

Earth's ancient dynamo with silicon precipitation

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1 Powering Earth's ancient dynamo with
2 silicon precipitation

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20 **Abstract**

21 Earth's core has produced a global magnetic field for the last 4 Gyrs,
22 presently sustained by inner core growth. Models of the core with high
23 thermal conductivity suggest potentially insufficient power available for
24 the geodynamo prior to inner core formation ~ 1 Ga. Precipitation of
25 SiO₂ from the liquid core might offer an alternative power source for the
26 magnetic field before inner core growth, however, no estimates of parti-
27 tion coefficient exist for conditions of the early core. We present the first
28 determination of the silicon partition coefficient at core-mantle boundary
29 conditions and use these results to build a thermodynamic model that

is integrated into a model of coupled core-mantle thermal evolution. We show that models including precipitation of silicon can satisfy constraints of inner core size, mantle convective heat flux, mantle temperature and a persistent ancient geodynamo whilst those excluding fail. Successful power from precipitation favours an oxygen poor initial core composition.

Keywords: Earth's core, geodynamo, thermal evolution, ab initio

1 Introduction

Earth's magnetic field is fundamental for the habitability of our planet, and yet the power to sustain it remains enigmatic for the majority of geological time. Palaeointensity data suggest the field has been maintained for at least the last 3.45 Gyrs [1] but the main power sources derive from growth of the solid inner core [2–4]. Growth of the inner core provides latent heat, however more influential is that light elements can be partitioned into the liquid [5] creating a chemical buoyancy source at the base of the outer core. Oxygen is considered a likely candidate because it can help to explain the density contrast between the inner and outer cores [6] although similar partitioning and convective influence can be explained by carbon [7]. Enrichment of the lowermost outer core in light elements provides power for outer core convection which is expected to be the major contributor to geodynamo power today [2, 8, 9].

Several first principles calculations and high pressure (P) and temperature (T) experimental results suggest that the core thermal conductivity may be significantly higher than previously thought [10–15]. Maintaining sufficient power for the dynamo with high conductivity implies rapid cooling and constrains the inner core to be far less than 1 Gyrs old. It also requires the geodynamo to be powered by heat loss from the core for most of Earth's history. This rapid cooling scenario means the mantle would have been subject to a super-solidus core-mantle boundary (CMB) temperature for much of Earth history [2, 4, 16].

57 The presence of a basal magma ocean (BMO) may provide a resolution to the
58 ancient geodynamo [17], although this approach relies upon the uncertain evo-
59 lution of the BMO as well as requiring a conductivity at the lower limit of the
60 recent high estimates. Secular cooling is not an efficient mechanism for pow-
61 ering the geodynamo, making thermal convection alone an unsuitable power
62 source [18].

63 In search of an alternate explanation for the long-lived geodynamo, prior
64 studies have investigated whether light elements in the liquid core, incorpo-
65 rated during a hot differentiation, might become insoluble during cooling and
66 precipitate. Convection is driven by the dense, iron-rich residual liquids sink-
67 ing following precipitation. Lower initial core temperatures and slower cooling
68 allowed by this power source imply a significantly older inner core. MgO pre-
69 cipitation has been suggested [18–20] although the dependence of magnesium
70 solubility on the oxygen content of the core has been argued to reduce the
71 overall power output, making MgO precipitation an insufficient power source
72 for the geodynamo alone [21, 22]. Additionally, incorporating sufficient Mg in
73 the core initially is difficult due to limited solubility in iron liquids. Others
74 have investigated the possibility of precipitating Si [23, 24] which is a more
75 widely accepted component in the liquid core (e.g. 25–27) as well as simulta-
76 neous precipitation of multiple elements [28]. At present, there is no consensus
77 on the possibility of Si precipitation, nor its onset time or associated power.
78 This is due to uncertainties on the initial composition of the core [26, 29, 30],
79 the method of modelling the partitioning behaviour, and the lack of data at
80 core conditions. Here we will address all three of these.

81 We produce the first determinations of Si partitioning at CMB conditions.
82 Ab initio molecular dynamic simulations of iron-rich liquids and silicate liq-
83 uids are used to calculate chemical potentials through free energy differences.

84 Equilibrium constants calculated from these chemical potentials are in good
 85 agreement with the extrapolation of previous experimental results at lower
 86 pressures and temperatures than core pressure. We derive a thermodynamic
 87 model for Si partitioning using a dataset which spans a wider range of physical
 88 and chemical conditions than was available to previous studies and confirm the
 89 extrapolation of this model to core conditions with our ab initio results. We
 90 use our thermodynamic model to describe Si precipitation in thermal history
 91 models of the cooling core. Previous studies of SiO_2 have evaluated the cooling
 92 rate needed to sustain a geodynamo from experimentally derived precipitation
 93 rates [23] and implemented a thermodynamic model of simultaneous precipi-
 94 tation of multiple light elements into a parameterised model of core thermal
 95 evolution [28]. We take a combined approach, using a thermal evolution model
 96 whilst choosing to focus solely on Si precipitation with a greater number of
 97 resolved interaction parameters. This includes C, O, Si, S, Mg in order to cap-
 98 ture important compositional effects relevant to all commonly considered light
 99 elements in the core. Si precipitation is considered over SiO_2 to isolate its effect
 100 on the thermal evolution of the core and avoid uncertainty associated with the
 101 type and source of reactants.

102 **2 Results and Discussion**

103 **2.1 Ab initio calculations**

104 Si distribution coefficients (K_d) are calculated for the first time at early core
 105 conditions using excess chemical potentials; the difference in chemical poten-
 106 tials of a species on either side of a reaction ($\delta\tilde{\mu}_{\text{SiO}_2} = \tilde{\mu}_{\text{SiO}_2}^{\text{metal}} - \tilde{\mu}_{\text{SiO}_2}^{\text{silicate}}$).
 107 Chemical potentials are calculated through free energies differences at
 108 represent significant computational expense. For a dissociation reaction

109 ($K_d^{dissociation} = \frac{x_{Si}^{metal} x_O^{metal2}}{x_{SiO_2}^{silicate}}$, other reactions computational details are dis-
 110 cussed in methods and supplementary information) $K_d = 0.50_{-0.09}^{+0.09}$ at 5500
 111 K and $0.029_{+0.028}^{-0.014}$ at 4500 K, both at 124 GPa. Differences in compositions
 112 make direct comparison difficult but indicate an overall agreement in trends.
 113 The highest PT experiments compare well to our results especially at 4500
 114 K, which lies within the scatter of experiments at similar temperatures. This
 115 dataset shows a strong temperature dependence and a weaker pressure effect,
 116 especially above 50 GPa, commensurate with an entropy dominated, configu-
 117 rational change in the iron-rich liquid and in agreement with other high PT
 118 partitioning studies (e.g. 20, 27).

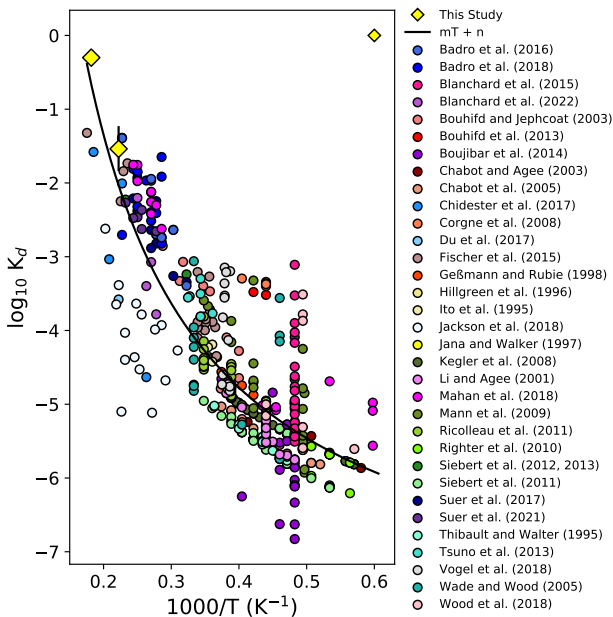


Fig. 1 Comparison of partition coefficients for the dissociation of Si and O into Fe-rich liquid calculated from our experimental dataset using our thermodynamic model with ab initio results of this study (yellow diamonds). The complete dataset is presented in the supplementary information (table S1). We show a fit of these values of K_d to a general temperature dependence (black line, $\log_{10} K_d = mT + n$ where $m = 609.5$ and $n = 218.4$).

2.2 Thermodynamic Model

To evaluate Si solubility in the liquid core, we must know the T, P and compositional influences on partitioning. Ab initio results provide T dependence of K_d naturally, however, a thermodynamic model is required for compositional effects. We construct a thermodynamic model of partitioning fit to lower P and T experimental data and validate extrapolation using our ab initio results. We use an interaction parameter model [31] which is commonly applied to high PT partitioning reactions (e.g. 20, 23, 27, 32). The interaction parameters are notionally universal and constant, however in reality, data are insufficient to fully resolve all possible parameters. This is because the existing data do not fully span P, T and composition space for the core. Varying starting compositions among studies also limits the interactions which can be resolved and affects partitioning behaviour, given that omission of one element can affect the interactions between retained elements. Additionally, differing experimental techniques introduce various uncertainties making any direct comparison challenging. Finally, the interaction parameter model is designed for solutes at low concentration, many studies include elements of interest in high concentration in order to better resolve their effects, but these may not be fully captured by this type of model. It is therefore inevitable that the interaction parameters will vary based on these factors. Indeed this is made apparent by previous studies [20, 27, 32] as well as in this study. To circumvent these difficulties, we have gathered the largest dataset yet (see supplementary information) in order to best constrain Si partitioning behaviour. Our model uses values which provide the best fit to our dataset. However, fixing specific parameters to the values found by previous studies can still produce models which predict precipitation rates within the error of our model.

145 We find that the aggregate temperature dependence of K_d from our model
146 is 0.0014 K^{-1} on average, which is within the uncertainty of our ab initio results
147 ($0.0016 - 0.00086 \text{ K}^{-1}$). The dominant compositional effect is that O limits the
148 solubility of Si in agreement prior studies [23]. Fig. 2 shows the prediction
149 of stable Si concentration and precipitation from our thermodynamic model.
150 For moderate O concentrations (0.4-1 wt. %) and temperatures between 3500
151 and 6000 K, we find precipitation rate in the range of 2×10^{-3} to 3×10^{-4}
152 wt.% K^{-1} . The precipitation rates predicted by functional models incorporating
153 interaction parameters from previous studies occupies a range narrower than
154 that imposed by the uncertainty of the initial O content of the core (fig. 2). One
155 notable prediction of our model is that the range of initial Si concentrations
156 predicted by accretionary modelling will encompass the compositions found
157 to be consistent with inner core density jumps of 0.8 and 1.0 g cm^{-1} , whilst
158 excluding higher contrasts. Considering more complex compositions will influ-
159 ence the absolute solubility of Si, although, significantly higher concentrations
160 are unlikely due to the dominant effect of temperature and O content.

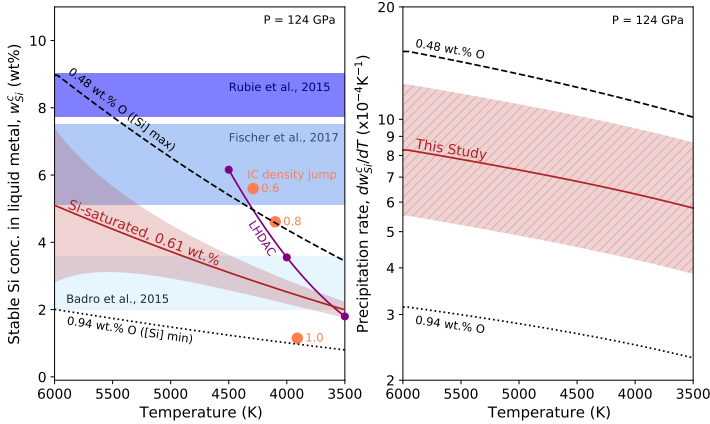


Fig. 2 Left: Stable concentration of Si in the liquid metal. Our model is evaluated for partitioning between an initially Si saturated iron-rich liquid containing 0.61 wt. % O and a pyrolite mantle (red solid line) at 124 GPa. Red shaded envelope is the uncertainty from the fitting parameters of our model. Horizontal shaded regions are estimated initial high [26] (dark blue), moderate [30] (mid blue) and low [29] (light blue) core Si content. Orange circles are estimates of present-day core composition [33] (within an Fe-Si/S-O core) based on the inner core density jump of 0.6, 0.8 and 1.0 g cm^{-3} . Laser heated diamond anvil cell experiments [23] are shown as purple circles. Dotted (dashed) line is the minimum (maximum) initial Si concentration [26, 29] with initial O concentration set to achieve this. Right: Precipitation rate from our model, hatched shaded region of 1.5x and 0.67x encompasses functional models using parameters fixed to values found from previous studies. Maximum and minimum initial Si cases are also shown

161 2.3 Thermal evolution of the core

162 To investigate the effect of precipitation on the thermal evolution of the core
 163 we combine two classical models of the core [17, 34] and the solid mantle [35].
 164 These parameterisations of the deep Earth are coupled at the CMB, where
 165 the mantle defines the heat transport across the CMB and the core defines the
 166 temperature of the CMB. For the core, energy balance is used to evolve the
 167 core temperature and composition alongside entropy balance to evaluate the
 168 entropy production due to the magnetic field. A moderately high conductivity

169 scenario is considered, where thermal conductivity is $70 \text{ W m}^{-1} \text{ K}^{-1}$ everywhere
170 in the core [15, 17]. Whilst a solid mantle is included, we do not include a sep-
171 arate magma ocean to minimise the contributions to geodynamo power such
172 that the effects of precipitation are clearly distinguishable and the number of
173 uncertain parameters is reduced. This setup is not fully consistent with our
174 thermodynamic model, which is based on liquid-liquid reactions in both exper-
175 iments and calculations, but is preferable to attempting to model the highly
176 uncertain physics associated with a magma ocean. Due to the high CMB tem-
177 peratures present in many of our models, we envisage (purely for convenience)
178 a simplistic, persistent thin melt layer at the base of the mantle, with negligible
179 latent heat release and an equal partitioning of radiogenic elements (which we
180 do not expect to be the case in reality) with the overlying mantle. We assume
181 that the core is mixed thoroughly on timescales far shorter than the timestep
182 of our simulation such that the liquid core has no compositional variation nor
183 chemically stable layers. We do observe sub adiabatic CMB heat flux prior to
184 inner core nucleation in our models implying thermally stratified layers at the
185 top of the liquid core.

186 Our description of precipitation is based solely on the thermodynamic sta-
187 bility of Si, depending on P, T and composition. We evaluate precipitation as
188 removing the fraction of Si above the stability limit from the metal and do not
189 include oxygen in this evaluation. This is done to pose the simplest case when
190 examining the power made available to the geodynamo and also to avoid the
191 need to include a description of phase (e.g. SiO_2 or SiC) or source of reactant
192 (e.g. mantle, core or boundary layer) both of which are highly uncertain.

193 The thermal history of two compositional scenarios is considered; high (10
194 mol%) and low (2 mol%) initial oxygen compositions of the liquid core, all with
195 a pyrolytic mantle composition. Table 1 provides the setup parameters for each

196 case. The mantle composition is held constant for a simple examination of the
 197 effect of core evolution. We expect that the mantle composition would not be
 198 greatly affected by precipitation because it is a significantly larger reservoir of
 199 Si than the core, however the effect of a freezing basal magma ocean may be
 200 more significant. Each initial core composition is evolved under conditions of
 201 initially over- and under-saturated Si content, and with ($\alpha_{ppt}^i \neq 0$) and without
 202 ($\alpha_{ppt}^i = 0$) the convective power of precipitation included. We vary the upper
 203 to lower mantle viscosity ratio (f_{visco}) and initial CMB temperature ($T_{t=0}^{cmb}$) to
 204 regulate the core temperature such that the final state of our models matches
 205 constraints of the present-day core. These constraints are: the inner core radius
 206 agreeing with the present-day value of 1221 km, a present-day mantle con-
 207 vective heat flow of 39 TW [36], a mid-mantle temperature of 2320 K, and a
 208 positive entropy from ohmic dissipation (or dynamo entropy, E_j) for all time
 209 preceding inner core nucleation.

	Symbol	O	Si	α_{ppt}^O	α_{ppt}^{Si}	$T_{t=0}^{CMB}$	f_{visco}
	Units	wt. %	wt. %			K	
Without Precipitation	A	5.314	0.165	0.0	0.0	5500	4
	B	5.303	0.085	0.0	0.0	5200	5
	C	1.126	4.339	0.0	0.0	7000	23
	D	1.070	2.137	0.0	0.0	6500	12
With Precipitation	A ^P	5.314	0.165	1.1	0.87	5000	5
	B ^P	5.303	0.085	1.1	0.87	4900	6
	C ^P	1.126	4.339	1.1	0.87	5400	13
	D ^P	1.070	2.137	1.1	0.87	5800	9

Table 1 Initial values for thermal evolution model runs (A-D^P) where all other quantities remain unchanged from the original models of core [4] and mantle [35] unless otherwise stated. Expansivity (α_{ppt}^i) [33] applies only to precipitation from the liquid core, non-zero values are applied to inner core growth for all cases. High (A,A^P,B,B^P) and low (C,C^P,D,D^P) oxygen cases are taken for Si over (A,A^P,C,C^P) and under (B,B^P,D,D^P) saturation with power from precipitation turned on (A^P-D^P) and off (A-D). Parameters $T_{t=0}^{CMB}$ and f_{visco} (ratio of upper to lower mantle viscosity) are varied to match present day constraints.

210 Fig. 3 shows examples of the time evolution of inner core radius, mid-
 211 mantle potential temperature, CMB temperature, mantle convective heat flow,
 212 CMB heat flow, and dynamo entropy for two cases that differ by the inclu-
 213 sion or emission of precipitation. We find that without precipitation all cases
 214 will fail to maintain a positive dynamo entropy before inner core nucleation.
 215 This is because secular cooling must be sufficiently diminished by rapid cool-
 216 ing to grow the inner core to the present day size. We find that including the
 217 energy and entropy effects of precipitation can maintain a positive E_j for the
 218 majority of Earth history preceding inner core formation, producing an older
 219 inner core. We find that high initial oxygen concentration cases strongly reduce
 220 available dissolved silicon and therefore power from precipitation. These cases
 221 require $f_{visco} < 7$ in order to grow the core to present-day size, meaning the
 222 mantle is responsible for maintaining rapid secular cooling. This highlights the
 223 requirement for modest O content for Si precipitation to reduce mantle and
 224 core temperatures, sustain a geodynamo and satisfy present-day constraints.
 225 We find that compared to cases without precipitation, continuous precipita-
 226 tion of Si from the liquid core can sustain the geodynamo throughout Earth's
 227 history and allow the core to be 300 K cooler and 500 Myrs older.

228 We also examine the effect of doubling and halving the calculated precip-
 229 itation rate to explore the uncertainty of our thermodynamic model (shaded
 230 region, fig. 2). Although this requires minor adjustment of initial T^{CMB} and
 231 f_{visco} , the same outcome of cases with precipitation meeting all four con-
 232 straints is held whilst inner core ages differ by < 100 Myrs and ancient core
 233 temperatures by < 50 K. This shows that different combinations of interac-
 234 tion parameters in the thermodynamic model can produce some variance in
 235 the calculated precipitation rate, but this is not large enough to change the
 236 outcome of the thermal evolution. We also show that the uncertainty on the

237 initial oxygen content (dashed and dotted lines, fig 2) of the core has a far
 238 greater effect on the outcome of thermal evolution models than the uncertainty
 239 of thermodynamic modelling.

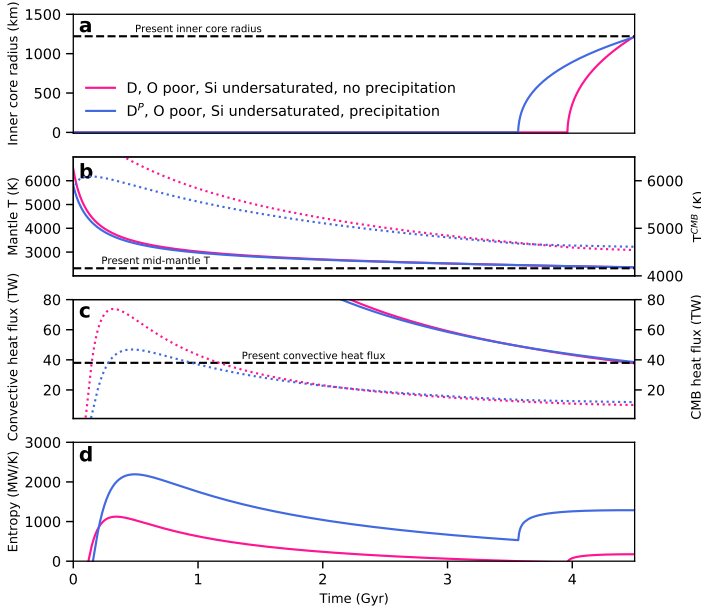


Fig. 3 Thermal evolution of the Earth's core with an initial condition of low O concentration (2 mol%) and Si saturation with inclusion (blue) and exclusion (pink) of power and entropy of precipitation (cases C and C^P from Table 1, respectively). Inner core radius (a), mid-mantle potential temperature (b, left, solid lines) and CMB temperature (b, right, dotted lines), convective mantle heat flux (c, left, solid lines) and CMB heat flow (c, right, dotted), and core entropy from ohmic dissipation (d). Black dashed lines show present-day target values.

240 We show the outcomes of thermal history cases from table 1 in fig. 4. When
 241 Si is initially saturated (cases A, A^P and C, C^P) the low O cases require high
 242 values of f_{visco} for the inner core to not grow too large by 4.5 Gyrs whilst
 243 in the high O case low temperatures are needed to freeze the inner core due
 244 to further melting point depression. When $Q_{ppt} \neq 0$ (again for Si saturated

245 initial conditions, cases A^P and C^P) cooling rates are lower and the inner core
246 is ~ 500 Myrs older for O poor conditions (more Si is available to precipitate).
247 For cases of initial Si undersaturation (B, B^P, D, D^P; meaning precipitation is
248 delayed by between 130 and 210 Myrs when $\alpha \neq 0$), a similar core temperature
249 is needed both with and without precipitation, however, in all compositional
250 configurations the inner core is older with the precipitation power included
251 [23]. When Si is initially saturated, including Q_p allows lower cooling rates
252 and an older inner core ($C^P = 1102$ Myrs). Whilst all considered cases are
253 able to produce a geodynamo within the first 2 Gyrs, cases where $Q_{ppt} = 0$
254 are unable to produce a magnetic field from at least 200 Myrs prior to inner
255 core formation (crossed symbols, fig. 4).

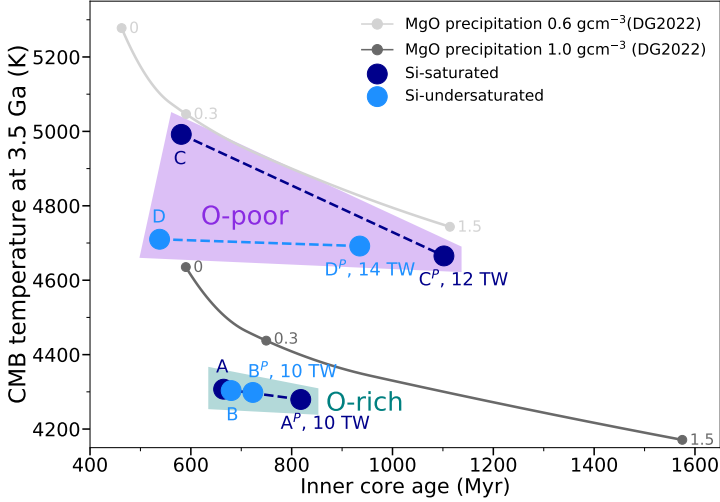


Fig. 4 Inner core age and core temperature at 3.5 Ga for our model with and without convective power from precipitation (connected by dashed lines). Initial Si saturation (undersaturation) is shown as dark (light) blue. O rich (poor) initial conditions are captured by teal (purple) regions. Labels correspond to setup conditions in table 1 and also give the CMB heat flow at 3.5 Ga for models which maintain positive E_j for all time. Also shown are the results from models examining MgO precipitation [17] for precipitation rates of 0, 0.3 and $1.5 \times 10^{-5} \text{ K}^{-1}$, colours denote the core properties in terms of the density jump at the inner core boundary (0.6 (light grey) and 1.0 g cm^{-3} (dark grey)) which represent bounding extremes of the density jump.

256 We find that the precipitation of Si allows the early core to cool more slowly
 257 than it would otherwise and can supply power to the geodynamo throughout
 258 Earth's history. High O concentration in the core can reduce ancient core
 259 temperatures but relies predominantly on secular cooling to power the ancient
 260 geodynamo. The more plausible low O cases result in higher ancient CMB
 261 temperatures due to lesser melting point depression. The rheological transition
 262 of the magma ocean should occur between 40% to 60% melt fraction [37,
 263 38], rather than at the intersection of the liquidus or solidus, which would
 264 correspond to the occurrence of complete crystallisation and first partial melt,

265 respectively. Our thermal histories for low O content in particular suggest a
 266 long lived basal magma ocean. A scenario where the ancient geodynamo is
 267 powered by Si precipitation places constraint on accretionary models of core
 268 composition. We show that an initial core composition of 4.3 wt. % Si and 1.1
 269 wt. % O is both thermodynamically stable and able to produce sufficient power
 270 for the ancient geodynamo to be sustained, however this limits compatible
 271 accretion models to those which predict intermediate initial core Si content
 272 and low O content.

273 3 Methods

274 3.1 Ab Initio Calculations

275 We conduct density functional theory [39, 40] spin-polarised, molecular
 276 dynamic simulations of silicate and iron-rich liquids to calculate the excess
 277 chemical potentials of individual chemical components. These calculations
 278 individually require significant computational resources, the two partitioning
 279 results we present represent millions of CPU hours spread across several HPC
 280 systems. Chemical potentials (μ_i) can be described as the free-energy change
 281 (∂F) of a system when the quantity of a species (i) is changed

$$\mu_i(v, T, x_i, x_j, \dots) = \left(\frac{\partial F}{\partial x_i} \right)_{V, T, x_i, x_j, \dots}, \quad (1)$$

282 in this case under conditions of constant volume (V , v is volume per atom),
 283 temperature (T) and composition (where x_i is the molar fraction of species i).
 284 Helmholtz free energy (F) is used for consistency with the constant volume
 285 conditions of our simulations. We use two complementary methods [41] to cal-
 286 culate μ_i . The first method compares F of a reference system against another

287 with a different number of solute atoms (dN_i) to isolate μ_i of the solute:

$$\mu_i(v, T, x_i, x_j, \dots) = \frac{F(V, T, x_i, x_j, \dots) - F(V, T, x_i - dN_i, x_j, \dots)}{dN} \quad (2)$$

288 The second method computes the change in free energy as a result of changing
 289 the number of solute atoms in the same system and calculating the change in
 290 free energy. The difference here is that the explicit free energies of two systems
 291 are not needed, only the change in free energy (for complete details, see 41).
 292 Values from both methods are combined for use here, where their variance
 293 gives an uncertainty. We find distribution coefficients (K_d) from our ab initio
 294 results of μ_i . When μ_i on either side of a reaction are equal, this component
 295 is in thermodynamic equilibrium and each concentration will be stable

$$\mu_{SiO_2}^{silicate}(V, T, x_{SiO_2}^{silicate}, x_j^{silicate}, \dots) = \mu_{SiO_2}^{metal}(V, T, x_{SiO_2}^{metal}, x_j^{metal}, \dots) \quad (3)$$

296 Here μ_i is dependent on V , T and composition. Separating out the configura-
 297 tional portion of μ_i gives

$$\begin{aligned} & 2(k_B T \ln x_O^{silicate} + \tilde{\mu}_O^{silicate}) + k_B T \ln x_{Si}^{silicate} \\ & = 2(k_B T \ln x_O^{metal} + \tilde{\mu}_O^{metal}) + k_B T \ln x_{Si}^{metal} \end{aligned} \quad (4)$$

298 whilst $\tilde{\mu}_{SiO_2} = \tilde{\mu}_{Si} + 2\tilde{\mu}_O$ in the liquid, which when rearranged becomes
 299 equal to the dissociation distribution coefficient

$$K_d^{dissociation} = \frac{x_{Si}^{metal} x_O^{metal^2}}{x_{SiO_2}^{silicate}} = \exp\left(-\frac{\tilde{\mu}_{SiO_2}^{metal} - \tilde{\mu}_{SiO_2}^{silicate}}{k_B T}\right) \quad (5)$$

300 allowing us to validate our thermodynamic model through comparison of model
 301 prediction, experimental value and ab initio calculation. The dissolution and
 302 exchange reactions take the forms

$$K_d^{dissolution} = \frac{x_{SiO_2}^{metal}}{x_{SiO_2}^{silicate}} = (x_O^{silicate})^2 \exp - \left(\frac{(\tilde{\mu}_{SiO_2}^{metal} - \tilde{\mu}_{SiO_2}^{silicate})}{k_B T} \right) \quad (6)$$

303 and

$$\begin{aligned}
 K_d^{exchange} &= \sum_{i=1}^{N-1} \frac{(x_{FeO}^{silicate})^2 x_{Si}^{metal}}{(x_{Fe}^{metal})^2 x_{SiO_2}^{silicate}} \\
 &= \left(\frac{x_O^{silicate}}{x_O^{metal}} \right)^2 \left(\frac{x_{Fe}^{silicate}}{x_{Fe}^{metal}} \right)^2 \exp - \left(\frac{(\tilde{\mu}_{SiO_2}^{metal} - \tilde{\mu}_{SiO_2}^{silicate})}{k_B T} \right) \quad (7)
 \end{aligned}$$

304 respectively.

305 We focus on pressure and temperatures relevant to the CMB (124 GPa
 306 and 4500-5500 K), as these are the most crucial for the evolution of the core.
 307 Simulations were performed using the VASP code [42] in the canonical ensemble
 308 using a Nosé thermostat [43] and with the Brillouin Zone sampled at the
 309 Γ point. A timestep of 1 fs was used and runs lasted between 10 and 100 ps.
 310 The plane wave cutoff was set to 500 eV and the projector augmented wave
 311 method [44] was used with the generalised gradient approximation functional
 312 PW91 [45]. The number of valence electrons and core radii for Fe, Si and O
 313 were 14, 4 and 6, and 1.16, 0.7 and 0.08 Angstroms, respectively. Simulations
 314 contained between 148 and 160 atoms, depending on composition (reported in
 315 supplementary information).

316 3.2 Thermodynamic Model

317 We use an interaction parameter model [31] to describe the solubility of Si in
 318 iron-rich liquids. We fit this thermodynamic model to experimental values of

319 K_d (calculated using eq. 5) through eq. S15 in the supplementary information.
 320 The parameters of this model capture the compositional effects of C, O, Si, S
 321 and Mg (chosen to represent likely light elements in the core and to account
 322 for common impurities in our experimental dataset) as well as pressure and
 323 temperature effects. We fit to a larger dataset than was available to previous
 324 studies (480 measurements from 33 studies) the details of which, choice of
 325 reaction and model parameters are provided in the supplementary information.

326 **3.3 Thermal Evolution model**

327 Thermal evolution modelling follows 4 where, if small terms are ignored, the
 328 heat flow across the CMB (Q^{cmb}) is found through the balance of energies

$$Q^{cmb} = Q_s + Q_L + Q_{ppt} + Q_g. \quad (8)$$

329 Q_s is the secular heat stored in the core and Q_L is the latent heat release due
 330 to inner core growth. Q_{ppt} is the gravitational energy from mixing the dense,
 331 iron-rich residual liquids post precipitation across the outer core [18]

$$Q_{ppt} = \int_{\infty} \psi \rho \alpha_{ppt}^i \left[C_{ppt} \left(\frac{dT_{cmb}}{dt} \right) \right] dV_c \quad (9)$$

332 where ρ is density, α_{ppt}^i is expansivity, ψ is gravitational potential, C_{ppt} is
 333 the precipitation rate of Si ($C_{ppt} = dw_{Si}^c/dT$ is evaluated through our ther-
 334 modynamic model), t is time and V_c is volume of the liquid core. Q_g is the
 335 gravitational power generated from the preferential partitioning of O into the
 336 lowermost liquid core upon freezing. We assume Si to partition evenly between
 337 the solid and liquid core [6] such that the growth of the inner core has no
 338 direct effect on the Si concentration of the liquid core. The entropy budget of

339 the core can be balanced [9] by

$$E_j + E_\alpha + E_k = E_s + E_L + E_{ppt} + E_g \quad (10)$$

340 where E_α is the entropy due to barodiffusion throughout the core which is
 341 negligible [4, 9] and so is ignored. E_k is the entropy from thermal conduction
 342 and the other terms follow the same notation as their energy counterparts. E_j
 343 is the entropy due to ohmic dissipation, used to evaluate whether a geodynamo
 344 can be sustained (when positive) and is the output of this balance.

345 4 Supplementary information

346 The dataset used in this study is available to download from the supplementary
 347 information where details of the ab initio calculations and thermodynamic
 348 model are also provided.

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6 Author Contributions

M.P. and D.A. conducted the ab initio portion of this project, producing chemical potentials. A.P. and A.J.W constructed the experimental database and S.G. developed the thermal evolution model codes. This project was the inception of C.D. who provided guidance alongside A.M.W.. A.J.W. analysed the experimental data, constructed the thermodynamic model, conducted thermal evolution simulations and analysis, and was primarily responsible for the writing of this manuscript, to which all authors contributed.

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