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4	A Joint Experimental-Modeling Investigation of the Effect of Light Elements
5	on Dynamos in Small Planets and Moons
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23 Abstract

24 We present a joint experimental-modeling investigation of core cooling in small terrestrial bodies. Significant amounts of light elements (S, O, Mg, Si) may compose the metallic cores of 25 26 terrestrial planets and moons. However, the effect of multiple light elements on transport 27 properties, in particular, electrical resistivity and thermal conductivity, is not well constrained. 28 Electrical experiments were conducted at 10 GPa and up to 1850 K on high-purity powder mixtures 29 in the Fe-S-O(+/-Mg, +/-Si) systems using the multi-anvil apparatus and the 4-electrode technique. 30 The sample compositions contained 5 wt.% S, up to 3 wt.% O, up to 2 wt.% Mg, and up to 1 wt.% 31 Si. We observe that above the eutectic temperature, electrical resistivity is significantly sensitive 32 to the nature and amount of light elements. For each composition, thermal conductivity-33 temperature equations were estimated using the experimental electrical results and a modified Wiedemann-Franz law. These equations were implemented in a thermochemical core cooling 34 35 model to study the evolution of the dynamo. Modeling results suggest that bulk chemistry 36 significantly affects the entropy available to power dynamo action during core cooling. In the case 37 of Mars, the presence of oxygen would delay the dynamo cessation by up to 1 billion years compared to an O-free, Fe-S core. Models with 3 wt% O can be reconciled with the inferred 38 39 cessation time of the Martian dynamo if the core-mantle boundary heat flow falls from >2 TW to ~0.1 TW in the first 0.5 Gyrs following core formation. 40

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Keywords: core cooling, dynamo, electrical resistivity, thermal conductivity, iron alloys, terrestrial
planets and moons.

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- 45

46 Plain language summary

47 Different elements (like S, O, Mg, Si) are present in the metallic (Fe) cores of some planets and 48 moons. The effect of these elements on the physical properties of the core is not well understood. 49 Here we performed electrical experiments under pressure and temperature on different core compositions. The samples contain small amounts of S, O, Mg and Si. Our experimental results 50 51 show that at high temperature, the electrical response of the sample is significantly sensitive to the 52 nature and amount of added elements. For each composition, we also estimated the ability of the 53 sample to conduct heat. All these results were used as part of core cooling models. Our modeling 54 results suggest that core chemistry significantly changes the energy available to power dynamo 55 action during cooling. Applied to the core of Mars, our model shows a significant effect of oxygen 56 on the activity of the core dynamo.

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60 **1. Introduction**

The transport properties of iron alloys, such as electrical resistivity and thermal 61 62 conductivity, strongly influence the evolutionary pathways of terrestrial planets and moons during 63 cooling. In particular, these properties affect the generation of an intrinsic magnetic field by 64 thermochemical convection in a fully or partially liquid core, as suggested by models of core 65 evolution for the Earth (e.g., Pozzo et al., 2012; deKoker et al., 2012; Labrosse, 2015; Davies, 66 2015), Mars (e.g., Williams and Nimmo, 2004 Davies and Pommier, 2018), Mercury (e.g., Knibbe 67 and van Westrenen, 2018, Ganymede (e.g., Rückriemen et al., 2015) and the Moon (e.g., 68 Laneuville et al., 2014). Understanding how transport properties respond to changes in the thermal 69 state, pressure, and core composition is fundamental to understanding core cooling processes and 70 the generation of a magnetic field, as previous experimental work indicates that these properties 71 are sensitive to temperature, pressure and chemistry (e.g., Ho et al., 1975; Gomi et al., 2016; 72 Pommier, 2018). The investigation of transport properties could also help estimate the content of 73 light elements in planetary cores, which is not well constrained.

74 The nature and amount of light elements in the metallic core of a terrestrial body depends 75 highly on the conditions during accretion and formation of the core. In particular, temperature, 76 pressure and redox conditions are among the main parameters that control the partitioning of light 77 elements into the metallic core and their solubility (e.g., Ohtani and Ringwood, 1984; Dreibus and 78 Wänke, 1985; Tsuno et al., 2007; Buono and Walker, 2015; Rubie et al., 2015; Pozzo et al., 2019). 79 A few wt.% sulfur, oxygen, and silicon are thought to compose the cores of terrestrial planets and 80 moons, because they partition to pure iron or iron-nickel alloys at pressure and temperature 81 conditions, are abundant in the Solar System, and are observed in meteorite geochemistry, (e.g., 82 Poirier, 1994; Badro et al., 2015; Hirose et al., 2013; Suehiro et al., 2017). Magnesium has also 83 been suggested to be a potential candidate in the Earth's core, with the very high temperatures at 84 the time of the core-mantle differentiation possibly allowing its partitioning into metal (O'Rourke 85 and Stevenson, 2016, Badro et al, 2016). Cosmochemistry studies have suggested that carbon, 86 hydrogen, and phosphorus are present in too small amounts (below 0.3 wt.%) to represent 87 significant components of terrestrial cores (e.g., McDonough, 2003). In the Earth, several studies 88 have pointed out that more than one element is likely present in the liquid outer core (e.g., Poirier, 89 1994; Alfé, 2002; Sanloup et al., 2004; Badro et al., 2007; Yokoo et al., 2019). Mercury's reducing 90 conditions are consistent with a silicon-rich, sulfur-bearing core (e.g., Hauck et al., 2013; Namur 91 et al., 2016; Cartier et al., 2019), while the more oxidizing conditions on Mars, the Moon, and

possibly Ganymede are compatible with the presence of sulfur (e.g., Lodders and Fegley, 1997;
Hauck et al., 2006; Kuskov and Belashchenko, 2016; Rückriemen et al., 2015) and oxygen in the
core (Tsuno et al., 2011; Pommier et al., 2018).

95 Several studies have measured or computed the electrical resistivity and thermal 96 conductivity of core analogues under pressure and temperature conditions. However, these 97 investigations have focused mostly on systems that do not combine several light elements, 98 considering either pure iron (e.g., deKoker et al., 2012; Pozzo et al., 2012 for computational 99 studies, and Deng et al., 2013; Ohta et al., 2016; Konôpková et al., 2016; Silber et al., 2018 for 100 laboratory studies) or binary systems such as Fe-S, Fe-Si, and Fe-O (e.g., deKoker et al., 2012; 101 Pozzo et al., 2013; Wagle et al., 2019 for computational studies, and Gomi et al., 2013, 2016; 102 Pommier 2018; Silber et al., 2019 for laboratory studies). As pointed out by Wagle et al. (2019) 103 using simulations at temperature ranging from 2000 to 8000 K and pressure from 23 up to >300 104 GPa, light elements do not affect electrical resistivity and thermal resistivity the same way: both S 105 and Si atoms substitute for Fe in the molten state, but S atoms tend to distribute more evenly in 106 liquid iron than Si atoms. In contrast, oxygen occupies interstitial sites, shortening Fe-O distances 107 in the liquid state, which affects diffusive transport, and hence, increases electrical resistivity. It is 108 unclear how light elements would affect transport properties when combined in metallic iron. The 109 few investigations of the electrical and thermal properties of ternary systems are mostly 110 computational and focused on the Fe-O-Si system at Earth's core pressure (Pozzo et al., 2013; 111 Gubbins et al., 2015; Davies et al., 2015) and Fe-Si-S (Suehiro et al., 2017). The latter study 112 performed electrical resistivity measurements at room temperature over the 40-110 GPa pressure 113 range and used simulations to predict the electrical response of the Fe-Si-S alloy at high 114 temperature. The electrical resistivity of an Fe-Si-S alloy was also measured experimentally at 6

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GPa up to ~1950 K (Pommier et al., 2019). All these studies of ternary systems suggest high electrical resistivities as well as lower thermal conductivities than that obtained on pure iron. However, there is currently no investigation at pressure and temperature conditions relevant to planetary cores of the electrical and thermal properties of alloys containing a mixture of the four major light elements candidates expected in metallic cores, i.e., S, O, Si and Mg.

120 An important challenge for the electrical and thermal investigation of iron alloys regards 121 the estimate of one physical property from the other. Electrical resistivity measurements are often 122 used to estimate thermal conductivity at defined temperature using the Wiedemann-Franz law 123 (Wiedemann and Franz, 1853), as thermal conductivity is particularly challenging to measure in 124 the laboratory (e.g., Ohta et al., 2016; Gomi and Hirose, 2015; Pommier, 2018; Manthilake et al., 125 2019). It has been demonstrated for Fe-Ni at atmospheric pressure and above 1673 K and for Fe-126 Si alloys under a few GPa and up to 2100 K that the Wiedemann-Franz law underestimates the 127 thermal conductivity of iron alloys, therefore providing a lower bound of thermal conductivity 128 (Secco, 2017; Watanabe et al., 2019). The validity of the Wiedemann-Franz law has also been 129 questioned for pure iron at high pressures and temperatures (Dobson, 2016; Konôpková et al., 2016; Ohta et al., 2016). This is due to the contribution of the thermal vibration of atoms to the 130 131 thermal conductivity of iron alloys that is not accounted for in the Wiedemann-Franz law. It is 132 likely that this equation also provides a lower bound for complex iron alloys containing several 133 alloying agents, not only for alloys in binary systems. One way to estimate the factor of correction 134 on computed thermal conductivity estimates consists of comparing experimentally-measured and 135 computed thermal conductivities using the current thermal dataset for iron alloys (e.g., Secco, 136 2017; Pommier, 2020).

137	Here we present a study of metallic cores containing multiple alloying agents using high-
138	pressure experiments and core cooling modeling. In a first step, we performed electrical
139	experiments on core analogues in the Fe-S-O(+/-Mg)(+/-Si) systems at 10 GPa and up to 1850 K.
140	In a second step, experimental results were used to estimate thermal resistivity of the different
141	alloys in the (partially) molten state, using a modified Wiedemann-Franz law. These estimates
142	were then implemented into a 1-D parameterized model of core cooling. The effect of core
143	chemistry on the generation and sustainability of the magnetic field in small terrestrial bodies is
144	discussed. In particular, we apply our results to a Mars-type core and propose a detailed thermal
145	history, following our previous study of the Martian core that considered an Fe-S chemistry
146	(Davies and Pommier, 2018).
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150	2. Joint experimental-modeling approach
151	2.1.Experiments on core analogues
152	2.1.1. <u>Starting materials</u>
153	Electrical experiments were performed on ten analogues of planetary cores. Starting
154	materials were powder mixtures of high purity (>99%) Fe, FeS, Fe ₂ O ₃ , MgO, SiO ₂ and FeSi ₂ . The
155	detailed compositions are listed in Table 1. The starting materials contained 5 wt.% S, up to 3 wt.%
156	O, up to 2 wt.% Mg, and up to 1 wt.% Si. Compositions with the highest amounts of Mg and Si
157	are considered end-member compositions of metallic cores. One starting material contained Si as

 $FeSi_2$ and all other Si-bearing samples contained Si as SiO_2 in order to test the effect of Si

speciation on bulk resistivity. All the powders were stored in a vacuum oven at 383 K until use tominimize oxidation.

161 It should be noted that the starting materials are a mixture of different powders, as single-162 phase samples of iron alloys are challenging to synthesize (e.g., Mori et al., 2017). The starting 163 materials not being single-phase alloys means that the materials below the melting temperature 164 correspond to several phases coexisting (Fe, FeS, Fe₂O₃, +/-MgO, +/-SiO₂ and +/-FeSi₂), instead 165 of a Fe–S-O(+/-Mg)(+/-Si) single phase. As previously shown for samples in the Fe-FeS system, 166 the difference in bulk resistivity between multi-phase materials and single-phase samples is not 167 significant at pressure up to 8 GPa and temperature up to 2123 K (Pommier, 2018). We make the 168 hypothesis that adding a small amount of O, Mg or Si is unlikely to change the observations from 169 Pommier (2018) about the effect of the number of phases on bulk resistivity at low temperature. 170 However, investigating this topic is out of the scope of this paper and the application of the 171 electrical results to planetary cores will only consider data collected at temperatures above 1900 172 K, i.e. when the samples are partially or fully molten and correspond to metallic alloys.

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2.1.2. Electrical experiments

174 Electrical experiments were conducted at 10 GPa and up to 1850 K in the multi-anvil 175 apparatus at the Planetary and Experimental Petrology Laboratory at UCSD-SIO. Eight tungsten 176 carbide cubes with a corner-truncation edge length of 8 mm and MgO octahedral pressure media 177 with an edge length of 14 mm were used. A sketch of the COMPRES electrical cell assembly 178 (Pommier et al., 2019) is presented in Figure 1. The cell is composed of three alumina rings that 179 help keep the geometry of the sample during the experiment and contain the melt phase at high 180 temperature. Two iron disks served as electrodes and a rhenium foil was used as a heater. 181 Temperature was monitored using two Type-C (W₉₅Re₅-W₇₄Re₂₆) thermocouples. All the MgO parts used in the cell assembly were fired at 1273 K for two hours or 1673 K for one hour. They
were stored in a desiccator until use.

184 The experiments were conducted under quasi-hydrostatic conditions in the multi-anvil 185 press using 4-electrode electrical measurements. A dwell time was first applied to the sample at a 186 temperature below the eutectic temperature (~873 K) until a stable electrical response was 187 obtained. In order to check the reproducibility of the electrical measurements, the electrical 188 response of the sample was collected during both cooling and heating. Experiments were quenched 189 at the highest temperature by shutting off the power to the heating system. The electrical resistance 190 R was measured at each temperature using an impedance spectrometer (1260 Solartron 191 Impedance/Gain-Phase Analyze) with a frequency range of about 40 Hz - 1 Hz. The voltage was 192 controlled by setting a DC potential of 1 V and an AC amplitude of either 500 or 1000 mV.

193 The electrical resistivity ρ is calculated using the equation

194

$$\rho = \mathbf{R} \times \mathbf{G} \tag{1}$$

195 where $G = 2\pi r/l$ (2)

with r being the radius of one electrode disk and l being the thickness of cylindrical sample. The uncertainty on the resistivity calculation, $\Delta \rho$, is listed for each experiment in Table 1. Because the iron electrode disks cover the surface of the sample and the middle alumina ring, they form a series circuit with the sample and sleeve, and their contribution to the measured bulk resistance was subtracted. The contribution of the alumina sleeve to the bulk resistance was neglected, since the resistance of alumina is several orders of magnitude higher than the resistance of the metallic sample (Pommier et al., 2019).

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2.1.3. <u>Sample analyses</u>

206 After quenching, the recovered experimental samples were mounted in epoxy resin and 207 carefully polished for analysis using Scanning Electron Microscope (SEM) imaging at the UCSD-208 Nanoengineering Department. A FEI Quanta 600 SEM was used to characterize the texture of the 209 samples. Energy Dispersive X-ray Spectrometry (EDS) with a voltage of 20 kV and an emission 210 current of about 3.2 nA was used to analyze the phases of recovered samples as well as the starting 211 composition of the powders. 212 213 214 2.2. Integration of experimental constraints into a core cooling model 215 2.2.1. Estimating the thermal conductivity of core analogues 216 The measured electrical resistivity data are used to calculate the thermal conductivity of 217 the iron alloys as a function of temperature. Thermal conductivity corresponds to the sum of 218 contributions of electrons and phonons scattering. In several metals, the electronic contribution to 219 heat transport is significantly larger than the one due to transport by phonons (e.g., deKoker et al., 220 2012), therefore suggesting that the electronic component represents a lower bound that is, at first 221 approximation, an estimate of thermal conductivity. This lower bound (k_{LB}) can be calculated using 222 the Wiedemann-Franz relationship: 223 $k_{LB}=L\times T/\rho$ (3) 224 with L the Lorenz number with the theoretical value for the limit of electron degeneracy, called the Sommerfeld value, of $L_0 = 2.445 \times 10^{-8}$ W. Ω .K⁻² (Secco, 2017). The validity of the assumption 225 that Equation (3) provides a reasonable estimate of the bulk thermal conductivity depends strongly 226 227 on temperature, composition, and pressure (Pozzo, 2012; de Koker et al., 2012; Secco, 2017;

228 Wagle et al., 2018). Using experimental values of electrical resistivity and thermal conductivity of 229 iron, Secco (2017) showed that L/L_0 can vary by as much as 1.22 in the solid Fe and 1.32 in the 230 molten state at pressures up to 6 GPa and temperatures up to 2100 K, and that the deviation of L_0 231 at 1atm is even higher than these values for Fe-Si alloys (but remains unclear under pressure). In 232 Fe-O liquids, computations of k and ρ by deKoker et al. (2012) predicted a percentage deviation 233 from L_0 of about 7%-17% at the pressure conditions of our experiments (10 GPa) and at 234 temperatures >2000 K. For Fe-Ni alloys, thermal conductivity measurements at 1 atm and under 235 temperature indicate a difference between experimental thermal conductivities and estimates using 236 Equation (3) of about 15%-30% (using Holder, 1977; Kita and Morita, 1984; Seifter et al., 1998; 237 Watanabe et al., 2019). Based on these observations from previous studies, we assume that the 238 thermal conductivity k of our Fe-S-O alloys at 10 GPa can be estimated from electrical resistivity 239 measurements ρ as a function of temperature assuming a 20% increase in the lower bound values 240 computed using Equation (3). This represents an upper estimate rather than an upper bound, as we 241 cannot rule out higher values of L. The effect of pressure on thermal conductivity can be estimated 242 using the effect of pressure on electrical resistivity from previous studies of Fe-S and Fe-O alloys 243 (Suehiro et al., 2017; Wagle et al., 2018, 2019). These works suggest that from 10 to 40 GPa, 244 electrical resistivity decreases by ~10%. Therefore, we calculated the evolution of k as a function 245 of both temperature and pressure over a pressure range of 10 - 40 GPa using the following 246 equation:

247
$$k(T,P) = k(T) - (P-10) \times 0.1/30 \times k(T)$$
 (4)

248 where
$$k(T) = 1.2 \times L_0 \times T/\rho$$

with T the temperature (K), P the pressure (GPa), 1.2 the temperature correction factor and (P10)× 0.1/30 the pressure correction factor.

(5)

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252 2.2.2. <u>Core cooling modeling</u>

We calculated the thermal and chemical evolution of a Mars-sized core over the last 4.5 Gyrs using a 1-D parameterized model. Full details of the model can be found in Davies and Pommier (2018) and so only a brief description is given here. The core is initially entirely liquid with a prescribed starting temperature and bulk composition. The liquid region of the core is always assumed to be vigorously convecting such that the composition is uniform and the temperature profile follows an adiabat. In the absence of core crystallization, the core-mantle boundary (CMB) heat flow Q_{cmb} is balanced by the heat Q_s stored in the core.

260 Although the model allows for core crystallization at arbitrary depth, we focus on top-down 261 crystallization as this core cooling regime has been suggested previously for Mars, Ganymede, and 262 the Moon (Stewart et al., 2007; Breuer et al., 2015; Rückriemen et al., 2015; Davies and Pommier, 263 2018). In this regime, freezing of the metallic core begins from the CMB because the melting curve 264 T_m is shallower than the adiabatic gradient (e.g., Stewart et al., 2007; Breuer et al., 2015). The solid phase is assumed to be heavier than the residual liquid and therefore "snows" into the deeper core 265 where it remelts. Generation of snow releases latent heat Q_L^s and gravitational energy Q_g^s as solid 266 particles sink through the snow zone. Remelting of snow absorbs an amount of latent heat Q_L^l and 267 releases further gravitational energy Q_g^l since the remelted liquid is enriched in iron (and therefore 268 denser) compared to the bulk core. An amount of latent heat Q_L^B is released at the base of the 269 270 growing snow zone, though this contribution is small enough to neglect (Davies and Pommier, 271 2018). These processes affect the power E_J ("dynamo entropy") that is available to generate the 272 intrinsic magnetic field.

273 The cooling model solves the global energy, entropy and mass balance equations that 274 describe the long-term evolution of the core (e.g. Nimmo, 2015; Breuer and Moore, 2015). The 275 core comprises a snow layer on the liquidus above a vigorously convecting core. The model relies 276 on the following four main assumptions: 1) All light elements remain in the liquid phase on 277 freezing; 2) Melting is fast, i.e. instantaneous relaxation to phase equilibrium; 3) Sinking and 278 remelting of solid iron is rapid; and 4) An adiabatic temperature profile exists throughout the core. 279 With these approximations the global energy and entropy balances are (Davies and Pommier, 280 2018):

$$Q_{cmb} = Q_s + Q_g^s + Q_g^l + Q_L^s + Q_L^l + Q_L^B = \tilde{Q} \frac{dT_c}{dt}$$
(6)

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$$E_{J} + E_{k} = E_{s} + \frac{Q_{g}^{s} + Q_{g}^{l}}{T_{c}} + E_{L}^{s} + E_{L}^{l} + Q_{L}^{B} \left(\frac{T_{c} - T(r_{s})}{T_{c}T(r_{s})}\right) = \tilde{E} \frac{dT_{c}}{dt}.$$
(7)

Here E_k is the entropy due to thermal conduction, which depends on the thermal conductivity, and the terms E_L^s and E_L^l are entropy terms that reflect the thermodynamic efficiency of the heat sources Q_L^s and Q_L^l in Equation (6). T_c is the CMB temperature and r_s is the radius of the base of the snow zone (if one exists). Note that k does not appear in the energy balance (Eq. 6) and hence models that differ only in the choice of k produce the same thermal history; however, these models produce different magnetic histories through Equation (7).

Equation (6) relates Q_{cmb} to the core cooling rate, dT_c/dt , which can be used to compute the dynamo entropy E_J , which must be positive for dynamo action. The time when E_J first passes from positive to negative values defines the termination point of the dynamo. In the case of Mars, the key observation pertaining to core dynamics is that the global magnetic field (and hence dynamo) 292 likely decayed around 4.1-3.8 Ga (Acuña et al., 1998; Weiss et al., 2002; Langlais et al., 2012). 293 The variables \tilde{Q} and \tilde{E} are integrals that depend on the properties of the core material. The model 294 also outputs the properties of a snow zone at the top of the core if one exists. The base of the snow 295 zone is defined as the radius where the adiabat intersects the melting curve; if the core does not 296 cool to the melting point at the CMB then no snow zone forms. All the default parameters used 297 are from Davies and Pommier (2018) with the exception of k and Q_{cmb} , which are described 298 below.

Here, unlike previous work, we explicitly model the temperature-dependence of k on the thermal evolution of the core. We use the new k values derived from electrical experiments under temperature. To do so, thermal conductivity estimates are expressed as a polynomial equation which is evaluated at the current temperature at each depth (Supplementary Table 1). This gives the radial variation of thermal conductivity as k(P(r),T(r)).

The CMB heat flow is an input to the model that must be specified over the 4.5 Gyr evolution. In principle Q_{cmb} can be calculated using a parameterized model of mantle convection that is coupled to the core evolution (e.g., Williams and Nimmo, 2004), thus allowing changes in core temperature to alter the heat flow. Here we choose a simpler approach that introduces fewer uncertain parameters than that used in a core-mantle parameterized model and allows us to focus on the role of core thermal conductivity in the core thermal-magnetic history. We write Q_{cmb} using a simple functional form,

$$Q_{cmb} = Q_p + Q_f e^{-t/\tau} \tag{8}$$

where *t* is time, $Q_p + Q_f$ is the heat flow at t = 0 and τ is a timescale. By varying Q_p , Q_f and τ it is possible to closely reproduce previously published time-series of Q_{cmb} for Mars (Williams and Nimmo, 2004; Leone et al, 2014; Thiriet et al, 2019). In particular, values of $Q_p = 0.2$ TW, $Q_f =$

1.3 TW and $\tau = 0.9$ Gyrs closely represent the time-series of Q_{cmb} from Williams and Nimmo
(2004) that was used in Davies and Pommier (2018). The prescription (8) also makes it easy to
develop new time-series that have certain desirable properties. We will show that the range of
experimental k values produce a broad range of dynamo termination times that cannot be
reconciled with the observations by simply changing core properties within reasonable bounds. By
using Equation (8) it is possible to reproduce the observed termination time for all of the different
k values.
3. Results
3.1. Experimental results
Textural and chemical analyses of retrieved samples after electrical experiments using the
EDS-SEM techniques are presented in Figure 2 and Supplementary Figure 1. The interface
between the sample and the alumina ring is characterized by a thin (<~30 micron thick) layer of
Al-bearing alloy, which does not affect the sample's bulk electrical response (Pommier and
Leinenweber, 2018). Some samples present a small amount of W in the dendritic phase, which is
consistent with unavoidable interactions with the thermocouple wires at high temperature. No
strong compositional heterogeneity is observed across the recovered samples. SEM images of
recovered samples are shown in Figure 2. The retrieved Fe-S-O and Fe-S-O-Si (with Si added as
FeSi ₂) samples present textures of fully molten alloys following rapid solidification. Mg-bearing
alloys and alloys containing Si as SiO ₂ were only partially molten (Figure 2), in agreement with
the fact that the melting point of MgO (~3800 K; Kimura et al., 2017) and SiO ₂ (~3100 K; Zhang

et al., 1993) at 10 GPa is higher than the melting point of the Fe electrode disks (~2100 K; Buono
and Walker, 2011), which constrains the quenching temperature of the experiments. The electrical
cell geometry was well-preserved during the experiment (Figure 2), minimizing uncertainty on the
geometric factor calculations and hence, on electrical resistivity. Dendritic patterns are visible in
all samples, and color contrasts are observed between dendritic structures and the surrounding
phase, indicating different chemistry (Supplementary Figure 1). In particular, the presence of S in
the quenched phase surrounding the dendrites increases the color contrast between the two phases.

344 Electrical resistivity results are presented as a function of temperature in Figure 3. In all 345 experiments, electrical data collected after the dwell time during cooling and second heating 346 demonstrate data reproducibility. Reproducibility was also checked by the repeat of the experiment 347 on the FeS₅O_{0.5} material. For all samples except the one containing Si as FeSi₂, electrical resistivity 348 increases significantly with increasing temperature until the α - γ transition. This phase 349 transformation of iron is clearly identified and it is located around 1000 K (+/-50 K). From 1000 350 to 1300 K, the Si-bearing alloys present a small decrease in resistivity, whereas the resistivity of 351 the other alloys is not temperature-dependent, at first approximation. The onset of melting is not 352 as clearly identified as the α - γ transition but corresponds for most samples to a slight inflexion in 353 resistivity at 1200-1300 K. This temperature is in good agreement with the eutectic temperature 354 for Fe-S at 10 GPa (e.g., Chen et al., 2008). Above 1200-1300 K, all alloys except the one 355 containing Si as SiO₂ display a temperature-independent electrical response.

Figure 3 also illustrates the effect of starting composition on electrical resistivity. The two samples of bulk composition $FeS_5O_3Si_1$ present contrasting resistivities below 1700 K and a similar electrical response at T>1700 K; the difference in electrical behavior can be attributed to Si, which is either added as SiO₂ (silicate) or FeSi₂ (metal). At T>1700 K, the melt phase dominates

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the samples' resistivity; their similar electrical response confirms that both samples have a similar bulk composition and suggests that, in the SiO₂-bearing sample, some Si partitioned into the metallic liquid. The SiO₂-bearing starting powder is more resistive below 1700 K and the α - γ transition is more visible than in the FeSi₂-bearing powder. An abrupt change in resistivity is observed in the SiO₂-bearing sample at ~1500-1673 K (Figure 3). Such a peak in electrical resistivity is not observed in the FeSi₂-bearing sample nor in any other SiO₂-bearing samples that all contain less Si than 1 wt.% (Table 1).

367 The effect of alloy chemistry on bulk electrical resistivity is presented in Figures 3 and 4. 368 Electrical results indicate that, at the conditions of the experiments, adding Mg tends to decrease 369 the resistivity of iron alloys. For instance, at 1100 K, the Fe-S-O alloy containing 2wt% Mg has a 370 resistivity that is 12.5% lower than the alloy containing 0.5wt.% Mg (Figure 3). In contrast, adding 371 O and/or Si increases the bulk electrical resistivity. Over the investigated temperature range, 372 FeS_5O_3 is about 4.8 times more resistive than $FeS_5O_{0.5}$ (Figure 3, top plot; Figure 4). This factor 373 decreases to 1.4-2.1 when 0.1 wt.% Si is added (Figure 3, bottom plot; Figure 4). Fe-S-O-Si 374 samples containing the same amount of S and O present an increase in resistivity with increasing 375 Si content when Si is added as SiO₂. The sample containing both Mg and Si is the least resistive 376 Si-bearing alloy. As illustrated in Figure 4, at defined temperature, Fe-S-O and Fe-S-O-Si samples 377 show a stronger dependence of resistivity to the total amount of alloying agent than Fe-S-O-Mg 378 samples.

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3.2. Thermal conductivity of core analogues

Thermal conductivity estimates are presented for the different compositions at T>1200 K
 and at 10 GPa in Figure 5. These estimates were obtained using the linear extrapolation of electrical

383 resistivity measured at T≥1100K to the temperature range of 1900-3100 K; the extrapolated values 384 of ρ were then implemented into Equations (4) and (5) to calculate k(T,P). The linear fits to 385 compute k using Equation (5) are listed in Supplementary Table 1. The FeS_5O_3 sample is 386 characterized by the lowest thermal conductivity, whereas $FeS_5O_{0.5}$ and the sample containing both 387 Mg and Si show the highest values. All other alloys display intermediate thermal conductivity 388 values. For all samples, heat transport increases with increasing temperature. Thermal conductivity 389 has been extrapolated to temperatures up to 3100 K for three selected samples: FeS_5O_3 , $FeS_5O_{0.5}$, 390 and FeS₅O₃Mg_{0.5}, representing respectively a lower bound, an upper bound, and an intermediate 391 case of thermal conductivity of core analogues. Over the 1000-3100 K range, thermal conductivity 392 increases by a factor of 3.4, 4.0, and 2.6 for FeS₅O_{0.5}, FeS₅O₃Mg_{0.5}, and FeS₅O₃, respectively. We 393 notice that thermal resistivity variations among samples increase only slightly with increasing 394 temperature: for example, at 1000 K, FeS₅O_{0.5} is 3.8 times more thermally conductive than FeS₅O₃ 395 and at 3100 K, this factor increases to 5 (Figure 5). For comparison, extrapolations using the 396 Wiedemann-Franz law (Equation 3) are plotted (dashed lines); as predicted by Equation (5), a 397 difference in thermal conductivity of up to 20% is observed between estimates using this equation 398 (which represents a lower bound) and the modified relationship.

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400 *3.3. Modeling results*

The core cooling model described by Section 2 was applied to a Mars-sized metallic core, considering the three selected core compositions (FeS₅O_{0.5}, FeS₅O₃Si₁, and FeS₅O₃) and *k* values obtained at 10 GPa, extrapolated up to 40 GPa and to 3100 K. Mg-bearing core compositions are not considered here as it is unlikely that much Mg is dissolved in the metal (e.g., Badro et al., 2016). Figure 6 presents the contributions of individual terms to the energy and entropy balances

for four models with constant values of k = 3, 12, 22 and 40 W m⁻¹ K⁻¹, which approximately 406 407 correspond to the mean k values for the compositions $FeS_5O_{0.5}$, $FeS_5O_3Si_1$, FeS_5O_3 , and the Fe-S 408 core considered in Davies and Pommier (2018) across the relevant temperature range. In this 409 figure, the CMB heat flow of Williams and Nimmo (2004) was represented using Equation (8) with $Q_p = 0.2$ TW, $Q_f = 1.3$ TW and $\tau = 0.9$ Gyrs, which closely reproduces the original time-410 series. As previously observed in our Fe-S core cooling study, the latent heat terms Q_1^s and Q_1^{l} 411 412 almost counter-balance each other since the same amount of mass is produced and destroyed; the 413 difference is due to the fact that heat is released throughout the snow zone but absorbed only at the 414 top of the liquid region. The corresponding entropy terms make a significant contribution to the entropy balance only in the most recent times as can be seen from the upturn in the E_I time-series. 415 The only difference between the four cases is in the time-series of E_k and E_j : the lower the thermal 416 conductivity, the lower the value of E_k and the longer the dynamo operates (Figure 6, right panels). 417 418 The key result is that, all other factors being equal, lowering k substantially increases the lifetime of the dynamo: for k = 40 W m⁻¹ K⁻¹, the dynamo fails after ~0.5 Gyrs; whereas the dynamo does 419 not stop when k = 12 and 3 W m⁻¹ K⁻¹. In terms of core chemistry, low k values are obtained for 420 421 O-rich alloy compositions (Figure 5).

The difference in dynamo termination times observed in Figure 6 cannot simply be reconciled by uncertainties in core material properties. We considered an 'extreme' parameter combination based on the values in Davies and Pommier (2018, Table 1) that would lead to the earliest dynamo termination time (see Figure 6 of Davies and Pommier, 2018). This parameter set consists of k = 22 W m⁻¹K⁻¹, a CMB pressure to 23 GPa (default value 21 GPa), a CMB radius to 1800 km (default 1627 km) and initial core temperature to 2500 K (default 2400 K). However, we found the extreme parameter combination reduced the dynamo lifetime by only ~0.4 Gyrs 429 compared to that shown in Figure 6, which is not nearly enough to account for the variability 430 induced by the differences in conductivity values. Since snow zones do not form until long after 431 the dynamo has failed (e.g., Figure 6) this result is independent of melting and partitioning 432 behavior. Therefore, in order to determine whether it is possible to find thermal-magnetic histories 433 with each value of k that are consistent with the observed dynamo termination time we considered 434 modifications to the CMB heat flow.

435 To investigate this point we used the default parameters from Davies and Pommier (2018) 436 and constant k except that the CMB heat flow is modified using Equation (8) in order to obtain an E_I that falls below zero around 4 Ga. The results are presented in Figure 7, in which Q_c was 437 438 changed using Equation (8) in order to ensure a dynamo cessation time of ~0.5 Gyrs, in agreement with Mars' magnetic history. Figure 7 shows that varying Q_{cmb} allows all three models to 439 440 reproduce successfully the dynamo cessation time, implying that core thermal histories based on 441 O-bearing alloys are consistent with this fundamental constraint on Martian core evolution. The 442 parameterized Q_{cmb} time-series are also broadly consistent with published values obtained from coupled core-mantle evolution models. For the $FeS_5O_{0.5}$ composition, the Q_{cmb} time-series lies 443 444 between those obtained by Williams and Nimmo (2004) and Leone et al (2014). For the FeS₅O_{0,3}Si₁ composition, the initial drop in Q_{cmb} is similar to the results of Thiriet et al. (2019) 445 446 while the long-term steady heat flow is reasonably consistent with this study and that of Leone et 447 al. (2014).

Figure 7 also illustrates the effect of k(T) on core cooling. The temperature-dependence of k is unimportant compared to the mean value (taken to be either 3, 12, or 22 W m⁻¹ K⁻¹, depending on the core composition). For all three cases, considering a constant k value or a temperaturedependent thermal conductivity (k(T)) leads to a similar cessation time for the dynamo. This result

452	is consistent with the small temperature-dependence of k (Figure 5): in the $FeS_5O_{0.5}$ case, a 1000
453	K drop in temperature leads to only a ~ 5 W m ⁻¹ K ⁻¹ drop in thermal conductivity.
454	Finally, we note that none of the models for the three cases in Figure 7 produce a snow
455	zone as the core temperature remains above the liquidus temperature of Fe-S-O system for all time
456	(Urakawa et al., 1987; Huang et al., 2010; Terasaki et al., 2011; Buono et al., 2015; Pommier et
457	al., 2018).
458	
459	
460	
461	4. Discussion
462	4.1. Electrical and thermal properties of S,O-bearing iron alloys at high temperature
463	The electrical resistivity of all investigated alloys at 10 GPa and 1200-1850 K varies from
464	$\sim 3 \times 10^{-6}$ to 15×10^{-6} ohm-m (or 300 to 1500 microhm-cm) (Figure 3) and is highly sensitive to bulk
465	composition (Figures 3 and 4). The strong dependence of resistivity to chemistry is in agreement
466	with previous studies of Fe, Fe-S, Fe-Si, and Fe-P alloys under a pressure of a few GPa and
467	confirms that adding light elements to pure iron increases resistivity (Deng et al., 2013; Pommier,
468	2018; Pommier et al., 2019; Manthilake et al. 2019; Silber et al., 2019; Yin et al., 2019). The alloys
469	in our study all contain 5 wt.% S (Table 1) and their resistivities are higher than the ones measured
470	for FeS ₅ at 8 GPa and up to 1573 K (<1×10 ⁻⁶ ohm-m, or 100 microhm-cm, Pommier, 2018). The
471	pressure difference is unlikely to explain the contrast in the electrical response, because increasing
472	pressure decreases Fe-S resistivity (Suehiro et al., 2017; Pommier, 2018). This comparison
473	between FeS ₅ and Fe-S-O alloys suggests that even a small amount of oxygen (0.5 wt.%) has a
474	strong effect on electrical and thermal properties. Moreover, the properties of Fe-S-O alloys are in

475 the same range of magnitude as the ones for FeS at 8 GPa (Pommier, 2018; Figure 5). The relative 476 effects of S and O can be explained from their respective structural behavior in the iron alloy. 477 Structural studies of Fe-S alloys pointed out that increasing the S content decreases the effective 478 electron mean free path in Fe-S liquids, which increases scattering due to impurity and hence, 479 increases electrical resistivity (Wagle et al., 2018). In contrast, oxygen is less capable than sulfur 480 to decrease the mean free path, because its bonding with iron is less efficient and contrary to sulfur, 481 its atomic size is not similar to the one of an iron atom (Alfè and Gillan, 1998; Wagle et al., 2018). 482 Our results also show a strong difference in transport properties between $FeS_5O_{0.5}$ and FeS_5O_3 483 (Figures 3 to 5). This is in agreement with first-principle simulations that predicted a significant 484 effect of the O content on the electrical and thermal properties of Fe-O liquids and observed that 485 increasing the amount of oxygen increases electrical resistivity and decreases thermal conductivity 486 (deKoker et al., 2012; Wagle et al., 2019). As highlighted by Wagle et al. (2019), oxygen atoms 487 occupy interstitial sites in the iron alloy. This shortens the Fe-O distances, which results in a less 488 efficient diffusive transport of charge than in an O-free iron alloy.

489 At T>1200 K, the Si-bearing and Mg-bearing Fe-S-O alloys present electrical resistivities 490 and thermal conductivities that range between the values obtained for FeSO_{0.5} and FeSO₃ (Figures 491 3 and 5). As illustrated in Figure 4, adding Si to an Fe-S-O alloy tends to decrease its electrical 492 resistivity, although a clear trend is not observed. Thermal conductivities of Si-bearing alloys 493 present a lower temperature-dependence than the conductivities calculated from electrical 494 measurements on FeSi at the same pressure (Pommier et al., 2019). These observations might 495 reflect a competing effect between Si and O atoms, though structural studies of Fe-S-O-Si liquids 496 are needed to fully explain the experimental data. Experimental and modeling structural data on 497 Fe-Si alloys proposed that Si is integrated in liquid iron via substitution mechanisms and that FeSi alloys approach the close-packing limit of 12-fold coordination (e.g., Morard et al., 2008; Wagle et al., 2019). For similar concentrations and the considered pressure range (10-40 GPa), silicon and sulfur are supposed to have a stronger effect on electrical resistivity than oxygen (Wagle et al., 2019), which leads to the hypothesis that the electrical data on Si-bearing alloys are controlled primarily by S and Si, not O. However, our experiments do not allow exploring the behavior of Si and or Mg in the liquid as samples had to be quenched before reaching the melting temperature of SiO₂ and of MgO (to avoid melting of the electrodes).

505 The peak in electrical resistivity observed at ~1500-1673 K in the $FeS_5O_3Si_1$ sample with 506 Si added as SiO_2 (Figure 3) is consistent with the temperature of the stishovite-coesite transition 507 at this pressure (Zhang et al., 1993). Understanding the magnitude of this electrical peak requires 508 further experiments and this is out of scope of the present study. At 10 GPa, phase equilibria studies 509 showed that the liquidus of SiO₂ is higher than the quenching temperature of the experiment (e.g., 510 Zhang et al., 1993; Table 2). Therefore, this alloy consists of an Fe,S,O-rich liquid that contains 511 small amounts of Si and a few isolated SiO₂ grains, as illustrated by SEM-EDS data (Figure 2). 512 Increasing temperature increases the ability of the liquid to dissolve oxygen (e.g., Pommier et al., 513 2018), which is consistent with the absence of solid Fe_2O_3 or FeO grains in the quenched samples. 514 The intermediate case in our core models has an FeS₅O₃Si₁ composition. At temperature

above the eutectic composition, this material is composed of two phases: a highly conductive metallic liquid and resistive SiO_2 grains. Several models have been developed to predict the bulk conductivity of multiphase materials as a function of a conductive interstitial phase (e.g. Glover et al., 2000; ten Grotenhuis et al., 2005, and references therein). Connectivity can be probed using the percolation theory (Stauffer and Aharony, 1992), in which the connectivity threshold depends on the geometry of the conductive network (e.g. Miller et al., 2015). In many ways, the geometry 521 we address here is analogous to the melt-grain networks analyzed by Miller et al. (2015), except 522 that the liquid phase in our materials is a metallic melt, not a silicate one. To understand the effect 523 of SiO_2 grains on the bulk electrical response of this core, we calculated the bulk electrical 524 resistivity as a function of melt fraction (Supplementary Figure 2). The metallic liquid was 525 considered to be either FeS_5O_3 or $FeS_5O_{0.5}$ and its resistivity comes from our experiments. The 526 electrical resistivity of SiO₂ at 20 GPa and 1800 K is from Scipioni et al., 2017 (it was extrapolated 527 to 1800 K). We used the geometric mean, which considers that an arbitrary shaped and oriented 528 volumes of solid is randomly distributed (Glover et al., 2000), and the modified Archie's law, in 529 which the value of cementation exponent *m* implicitly relates to the electrical connectivity of the 530 conductive phase and is thus, relevant to express bulk conductivity as melt fraction (e.g., Glover 531 et al., 2000; Miller et al., 2015). These models correspond respectively to the following equations 532 (9) and (10)

533
$$\sigma_{bulk} = \sigma_{liq}^{X_{liq}} \times \sigma_{SiO2}^{1-X_{liq}}$$
(9)

534
$$\sigma_{bulk} = \sigma_{SiO2} (1 - X_{liq})^p + \sigma_{liq} X_{liq}^m \tag{10}$$

535 with
$$p = \frac{\log(1 - X_{liq}^m)}{\log(1 - X_{liq})}$$
 (11)

In these equations, X_{liq} is the volume fraction of liquid, σ_i is the conductivity of phase *i*, and *m* is 536 537 the cementation exponent. The melt phase being well connected, we considered a value of m=1538 (+/-0.3) (full connectivity is achieved for m=1; Glover et al., 2000). We observe that for both 539 models, the metallic melt phase, which is several orders of magnitudes more conductive (or less 540 resistive) than solid SiO₂, controls the bulk electrical response at the conditions relevant to 541 planetary cores (i.e., for relatively small amounts of SiO_2). As a consequence, we assume that for 542 small amounts of SiO₂, the measured bulk resistivity of partially molten samples containing Si is 543 similar to that of the fully molten state.

544 Previous phase equilibria experiments in the Fe-S-O system under pressure and 545 temperature conditions relevant to the cores of small terrestrial bodies have reported the presence 546 of FeO grains coexisting with Fe grains as well as the liquid phase, and possibly forming a layer 547 at the solid iron-liquid interface (Urakawa et al., 1987; Tsuno and Ohtani, 2009; Pommier et al., 548 2018). Our quenched Fe-S-O(-Si) samples do not show the presence of solid FeO coexisting with 549 the liquid phase, which can be explained by the high quenching temperatures of the experiments 550 (the Mg-bearing samples were quenched at too low T to have a significant proportion of melt). 551 Liquid immiscibility in Fe-S-O alloys has also been reported at T>2100 K and over the 15-21 GPa 552 pressure range, with the immiscibility gap disappearing at pressure higher than 21 GPa (e.g. Tsuno 553 et al., 2007). Immiscibility depends on the pressure and temperature conditions as well as the 554 respective amounts of S and O, as previously observed for the Fe-S-Si system (e.g., Morard et al., 555 2008; Morard and Katsura, 2010). Liquid immiscibility was not observed in the Fe-S-O samples 556 that were quenched at a temperature significantly lower than 2100 K, and thus, it is not a parameter 557 in the models. We identified it in the Mg,Si-bearing material (Figure 2) but further work is required 558 to constrain the phase diagram for this composition.

559

560

4.2. The effect of multiple alloys on the cooling and dynamo of small terrestrial bodies

Applied to Mars, our results suggest that the thermal conductivity values (Figure 5) are significantly lower than the values of 40-50 W m⁻¹ K⁻¹ used in previous studies of Martian core thermal-magnetic evolution (Williams and Nimmo, 2004; Davies and Pommier, 2018, O'Rourke and Shim, 2019). This observation can be explained by the fact that these studies either varied thermal conductivity in order to get the dynamo to fail at a specific time, rather than drawing on experimental results (O'Rourke and Shim, 2019), or used thermal conductivity estimates from 567 previous studies on Fe and binary alloys (Williams and Nimmo, 2004; Davies and Pommier, 2018). 568 We have shown that it is possible to reconcile the inferred termination time of the dynamo with the low k values by varying the CMB heat flow, Q_{cmb} , based on a simple empirical relation. In 569 570 reality, the CMB heat flow is set by mantle convection and future work modelling 3-D mantle convection is required to establish whether the obtained time-series of CMB are dynamically 571 consistent. We find that our Q_{cmb} time series for the FeS₅O_{0.5} composition is consistent with the 572 results from Williams and Nimmo (2004) and Leone et al (2014), while the time-series for the 573 574 $FeS_5O_{0,3}Si_1$ composition exhibits similar long-term behavior compared to the Leone et al (2014) result but with a sharper initial decline that is similar to the calculation of Thiriet et al. (2019). The 575 576 magnitude of the initial decline in heat flow depends on the degree to which the core is superheated 577 compared to the mantle, which is poorly constrained. We therefore suggest that the heat flows we 578 have obtained are plausible and that the reported Martian thermal-magnetic evolutionary scenarios 579 for each of the three chosen compositions are compatible with the inferred termination time of the 580 dynamo. Regarding core chemistry, the fact that none of the models from Figure 7 produced a 581 snow zone suggests that low oxygen concentrations are required for the Martian core to preserve 582 a snow zone at the present day.

For the Moon, it has been suggested that a magnetic field existed between at least 4.2 and 3.56 Ga ago (Laneuville et al., 2014). Assuming an Fe-FeS composition and a *k* value of 50 W m⁻¹ K⁻¹ (using deKoker et al., 2012), Laneuville and coworkers proposed a possible core cooling scenario to reproduce the paleomagnetic constraints that consists of the growth of an inner core by a transition between a bottom–up and top–down core crystallization (Laneuville et al., 2014). Our results suggest that much lower *k* values than 50 W m⁻¹ K⁻¹ are to be expected for an O-bearing lunar core, even if the effect of pressure on *k* should increase thermal conductivity by a factor of ~ 2 at the pressure conditions of the Moon, considering the effect of pressure on *k* from previous studies (e.g., Secco, 2017; Pommier, 2018). These low *k* values could question the need for a transition in the core crystallization regime. The Galilean satellite Ganymede presents an intrinsic magnetic field that is consistent with a snow regime in its core, assuming a pure Fe composition (Rückriemen et al., 2015). In this modeling study, *k* was varied from 20 to 60 W m⁻¹ K⁻¹. Based on our results, we can speculate that in the case of an O-bearing core, much lower thermal conductivities could maintain the dynamo active through time.

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599 **5.** Conclusions

600 This multi-disciplinary investigation of iron alloys containing multiple alloying agents (S, 601 O, Si, Mg) shows that at T>1200 K and P=10 GPa, electrical resistivity of O-bearing iron alloys 602 increases slightly with increasing T and significantly with the total amount of alloying agents, 603 indicating that the effect of chemistry on the electrical properties is important and should be 604 accounted for as part of core cooling models. The electrical measurements and thermal 605 conductivity estimates of these alloys reveal a complex interplay and a different structural behavior 606 of S, O, Si, and possibly, Mg. Applied to the metallic core of a small terrestrial body, our results 607 suggest that bulk chemistry significantly affects the power available to drive the dynamo during 608 core cooling. In particular, an application to the Martian core using the CMB heat flow from 609 Williams and Nimmo (2004) indicates that the presence of oxygen would delay considerably the 610 dynamo cessation as well as the formation of a snow zone, compared to an O-free, Fe-S core. It is 611 possible to match the dynamo termination time for each k value by changing the CMB heat flow, 612 with high oxygen concentrations requiring a high initial heat flow and more rapid decline in order to match the inferred timing of Martian dynamo failure. Our results demonstrate that thermalconductivities can change the dynamo cessation time significantly, by a billion years or more.

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880 Figure captions:

881 Figure 1: COMPRES electrical cell used for the 4-electrode experiments in 14/8 multi-anvil 882 assemblies. Thermocouple wires are also used as electrodes and are in contact with two Fe disks. 883

Figure 2: SEM images of selected recovered samples. Top left: Fe-S-O-Si sample quenched at 10
GPa and 1772 K. The two electrode disks and thermocouple wires are visible. A small layer (Albearing alloy) is formed at the sample-alumina interface and has a negligible effect on the electrical
measurement (Pommier and Leinenweber, 2018). Top right: Fe-S melt and SiO₂ grains in
FeS₅O₃Si₁ sample. Bottom left: quenched melt texture in an Fe-S-O sample. Bottom right:
quenched melt in the Fe-S-O-Si sample.

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Figure 3: Electrical resistivity results as a function of temperature for the different alloy compositions. The α - γ transition is indicated with black arrows. Eutectic temperature for Fe-S at 10 GPa is from Chen et al. (2008) and refs. therein. Top: results for the two Fe-S-O alloys and three Mg-bearing alloys. Bottom: results for the five Si-bearing alloys.

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Figure 4: Electrical resistivity as a function of the total amount of alloying agents. Colorscorrespond to different temperatures. The shaded areas only represent a guide for the eye.

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Figure 5: Thermal conductivity of iron alloys at 10 GPa as a function of temperature and extrapolation for selected samples up to 3100 K. The color code is similar to the one used in Figure 3. Solid lines correspond to extrapolation using Equation 4, dashed lines correspond to extrapolations using the Wiedemann-Franz law. As a comparison, thermal conductivity estimates were calculated for FeSi using electrical resistivity data at 10 GPa from Pommier et al. (2019), for FeS using electrical resistivity data at 8 GPa (Pommier, 2018), and for Fe using electrical resistivity
data at 9 and 11 GPa from Silber et al. (2018).

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Figure 6: Modeling results for constant *k* values ranging from 3 to 40 W m⁻¹ K⁻¹ corresponding to different core chemistry. The dynamo stops for all cases except k = 3 W m⁻¹ K⁻¹. Our model reproduces the data of Davies and Pommier (2018) for k = 40 W m⁻¹ K⁻¹. See text for details.

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911 **Figure 7:** Modeling results for a FeS₅O_{0.5} core (left panels), a FeS₅O₃Si₁ core (middle panels), and 912 a FeS₅O₃ core (right panels). Top plots show the Core-Mantle Boundary heat flow Qc from the 913 published models of Williams and Nimmo (2004) (WN04), Leone et al. (2014) (LT13), Thiriet et 914 al. (2019) (T19) together with the parameterized curve (red) that gives a dynamo cessation time around 4 Ga with a constant value of k (either 22, 12 or 3 W m⁻¹ K⁻¹). The bottom panels show 915 916 the dynamo entropy E_J over time for the case of a constant k value (blue) and two temperature-917 dependent k values (red). The dynamo cessation occurs when E_J becomes negative. The grey areas 918 in the bottom panels correspond to the dynamo cessation time predicted for an Fe-FeS Martian 919 core by Davies and Pommier (2018) (see text for details).

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922 Supplementary Figure captions:

923 Supplementary Figure 1: EDS map analyses for the retrieved FeS₅O₃ sample. Top left: BSE
924 image showing the texture of the selected area. Top right: Fe map. Bottom left: S map. Bottom
925 right: O map.

Supplementary Figure 2: Electrical resistivity estimates for an SiO₂-bearing core at 1800 K. Resistivity of the metallic liquid (fully molten FeS₅O₃ or FeS₅O_{0.5}) comes from our experiments and resistivity of SiO₂ is from previous works under high pressure and temperature (Scipioni et al., 2017). The geometric mean refers to the distribution of solid and liquid phases (e.g., Glover et al., 2000).