni}_4\text{Si}_{10}\text{O}_2\text{C}_2\text{S}_3$ melts only
121 increase by ~ 15 N/m (Extended Data Fig. 5).

122 Sulfur isotope fractionation during core formation

123 Using the high-temperature approximation of the Bigeleisen–Mayer equation²⁷,
124 we calculated the reduced partition function ratio ($10^3 \ln \beta$ or β factor) of $^{34}\text{S}/^{32}\text{S}$ from
125 the $\langle F \rangle$ (Extended Data Fig. 6) and the equilibrium S isotope fractionation factors
126 ($10^3 \ln \alpha$) between silicate and metallic melts at different pressures (Fig. 2). Our results
127 demonstrate that the oxidizing $\text{Mg}_{32}\text{Si}_{32}\text{O}_{96}\text{SO}_2$ silicate melt is enriched in ^{34}S relative
128 to metallic melts, but there is no measurable equilibrium S isotope fractionation
129 between the reducing silicate and metallic melts within the range of < 80 GPa. The
130 substantial changes in melt structural properties under compression only mildly affect
131 the $10^3 \ln \alpha$ between silicate and metallic melts. At 3000 K and 0-90 GPa, the $10^3 \ln \alpha$
132 between the reducing silicate and metallic melts is smaller than 0.05‰, while the value
133 between $\text{Mg}_{32}\text{Si}_{32}\text{O}_{96}\text{SO}_2$ and $\text{Fe}_{97}\text{S}_3/\text{Fe}_{87}\text{Ni}_4\text{Si}_{10}\text{O}_2\text{C}_2\text{S}_3$ is 0.35 ± 0.02 ‰. Thus, the S
134 isotope fractionation between the mantle and core is dominated by the S speciation in
135 the silicate melt.

136 The speciation of S in silicate melt is strongly controlled by the oxygen fugacity
137 ($f\text{O}_2$)^{28,29}. At $\log f\text{O}_2 < \text{FMQ}-1$ (1 log unit lower than the Fayalite–Magnetite–Quartz
138 buffer), S^{2-} is the dominant species; at $\log f\text{O}_2 > \text{FMQ}+2$, S occurs as S^{6+} , whereas at
139 $\text{FMQ}-1 < \log f\text{O}_2 < \text{FMQ}+2$, S^{2-} and S^{6+} coexist, and S^{6+} content increases sharply with
140 $\log f\text{O}_2$. Under the redox conditions of core formation for Earth, Mars, and Moon ($<$
141 $\text{FMQ}-4$)^{30,31}, S^{2-} should be the dominant species in silicate melt, and our results show

142 no measurable S isotope fractionation between silicate and metallic melts is predicted
143 (Fig. 2), and this conclusion is independent of the pressure of core formation^{2,32}.
144 Calculations using two endmember models (equilibrium and Rayleigh distillation)^{2,33,34}
145 show that core-mantle differentiation can only cause a very small positive shift of
146 +0.02-0.1‰ in $\delta^{34}\text{S}$ of the silicate mantle (Fig. 2c), which cannot explain the negative
147 $\delta^{34}\text{S}$ of the BSE relative to chondrites (Fig. 1).

148 **Mechanisms for sulfur isotope signatures in Earth and Moon**

149 In addition to ruling out core formation as the cause of the negative $\delta^{34}\text{S}$ of the
150 BSE, the very small fractionation of S isotopes caused by core formation means that
151 metallic cores have similar S isotopic ratios to their silicate mantles. Consequently, the
152 measured BSE isotopic composition¹⁵ of $-1.40 \pm 0.50\text{‰}$ should be representative of the
153 bulk Earth. Such a negative $\delta^{34}\text{S}_{\text{Earth}}$ cannot be explained by late delivery of S to the
154 BSE^{11,35,36} because most late-veener materials have heavier $\delta^{34}\text{S}$ than the Earth (Fig. 1).
155 Although the negative $\delta^{34}\text{S}$ of CM chondrites could be as low as $-1.11 \pm 0.30\text{‰}$, most
156 CM chondrites are characterized by a non-zero $\Delta^{33}\text{S}$ (from $-0.005 \pm 0.02\text{‰}$ to $0.213 \pm$
157 0.02‰ ; $\Delta^{33}\text{S} = 1000 \times [\delta^{33}\text{S} - [(\delta^{34}\text{S} + 1)^{0.515} - 1]]\text{‰}$), which is inconsistent with the
158 zero $\Delta^{33}\text{S}$ measured in terrestrial MORB ($0.005 \pm 0.008\text{‰}$)¹⁹. The average $\Delta^{33}\text{S}$ and
159 $\delta^{34}\text{S}$ values of CM chondrites¹⁹ are $0.021 \pm 0.068\text{‰}$ and $-0.08 \pm 0.44\text{‰}$, respectively,
160 which could produce zero $\Delta^{33}\text{S}$ but cannot reproduce the $\delta^{34}\text{S}_{\text{Earth}}$ value. We therefore
161 now consider whether this sub-chondritic $\delta^{34}\text{S}_{\text{Earth}}$ may be associated with volatile loss
162 during Earth's accretion.

163 Small precursor bodies with heat sources such as radiogenic $^{26}\text{Al}^4$ would have
164 undergone partial melting and vaporization, in which gravitational escape of volatiles
165 is possible if these precursor bodies have relatively small radii ($< 1000\text{ km}$)²⁶. Our
166 thermodynamic calculations (see Methods) show that S mainly occurs as H_2S in the
167 vapor phase (Extended Data Fig. 7 and Supplementary Table 2) in the presence of
168 nebular H_2 with a total pressure of about 10^{-4} bar ^{12,37}. Under such conditions, the net
169 fractionation as a consequence of planetesimal evaporation would be equal to the
170 equilibrium isotope fractionation between vapor phase and melt²⁶. This kind of

171 planetesimal evaporation can explain the concentrations of Mg and Si and their isotopic
172 signatures of the bulk Earth²⁶. Combining the fractions of each major S species with
173 their $\langle F \rangle$ (Supplementary Table 1), we estimated the equilibrium vapor-melt S isotope
174 fractionation ($\Delta^{34}\text{S}_{\text{vapor-melt}}^{\text{eq}}$) to be $\sim +0.45\%$ at 1400 K (Extended Data Fig. 8).
175 Therefore, S evaporation from planetesimal melts would enrich the melt phase with
176 light S isotopes. About 90% loss of S can explain the $\delta^{34}\text{S}$ difference between the bulk
177 Earth and chondrites (Fig. 3). This S evaporation process would leave a bulk Earth
178 accreted from enstatite-chondritic materials (3.3-5.8 wt% S, Wang and Becker¹³) with
179 a S concentration of 3300-5800 ppm. Such an initial S concentration can reproduce the
180 S abundance of the BSE³⁸ after S sequestration into the core^{7,9} without a contribution
181 from a late veneer.

182 While our model does not require a late veneer, a late delivery of S is still allowed
183 if the amount of S loss during evaporation is greater than 90%. In this case, the proto-
184 Earth would have an even lower $\delta^{34}\text{S}$ that would then be increased by the late-veneer
185 addition with a chondrite-like heavier $\delta^{34}\text{S}$. The more S is evaporated, the more S is
186 required to be added by a late veneer to match the S abundance in the BSE. However,
187 the $\delta^{34}\text{S}$ in the BSE will be close to those of chondrites if the amount of S added by the
188 late veneer is too high, and so to reproduce the S abundance and $\delta^{34}\text{S}$ value of the BSE,
189 the amount of S added by a late veneer to the BSE should not exceed $\sim 30\%$ of the
190 present-day BSE's S budget. As such, if the late veneer is characterized by chondrite-
191 like materials with 1.0 wt% S, the mass of late-veneer materials should not exceed 0.4%
192 of Earth's mass, consistent with estimates based on abundances of highly siderophile
193 elements³⁹.

194 We can also explain the large $\Delta^{34}\text{S}_{\text{Moon-Earth}}$ with the loss of volatile elements during
195 the Moon-forming giant impact (Fig. 3). It was suggested that evaporation
196 of moderately volatile elements under a vapor saturation of $\sim 99\%$ can explain the
197 enrichment of their heavy isotopes in the lunar mantle relative to the BSE⁴⁰⁻⁴². A high-
198 energy, high-angular-momentum model⁴³ suggests that the Moon condensed from a
199 vapor of BSE composition at distances beyond the Roche limit under high temperature

200 (~ 3700 K), Under such conditions, S evaporates as multiple species⁴⁴, including S, SO,
201 and SO₂. Because of the high temperature, the $\Delta^{34}\text{S}_{\text{vapor-melt}}^{\text{eq}}$, which is derived from the
202 $\langle F \rangle$ differences between all possible S species and silicate melt (Extended Data Fig.
203 11), is only -0.08–0.2‰. Consequently, the $\Delta^{34}\text{S}_{\text{vapor-melt}}$ is controlled by the kinetic S
204 isotope fractionation during free evaporation ($\Delta^{34}\text{S}_{\text{kin}} = [(32/34)^{1/2} - 1] * 1000 = -29.8\text{‰}$)
205 and the vapor saturation degree (see Methods). If the S concentration ratio between the
206 primitive lunar mantle⁴⁵ and the BSE³⁸ is used to estimate the fraction of S loss, the
207 $\Delta^{34}\text{S}_{\text{vapor-melt}}$ required to explain the $\Delta^{34}\text{S}_{\text{Moon-Earth}}$ ranges from -0.64‰ to -1.65‰,
208 corresponding to a vapor saturation degree of 0.941-0.977 (Fig. 3), which is similar to
209 that constrained by the isotopic data of several moderately volatile elements ($0.989 \pm$
210 0.002)⁴⁰. The small difference may be related to the uncertainties in the estimated lunar
211 $\delta^{34}\text{S}$, since S isotopes can be fractionated by magmatic events that complicates the
212 estimation of lunar $\delta^{34}\text{S}$ ⁴⁶. Overall, S evaporation during the Moon-forming event can
213 provide a first-order explanation for the enrichment of heavy S isotopes in the Moon.

214 In conclusion, we show that core formation does not significantly fractionate S
215 isotopes, and the bulk Earth is enriched in light S isotopes relative to chondrites and the
216 Moon. Evaporative loss of 90% S or greater from planetesimals with H₂S as the major
217 evaporative species in the presence of nebular H₂ with a pressure of about 10⁻⁴ bar can
218 reproduce the sub-chondritic $\delta^{34}\text{S}_{\text{Earth}}$ and the S concentration of the BSE. The large
219 $\Delta^{34}\text{S}_{\text{Moon-Earth}}$ can also be explained by S evaporation under vapor-unsaturated
220 conditions (94-98%) during the Moon-forming event (Fig. 4). This work strongly
221 supports the profound role of a melt-vapor reaction^{5,6} in establishing Earth's volatile
222 element depletion pattern².

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231 **Author contributions:** W.W. and C.-H.L. conceived and designed this project. W.W.
232 performed the theoretical calculations. S.H. and M.L. did the GRAINS calculations.
233 W.W. wrote the manuscript with the help of C.-H.L. and all authors contributed to the
234 discussion of the results and revision of the manuscript.

235 **Competing interests.** The authors declare no competing interests.

236 **Figure captions**

237 **Figure 1. Sulfur isotope compositions ($\delta^{34}\text{S}$) of planetary materials.** The $\delta^{34}\text{S}$ of the
238 BSE is defined by terrestrial mid-ocean ridge basalts^{15,16}, while the $\delta^{34}\text{S}$ of the silicate
239 Moon is defined by mare basalts⁴⁷. The $\delta^{34}\text{S}$ of sulfides in shergottites are from Franz
240 et al.⁴⁸. The average $\delta^{34}\text{S}$ of Vesta is defined by eucrites and diogenites^{49,50}. The $\delta^{34}\text{S}$
241 values of carbonaceous (CI, CV, CO and CM), ordinary, and enstatite chondrites are
242 from Gao and Thiemens^{17,18}, Labidi et al.¹⁹, and Defouilloy et al.⁵¹. The average $\delta^{34}\text{S}$
243 of carbonaceous chondrites given by Gao and Thiemens^{17,18} is $+0.49 \pm 0.16$ ‰. The
244 average of CM from Labidi et al.¹⁹ is -0.08 ± 0.44 ‰; however, most CM samples have
245 non-zero $\Delta^{33}\text{S}$ (mass independent sulfur isotope composition, $\Delta^{33}\text{S} = 1000 \times [\delta^{33}\text{S} -$
246 $[(\delta^{34}\text{S} + 1)^{0.515} - 1]]$ ‰), reflecting the effect of photochemistry¹⁹. The average of all
247 chondrites (light grey, -0.20 ± 0.20 ‰) is based on samples with Earth-like $\Delta^{33}\text{S}$
248 values^{15,16}. The $\delta^{34}\text{S}$ values of iron meteorites and pallasites are from Antonelli et al.⁵²
249 and Dottin et al.⁵³, respectively. Error bars represent $\pm 1\sigma$ deviation.

250 **Figure 2. Equilibrium sulfur isotope fractionation factors ($10^3 \ln \alpha$ of $^{34}\text{S}/^{32}\text{S}$)**
251 **between silicate and metallic melts.** (a) temperature dependence of $10^3 \ln \alpha_{\text{silicate-metal}}$ at
252 different pressures (b) pressure dependence of $10^3 \ln \alpha_{\text{silicate-metal}}$ at different temperatures.
253 $\text{Mg}_{32}\text{Si}_{32}\text{O}_{95}\text{S}$ and $\text{Mg}_{32}\text{Si}_{32}\text{O}_{96}\text{SO}_2$ represent S-bearing silicate melts under relatively
254 reducing and oxidizing conditions, respectively. Error bars represent $\pm 1\sigma$ deviation
255 obtained by propagation of $\pm 1\sigma$ deviation on the force constant. (c) modelled $\delta^{34}\text{S}$
256 difference between the BSE and chondrites ($\Delta^{34}\text{S}_{\text{BSE-chondrites}}$) as a function of remaining
257 S fraction (f) in the BSE after core formation. Equilibrium and Rayleigh distillation
258 models are considered as two endmember models. In the equilibrium model, $\Delta^{34}\text{S}_{\text{BSE-}}$
259 $\text{chondrites} = (1-f) * \Delta^{34}\text{S}_{\text{silicate-metal}}$; in the Rayleigh distillation model, $\delta^{34}\text{S}_{\text{BSE-chondrites}} =$
260 $\Delta^{34}\text{S}_{\text{silicate-metal}} * \ln(f)$. From (a) and (b), $\Delta^{34}\text{S}_{\text{silicate-metal}}$ is $< +0.02$ ‰ at > 3500 K and 0-60
261 GPa, which leads to a positive shift of 0.02-0.1 ‰ in $\delta^{34}\text{S}_{\text{BSE}}$.

262 **Figure 3. Sulfur isotope fractionation caused by volatile loss during planetesimal**
263 **evaporation and the Moon-forming impact.** (a) the modelled $\Delta^{34}\text{S}_{\text{Earth-chondrites}}$ as a
264 function of the S fraction remaining after S evaporation from molten planetesimals

265 under different temperatures (1300 K, 1400 K, and 1500 K). At a total gas pressure of
266 about 10^{-4} bar¹², the net evaporation fractionation factor of S isotopes would be equal
267 to the equilibrium vapor-melt S isotope fractionation factor ($\Delta^{34}\text{S}^{\text{eq}}_{\text{vapor-melt}}$), and
268 $\Delta^{34}\text{S}_{\text{Earth-chondrites}} = \Delta^{34}\text{S}^{\text{eq}}_{\text{vapor-melt}} * \ln f$, where f is the S fraction remaining. The β factor of
269 vapor phase is estimated based on the fractions of major S species in the vapor phase
270 and their $\langle F \rangle$, and $\Delta^{34}\text{S}^{\text{eq}}_{\text{vapor-melt}} = 10^3 \ln \beta_{\text{vapor}} - 10^3 \ln \beta_{\text{melt}}$. (b) the modelled $\Delta^{34}\text{S}_{\text{Moon-Earth}}$
271 as a function of the S fraction remaining after vapor loss (f) and vapor saturation degree
272 (D). The loss of abundant S as atomic gas during the Moon-forming impact can result
273 in a large $\Delta^{34}\text{S}_{\text{Moon-Earth}}$. Following a Rayleigh distillation model, $\Delta^{34}\text{S}_{\text{Moon-}}$
274 $\text{Earth} = \Delta^{34}\text{S}_{\text{vapor-melt}} * \ln f$. $\Delta^{34}\text{S}_{\text{vapor-melt}}$ ranges from $\Delta^{34}\text{S}^{\text{kin}}$ ($= [(32/34)^{1/2} - 1] * 1000 = -29.8\%$)
275 to $\Delta^{34}\text{S}^{\text{eq}}_{\text{vapor-melt}}$ ($= -113000/T^2$, T is temperature in Kelvin), depending on the vapor
276 saturation degree ($\Delta^{34}\text{S}_{\text{vapor-melt}} = \Delta^{34}\text{S}^{\text{eq}} + (1-D) * \Delta^{34}\text{S}^{\text{kin}}$)⁴⁰. The S loss fraction that is
277 required to explain the observed $\Delta^{34}\text{S}_{\text{Moon-Earth}}$ ($+1.98 \pm 0.50\%$, dash and solid blue lines)
278 depends on the vapor saturation degree.

279 **Figure 4. Schematic diagram of sulfur isotopic behaviors during evaporation on**
280 **small precursor bodies or during the Moon-forming impact. A:** partial melting and
281 S vaporization on molten planetesimals mainly as H₂S under vapor-saturated conditions
282 in the presence of nebular H₂ with a pressure of 10^{-4} bar¹². This process would cause
283 the enrichment of ³²S in proto-Earth and about 90% loss of S could explain the $\Delta^{34}\text{S}_{\text{Earth-}}$
284 chondrites . Followed by core formation^{7,8}, the S abundance of the BSE³⁸ can be reproduced
285 without the need of the accretion of CI-like materials. **B:** the growing molten Moon
286 condensed from the vapor of BSE composition at locales beyond the Roche limit under
287 high temperature, in which a large amount of S was lost under vapor-undersaturated
288 conditions (a vapor saturation degree of 0.941-0.977).

289 **Data availability.** The data that support the findings of this study is available in the
290 article and Supplementary Information files. All new data associated with this paper
291 will be made publicly available at <https://doi.org/10.6084/m9.figshare.16566336.v1>.

292 **Code availability.** The Vienna Ab Initio Simulation Package is a proprietary software
293 available for purchase at <https://www.vasp.at/>.

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441 **Methods**

442 **Equilibrium isotope fractionation factor**

443 Bigeleisen–Mayer equation²⁷ has been widely used to calculate the reduced
444 partition function ratio (β) of element X in phase A, which represents the equilibrium
445 isotope fractionation factor of element X between the phase A and an ideal gas of X
446 atoms. Under the high-temperature approximation, the Bigeleisen–Mayer equation can
447 be expressed as:

$$448 \quad \beta = 1 + \left(\frac{1}{m} - \frac{1}{m'}\right) \frac{\hbar^2}{24k^2T^2} (f_{xx} + f_{yy} + f_{zz}) \quad (1)$$

449 where m and m' refer to the light and heavy isotopes, respectively; f_{xx} , f_{yy} , and
450 f_{zz} are the diagonal elements of the force constant matrix; T is temperature in Kelvin,
451 and \hbar and k are the reduced Planck constant and Boltzmann constant, respectively.
452 Thus, the equilibrium isotope fractionation factor between phase A and B can be derived
453 from:

$$454 \quad 10^3 \ln \alpha_{A-B} = 10^3 \ln \beta_A - 10^3 \ln \beta_B = \left(\frac{1}{m} - \frac{1}{m'}\right) \frac{\hbar^2}{8k^2T^2} (\langle F \rangle_A - \langle F \rangle_B) \quad (2)$$

455 Here $\langle F \rangle$ is defined as the average value of diagonal elements of the force constant
456 matrix $(f_{xx} + f_{yy} + f_{zz})/3$. The use of Eq. (2) requires the validity criteria
457 that frequencies related to the element of interest ω_i (cm^{-1}) $\leq 1.39 T$ (T is the
458 temperature in Kelvin). For the temperature of core formation (> 3000 K), the upper
459 limit of frequencies is > 4200 cm^{-1} , which is higher than any vibrational frequency
460 associated with S atom in secular materials. This method has been also successfully
461 applied to predict the equilibrium barium isotope fractionation between minerals and
462 aqueous solution at low temperature⁵⁴ and the nickel isotope fractionation between
463 silicate and metallic melts⁵⁵.

464 **First-principles molecular dynamics simulations**

465 Equilibrium sulfur (S) isotope fractionation factors between silicate and metallic
466 melts can be estimated from the $\langle F \rangle$ difference between these two melts using Eq. (2).
467 Because melts do not have regular structures as solid crystals, we conducted first-
468 principles molecular dynamics (FPMD) simulations based on the density functional
469 theory (DFT) using VASP with the projector-augmented wave (PAW) method⁵⁶ to

470 predict the structures of S-bearing silicate and metallic melts. The generalized-gradient
471 approximation (GGA)⁵⁷ was adopted for the exchange-correlation functional and the
472 PBE pseudopotentials were used. The energy cutoff for the plane wave was 600 eV.
473 The Brillouin zone summations over the electronic states were performed at gamma
474 point. Here we firstly focus on three different melts, including metallic melt with a
475 chemical formula of Fe₉₇S₃ and two silicate melts with chemical formulas of
476 Mg₃₂Si₃₂O₉₅S and Mg₃₂Si₃₂O₉₆SO₂. The former silicate melt represents the S-bearing
477 silicate melt under relatively reducing condition and the latter refers to relatively
478 oxidizing condition. The chemical composition of MgSiO₃ was chosen for silicate melts
479 because it has similar MgO and SiO₂ contents to primitive chondrites. In order to check
480 the effect of other minor elements on the structural properties obtained for S in silicate
481 and metallic melt, we also conducted FPMD simulations on a pyrolitic composition
482 (Mg₄₁Ca₂Fe₅Si₃₂Al₄O₁₁₇S) and a multicomponent alloy (Fe₈₇Ni₄Si₁₀O₂C₂S₃) under
483 relatively reducing condition. All FPMD simulations were performed in the NVT
484 thermodynamic ensemble with a fixed temperature controlled by a Nosé thermostat.
485 The simulations for Fe-bearing systems are spin-polarized, with the spin on each Fe
486 atom being allowed to freely fluctuate at each step. We did not introduce a Hubbard U
487 correction for Fe atoms in our calculations. Caracas et al.⁵⁸ checked the behavior of the
488 Fe-bearing melt based on DFT+U and found that a +U correction does not significantly
489 change the calculated results. Cell parameters and volumes of simulated boxes are listed
490 in Supplementary Table 1. The time step was set to be 1 fs and the initial liquid
491 configurations at different volumes were prepared by melting the structures at 6000 K
492 for 20 ps. After that, all simulations were conducted at 3000 K for at least 60 ps.
493 Pressures at different volumes can be derived by averaging the pressure for each time
494 step after the equilibration.

495 To obtain the force constant of S atom in silicate and metallic melts, large numbers
496 of snapshots were extracted from the FPMD trajectories every 250 steps after
497 equilibration for the single-atom optimization, in which only S atomic positions were
498 relaxed with fixed cubic boxes. Then the force constant matrix of S in each snapshot
499 can be calculated using the small displacement method (see Supplementary Information)

500 and the statistical average on all snapshots is the average force constant of S atom in
501 the melts.

502 Our results suggest the Si-O distance initially increases from ~ 1.62 Å at 6.28 GPa
503 to ~ 1.67 Å at 66.85 GPa and then maintains at ~ 1.66 Å with further compression
504 (Supplementary Fig. 1 and 2), whereas the Mg-O bond length significantly decreases
505 from 1.97 to 1.88 Å when the pressure increases from 6.28 GPa to 105.03 GPa.
506 Meanwhile, the coordination numbers (CNs) for Si-O and Mg-O pairs increase from \sim
507 4.1 to 6 and from ~ 4.1 to 7.1 at that pressure range (Supplementary Fig. 1 and 2),
508 respectively. The calculated structural properties agree well with previous experimental
509 measurements²² and theoretical studies^{23,24}, ensuring the accuracy and reliability of our
510 calculations. In $\text{Mg}_{32}\text{Si}_{32}\text{O}_{96}\text{SO}_2$ melt, the S-O distance (~ 1.5 Å) is much shorter than
511 the S-Mg (> 2.5 Å) and S-Si distances (> 2.8 Å) and the coordination number (CN) for
512 S-O pair is ~ 3 if the cutoff is 2.0 Å (Extended Data Fig. 1), suggesting that S atom is
513 directly bonded to O atoms as sulfate under relatively oxidizing conditions. In contrast,
514 the S-O distance in $\text{Mg}_{32}\text{Si}_{32}\text{O}_{95}\text{S}$ melt (~ 2.6 Å) is much longer than that in the
515 $\text{Mg}_{32}\text{Si}_{32}\text{O}_{96}\text{SO}_2$ melt, while the S-Mg (~ 2.4 Å) and S-Si distances (~ 2.05 Å) are much
516 shorter than those in $\text{Mg}_{32}\text{Si}_{32}\text{O}_{96}\text{SO}_2$ melt (Extended Data Fig. 2). When the cutoff for
517 the coordination shell is 2.5 Å, the CNs for S-Mg and S-Si pairs are both ~ 1 , suggesting
518 that the S atom is bonded to Si and Mg atoms, which is self-consistent with the valence
519 state of S (S^{2-}). The S atom in $\text{Mg}_{41}\text{Ca}_2\text{Fe}_5\text{Si}_{32}\text{Al}_4\text{O}_{117}\text{S}$ melt is preferentially bonded to
520 Fe and Mg atoms (Extended Data Fig. 4), but the S-Fe distance (~ 2.10 Å) is shorter
521 than the S-Mg distance (~ 2.37 Å). The CNs for S-Fe and S-Mg pairs are ~ 2 and 1,
522 respectively, when the cutoff for the coordination shell is 2.5 Å. In Fe_{97}S_3 melt, the S-
523 Fe distance (2.09-2.15 Å) is comparable to the S-Fe distance in
524 $\text{Mg}_{41}\text{Ca}_2\text{Fe}_5\text{Si}_{32}\text{Al}_4\text{O}_{117}\text{S}$ melt and the CNs are 4-5 if the cutoff is 2.4 Å (Extended Data
525 Fig. 3). In $\text{Fe}_{87}\text{Ni}_4\text{Si}_{10}\text{O}_2\text{C}_2\text{S}_3$ melt, the S atom is dominantly bonded to Fe and Ni atoms
526 with a S-Fe/Ni distance of ~ 2.11 Å (Extended Data Fig. 4), similar to the S-Fe distance
527 in Fe_{97}S_3 melt.

528 The $\langle F \rangle$ of S in each snapshot and the statistical average are shown in
529 Supplementary Fig. 3-6. Our results show that the $\langle F \rangle$ difference between silicate and

530 metallic melts is smaller than 25 N/m at < 80 GPa (Extended Data Fig. 5 and
531 Supplementary Table 1) when S^{2-} is the dominant species, suggesting no significant
532 equilibrium S isotope fractionation between these two phases (Fig. 2). The $\langle F \rangle$ of S in
533 $Mg_{41}Ca_2Fe_5Si_{32}Al_4O_{117}S$ and $Fe_{87}Ni_4Si_{10}O_2C_2S_3$ melts are 291.6 N/m at 46.6 GPa and
534 253.8 N/m at 41.8 N/m, which are only ~ 15 N/m higher than the values for
535 $Mg_{32}Si_{32}O_{95}S$ and $Fe_{97}S_3$ systems (Extended Data Fig. 5). This indicates that the
536 presence of other components does not significantly affect the the $10^3 \ln \alpha$ between
537 silicate and metallic melts under relatively reducing condition. Previous experimental
538 work argued that Fe metal is preferentially enriched in ^{34}S relative to silicate melt and
539 the fractionation is up to +0.64 ‰ at 1923 K. If this is correct, the $\langle F \rangle$ of S in silicate
540 melt should be at least 290 N/m lower than that the one in metallic melt, which deviates
541 from the direction of our predictions. This is likely because the isotope exchange during
542 experiments had not reached the equilibrium state.

543

544 **Sulfur species in vapor phases**

545 In order to estimate the equilibrium S isotope fractionation between the vapor
546 phase and silicate melt, we first determined the S species in the vapor phase. We used
547 the GRAINS code⁵⁹ to calculate the minimum Gibbs free energy of the system with
548 solar abundance for the elements¹² at specific temperature and $1e^{-4}$ bar. This code
549 considered 33 elements (H, He, C, N, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe,
550 Co, Ni, Cu, Ga, Ge, Mo, Ru, Pd, Hf, W, Re, Os, Ir, Pt, Au). The code considers 242 gas
551 species and 520 condensed (liquid or solid) species freely and outputs all the species
552 when the system achieves chemical equilibrium through Gibbs free energy
553 minimization. We used the solar abundances for the elements to calculate the
554 equilibrium gas phases because the solar nebular would not have completely dissipated
555 during planetesimal evaporation in the first several million years³⁷. The evaporation of
556 planetesimals investigated here requires the presence of nebular H_2 under a total
557 pressure of $1e^{-4}$ bar. The results of all S species at 1000-1600 K and $1e^{-4}$ bar are listed
558 in Supplementary Table 2. The important species for S in the vapor includes H_2S (g),
559 HS (g), SiS (g), and S_2 (g), among which the fraction of H_2S is the largest at 1000-1500

560 K. To check the effect of H concentration on the S species in the vapor phase, we also
561 conducted thermodynamic calculations using GRAINS with solar elemental
562 abundances but with H concentration decreased by one and four orders of magnitude,
563 conditions that are more oxidizing than the solar nebular. The results show that S in the
564 vapor phase mainly occurs as H₂S and/or HS at 1000-1500 K when H concentration is
565 decreased by 90%, while SO, SO₂, and S₂ are the main S species when only 0.01% H
566 is retained (Extended Data Fig. 7). On the basis of these results, we conducted first-
567 principles calculations for these S species in the vapor phase. For each S species, we
568 put a molecule in a cubic box (20 Å×20 Å×20 Å) and relaxed the atomic positions. The
569 <F> of S can be estimated using the small displacement method (Supplementary Table
570 1). We checked the effect of box size and found that the results will not change with the
571 size when the cell parameter is larger than 20 Å. The atomic S gas has a <F> of 0 N/m
572 and the β factor is 0, because there is no atomic bonding in this system. Thus, the <F>
573 of S in the vapor with the presence of nebular H₂ can be calculated based on the
574 fractions of each species (Supplementary Table 2).

575

576 **Isotope fractionation during evaporation and condensation**

577 Young et al.²⁶ investigated the nature of evaporation process and how evaporation
578 and condensation fractionate isotopes using numerical simulations. Following that
579 work, the S isotope fractionation during evaporation and condensation ($\Delta^{34}\text{S}_{\text{vapor-melt}}$)
580 can be approximately expressed as:

$$581 \quad \Delta^{34}\text{S}_{\text{vapor-melt}} = \Delta^{34}\text{S}^{\text{eq}} + (1-D) * \Delta^{34}\text{S}^{\text{kin}} \quad (3)$$

582 where $\Delta^{34}\text{S}^{\text{eq}}$ is the equilibrium S isotope fractionation between vapor phase and melt,
583 $\Delta^{34}\text{S}^{\text{kin}}$ is the kinetic S isotope fractionation, and D is the degree vapor saturation
584 ($D=P/P_{\text{sat}}$, P is the pressure of the evaporating species at the surface of the melt and P_{sat}
585 is the saturation vapor pressure). $\Delta^{34}\text{S}^{\text{kin}}$ can be estimated from: $\Delta^{34}\text{S}^{\text{kin}} =$
586 $1000 * [(m_{\text{S32}}/m_{\text{S34}})^{1/2} - 1]$, where is the atomic or molecular mass of the vapor species.
587 This simplified approach gives the instantaneous isotopic fractionation between vapor
588 and melt.

589 The effect of planetesimal evaporation on the $\delta^{34}\text{S}$ of proto-Earth and other

590 differentiated bodies depends on the degree vapor saturation and S species in the vapor
591 phase that are a function of oxygen fugacity and temperature. If D is lower than 100%,
592 the net evaporation fractionation factor of S isotopes ($\Delta^{34}\text{S}_{\text{vapor-melt}}$) would be affected
593 by the large negative kinetic fractionation, and the final $\Delta^{34}\text{S}_{\text{vapor-melt}}$ could be positive,
594 zero, or negative even when the S evaporates mainly as H_2S from planetesimals. On the
595 other hand, when D is 100%, $\Delta^{34}\text{S}_{\text{vapor-melt}}$ is controlled by the S species in the vapor
596 phase. The evaporation of atomic S will enrich the melt in heavy S isotopes, whereas
597 H_2S evaporation will enrich the melt in light S isotopes.

598 Differentiated planetesimals may have undergone S evaporation under a range of
599 conditions, which may show different effects on their $\delta^{34}\text{S}$ values. When planetesimals
600 undergo evaporation in the presence of nebular H_2 under a total pressure of about 10^{-4}
601 bar, numerical simulations²⁶ show that the vapor saturation degree will be
602 approximately 100%, and the net isotope fractionation is equal to the equilibrium
603 isotope fractionation between vapor and melt. The evaporation of planetesimal melts in
604 the presence of nebular H_2 can also explain the Mg and Si isotopic and elemental
605 compositions of the bulk Earth²⁶. The observed bulk Earth S isotope signature and
606 abundance can be reproduced by the evaporative loss of ~90% S, mainly as H_2S , from
607 molten planetesimals in a H_2 atmosphere. For Mars, previous studies reported that most
608 sulfides in shergottiites have negative $\delta^{34}\text{S}$ values, indicating that the Martian mantle is
609 also likely to have a negative $\delta^{34}\text{S}$ value. The average S concentration for all
610 shergottiites⁴⁸ is about four times the S abundance in the BSE. As such, the evaporative
611 loss of S (~60%) would be significantly lower than the estimate for Earth and the effect
612 of evaporation on the $\delta^{34}\text{S}$ value ($\Delta^{34}\text{S}_{\text{Mars-chondrites}} = \Delta^{34}\text{S}_{\text{vapor-melt}}^{\text{eq}} * \text{Inf}$, where f is the S
613 fraction remaining) would be smaller than that for Earth. So overall, the literature data
614 of sulfides in shergottiites primary supports our conclusions.

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