A thermally conductive Martian core and implications for its dynamo cessation

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Abstract

Mars experienced a dynamo process that generated a global magnetic field $^{4.3-3.6}$ Ga. The cessation of this dynamo strongly impacted Mars' history and is expected to be linked to thermochemical evolution of Mars' iron-rich liquid core, which is strongly influenced by its thermal conductivity. Here we directly measured thermal conductivities of solid iron-sulfur alloys to pressures relevant to the Martian core and temperatures to 1023 K. Our results show that a Martian core with 16 wt% sulfur has a thermal conductivity of $^{-19}$ to 32 W m⁻¹ K⁻¹ from its top to the center, much higher than previously inferred from electrical resistivity measurements. Our modelled thermal conductivity profile throughout the Martian deep-mantle and core indicates a $^{-4}$ to 6-fold discontinuity across the core-mantle-boundary. The core's efficient cooling resulting from the depth-dependent, high conductivity diminishes thermal convection and forms thermal stratification, significantly contributing to cessation of Martian dynamo.

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20 21

22 Abstract

Mars experienced a dynamo process that generated a global magnetic field ~4.3–3.6 Ga. The 23 cessation of this dynamo strongly impacted Mars' history and is expected to be linked to 24 thermochemical evolution of Mars' iron-rich liquid core, which is strongly influenced by its 25 thermal conductivity. Here we directly measured thermal conductivities of solid iron-sulfur alloys 26 to pressures relevant to the Martian core and temperatures to 1023 K. Our results show that a 27 Martian core with 16 wt% sulfur has a thermal conductivity of ~19 to 32 W m⁻¹ K⁻¹ from its top to 28 the center, much higher than previously inferred from electrical resistivity measurements. Our 29 modelled thermal conductivity profile throughout the Martian deep-mantle and core indicates a ~ 4 30 to 6-fold discontinuity across the core-mantle-boundary. The core's efficient cooling resulting 31 from the depth-dependent, high conductivity diminishes thermal convection and forms thermal 32 33 stratification, significantly contributing to cessation of Martian dynamo.

- 34
- 3536 Teaser
- 37 38

Mars' core is much more thermally-conductive than previously inferred, which critically contributes to stop its early dynamo.

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44 MAIN TEXT 45 Introduction 46 Thermal conductivity of rocky planets' cores controls their thermal evolution and dynamics, 47 which drive and maintain the dynamo action and magnetic fields of these planets (1-3). 48 Convection of an iron (Fe)-rich liquid core is predominantly operated by thermal and 49 compositional buoyancy (4-7). Thermal buoyancy is produced as the super-isentropic heat flux 50 extracted across the core-mantle-boundary (CMB) to the mantle is larger than a minimum value. 51 The compositional buoyancy, on the other hand, is generated by a gravitationally unstable density 52 distribution via either phase transition (e.g., crystallization of the liquid core), or exsolution of 53 materials and immiscibility of elements (8-10). Interestingly, the evolution history of the dynamo 54 and magnetic fields of Mars are strikingly different from those of the Earth: satellites magnetic 55 data on the Martian crustal rocks suggested an early, short-lived dynamo that once operated ~ 4.3 -56 3.6 Ga (see, e.g., Ref (11-14) for details of the dynamo history), while the Earth's dynamo, 57 predominantly powered by inner core crystallization, remains active today. Paleomagnetic data 58 (15) suggested that Earth's dynamo slowly decayed from 2.5 to 0.5 Ga, but recovered as the inner 59 core started to grow. Hemingway and Driscoll (16) suggested that Martian dynamo may be 60 intermittent. They showed that the presence of a solid inner core in Mars is compatible with the 61 absence of a present-day dynamo, and that a compositionally powered dynamo could become 62 effective in the next ~1 Gyrs. Note, however, that InSight data suggested that Martian core is 63 entirely molten and lighter than expected (17), indicating that it may be richer in light elements. 64 Finally, it is worth pointing out that Mercury, which is smaller than Mars but has an inner core, 65 66 has a faint magnetic field triggered by a core dynamo, while Venus, whose size is similar to Earth, does not. These suggest that the size of a planet is not the primary parameter controlling the 67 68 presence of dynamo, and that other aspects, including core composition and its effects on physical 69 properties, play crucial roles in maintaining a dynamo. Martian core's thermal conductivity holds

a key to estimate the available thermal and compositional energy to operate its dynamo, and thus
to reconstruct its thermochemical history. Recent numerical simulations (*I*) explored the
influence of thermal conductivity on core evolution by doing a systematic parameter survey over
a broad range of potential thermal conductivity values and revealed that a high core thermal
conductivity (16–35 W m⁻¹ K⁻¹) could be a critical factor to cease its global magnetic field. The
assumption that thermal conductivity at Martian core's condition is high has, however, never been
experimentally verified.

Recent seismic observations by the InSight lander (17) and the geodetic data inferred a liquid 77 Martian core that is larger than previously expected. Furthermore, it is implied that the entire 78 Martian mantle has a mineralogy similar to that in the Earth's upper mantle and transition zone, 79 i.e., ringwoodite is the major mineral in Martian deep mantle, while bridgmanite, the predominant 80 mineral in Earth's lower mantle, is not present within Mars. Given the limited cosmochemical and 81 geophysical data as well as different model assumptions, the composition of the Martian core 82 remains poorly constrained (see Ref (18, 19) and references therein). However, it is commonly 83 considered to be made of Fe alloyed with significant amounts of light elements, including sulfur 84 (S) as the major one, along with small amounts of oxygen (O), carbon (C), and hydrogen (H). Due 85 to the abundance and siderophile characteristic of S, its proposed content in the Martian core 86 typically falls in the range of ~10–25 wt% (18–20). This motivates us to choose, for simplicity, 87 eutectic Fe₃S (~16 wt%) and FeS (~36 wt%) as representative compositions, and to study their 88 thermal conductivity at Martian core pressure-temperature (P-T) conditions, providing pivotal 89 90 insights to their impacts on the fate of Martian dynamo.

The heat flux across the Martian CMB, Q_c , is crucial for determining the evolution of the thermal state and dynamo action in the Martian core. This flux is controlled by heat transfer through the mantle, which itself depends on the lowermost mantle thermal conductivity, as it controls the conductive heat transfer through thermal boundary layers, as well as on the efficiency

95	of mantle convection (if happening at all). The lowermost mantle thermal conductivity may be					
96	estimated from mineral physics measurements of ringwoodite's thermal conductivity (21). On the					
97	core side, heat transfer and dissipation, which play a crucial role on the core and dynamo					
98	evolutions, depend on the core's thermal conductivity. The thermal conductivity of Fe-S alloys					
99	may bring important constraints on this conductivity, but has never been directly measured under					
100	Martian core's high P-T conditions. Previous studies have largely focused on the determination					
101	the electrical resistivity ρ of Fe-S alloys, which is then used to infer its thermal conductivity					
102	through the Wiedemann-Franz (WF) law with ideal Lorenz number (see, e.g., Ref (22) and					
103	references therein). First-principles theoretical calculations showed that at Martian core					
104	conditions the ρ of liquid Fe ₃ S and Fe ₇ S remains at ~107 $\mu\Omega$ cm and ~88 $\mu\Omega$ cm, respectively					
105	(23); these results infer a relatively high Martian core's thermal conductivity (~50 W m ⁻¹ K ⁻¹).					
106	Note that with similar approaches, Earth's core thermal conductivity was inferred to be ~80–300					
107	W m ⁻¹ K ⁻¹ (22). Experimental high <i>P</i> - <i>T</i> measurements on the ρ of solid Fe-S alloys were,					
108	however, typically limited to ≤ 10 GPa (24–26). Extrapolation of such low-pressure data to					
109	Martian core's high-pressure conditions (~18-40 GPa) suggested a low thermal conductivity of					
110	~10 W m ⁻¹ K ⁻¹ in Martian core. These contradictory results lead to distinct implications for the					
111	energy budget of the Martian core and Q_c , and different scenarios for the evolution of the					
112	dynamo. Since the validity of applying the WF law with ideal Lorenz number on the Fe-light					
113	element alloys (e.g., Fe-S alloys) under extreme conditions remains uncertain and is being					
114	challenged (2), direct and precise determination of their thermal conductivity at high $P-T$					
115	conditions relevant to the Martian core is key to constrain its thermal conductivity and understand					
116	the mechanisms that stop its dynamo.					
117	In this work, our direct high <i>P</i> - <i>T</i> thermal conductivity measurements of Fe-S alloys					

118 combined with data modeling allow us to build a depth-dependent thermal conductivity profile 119 from the Martian deep-mantle to its core, providing the first direct experimental evidence for a highly thermally-conductive Martian core. Such high thermal conductivity enables efficient
 cooling of the Martian core and formation of thermal stratification layer, leading to a short-lived
 (~0.5–0.8 Gyr) dynamo that ceased ~4 Gyr ago.

- 123
- 124 **Results**125

126 Thermal conductivity at high pressure and room temperature

We used time-domain thermoreflectance (TDTR) coupled with diamond anvil cell (DAC) (2, 127 27, 28) (see Methods) to precisely measure the thermal conductivity of polycrystalline Fe₃S and 128 FeS to ~40 GPa at room temperature. We find that the thermal conductivity of Fe₃S (~16 wt% S) 129 at ambient conditions is ~6.8 W m⁻¹ K⁻¹ (Fig. 1(a)), which is more than an order of magnitude 130 smaller than that of pure Fe (\sim 76 W m⁻¹ K⁻¹) (2), indicating a strong reduction of thermal 131 conductivity caused by the sulfur impurity. Application of pressure monotonically enhances the 132 thermal conductivity, which reaches $\sim 25 \text{ W m}^{-1} \text{ K}^{-1}$ at 40.5 GPa, the pressure at the center of the 133 Mars. Moreover, with ~36 wt% S impurity, the FeS shows drastically distinct values of thermal 134 conductivity and pressure dependence (Fig. 1(b)). The thermal conductivity of FeS at ambient 135 conditions (FeS I phase) is even lower than that of Fe₃S, down to ~ 2.9 W m⁻¹ K⁻¹. Upon 136 compression across ~3.4 GPa, the thermal conductivity suddenly increases to 9 W m⁻¹ K⁻¹ at 5.2 137 GPa (FeS II phase). After the transition at ~6.7 GPa to FeS III phase, considering the data 138 uncertainty, the thermal conductivity remains approximately at 7.5 W m⁻¹ K⁻¹ until \sim 25 GPa, after 139 which it significantly increases to 12 W m⁻¹ K⁻¹ at 43 GPa, half of the Fe₃S at similar pressures. 140 It's worth noting that, similar to the effect of silicon alloying (2), presence of ~ 16 wt% (Fe₃S) 141 and ~ 36 wt% S (FeS) in Fe significantly reduces the thermal conductivity, presumably due to the 142 strong inelastic scattering between electrons and impurities (29-31). The impurity effects also 143 alter the pressure dependences of Fe_3S and FeS, which are considerably different from that of 144 pure Fe, where a concave pressure dependence with a minimum at ~ 40 GPa was observed (2). 145

147 Thermal conductivity at high pressure-temperature conditions

148	To quantify the effects of temperature and sulfur alloying, we further performed high $P-T$					
149	thermal conductivity measurements on the Fe ₃ S and FeS in externally-heated DACs (Fig. 2). The					
150	thermal conductivities of Fe ₃ S and FeS both increase with temperature, similar, again, to the					
151	behaviors of Fe-Si alloys (2, 32). Note that along the $P-T$ path of our measurements (i.e., first					
152	compressing the sample to a fixed pressure and then raising the temperature), the Fe ₃ S stayed in					
153	the tetragonal structure (33), while the FeS transitioned from FeS III to IV phase at ~730 K (34).					
154	Though our measurement temperature was only up to ~1023 K, we observed clear temperature					
155	dependences that change with the pressure and S content. We should note that the estimated					
156	Martian core temperature was ~2000–2400 K (35). If we assume the thermal conductivity can be					
157	phenomenologically modelled as $\Lambda(T) = aT^n$, where <i>a</i> is a normalization constant, the exponent					
158	value <i>n</i> can be determined by the linear slope in the $\ln\Lambda$ - $\ln T$ plot. Interestingly, for Fe ₃ S, <i>n</i> = 0.25					
159	(±0.07) at 15.4 GPa and slightly decreases with pressure to $n = 0.2$ (±0.04) at 35.5 GPa (Fig.					
160	2(a)). With higher content of S impurity that results in stronger carrier scattering, the FeS IV					
161	phase has a stronger temperature dependence than the Fe ₃ S at similar pressures: $n = 0.36 (\pm 0.07)$					
162	at 27 GPa and $n = 0.33 (\pm 0.05)$ at 28 GPa, respectively (Fig. 2(b)). Though the crystal structure of					
163	Fe ₃ S and FeS is different, our results suggest that at a given pressure, the higher content of					
164	impurity would have a stronger temperature dependence, which has also been reported in Fe-Si					
165	alloys (2, 32) (see discussion).					

166

167 Discussion and implications for the Martian dynamo evolution

168 **Temperature dependence of thermal conductivity**

169 The Wiedemann-Franz (WF) law relates the electronic thermal conductivity Λ_e of a material 170 with its electrical resistivity ρ by $\Lambda_e = L \times T/\rho$, where *L* is the Lorenz number that may vary with 171 pressure and temperature, and *T* the absolute temperature. Typically, when the temperature is

172	comparable or higher than the Debye temperature of the material, its electrical resistivity can be
173	expressed approximately as $\rho = \rho_0 + \alpha + \beta T$, where ρ_0 is the residual resistivity arisen from defect-
174	scattering, α a phenomenological constant associated with the shift in the resistivity due to
175	temperature effect, and β a temperature coefficient (36, 37). Therefore, Λ_e can be rewritten as Λ_e
176	~ $L \times T/(\rho_0 + \alpha + \beta T)$. Since our measurement temperature (300–1023 K) is higher than 1/3 of the
177	Debye temperature of Fe-S alloys (~ 400 K) (38), the high contents of S impurity in Fe makes the
178	sum of $(\rho_0 + \alpha)$ larger than βT (37). The Λ_e of F-S alloys is thus expected to increase with
179	increasing temperature. Furthermore, with increasing S content, the relative contribution of βT to
180	the total electrical resistivity would be further reduced, leading to a stronger temperature
181	dependence. On the other hand, for both Fe_3S and FeS , the temperature exponent <i>n</i> decreases with
182	pressure, in line with the general trend observed for the $Fe_{0.85}Si_{0.15}(2)$. This is presumably caused
183	by the fact that pressure reduces the effective density of impurity in momentum space (less
184	impurity-scattering) and enhances the relative contribution of βT , leading to a weaker temperature
185	dependence of thermal conductivity (36).

186

187 Thermal conductivity profiles in Martian core and mantle

The recent geophysical observations by the InSight mission (17) suggest that the Martian 188 core is larger than previously thought and confirm that, by contrast to the Earth, the Martian 189 mantle is too thin to allow a transition from ringwoodite to bridgmanite, i.e., ringwoodite is the 190 major mineral in its deep mantle. The mean Martian core density derived from InSight 191 observations spans from \sim 5.7–6.3 g cm⁻³, where a number of potential combinations of S, O, and 192 H contents alloyed in an Fe-Ni core is discussed (17). Geochemically defensible amounts of these 193 light elements with a mean core density >6 g cm⁻³ are at the upper end of such density range. With 194 a lower bulk mantle FeO content, the Insight observations preliminarily suggests that the core is 195 majorly composed of Fe-Ni along with ~10–15 wt% S, <5 wt% O, and <1 wt% H and C (17). To 196

197	understand the thermal evolution history of Mars and its early dynamo, we first model the thermal
198	conductivity of the Martian core and mantle along an estimated Martian areotherm taken from
199	Ref (35) (an estimated present-day radial temperature profile within Mars), based on our present
200	high <i>P-T</i> thermal conductivity of solid Fe-S alloys and previous data for ringwoodite (21). Note
201	that if the core temperature were as high as 3000 K early in Mars' history, our modelled thermal
202	conductivity of Martian core would be increased by only ~6%, which is within our data
203	uncertainty. In other words, the temporal changes in the Martian areotherm as it cools down since
204	its early stage have minor effects on our modelled thermal conductivity and numerical simulations
205	on its thermal evolution. For the solid Fe ₃ S and FeS, we assume their temperature dependences of
206	thermal conductivity at Martian core <i>P</i> - <i>T</i> conditions follow those shown in Fig. 2, i.e., scaling
207	with $T^{0.21}$ and $T^{0.33}$, respectively. The thermal conductivity of ringwoodite, on the other hand, is
208	assumed to follow a $T^{-0.5}$ dependence, typical of Fe-bearing minerals (27, 39–41). The modelled
209	thermal conductivities of ringwoodite (blue curves), solid Fe ₃ S (black curve), and solid FeS
210	(orange curve) along a Martian areotherm are plotted in Fig. 3.
211	Literature experimental investigations on the high <i>P</i> - <i>T</i> electrical resistivity ρ of solid Fe-S
212	alloys have been largely limited to ≤ 10 GPa (24–26). For instance, ρ of Fe-20wt%S at 4.5 GPa
213	was found to be ~400 $\mu\Omega$ cm up to ~1400 K (24), and ρ of FeS at 5 GPa (26) and 8 GPa (24)
214	remained at ~400 $\mu\Omega$ cm and ~700 $\mu\Omega$ cm, respectively, up to ~1700 K. Their corresponding
215	thermal conductivities were then further inferred to be $\sim 6-11$ W m ⁻¹ K ⁻¹ via the WF law with an
216	ideal Lorenz number. In addition, based on high pressure but room temperature electrical
217	resistivity measurements, ρ of solid Fe-14.2wt%S at Martian core conditions was estimated to
218	~100 $\mu\Omega$ cm, suggesting a thermal conductivity of 46 W m $^{-1}$ K $^{-1}$ at the Martian CMB and 62 W m $^{-1}$
219	¹ K ⁻¹ at the center (42). Using first-principles calculations, ρ of liquid Fe ₃ S and Fe ₇ S were
220	determined to stay at ~107 $\mu\Omega$ cm and ~88 $\mu\Omega$ cm, respectively, throughout the Martian core
221	conditions (23). Again, it is important to note that our present study represents the first direct high

222	<i>P-T</i> thermal conductivity measurements of solid Fe-S alloys that do not rely on the WF law and
223	assumption of ideal Lorenz number. Our results for the thermal conductivities of solid Fe-S alloys
224	(solid black and orange curves in Fig. 3) under similar <i>P</i> - <i>T</i> conditions and S content are much
225	higher than those inferred from high $P-T$ experimental electrical resistivity data (24), while only
226	about half of those estimated from room temperature resistivity data (42) and calculated by first-
227	principles (for liquid phase) (23). Table 1 summarizes thermal conductivity of Fe-S alloys at
228	Martian CMB conditions. Here we only include literature results available at CMB <i>P</i> - <i>T</i> conditions
229	with an S content similar to our present study, as the chemical composition could significantly
230	influence the thermal conductivity of Fe alloys.
231	Moreover, prior studies have suggested that the effect of melting would reduce the thermal
232	conductivity of Fe and Fe alloys by ~20% or less (see, e.g., Ref. (2) and references therein).
233	Assuming S is the major light element with ~16 wt% (~25 at%) (20) in the Martian core and a
234	15% conductivity reduction upon melting, our present data suggest that the thermal conductivity
235	of liquid Fe ₃ S (red dashed curve in Fig. 3) would be ~19 W m ⁻¹ K ⁻¹ at the top of the Martian core,
236	and that it increases by ~70% to ~32 W m ⁻¹ K ⁻¹ at the center, leading to a much more thermally-
237	conductive Martian core than previously inferred. In addition, if the mineralogy of the Martian
238	mantle is similar to that of the Earth's upper mantle, which is predominantly composed of olivine
239	and its high-pressure polymorph ringwoodite, the thermal conductivity of ringwoodite in dry
240	phase at the bottom of the mantle would be ~4.5 W m ⁻¹ K ⁻¹ (blue solid curve in Fig. 3). Note that
241	if the ringwoodite in the Martian mantle contains substantial amounts of water, its thermal
242	conductivity would be lower. For instance, the presence of 1.73 wt% water would lead to a
243	conductivity of ~3 W m ⁻¹ K ⁻¹ at the bottom of the Martian mantle (see the blue dashed curve).
244	Furthermore, if the ringwoodite in the Martian mantle contains more iron than that in the Earth,
245	its thermal conductivity would be even lower. Overall, a ~4 to 6-fold thermal conductivity
246	discontinuity is expected across the Martian CMB (liquid Fe ₃ S vs. ringwoodite), which would

suppress heat released from the core and promote thermal stratification. Such findings yield 247 distinct behaviors concerning the Q_c (see geodynamic modeling below). In addition, our results 248 for Fe₃S and FeS at Martian core's *P*-*T* conditions provide a platform to model the thermal 249 conductivity of the Fe-S alloys with different S contents, since under different model assumptions 250 the not-well-constrained S content in the Martian core may vary over the range we explored 251 (~16–36 wt%) during Mars history. If the Martian core also contains few amounts of other 252 elements (e.g., O, H, and C, etc.), these impurities are expected to further slightly reduce the 253 thermal conductivity of Martian core, while their exact effects require future experimental and 254 computational studies. 255

256

257 Implications for Martian thermal evolution and dynamo cessation

Dynamo operation and duration strongly depend on core thermal conductivity. Higher 258 thermal conductivity promotes faster dynamo decay through ohmic dissipation, and in absence of 259 gravitational energy released from core crystallization the dynamo may rapidly switch off. Recent 260 simulations of Mars core-mantle coupled evolution (1) indicate that the cessation time of the 261 Martian magnetic field (11–13) can be explained with a core thermal conductivity in the range of 262 16–35 W m⁻¹ K⁻¹, provided that the mantle reference viscosity, η_0 , is between 10¹⁹ and 10²¹ Pa s. 263 Modelling details further show that the pressure dependence of mantle viscosity (with an 264 activation volume fixed to 6 cm³ mol⁻¹) requires a lower range of reference viscosity $(10^{19}-10^{20})$ 265 Pa s) and thermal conductivity ($< 20 \text{ W m}^{-1} \text{ K}^{-1}$) to explain this cessation time. 266 Here we investigate how the radial profile of the core thermal conductivity, Λ_c (red dashed 267 curve in Fig. 3), impacts Mars thermal evolution. For this, we performed simulations coupling 268 parameterized models of core and mantle evolution following the method developed in Ref (1)269 270 (also see method section), with the exception that the thermal conductivity is now allowed to vary with depth. Figure 4 plots evolution of key parameters ((a) heat flow Q_c , (b) entropy arising from 271

272	ohmic dissipation, E_j , (c) bottom radius of the thermally stratified layer, r_s , and (d) temperature at					
273	the CMB) for three different scenarios, including the reference case in Ref (1) (green curves).					
274	Thermal stratification is a consequence of a sub-isentropic heat flow (i.e., Q_c is lower than the					
275	heat flow along an isentropic temperature gradient, Q_a), and results in higher core temperatures.					
276	All cases were performed with the "standard" configuration of Ref (1) , i.e., the mantle viscosity					
277	does not depend on pressure (activation volume is set to zero), and the mantle abundance in heat-					
278	producing elements is that of Ref (43) . In addition, the initial mantle temperature and temperature					
279	jump at the CMB were set to 2327 K and 182 K, respectively, corresponding to the standard					
280	reference case in Ref (1), and leading to an initial CMB temperature of 2509 K. Dynamo switches					
281	off when E_j is below a small value $E_{j,min}$, corresponding to the minimum ohmic dissipation needed					
282	to self-sustain feedbacks between magnetohydrodynamic processes. For Earth, and in the case of					
283	a poloidal field, this value was estimated to 1.0 MW K^{-1} (44), which we adopted in our estimation					
284	of the Martian dynamo cessation time. Greenwood et al. (1) pointed out that because $E_{j,min}$ is					
285	much smaller than the dissipation provided by secular cooling, its exact value does not					
286	substantially influence the dynamo cessation time. The condition $E_j < 1.0 \text{ MW K}^{-1}$ occurs around					
287	the transition from super- to sub-isentropic heat flow (i.e., Q_c being slightly higher or lower than					
288	Q_a). For the reference case (Λ_c is a constant of 24 W m ⁻¹ K ⁻¹ throughout the core and $\eta_0 = 2.5 \times 10^{20}$					
289	Pa s; green curves in Fig. 4), this happens ~0.9 Gyr, well within the estimated cessation range					
290	(11–13). For the depth-dependent profile of Λ_c based on our experimental data and still with η_0 =					
291	2.5×10^{20} Pa s, dynamo cessation occurs later, ~1.1 Gyr (blue curves in Fig. 4). Within error bars					
292	(blue shaded area), however, the cessation time expected from our Λ_c profile agrees with the					
293	observed range. In addition, good agreement can be obtained by assuming a slightly higher					
294	mantle viscosity (red curves in Fig. 4, the same Λ_c profile as the blue curves, but with η_0 =					
295	3.5×10^{20} Pa s). Thermal stratification starts when Q_c becomes lower than Q_a . Our calculations					
296	indicate that Q_a is lower with depth-increasing conductivity, which delays the onset of					

297	stratification. For the reference case, stratification starts ~0.3 Gyr before dynamo cessation, while					
298	it starts ~0.4–0.6 Gyr after dynamo cessation when the depth-dependent Λ_c is accounted for.					
299	Moreover, core thermal stratification is much faster with the depth-dependent Λ_c . For instance,					
300	the entire core is thermally stratified by 2.8 Gyr with our Λ_c profile and $\eta_0=2.5\times10^{20}$ Pa s (blue					
301	curve in Fig. 4(c)), compared to ~4.5 Gyr for the reference case (green curve). A possible					
302	explanation for this faster stratification is that, compared to the constant Λ_c case, due to the depth-					
303	increasing Λ_c , the increase in cooling rate of the convecting core is greater than that of the stable					
304	layer, meaning the thermal stratification completes earlier.					
305	One aspect that is not accounted for in our simulations is the possible presence of a basal					
306	layer enriched in iron and heat producing elements at the base of the mantle (45). Such a layer					
307	may result from the crystallization of Martian magma ocean, and is expected to be partially					
308	molten due to high temperatures in the CMB region, and to transfer heat by conduction. Because					
309	it is partially molten and enriched in iron, one would further expect the thermal conductivity of					
310	this layer to be much lower than that of ringwoodite (blue curve in Fig. 3). In other words, if such					
311	a layer exists, it would act as a thermal blanket, opposing core cooling and dynamo action.					
312	Combined with our present core thermal conductivity, it would, in turn, request a lower mantle					
313	viscosity to explain the observed dynamo cessation time. Future direct measurements and					
314	computational studies on the thermal conductivity of other Fe-S-light element systems under					
315	relevant <i>P</i> - <i>T</i> conditions are required to better constrain the thermal evolution and energy budget					
316	of the Mars.					
317 318 319 320	Materials and Methods					
320 321	Starting materials and sample preparation					
322	The Fe ₃ S polycrystals were synthesized by a Kawai apparatus with a 5000 ton press (run					
323	number 5K3187). The starting material is a powder mixture of Fe and S with an atomic ratio of					

324	3:1. The sample was compressed to 22 GPa, and first heated to 1000°C, followed by a cooling
325	process from 1000°C to 855°C for 9.5 hrs, and finally kept at 700°C for 2hrs. The starting FeS
326	troilite powder was extracted from the Cape York IIIAB iron meteorite, also known as the
327	Innaanganeq meteorite, in the Geological Museum of the University of Copenhagen, Denmark.
328	Troilite in iron meteorites is known to be very chemically stoichiometric FeS, which is more
329	suitable for the present study than commercial pyrrhotite samples (Fe _{1-x} S) with iron deficiency (X
330	= 0 to 0.2). The chemical composition of Fe ₃ S and FeS was characterized to be Fe _{2.97} S (with a
331	small amount of Fe ₃ S ₂) and Fe _{0.995} S, respectively, by electron probe microanalyzer in Academia
332	Sinica.

To prepare samples for thermal conductivity measurements at high pressure and room 333 temperature, each sample was firstly hand-polished down to ~10 µm thick, and then thermally 334 evaporated with a 90 nm thick Al film. The sample along with several ruby spheres was loaded 335 into a symmetric diamond anvil cell (DAC) where a pair of 300 µm culet anvils and a Re gasket 336 were used. Due to its relatively low thermal conductivity at high pressures, silicone oil (CAS No. 337 63148-62-9 from ACROS ORGANICS) was loaded as the pressure transmitting medium, which 338 remains in a reasonably well quasi-hydrostatic condition over the pressure range we studied (<45 339 GPa). The pressure within the sample chamber of the DAC was monitored by fluorescence(46) 340 and Raman of the ruby with a typical uncertainty of <5%. 341

In our high *P-T* measurements, the ~10 μ m-thick sample and ruby spheres were loaded into an externally-heated DAC (EHDAC). Here polycrystalline NaCl powder (thermally dried at ~120°C for one hour before being loaded) was used as the pressure medium. The EHDAC provides a spatially homogeneous temperature distribution over the sample chamber. Since the pressure within the sample chamber may change upon heating, a gas membrane that enables *in situ* control on the pressure within the EHDAC was also used. The combination of these techniques allows us to investigate the temperature dependence of thermal conductivity of Fe₃S and FeS at a given pressure up to ~1023 K. Details of the EHDAC assemblage and pressuretemperature measurement, as well as the sample geometry and experimental setup can be found in
Ref (*39*, *47*).

352

353 Thermal conductivity measurements

We used time-domain thermoreflectance (TDTR) to measure the thermal conductivity of 354 Fe₃S and Fe₅ over a wide range of *P*-*T* conditions presented in this work. TDTR is a widely used 355 thermal metrology method that provides thermal conductivity measurements of various materials 356 with high precision. In the past decade, it has also been successfully coupled with high P-T357 techniques, see, e.g., Ref (2, 27, 39, 48). In short, TDTR is an ultrafast optical pump-probe 358 spectroscopy, which uses a split pump pulse to heat up the Al film coated on the sample, and a 359 split probe pulse to detect the heat diffusion dynamics through the sample. By comparing the 360 temporal evolution of the Al's reflectivity change with numerical calculations based on a bi-361 directional thermal model, the thermal conductivity of the sample of interest is determined. More 362 details of the principle, experimental setup, and data analysis of the TDTR are described in 363 literatures, e.g., Ref (2, 47-50) and references therein. 364

Supplementary Materials Fig. S1 shows a set of representative TDTR spectrum for Fe₃S at 365 40.5 GPa and room temperature along with data fitting by the thermal model calculations. In the 366 thermal model, the volumetric heat capacity of the sample of interest (Fe-S alloys) is an important 367 parameter. At ambient conditions, the volumetric heat capacity of FeS is 2.78 J cm⁻³ K⁻¹ taken 368 from Ref (51), while that of Fe₃S is estimated to be $3.16 \text{ J cm}^{-3} \text{ K}^{-1}$ by linear interpolation between 369 pure Fe (3.54 J cm⁻³ K⁻¹) and FeS. The heat capacity of both FeS and Fe₃S at high *P*-*T* conditions 370 are not known, and thus assumed to be a constant as their ambient values. We note that the 371 372 uncertainty in our data majorly arises from the analysis uncertainty, rather than the measurement 373 uncertainty. Based on the method (52, 53) described in Supplementary Materials Fig. S1 and S2,

the uncertainties in all the parameters in our thermal model calculations would translate <10%
error in the derived thermal conductivity of Fe-S alloys before 20 GPa, and ~10–17% error at 20–
40 GPa.

377

378 Modelling of core evolution

To investigate the evolution of the Martian core, including the growth of a stable layer, and to estimate the cessation time of Martian dynamo, we used the approach in Ref (1), which is coupling models of parameterized convection for the core and for the mantle.

For the mantle, this approach uses a parameterization based on stagnant lid thermal 382 383 convection (54, 55) with a simplified lithosphere. The mantle is heated both from below (heat extracted from the core) and from within (radiogenic heating due to the decay of U, Th and K). 384 Concentration in heat producing elements is taken from the compositional model of Ref (43). The 385 convective interior is assumed isothermal, and temperature increases linearly with depth within 386 thermal boundary layers. The crust thickness is considered as constant over time, and melting and 387 crust growth are neglected. The thickness of the stagnant lid (modelling the lithosphere) is set to 388 300 km. Ref (1) showed that the thickness of the stagnant lid does not have a strong impact on the 389 390 evolution of the mantle convective interior and of the core. Mantle viscosity depends on temperature following an Arrhenius law with activation energy fixed to 300 kJ mol⁻¹, and is 391 specified (reference viscosity n_0) at a temperature of 1600 K. Viscosity is further allowed to 392 393 increase with temperature, but, for simplicity, here is neglected this dependence (activation volume V_a is set to 0). The time for dynamo's cessation strongly depends on η_0 and, to a lesser 394 extent on activation volume (1). For core thermal conductivity in the range of 16-35 W m⁻¹ K⁻¹, 395 calculated cessation time agrees with that estimated for Martian dynamo with viscosity in the 396 range of 10^{20} - 10^{21} Pa s. Accounting for viscosity pressure dependence ($V_a=6$ cm³ mol⁻¹) reduces 397

this range by one order of magnitude. In calculations, we tested values of the reference viscosity, $\eta_0=2.5\times10^{20}$ Pa s and $\eta_0=3.5\times10^{20}$ Pa s.

400	The core is initially well mixed with an adiabatic temperature profile and is animated with					
401	convection. The core is initially assumed super-heated compared to the mantle with a temperature					
402	difference dT , which we fixed to 182 K, based on the standard model from Ref (1), and the					
403	temperature at the CMB is re-adjusted according to this treatment. The heat flow at CMB, Q_c , is					
404	calculated from scaling relationships built for mantle convection (55) and is further depending on					
405	the temperature at the CMB, T_{CMB} , which is determined from the core evolution. As Q_{c} becomes					
406	lowe	or than the heat flow calculated along an isentropic temperature profile, $Q_{\rm a}$, a stable				
407	conductive layer starts to grow and core convection is confined beneath this layer. The evolution					
408	of th	e stable layer follows the treatment in Ref (56). The ohmic dissipation related to magnetic				
409	field is measured with the entropy balance E_j between the entropies originating from secular					
410	cooling and thermal conduction, E_s and E_k , which are calculated following Ref (56). Because E_k is					
411	proportional to the core thermal conductivity, Λ_c , larger conductivity leads to larger E_k and thus					
412	lower E_j . In other words, dynamo action is reduced with increasing Λ_c and may stop if conduction					
413	is too large.					
414						
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590591 Figures and Tables





593 Figure 1. Thermal conductivity of (a) Fe₃S and (b) FeS at high pressure and room

temperature. For both compositions, several runs of measurements show consistent results, where each run is represented by a symbol set. Vertical bars show uncertainties which are mainly from the error propagations in spectral modelling analysis: <10% before 20 GPa and ~10–17% at 20–40 GPa. Note that at ~40 GPa, the thermal conductivity of FeS is only half of the Fe₃S, indicating a strong reduction by the sulfur impurity. For FeS in (b), the two vertical dashed lines represent the phase transition pressures for FeS I-II at ~3.4 GPa and II-III at ~6.7 GPa (*34*), respectively.



603 604



Figure 2. Temperature dependence of the thermal conductivity of Fe-S alloys at high pressures. Assuming the thermal conductivity scales with T^n , the *n* for (a) Fe₃S decreases from 0.25(±0.07) at 15.4 GPa to 0.2(±0.04) at 35.5 GPa. (b) The FeS IV phase (at T > 730 K) has a larger temperature exponent *n* (0.33 at 28 GPa and 0.36 at 27 GPa) than that of Fe₃S (0.2–0.25) at relevant Martian core's pressures. Vertical bars represent analysis uncertainties of the data at ~10–15%.



614

613

Figure 3. Modeled thermal conductivity profile in Martian mantle and core. Assuming the 615 Martian liquid core is majorly composed of Fe₃S (20), its thermal conductivity (red dashed curve) 616 spans from ~19 W m⁻¹ K⁻¹ at the top to ~32 W m⁻¹ K⁻¹ at the center. The thermal conductivity of 617 FeS in solid (orange curve) and liquid (green dashed curve) phase, respectively, are plotted for 618 comparison. Note that the thermal conductivity of liquid FeS was estimated by a 15% reduction 619 from that of the FeS V phase, which was assumed to have the same temperature dependence as 620 FeS IV phase. The shaded areas represent the uncertainty ranges considering the small variation 621 of the temperature exponent n. The solid and dashed blue curves are the thermal conductivity of 622 ringwoodite with 0.11 wt% (dry) and 1.73 wt% (hydrous) water (21), respectively, along an 623 624 estimated Martian mantle areotherm (magenta dashed curve with the temperature scale at the top axis) taken from Ref (35). A ~4 to 6-fold discontinuity in the thermal conductivity across the 625 Martian CMB (liquid Fe₃S vs. ringwoodite) is estimated. 626 627



630 Figure 4. Thermal evolution scenarios of the Martian core. Three scenarios are described in 631 the text in detail. (a) Heat flow across the Martian CMB, Q_c (solid curves), vs. isentropic heat 632 flow, O_a (dashed curves). (b) Entropy due to the Ohmic dissipation, E_i. The dynamo will stop as 633 $E_{\rm i}$ < 1.0 MW K⁻¹ (horizontal dashed line), which occurs around the transition from super- to sub-634 isentropic heat flow, i.e., O_c being slightly higher or lower than O_a . The grev zone indicates the 635 range of cessation time of dynamo based on remnant crustal magnetism. (c) Ratio of the radius of 636 the base of thermal stratification layer (r_s) to the radius of the core (r_c). Thermal stratification 637 starts when Q_c becomes lower than Q_a . The shaded region in all the figures represents the 638 uncertainty of each curve. (d) Temperature at the Martian CMB, where the green and blue curves 639 are close to each other. 640 641

642

Table 1. Recent experimental and computational results of electrical resistivity ρ and thermal conductivity Λ of Fe-S alloys at Martian CMB conditions

Composition	ρ (μΩ cm)	$\Lambda (W m^{-1} K^{-1})$	Method	Reference
solid Fe-16wt%S	NA	~22.7	DTCM+E	This study
solid Fe-36wt%S	NA	~13.7	DTCM+E	This study
solid Fe-14.2wt%S	~100	~46*	ERM+E	(42)
liquid Fe-16.1wt%S	~107	~43.3*	С	(23)
liquid Fe-7.6wt%S	~88	~52.7*	С	(23)

*Thermal conductivity was inferred from electrical resistivity via WF law with ideal Lorenz
 number.

Method: DTCM: direct thermal conductivity measurement; E: extrapolation; ERM: electrical
 resistivity measurement; C: calculation

649 NA: not applicable



Supplementary Materials for

A thermally-conductive Martian core and implications for its dynamo cessation

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This PDF file includes:

Figs. S1 and S2 Table S1



Fig. S1. Example TDTR spectrum (open circles) along with thermal model calculations (color solid curves) for Fe₃S at 40.5 GPa. Using the input parameters listed in Table S1, $\Lambda_{\text{Fe3S}}=25 \text{ W m}^{-1} \text{ K}^{-1}$ (red curve) enables a best-fit to the TDTR data. The spectrum ratio $-V_{in}/V_{out}$ is most sensitive to the sample's thermal conductivity at delay times of few hundred picoseconds (ps), see Ref (48, 49) for details. A test variation of 10% in Λ_{Fe3S} , i.e., green and blue curves, results in a clear deviation from the data. Such high sensitivity indicates our thermal model fitting and the derived Λ_{Fe3S} are precise and reliable based on the high-quality data.



Fig. S2. Sensitivity tests of the thermal model to input parameters for Fe₃S at 40.5 GPa. Thermal conductivity of Fe₃S, Λ_{Fe3S} , is fixed at 25 W m⁻¹ K⁻¹, as shown in Fig. S1. (a) and (b) Changes in

the thicknesses of silicone oil ($h_{Si oil}$) and Fe₃S (h_{Fe3S}) by 33% and 50%, respectively, have essentially no influence on the model calculations, i.e., the derived Λ_{Fe3S} is not affected by the uncertainties in the $h_{Si oil}$ and h_{Fe3S} . (c) Large uncertainty in the high thermal conductivity of Al film has very minor effect on the Λ_{Fe3S} . (d) If the thermal effusivity of the pressure medium silicone oil, $e=(\Lambda_{Si}C_{Si})^{1/2}$, has 10% uncertainty, it requires the Λ_{Fe3S} to decrease to 24.5 W m⁻¹ K⁻¹ to re-fit the data, i.e., producing 2% uncertainty. (e) If the volumetric heat capacity of Fe₃S, C_{Fe3S} , is 5%, a $\Lambda_{Fe3S}=24.3$ W m⁻¹ K⁻¹ can re-fit the data, i.e., propagating 3% uncertainty. (f) In our analysis, the major uncertainty is from the uncertainty in the heat capacity of Al film per unit area, i.e., product of volumetric heat capacity and thickness, $C_{A1}h_{A1}$. This is because the ratio - V_{in} / V_{out} at few hundred picosecond delay time scales inversely with the $C_{A1}h_{A1}(49)$. If there is a 10% uncertainty, it requires ~16% change in the Λ_{Fe3S} to fit the data. (g) Changing the laser spot size by 15% does not influence the model calculation, i.e., its uncertainty has essentially no effect on the Λ_{Fe3S} . (h) 10% variation in the thermal conductance of Al/Fe₃S and Al/silicone oil interfaces, *G*, lead to a very minor change in the model calculation, propagating only ~4% uncertainty in the Λ_{Fe3S} .

Table S1. Input parameters in the thermal model for Fe₃S at 40.5 GPa and 300 K in TDTR measurements

P (GPa)	$C_{\rm Fe3S}$	$C_{ m Al}$	$h_{ m Al}$	$e=(\Lambda_{\rm Si}C_{\rm Si})^{1/2}$	r	$h_{ m Fe3S/Si}$ oil	$\Lambda_{ m Al}$	G	_
	(J cm ⁻³ K ⁻¹)	(J cm ⁻³ K ⁻¹)	(nm)*	(J m ⁻² K ⁻¹ s ^{-1/2})	(µm)	(µm)	(W m ⁻¹ K ⁻¹)	(MW m ⁻² K ⁻¹)	
40.5	3.16	2.68	79.0	2260	7.6	10/15	200	250	

*In this experimental run, the Al thickness at ambient pressure is 90 nm. C_{Fe3S} : Fe₃S heat capacity, C_{Al} : Al heat capacity, h_{Al} : Al thickness, e: silicone oil thermal effusivity, r: laser spot size, h_{Fe3S} : Fe₃S thickness, $h_{\text{Si oil}}$: silicone oil thickness, Λ_{Al} : Al thermal conductivity, G: thermal conductance of Al/Fe₃S and Al/silicone oil interfaces.