Large-scale atomistic simulations of magnesium oxide exsolution driven by machine learning potentials: Implications for the early geodynamo

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April 26, 2024

Abstract

The precipitation of magnesium oxide (MgO) from the Earth's core has been proposed as a potential energy source to power the geodynamo prior to the inner core solidification. Yet, the stable phase and exact amount of MgO exsolution remain elusive. Here we utilize an iterative learning scheme to develop a unified deep learning interatomic potential for the Mg-Fe-O system valid over a wide pressure-temperature range. This potential enables direct, large-scale simulations of MgO exsolution processes at the Earth's core-mantle boundary. Our results suggest that Mg exsolves in the form of crystalline Fe-poor ferropericlase as opposed to a liquid MgO component presumed previously. The solubility of Mg in the core is limited, and the present-day core is nearly Mg-free. The resulting exsolution rate is small yet nonnegligible, suggesting that MgO exsolution can provide a potentially important energy source, although it alone may be difficult to drive an early geodynamo.

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9 10	Email: jie.deng@princeton.edu							
11	Key points (140 character with no abbreviations):							
12	• A machine learning potential of <i>ab initio</i> quality is developed for the Mg-Fe-O system							
13 14 15	 Mg exsolves in the form of crystalline Fe-poor ferropericlase with a small exsolution rate assuming only Mg and O are present in the core MgO exsolution can serve as an important source of buoyant flux to drive the early geodynamo 							
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18 Abstract (150 words)

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The precipitation of magnesium oxide (MgO) from the Earth's core has been proposed as a potential energy 20 21 source to power the geodynamo prior to the inner core solidification. Yet, the stable phase and exact amount 22 of MgO exsolution remain elusive. Here we utilize an iterative learning scheme to develop a unified deep 23 learning interatomic potential for the Mg-Fe-O system valid over a wide pressure-temperature range. This 24 potential enables direct, large-scale simulations of MgO exsolution processes at the Earth's core-mantle 25 boundary. Our results suggest that Mg exsolves in the form of crystalline Fe-poor ferropericlase as opposed 26 to a liquid MgO component presumed previously. The solubility of Mg in the core is limited, and the 27 present-day core is nearly Mg-free. The resulting exsolution rate is small yet nonnegligible, suggesting that 28 MgO exsolution can provide a potentially important energy source, although it alone may be difficult to 29 drive an early geodynamo.

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33 Plain language summary (200 words)

34 The paleomagnetic records suggest that Earth's magnetic field dates back to at least 3.4 billion years ago. 35 Yet, the energy source of this early geodynamo is still puzzling. One popular hypothesis is that buoyant 36 magnesium oxide may exsolve out of the Earth's core as the core cools, releasing gravitational potential 37 energy to drive the core convection and power the early geodynamo. However, the amount of MgO 38 exsolved is uncertain due to experimental and computational challenges. Here, for the first time, we directly 39 simulate the MgO exsolution processes using large-scale molecular dynamics simulations, made possible 40 by interatomic potentials built upon machine learning methods. The results show that MgO exsolves as a 41 component of a crystalline ferropericlase, in contrast to early studies which generally assume that MgO 42 exsolved as a component of silicate melts. We find that MgO solubility in the core is low. The exsolution 43 rate is small and MgO alone may be insufficient to sustain a long-lasting magnetic field at the Earth's 44 surface in its early history.

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50 1. Introduction

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52 Chemical buoyancy due to the crystallization of the inner core is believed to have supplied energy to power 53 the geodynamo in the last 0.5-1 billion years (Nimmo, 2015). Paleomagnetic records suggest the existence 54 of a very early (3.4 Ga) magnetic field in the Earth's history prior to the inner core crystallization (Tarduno 55 et al., 2010). The energy source of this early geodynamo is enigmatic. Radiogenic heat production in the 56 core may not be sufficient to sustain an early dynamo (Frost et al., 2022). The basal magma ocean may be 57 electrically conductive (Stixrude et al., 2020), but the scale and longevity of a convective basal magma 58 ocean are uncertain.

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Recent studies propose that exsolution of oxides from the core upon cooling, such as MgO (O'Rourke and
Stevenson, 2016) or SiO₂ (Hirose et al., 2017), may be a viable mechanism to power an early dynamo.
Experimental studies on metal-silicate partitioning suggest that the solubility of Mg is highly sensitive to
temperature (Badro et al., 2016; Du et al., 2017). The high-temperature equilibration between the metallic
and silicate melts during the core formation process may result in a few wt% of MgO dissolved in the core.
Upon cooling, Mg is expected to precipitate out of the core as its solubility drops. However, the efficiency
of this mechanism, especially for MgO oxide, remains controversial (Badro et al., 2016; Du et al., 2017).

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68 The precipitation rate of MgO has been widely estimated using Mg partitioning behaviors in the metal-69 silicate system (Badro et al., 2018; Du et al., 2019; Liu et al., 2019). This estimation, strictly speaking, is 70 unjustified. In contrast to the core formation process, where metallic and silicate melts equilibrate, the 71 precipitation process involves the equilibration between the metallic melt and exsolution, where the exact 72 phase and chemistry of exsolution depend on bulk compositions and thermodynamic conditions (Helffrich 73 et al., 2020). Previous estimates, however, implicitly assume that exsolved MgO is a component of liquid 74 silicate (Badro et al., 2018; Du et al., 2019; Liu et al., 2019). This assumption is questionable, as MgO is 75 more refractory than SiO_2 which may exsolve out of the core in solid-sate (Hirose et al., 2017). Therefore, 76 a careful examination of the Mg exsolution process is necessary.

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In this study, we combine enhanced sampling, feature selection, and deep learning to develop a unified
machine learning potential (MLP) for the Mg-Fe-O system. This MLP is used to perform large-scale
molecular dynamics simulations to study the exsolution of Mg from core fluids. Unlike previous
computational studies based on free energy calculations (Davies et al., 2018; Wahl and Militzer, 2015;
Wilson et al., 2023), this method does not prescribe the state of the exsolved phase (Sun et al., 2022). The
results inform the stable state of MgO precipitation, Mg and O partitioning between core fluid and
exsolution, and the efficiency of MgO exsolution in powering an early geodynamo.

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86 2. Methodology

87 2.1. Development of Machine Learning Potential

88 A machine learning potential (MLP) is a non-parametric model that approximates the Born-Oppenheimer 89 potential energy surface. We follow the same approaches outlined in our previous work on Mg-Si-O (Deng 90 et al., 2023) and Mg-Si-O-H (Peng and Deng, 2024) where details of the machine learning process can be 91 found. To briefly summarize our approach, the MLP is trained on a set of configurations drawn from 92 multithermal and multibaric (MTMP) simulations (Piaggi and Parrinello, 2019), which are used to 93 efficiently sample the multi-phase configuration space. We use the structure factor of B1 MgO as the 94 collective variable to drive the sampling, and an iterative learning scheme as described by (Deng et al., 95 2023) to efficiently select distinct samples from molecular dynamics trajectories. High-accuracy ab initio 96 calculations are performed on the selected sample configurations to derive the corresponding energies,

97 atomic forces, and stresses. The DeePMD approach is employed to train an MLP which takes a 98 configuration (a structure of a given atomic arrangement) and predicts its energy, atomic forces, and stresses without iterating through the time-consuming self-consistent field calculation (Wang et al., 2018; Zhang et 99 100 al., 2018). The details of DeePMD approach and density functional theory (DFT) calculations can be found 101 at Supplementary Information (Text S1, Figure S1). Our MLP explores a wide compositional space, trained on Mg-Fe-O systems of varying Mg:Fe:O ratios, including the pure endmembers, Fe and MgO, as well as 102 103 intermediate compositions denoted by $(MgO)_aFe_bO_c$, where a=0-64, b = 0-64, c = 0-16 with 2a+b \geq 64. The 104 final training set consists of 4466 configurations generated at pressure up to 200 GPa and temperature up

105 to 8000 K.

106 2.2. Two-phase molecular dynamics simulation

107 Two-phase simulations are performed on a pure MgO system to determine the melting point of B1 MgO. 108 Alfè (2005) found that systems of 432 atoms are sufficient to yield converged melting points as those larger systems. Here, supercells of 432 atoms are constructed and then relaxed for 1000 steps at desired pressure 109 and temperature conditions in the NPT ensemble. The relaxed cell is then used to perform NVT simulations 110 111 at high temperatures far exceeding the melting temperatures, with the atoms of half the cell fixed and the 112 force applied to these atoms set to 0. The resulting structure is half-molten and half-crystalline. We relax 113 this structure again at the target pressure and temperature for 1000 steps to obtain the initial configuration for two-phase simulations. Simulations on the two-phase supercell of solid-liquid coexistence were then 114 performed. If the whole cell is molten (or crystallized) at the end, the simulation temperature is above (or 115 116 below) the melting point. The state of the system can be determined by analyzing the radial distribution

117 functions, allowing us to pinpoint the upper and lower bounds of the melting point.

118 2.3 Exsolution simulation

119 We construct systems of various Mg:Fe:O ratios by substituting/removing Mg and/or O atoms of supercells

120 of B1 MgO. Initial configurations are melted at 8000 K and 140 GPa under the NPT ensemble for ~10 ps.

121 We inspect trajectories and radial distribution functions to ensure systems are fully molten and well relaxed.

122 The resulting configurations are further used to perform simulations at 140 GPa and target temperatures

123 under the NPT ensemble for up to several nanoseconds to simulate the exsolution process.

124 2.4 Gibbs dividing surface

To determine the composition of the two coexisting phases, for every frame we locate the Gibbs dividing surface (GDS) that separates the whole cell into an oxide region, a metallic region, and two interfaces in between (Sega et al., 2018; Willard and Chandler, 2010). For every snapshot, we calculate the coarsegrained instantaneous density field at point **r** by

128 grained instantaneous density field at point \mathbf{r} by

$$\rho(\mathbf{r}) = \sum_{i} (2\pi)^{-\frac{3}{2}} \exp\left(-\frac{|\mathbf{r} - \mathbf{r}_i|^2}{2\sigma^2}\right),\tag{1}$$

where \mathbf{r}_i is the position of the *i*th atom; σ is the coarse-graining length, and is set as 2.5 Å here (Willard and Chandler, 2010). The instantaneous surface $\mathbf{s}(t)$ is defined as a contour surface of the instantaneous

- 150 and Chandler, 2010). The instantaneous surface s(t) is defined as a contour surface s(t) is defined as a contour surface is
- 131 coarse-grained density. The proximity of *i*th atom to this surface is

$$a_i = \{ [\boldsymbol{s}(t) - \boldsymbol{r}_i(t)] \cdot \boldsymbol{n}(t) \} |_{\boldsymbol{s}(t) = \boldsymbol{s}_i^*(t)},$$
(2)

- 132 where n(t) is the surface normal in the direction of the density gradient at that point. This instantaneous
- density field is then projected onto each atom and associated with the corresponding proximity. We find
- 134 that $\rho(a)$ follows the expected form

$$\rho(a) = \rho_{oxide} + \frac{1}{2}(\rho_{metal} - \rho_{oxide}) \left[\tanh\left(\frac{a-a0}{w}\right) - \tanh\left(\frac{a-a1}{w}\right) \right], \tag{3}$$

where ρ_{oxide} and ρ_{metal} are the density of the oxide phase and metal phase, respectively; a_0 and a_1 are the positions of the Gibbs dividing surfaces; w is the thickness of the interface. Fitting $\rho(a)$ to Eq. (3) yields the location of the Gibbs dividing surfaces, as well as the density of each phase. The metal and oxide phases are defined by $a_i > 2w$ and $a_i < -2w$, respectively. We count the number of atoms of metal and oxide phases of each frame. A long trajectory after the system is equilibrated and used to determine the average concentrations in each phase and associated standard deviations. For more details, the reader is referred to (Deng and Du, 2023; Sega et al., 2018; Willard and Chandler, 2010; Xiao and Stixrude, 2018).

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143 **3.** Results and discussion

144 3.1. Benchmarks of the Machine Learning Potential

145 We compare the energies, atomic forces, and stresses from the MLP to those from DFT calculations for

146 15078 configurations that are not included in the training set (Figure S2). The root-mean-square errors of 147 the energies, atomic forces, and stresses are $6.34 \text{ meV/atom}^{-1}$, 0.27 eV/Å^{-1} , and 0.48 GPa, respectively.

148 We perform two additional tests to further examine the reliability of the MLP. First, we perform MD 149 simulations with supercells of B1 MgO solid, MgO liquid, and a Mg-Fe-O liquid mixture, respectively. 150 These supercells are larger than the training configurations. The root-mean-square error of energy 151 prediction by the MLP with respect to the DFT calculations is similar to the error in the testing sets (Figure 152 S3). This verification test further proved the accuracy of energy prediction and also demonstrated the 153 transferability of the MLP to structures larger than the train/test sets. Second, we calculate the melting point 154 of B1 MgO at 140 GPa using the solid-liquid two-phase coexistence method with a supercell of 432 atoms. 155 For both DFT and MLP, the system crystalizes at 7700 K and melts at 7800 K, suggesting a melting point 156 of 7750±50 K at 140 GPa and further validating the robustness of the MLP. The melting temperature is also 157 consistent with previous studies (Alfè, 2005; Du and Lee, 2014).

158 **3.2.** System convergence of the exsolution simulation

159 The robust MLP of Mg-Fe-O system allows for large-scale exsolution simulations. We first examine the 160 convergence of Fe liquid composition with respect to the simulation cell size by performing exsolution 161 simulations at 5000 K and 140 GPa with five Mg-Fe-O liquid mixtures, where ratios of Mg, O and Fe atoms 162 are fixed as 2:2:3, i.e., Mg₆₄O₆₄Fe₉₆, Mg₅₁₂O₅₁₂Fe₇₆₈, Mg₁₇₂₈O₁₇₂₈Fe₂₅₉₂, Mg₂₃₀₄O₂₃₀₄Fe₃₄₅₆, Mg₃₁₃₆O₃₁₃₆Fe₄₇₀₄. 163 For all simulation, the system quickly demixes to form MgO-rich and Fe-rich region, and subsequently, MgO-rich region spontaneously crystallizes to form ferropericlase while metallic phase remains liquid. The 164 resulting atomic fraction of Mg, O in the metallic phase converges when system size reaches 2000 atoms 165 166 (Figure S4). Large systems also yield better statistics and thus the smaller uncertainties in the atomic 167 fraction. Based on this test, all the partitioning results reported here are derived from simulations performed 168 with systems of more than 2000 atoms to ensure convergence and robust statistics.

169 **3.3 Exsolution process**

170 In all simulations considered, exsolution spontaneously occurs within a few picoseconds at 4000 K to a few 171 nanoseconds at 5500 K. Exsolutions are all solid ferropericlase with small amounts of FeO. The interfaces between exsolution and Fe liquid are typically irregular as they form spontaneously without interference. 172 173 Taking the exsolution simulation of Mg₂₀₈₈Fe₃₄₅₆O₂₅₂₀ liquid at 140 GPa and 5500 K as an example (Figure 174 1; Supplementary movie 1). It starts with a homogeneous liquid (Figure 1a), and quickly demixes to form 175 patches of MgO-rich liquid and Fe-rich liquid with a continuous drop of potential energy. Within around 176 250 ps, MgO-rich patches and Fe-rich patches conglomerate, respectively, dividing the whole cell into two 177 regions: one enriched in MgO and the other Fe. MgO-rich region remains liquid for another 750 ps until a 178 sudden crystallization occurs to form ferropericlase (Figure 1b). The crystallization is a rapid process 179 accompanied by a significant drop in potential energy. Quickly after ferropericlase crystallizes, the potential 180 energy plateaus. The element exchange between ferropericlase and residual Fe liquid continues within the 181 interface region. We analyze the trajectories at this stage, calculate the Gibbs dividing surface, and 182 determine the average composition of each phase for the last 100 ps. The chemical compositions of both 183 phases are shown in Figure 1c. The metallic liquid is oxygen rich and magnesium poor. The exsolved ferropericlase is of B1 structure and is nearly stochiometric (Mg_{0.974}Fe_{0.026})O. Similar analyses have been 184 185 applied to all other exsolution simulations, and the compositions of simulation products are summarized in 186 Table S1.





Figure 1. Molecular dynamics simulation of spontaneous ferropericlase exsolution from a homogeneous Mg₂₀₈₈Fe₃₄₅₆O₂₅₂₀ liquid at 140 GPa and 5500 K (NPT ensemble). (a) The initial configuration at 1 fs with a homogeneous distribution of Mg (green), Fe (yellow), and O (red) atoms. (b) The final configuration at 1.5 ns. Dark red planes are the Gibbs diving surfaces that separates the whole systems into crystalline ferropericlase, interface, and metallic liquid. The cell dimension is 50.9 Å × 39.9 Å × 35.3 Å initially (a) and becomes 47.9 Å × 37.6 Å × 33.3 Å at the end of the simulation (b). (c) Evolution of number of atoms in liquid (liq) and solid exsolution (sol) in the last 100 ps. (d) Evolution of potential energy. Energy drops

195 with the separation of ferropericlase and metallic liquid. The sudden drop of internal energy corresponds to 196 the crystallization of ferropericlase.

197 3.4 Element partitioning

We further analyze the element partitioning between the exsolved ferropericlase and Fe liquid considering 198 two dissociation reactions: MgO^{ox} = Mg^{met} + O^{met} and FeO^{ox} = Fe^{met} + O^{met}, where superscripts ox and met 199 indicate oxide and metal, respectively. We also consider Mg exchange reaction with $MgO^{ox} + Fe^{met} = FeO^{ox}$ 200 + Mg^{met}, but the fit is poor, as also reported in other studies (Badro et al., 2018; Liu et al., 2019). The 201 exchange coefficients for Mg ($K_D^{Mg} = X_{Mg}^{met} X_0^{met} / X_{Mg}^{ox}$) and O ($K_D^0 = X_{Fe}^{met} X_0^{ox} / X_{Fe0}^{ox}$) are summarized in 202 Figure 2, where X_i^k is the molar fraction of element *i* in phase *k*. Both K_D^{Mg} and K_D^O increase with 203 temperature and oxygen concentration in the metallic liquid. K_D^{Mg} and K_D^{O} are fitted simultaneously to a 204 205 standard thermodynamic model with the non-ideality described by the epsilon formalism of (Ma, 2001). 206 The phase relation between ferropericlase and Fe liquid has been studied mostly at low pressures and low 207 temperatures (Asahara et al., 2007; Frost et al., 2010; Ozawa et al., 2008). Unfortunately, Mg contents in metallic melts were not reported and only K_D^0 were reported in these studies. Thus, we only include K_D^0 of 208 these experiments in the fitting (Texts S2, S3; Tables S2). 209

Our calculated K_D^{Mg} is slightly larger than that reported by a recent *ab initio* calculation (Wilson et al., 2023) 210 where the pure B1 MgO is assumed as the exsolved phase, while our exsolution simulations show that 211 212 precipitates contain small amounts of FeO (Figure 1, Table S1). The incorporation of FeO in the exsolved phase likely changes the free energy of the system, leading to different in K_D^{Mg} . Wahl and Militzer (2015) 213 also perform ab initio simulations on the Mg-Fe-O system but focus on high temperatures close to the 214 solvus closure and do not report Mg partitioning results at the conditions overlapping this study, which 215 precludes a direct comparison. Compared with the previously determined K_D^{Mg} between Fe liquid and 216 silicate melt (Badro et al., 2018; Du et al., 2019; Liu et al., 2019), K_D^{Mg} between Fe liquid and solid 217 ferropericlase shows similar temperature dependence but is overall approximately one order of magnitude 218 lower (Figure 2a), indicating a low Mg content in Fe liquid when equilibrated with ferropericlase. This is 219 220 expected as MgO preferentially enters ferropericlase when silicate melt crystalizes (Boukaré et al., 2015).

221 Oxygen partitioning between ferropericlase and liquid Fe is strongly controlled by temperature, in 222 agreement with previous experiments (Asahara et al., 2007; Frost et al., 2010; Ozawa et al., 2008) and calculations (Davies et al., 2018). K_D^0 between Fe liquid and silicate melt derived by (Liu et al., 2019) 223 generally aligns with K_D^0 between Fe liquid and solid ferropericlase, especially at high temperatures. Our 224 K_D^0 can be well fitted with previous experimental data to a unified thermodynamic model (Asahara et al., 225 2007; Ozawa et al., 2008), except for the four data points reported by (Frost et al., 2010) (Text S3; Table 226 S3). At around 30-70 GPa and with similar oxygen contents in the liquid Fe, K_D^0 of (Frost et al., 2010) are 227 around half log unit higher than those of (Ozawa et al., 2008) and our extrapolated results. The source of 228 this discrepancy is unknown but may arise from the carbon contamination. K_D^0 reported by an early DFT 229 230 calculation (Davies et al., 2018) is around 0.3-0.6 log unit higher than those of (Ozawa et al., 2008) and our results at similar conditions. We note that Davies et al. (2018) calculated the chemical potential of FeO for 231 232 defect-free (Mg,Fe)O. Yet, both our simulations and previous studies (Karki and Khanduja, 2006; Van 233 Orman et al., 2003) support the existence of defects in ferropericlase at high temperatures, which may lower the free energy of the host mineral and enrich FeO in ferropericlase, leading to a reduced K_D^0 . 234



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236 Figure 2. Mg (a) and O (b) exchange coefficients as a function of oxygen content in the iron (X_0) and 237 temperature at 140 GPa. Solid circles are the results from this study, and solid lines are the best-fit curves 238 (Supplementary Texts S2, S3). The color of curves and symbols represents the value of X_0 . Previous 239 calculations and experiments are also shown for comparison. (a) W23 denotes the DFT calculation result 240 by (Wilson et al., 2023) (upward triangle). B18 (dotted line), L19 (dashed line), and D19 (dotted-dashed 241 line) represents the Mg exchange coefficient between silicate melt and Fe liquid calibrated by (Badro et al., 242 2018), (Liu et al., 2019), and (Du et al., 2019), respectively. (b) Experimental studies include (Ozawa et al., 2008) (O08, downward triangle), (Asahara et al., 2007) (A07, diamond), (Frost et al., 2010) (F10, 243 244 upward triangle). DFT study includes (Davies et al., 2018) (D18, square). All previous results are 245 normalized to 140 GPa for a direct comparison using the best-fit pressure dependence, $\log_{10} K_D^0(140 \text{ GPa}) = \log_{10} K_D^0(\text{experiment}) - \frac{c_0(140-P)}{T}$, where P/T are experimental/calculation 246 pressure/temperature, and c_0 is a fitted constant (Table S3). L19 (dashed line) indicates the O exchange 247 248 coefficient of silicate-melt calibrated by (Liu et al., 2019). Uncertainties of the exchange coefficients of this 249 study are roughly represented by the symbol size.

251 4. Exsolution rate and geodynamo

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253 Earth's accretion and differentiation in its early history likely resulted in a core much hotter than it is today. 254 The precipitation of light elements due to the secular cooling of the core may have provided a vital energy 255 source to drive the geodynamo. The energetics of the exsolution-powered dynamo hinge on the cooling rate 256 and the exsolution rate. Here, we adopt a core thermal evolution model proposed by O'Rourke et al. (2017) 257 where the CMB temperature (T_{CMB}) drops from around 5000 K to around 4100 K over the first ~3.8 billion years (Gyr) with a cooling rate of ~230 K Gyr⁻¹. Given this thermal history of the core, the phase of 258 259 exsolution and the associated exsolution rate can be further determined using the element partitioning 260 models, along with knowledge of the initial core composition. All previous modeling of Mg exsolution 261 from the core assume that MgO exsolve as a component of silicate melts. However, our simulations show that MgO should exsolve as a component of crystalline ferropericlase, at least when light elements other 262 than Mg and O are absent (Badro et al., 2018; Du et al., 2019; Liu et al., 2019; Mittal et al., 2020). Here, 263 264 we first examine the Mg exsolution and its potential to drive the early geodynamo for an Mg- and O-bearing 265 core, and then we discuss the effects of additional light elements.

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To model Mg exsolution from a core fluid with only Mg and O as light elements, we first determine the saturation conditions under which Mg precipitates. Previous N-body simulations and metal-silicate equilibrium experiments suggest that the Earth's core following its formation may contain 1.6-5 wt% O 270 (Fischer et al., 2017; Liu et al., 2019; Rubie et al., 2015). The corresponding saturation magnesium concentration in the core is 0.04-0.19 wt% at 140 GPa, as determined using the K_D^{Mg} between metal and 271 ferropericlase, which is significantly lower than that determined by K_D^{Mg} between metal and silicate melt 272 (Liu et al., 2019) (Figure 3a). This difference is expected, as the former K_D^{Mg} value is about one order of 273 274 magnitude smaller than the latter (Figure 2a). Hence, our work implies that a substantial amount of Mg may 275 have already been exsolved by the time the core cools to a $T_{\rm CMB}$ of 5000 K. Further cooling reduces the Mg 276 solubility in the core, with concentrations approaching 0.02-0.003 wt% at a $T_{\rm CMB}$ of 4000 K. This suggests a diminishingly small amount of Mg in the present-day outer core. We use these saturation magnesium 277 278 conditions as the initial core composition in our exsolution modeling.

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280 Despite the contrasting Mg solubilities in the core, the compositions of the exsolutions are similar and 281 exhibit a comparable trend with temperature. Specifically, the exsolved phase in both models becomes 282 increasingly FeO-rich with cooling. At 4000 K, the exsolution contains up to 20 wt% FeO (Figure 3b). 283 Throughout the thermal history, T_{CMB} is lower than the solidus of exsolved ferropericlase (Deng et al., 2019), 284 indicating that exsolutions remain solid.

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The resulting exsolution rates decrease with temperature, with the values dropping from $1.4-5.6 \times 10^{-6} \text{ K}^{-1}$ 286 at 5000 K to 0.2-1.0 $\times 10^{-6}$ K⁻¹ at 4000 K. Exsolution rates of ferropericlase are approximately one order of 287 288 magnitude smaller than those predicted for silicate melt exsolution (Figure 3c). Exsolutions are depleted in 289 iron and enriched in Mg. As a result, they are lighter than the outer core fluid and thus provide the buoyancy 290 flux that may sustain an exsolution-driven dynamo (O'Rourke and Stevenson, 2016). Converting the 291 exsolution rate to the magnetic field intensity is model dependent, however. The upper bound of the 292 exsolution rates $(1-5.6 \times 10^{-6} \text{ K}^{-1})$ derived here are similar to the previous reports (Badro et al., 2016; Du et 293 al., 2017). While Du et al. (2019) conclude that this exsolution rate is not sufficient to power the early 294 geodynamo alone, Badro et al. (2018) use a scaling law that relates the exsolution rate to dipolar magnetic field intensity $(B_{\text{surface}}^{\text{dipole}})$ and argue that MgO exsolution can well produce the dipolar magnetic field 295 intensity at Earth's surface consistent with observations. We follow (Badro et al., 2018) to convert the 296 exsolution rate to $B_{\text{surface}}^{\text{dipole}}$ (Figure 3d). The results show that $B_{\text{surface}}^{\text{dipole}}$ generated by the upper bound exsolution rate is broadly consistent with the paleo-intensities records dating back to 3.4 Gyr (Tarduno et 297 298 299 al., 2010), and that generated by the lower bound rate is overall smaller than the observations and thus may 300 not be sufficient (Tarduno et al., 2015). Overall, we find that MgO exsolution alone may be difficult to 301 power the early geodynamo, but it is nevertheless an important energy source. 302

303 While the exact composition of the core remains unknown, it may contain other light elements, such as S, 304 Si, C, and H (Hirose et al., 2021). As the core cools, the solubility of these light elements tends to decrease, 305 leading to their exsolution. For example, in a core composed solely of Si, O, and Fe, the exsolved phase 306 would likely be solid SiO₂ (Hirose et al., 2017; Zhang et al., 2022). The study by Helffrich et al. (2020) on the joint solubility of Mg. O, and Si in liquid Fe suggests that the presence of Si enhances the retention of 307 308 Mg in metal, thereby reducing the extent of MgO exsolution. It is crucial to note, however, that their 309 thermodynamic model is based on data from the silicate melt-Fe system and the SiO₂-Fe system without 310 considering ferropericlase. As a result, in their model, MgO is implicitly treated as a component of liquid 311 rather than as solid ferropericlase. Adding further complexity, instead of precipitating separate MgO and 312 SiO₂ solids, a Mg-Fe-Si-O system may yield exsolutions of MgSiO₃ bridgmanite or post-perovskite. Indeed, bridgmanite and post-perovskite with low iron content are quite refractory, with melting temperatures 313 exceeding the $T_{\rm CMB}$ assumed here and thus may form stable exsolution phases (Deng et al., 2023; Zerr and 314 Boehler, 1993). Whether bridgmanite, post-perovskite, solid SiO₂, B1 MgO, or liquid is the stable 315 316 exsolution phase depends on their free energies and is still open to question. Consequently, a comprehensive 317 re-evaluation of the phase relations in the Mg-Si-O-Fe system and more broadly, in the Mg-Si-O-C-H-S-318 Fe system, which considers exsolutions as solids, is warranted. This study marks a first attempt to

319 demonstrate the significance of solid exsolutions and the substantially different behaviors they exhibit 320 during exsolution.



Figure 3. MgO solubility (a), chemical composition of the exsolution (b), exsolution rate (c), intensity of the dipolar magnetic field at Earth's surface produced by exsolution-driven dynamo (d) based on the element partitioning models from this study with crystalline ferropericlase as the exsolved phase (solid lines) and those from a recent study with silicate melts as the exsolved phase (dashed lines) (Liu et al., 2019), respectively. Red and green denote initial oxygen concentration in the core of 5 wt% and 1.6 wt% at 5000 K, respectively.

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330 5. Conclusion

331 We developed a machine learning potential of *ab initio* quality for Mg-Fe-O system using the iterative 332 training scheme, which enables large-scale atomistic simulations of Mg exsolution processes at 4000-5500 333 K and 140 GPa without any *ad hoc* assumptions regarding the stable exsolution phase. The exsolved phase 334 is solid Fe-poor ferropericlase across all the thermodynamic conditions considered. Using the Gibbs 335 dividing surface method, we analyze simulation trajectories, obtain the chemical composition of exsolved phases and liquid phases, and determine Mg and O exchange coefficients. The results show that partitioning 336 337 of Mg into the exsolved phase is significantly enhanced when compared to scenarios where the exsolved 338 phase is assumed to be liquid, as in previous studies (Badro et al., 2018; Du et al., 2019; Liu et al., 2019; 339 Mittal et al., 2020). The resulting small Mg exchange coefficients suggest a reduced Mg solubility in the

- core. Assuming a reasonable initial core composition with 1.6-5 wt% oxygen, the MgO exsolution rate may
- be insufficient to generate the dipolar magnetic field at the Earth's surface with intensities that align with
- the paleomagnetic record.

Though not the focus of this study, it is noteworthy that our oxygen exchange coefficients are smaller than the previous *ab initio* results, indicating a reduced transport of FeO from ferropericlase into the core fluid (Davies et al., 2018), with implications for the dynamics of long-term core-mantle interaction. Moreover,

- solid exsolution may encapsulate distinctive core-characteristic signatures and transport them into the
- certain regions of the overlaying mantle (Helffrich et al., 2018), offering a valuable window to probe the
- 348 core-mantle interaction (Deng and Du, 2023).

349 Acknowledgments

350 This work was funded by the National Science Foundation under Grant EAR- 2242946. The simulations

- 351 presented in this article were performed on computational resources managed and supported by Princeton
- Research Computing, a consortium of groups including the Princeton Institute for Computational Science
- and Engineering (PICSciE) and the Office of Information Technology's High-Performance Computing
- **354** Center and Visualization Laboratory at Princeton University.

355 Data Availability Statement 356

357 All the data and source codes used in this study are stored at the Open Science Framework 358 (https://osf.io/msrv4/) via DOI 10.17605/OSF.IO/MSRV4 (Deng, 2024). For the software packages used 359 in this study, VASP is a commercial code available at https://www.vasp.at; DeePMD-kit is developed 360 at https://github.com/deepmodeling/deepmd-kit; LAMMPS is developed openly openly at 361 https://github.com/lammps/lammps; PLUMED 2 is developed openly at 362 https://github.com/plumed/plumed2; ASAP is developed openly at https:// github.com/BingqingCheng/ASAP; PYTIM is developed openly at https://github.com/Marcello-363 364 Sega/pytim.

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- 488 489

1 2 3 4 5 6	Large-scale atomistic simulations of magnesium oxide exsolution driven by machine learning potentials: Implications for the early geodynamo Author: Jie Deng							
7	Affiliation:							
8	Department of Geosciences, Princeton University, Princeton, NJ 08544, USA.							
9 10	Email: jie.deng@princeton.edu							
11	Key points (140 character with no abbreviations):							
12	• A machine learning potential of <i>ab initio</i> quality is developed for the Mg-Fe-O system							
13 14 15	 Mg exsolves in the form of crystalline Fe-poor ferropericlase with a small exsolution rate assuming only Mg and O are present in the core MgO exsolution can serve as an important source of buoyant flux to drive the early geodynamo 							
16 17								

18 Abstract (150 words)

19

The precipitation of magnesium oxide (MgO) from the Earth's core has been proposed as a potential energy 20 21 source to power the geodynamo prior to the inner core solidification. Yet, the stable phase and exact amount 22 of MgO exsolution remain elusive. Here we utilize an iterative learning scheme to develop a unified deep 23 learning interatomic potential for the Mg-Fe-O system valid over a wide pressure-temperature range. This 24 potential enables direct, large-scale simulations of MgO exsolution processes at the Earth's core-mantle 25 boundary. Our results suggest that Mg exsolves in the form of crystalline Fe-poor ferropericlase as opposed 26 to a liquid MgO component presumed previously. The solubility of Mg in the core is limited, and the 27 present-day core is nearly Mg-free. The resulting exsolution rate is small yet nonnegligible, suggesting that 28 MgO exsolution can provide a potentially important energy source, although it alone may be difficult to 29 drive an early geodynamo.

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- 32

33 Plain language summary (200 words)

34 The paleomagnetic records suggest that Earth's magnetic field dates back to at least 3.4 billion years ago. 35 Yet, the energy source of this early geodynamo is still puzzling. One popular hypothesis is that buoyant 36 magnesium oxide may exsolve out of the Earth's core as the core cools, releasing gravitational potential 37 energy to drive the core convection and power the early geodynamo. However, the amount of MgO 38 exsolved is uncertain due to experimental and computational challenges. Here, for the first time, we directly 39 simulate the MgO exsolution processes using large-scale molecular dynamics simulations, made possible 40 by interatomic potentials built upon machine learning methods. The results show that MgO exsolves as a 41 component of a crystalline ferropericlase, in contrast to early studies which generally assume that MgO 42 exsolved as a component of silicate melts. We find that MgO solubility in the core is low. The exsolution 43 rate is small and MgO alone may be insufficient to sustain a long-lasting magnetic field at the Earth's 44 surface in its early history.

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- 46

47

50 1. Introduction

51

52 Chemical buoyancy due to the crystallization of the inner core is believed to have supplied energy to power 53 the geodynamo in the last 0.5-1 billion years (Nimmo, 2015). Paleomagnetic records suggest the existence 54 of a very early (3.4 Ga) magnetic field in the Earth's history prior to the inner core crystallization (Tarduno 55 et al., 2010). The energy source of this early geodynamo is enigmatic. Radiogenic heat production in the 56 core may not be sufficient to sustain an early dynamo (Frost et al., 2022). The basal magma ocean may be 57 electrically conductive (Stixrude et al., 2020), but the scale and longevity of a convective basal magma 58 ocean are uncertain.

59

Recent studies propose that exsolution of oxides from the core upon cooling, such as MgO (O'Rourke and
Stevenson, 2016) or SiO₂ (Hirose et al., 2017), may be a viable mechanism to power an early dynamo.
Experimental studies on metal-silicate partitioning suggest that the solubility of Mg is highly sensitive to
temperature (Badro et al., 2016; Du et al., 2017). The high-temperature equilibration between the metallic
and silicate melts during the core formation process may result in a few wt% of MgO dissolved in the core.
Upon cooling, Mg is expected to precipitate out of the core as its solubility drops. However, the efficiency
of this mechanism, especially for MgO oxide, remains controversial (Badro et al., 2016; Du et al., 2017).

67

68 The precipitation rate of MgO has been widely estimated using Mg partitioning behaviors in the metal-69 silicate system (Badro et al., 2018; Du et al., 2019; Liu et al., 2019). This estimation, strictly speaking, is 70 unjustified. In contrast to the core formation process, where metallic and silicate melts equilibrate, the 71 precipitation process involves the equilibration between the metallic melt and exsolution, where the exact 72 phase and chemistry of exsolution depend on bulk compositions and thermodynamic conditions (Helffrich 73 et al., 2020). Previous estimates, however, implicitly assume that exsolved MgO is a component of liquid 74 silicate (Badro et al., 2018; Du et al., 2019; Liu et al., 2019). This assumption is questionable, as MgO is 75 more refractory than SiO₂ which may exsolve out of the core in solid-sate (Hirose et al., 2017). Therefore, 76 a careful examination of the Mg exsolution process is necessary.

77

In this study, we combine enhanced sampling, feature selection, and deep learning to develop a unified
machine learning potential (MLP) for the Mg-Fe-O system. This MLP is used to perform large-scale
molecular dynamics simulations to study the exsolution of Mg from core fluids. Unlike previous
computational studies based on free energy calculations (Davies et al., 2018; Wahl and Militzer, 2015;
Wilson et al., 2023), this method does not prescribe the state of the exsolved phase (Sun et al., 2022). The
results inform the stable state of MgO precipitation, Mg and O partitioning between core fluid and
exsolution, and the efficiency of MgO exsolution in powering an early geodynamo.

85

86 2. Methodology

87 2.1. Development of Machine Learning Potential

88 A machine learning potential (MLP) is a non-parametric model that approximates the Born-Oppenheimer 89 potential energy surface. We follow the same approaches outlined in our previous work on Mg-Si-O (Deng 90 et al., 2023) and Mg-Si-O-H (Peng and Deng, 2024) where details of the machine learning process can be 91 found. To briefly summarize our approach, the MLP is trained on a set of configurations drawn from 92 multithermal and multibaric (MTMP) simulations (Piaggi and Parrinello, 2019), which are used to 93 efficiently sample the multi-phase configuration space. We use the structure factor of B1 MgO as the 94 collective variable to drive the sampling, and an iterative learning scheme as described by (Deng et al., 95 2023) to efficiently select distinct samples from molecular dynamics trajectories. High-accuracy ab initio 96 calculations are performed on the selected sample configurations to derive the corresponding energies,

97 atomic forces, and stresses. The DeePMD approach is employed to train an MLP which takes a 98 configuration (a structure of a given atomic arrangement) and predicts its energy, atomic forces, and stresses without iterating through the time-consuming self-consistent field calculation (Wang et al., 2018; Zhang et 99 100 al., 2018). The details of DeePMD approach and density functional theory (DFT) calculations can be found 101 at Supplementary Information (Text S1, Figure S1). Our MLP explores a wide compositional space, trained on Mg-Fe-O systems of varying Mg:Fe:O ratios, including the pure endmembers, Fe and MgO, as well as 102 103 intermediate compositions denoted by $(MgO)_aFe_bO_c$, where a=0-64, b = 0-64, c = 0-16 with 2a+b \geq 64. The 104 final training set consists of 4466 configurations generated at pressure up to 200 GPa and temperature up

105 to 8000 K.

106 2.2. Two-phase molecular dynamics simulation

107 Two-phase simulations are performed on a pure MgO system to determine the melting point of B1 MgO. 108 Alfè (2005) found that systems of 432 atoms are sufficient to yield converged melting points as those larger systems. Here, supercells of 432 atoms are constructed and then relaxed for 1000 steps at desired pressure 109 and temperature conditions in the NPT ensemble. The relaxed cell is then used to perform NVT simulations 110 111 at high temperatures far exceeding the melting temperatures, with the atoms of half the cell fixed and the 112 force applied to these atoms set to 0. The resulting structure is half-molten and half-crystalline. We relax 113 this structure again at the target pressure and temperature for 1000 steps to obtain the initial configuration for two-phase simulations. Simulations on the two-phase supercell of solid-liquid coexistence were then 114 performed. If the whole cell is molten (or crystallized) at the end, the simulation temperature is above (or 115 116 below) the melting point. The state of the system can be determined by analyzing the radial distribution

117 functions, allowing us to pinpoint the upper and lower bounds of the melting point.

118 2.3 Exsolution simulation

119 We construct systems of various Mg:Fe:O ratios by substituting/removing Mg and/or O atoms of supercells

120 of B1 MgO. Initial configurations are melted at 8000 K and 140 GPa under the NPT ensemble for ~10 ps.

121 We inspect trajectories and radial distribution functions to ensure systems are fully molten and well relaxed.

122 The resulting configurations are further used to perform simulations at 140 GPa and target temperatures

123 under the NPT ensemble for up to several nanoseconds to simulate the exsolution process.

124 2.4 Gibbs dividing surface

To determine the composition of the two coexisting phases, for every frame we locate the Gibbs dividing surface (GDS) that separates the whole cell into an oxide region, a metallic region, and two interfaces in between (Sega et al., 2018; Willard and Chandler, 2010). For every snapshot, we calculate the coarsegrained instantaneous density field at point **r** by

128 grained instantaneous density field at point \mathbf{r} by

$$\rho(\mathbf{r}) = \sum_{i} (2\pi)^{-\frac{3}{2}} \exp\left(-\frac{|\mathbf{r} - \mathbf{r}_i|^2}{2\sigma^2}\right),\tag{1}$$

where \mathbf{r}_i is the position of the *i*th atom; σ is the coarse-graining length, and is set as 2.5 Å here (Willard and Chandler, 2010). The instantaneous surface $\mathbf{s}(t)$ is defined as a contour surface of the instantaneous

- 150 and Chandler, 2010). The instantaneous surface s(t) is defined as a contour surface s(t) is defined as a contour surface is
- 131 coarse-grained density. The proximity of *i*th atom to this surface is

$$a_i = \{ [\boldsymbol{s}(t) - \boldsymbol{r}_i(t)] \cdot \boldsymbol{n}(t) \} |_{\boldsymbol{s}(t) = \boldsymbol{s}_i^*(t)},$$
(2)

- 132 where n(t) is the surface normal in the direction of the density gradient at that point. This instantaneous
- density field is then projected onto each atom and associated with the corresponding proximity. We find
- 134 that $\rho(a)$ follows the expected form

$$\rho(a) = \rho_{oxide} + \frac{1}{2}(\rho_{metal} - \rho_{oxide}) \left[\tanh\left(\frac{a-a0}{w}\right) - \tanh\left(\frac{a-a1}{w}\right) \right], \tag{3}$$

where ρ_{oxide} and ρ_{metal} are the density of the oxide phase and metal phase, respectively; a_0 and a_1 are the positions of the Gibbs dividing surfaces; w is the thickness of the interface. Fitting $\rho(a)$ to Eq. (3) yields the location of the Gibbs dividing surfaces, as well as the density of each phase. The metal and oxide phases are defined by $a_i > 2w$ and $a_i < -2w$, respectively. We count the number of atoms of metal and oxide phases of each frame. A long trajectory after the system is equilibrated and used to determine the average concentrations in each phase and associated standard deviations. For more details, the reader is referred to (Deng and Du, 2023; Sega et al., 2018; Willard and Chandler, 2010; Xiao and Stixrude, 2018).

142

143 **3.** Results and discussion

144 3.1. Benchmarks of the Machine Learning Potential

145 We compare the energies, atomic forces, and stresses from the MLP to those from DFT calculations for

146 15078 configurations that are not included in the training set (Figure S2). The root-mean-square errors of 147 the energies, atomic forces, and stresses are $6.34 \text{ meV/atom}^{-1}$, 0.27 eV/Å^{-1} , and 0.48 GPa, respectively.

148 We perform two additional tests to further examine the reliability of the MLP. First, we perform MD 149 simulations with supercells of B1 MgO solid, MgO liquid, and a Mg-Fe-O liquid mixture, respectively. 150 These supercells are larger than the training configurations. The root-mean-square error of energy 151 prediction by the MLP with respect to the DFT calculations is similar to the error in the testing sets (Figure 152 S3). This verification test further proved the accuracy of energy prediction and also demonstrated the 153 transferability of the MLP to structures larger than the train/test sets. Second, we calculate the melting point 154 of B1 MgO at 140 GPa using the solid-liquid two-phase coexistence method with a supercell of 432 atoms. 155 For both DFT and MLP, the system crystalizes at 7700 K and melts at 7800 K, suggesting a melting point 156 of 7750±50 K at 140 GPa and further validating the robustness of the MLP. The melting temperature is also 157 consistent with previous studies (Alfè, 2005; Du and Lee, 2014).

158 **3.2.** System convergence of the exsolution simulation

159 The robust MLP of Mg-Fe-O system allows for large-scale exsolution simulations. We first examine the 160 convergence of Fe liquid composition with respect to the simulation cell size by performing exsolution 161 simulations at 5000 K and 140 GPa with five Mg-Fe-O liquid mixtures, where ratios of Mg, O and Fe atoms 162 are fixed as 2:2:3, i.e., Mg₆₄O₆₄Fe₉₆, Mg₅₁₂O₅₁₂Fe₇₆₈, Mg₁₇₂₈O₁₇₂₈Fe₂₅₉₂, Mg₂₃₀₄O₂₃₀₄Fe₃₄₅₆, Mg₃₁₃₆O₃₁₃₆Fe₄₇₀₄. 163 For all simulation, the system quickly demixes to form MgO-rich and Fe-rich region, and subsequently, MgO-rich region spontaneously crystallizes to form ferropericlase while metallic phase remains liquid. The 164 resulting atomic fraction of Mg, O in the metallic phase converges when system size reaches 2000 atoms 165 166 (Figure S4). Large systems also yield better statistics and thus the smaller uncertainties in the atomic 167 fraction. Based on this test, all the partitioning results reported here are derived from simulations performed 168 with systems of more than 2000 atoms to ensure convergence and robust statistics.

169 **3.3 Exsolution process**

170 In all simulations considered, exsolution spontaneously occurs within a few picoseconds at 4000 K to a few 171 nanoseconds at 5500 K. Exsolutions are all solid ferropericlase with small amounts of FeO. The interfaces between exsolution and Fe liquid are typically irregular as they form spontaneously without interference. 172 173 Taking the exsolution simulation of Mg₂₀₈₈Fe₃₄₅₆O₂₅₂₀ liquid at 140 GPa and 5500 K as an example (Figure 174 1; Supplementary movie 1). It starts with a homogeneous liquid (Figure 1a), and quickly demixes to form 175 patches of MgO-rich liquid and Fe-rich liquid with a continuous drop of potential energy. Within around 176 250 ps, MgO-rich patches and Fe-rich patches conglomerate, respectively, dividing the whole cell into two 177 regions: one enriched in MgO and the other Fe. MgO-rich region remains liquid for another 750 ps until a 178 sudden crystallization occurs to form ferropericlase (Figure 1b). The crystallization is a rapid process 179 accompanied by a significant drop in potential energy. Quickly after ferropericlase crystallizes, the potential 180 energy plateaus. The element exchange between ferropericlase and residual Fe liquid continues within the 181 interface region. We analyze the trajectories at this stage, calculate the Gibbs dividing surface, and 182 determine the average composition of each phase for the last 100 ps. The chemical compositions of both 183 phases are shown in Figure 1c. The metallic liquid is oxygen rich and magnesium poor. The exsolved ferropericlase is of B1 structure and is nearly stochiometric (Mg_{0.974}Fe_{0.026})O. Similar analyses have been 184 185 applied to all other exsolution simulations, and the compositions of simulation products are summarized in 186 Table S1.





Figure 1. Molecular dynamics simulation of spontaneous ferropericlase exsolution from a homogeneous Mg₂₀₈₈Fe₃₄₅₆O₂₅₂₀ liquid at 140 GPa and 5500 K (NPT ensemble). (a) The initial configuration at 1 fs with a homogeneous distribution of Mg (green), Fe (yellow), and O (red) atoms. (b) The final configuration at 1.5 ns. Dark red planes are the Gibbs diving surfaces that separates the whole systems into crystalline ferropericlase, interface, and metallic liquid. The cell dimension is 50.9 Å × 39.9 Å × 35.3 Å initially (a) and becomes 47.9 Å × 37.6 Å × 33.3 Å at the end of the simulation (b). (c) Evolution of number of atoms in liquid (liq) and solid exsolution (sol) in the last 100 ps. (d) Evolution of potential energy. Energy drops

195 with the separation of ferropericlase and metallic liquid. The sudden drop of internal energy corresponds to 196 the crystallization of ferropericlase.

197 3.4 Element partitioning

We further analyze the element partitioning between the exsolved ferropericlase and Fe liquid considering 198 two dissociation reactions: MgO^{ox} = Mg^{met} + O^{met} and FeO^{ox} = Fe^{met} + O^{met}, where superscripts ox and met 199 indicate oxide and metal, respectively. We also consider Mg exchange reaction with $MgO^{ox} + Fe^{met} = FeO^{ox}$ 200 + Mg^{met}, but the fit is poor, as also reported in other studies (Badro et al., 2018; Liu et al., 2019). The 201 exchange coefficients for Mg ($K_D^{Mg} = X_{Mg}^{met} X_0^{met} / X_{Mg}^{ox}$) and O ($K_D^0 = X_{Fe}^{met} X_0^{ox} / X_{Fe0}^{ox}$) are summarized in 202 Figure 2, where X_i^k is the molar fraction of element *i* in phase *k*. Both K_D^{Mg} and K_D^O increase with 203 temperature and oxygen concentration in the metallic liquid. K_D^{Mg} and K_D^{O} are fitted simultaneously to a 204 205 standard thermodynamic model with the non-ideality described by the epsilon formalism of (Ma, 2001). 206 The phase relation between ferropericlase and Fe liquid has been studied mostly at low pressures and low 207 temperatures (Asahara et al., 2007; Frost et al., 2010; Ozawa et al., 2008). Unfortunately, Mg contents in metallic melts were not reported and only K_D^0 were reported in these studies. Thus, we only include K_D^0 of 208 these experiments in the fitting (Texts S2, S3; Tables S2). 209

Our calculated K_D^{Mg} is slightly larger than that reported by a recent *ab initio* calculation (Wilson et al., 2023) 210 where the pure B1 MgO is assumed as the exsolved phase, while our exsolution simulations show that 211 212 precipitates contain small amounts of FeO (Figure 1, Table S1). The incorporation of FeO in the exsolved phase likely changes the free energy of the system, leading to different in K_D^{Mg} . Wahl and Militzer (2015) 213 also perform ab initio simulations on the Mg-Fe-O system but focus on high temperatures close to the 214 solvus closure and do not report Mg partitioning results at the conditions overlapping this study, which 215 precludes a direct comparison. Compared with the previously determined K_D^{Mg} between Fe liquid and 216 silicate melt (Badro et al., 2018; Du et al., 2019; Liu et al., 2019), K_D^{Mg} between Fe liquid and solid 217 ferropericlase shows similar temperature dependence but is overall approximately one order of magnitude 218 lower (Figure 2a), indicating a low Mg content in Fe liquid when equilibrated with ferropericlase. This is 219 220 expected as MgO preferentially enters ferropericlase when silicate melt crystalizes (Boukaré et al., 2015).

221 Oxygen partitioning between ferropericlase and liquid Fe is strongly controlled by temperature, in 222 agreement with previous experiments (Asahara et al., 2007; Frost et al., 2010; Ozawa et al., 2008) and calculations (Davies et al., 2018). K_D^0 between Fe liquid and silicate melt derived by (Liu et al., 2019) 223 generally aligns with K_D^0 between Fe liquid and solid ferropericlase, especially at high temperatures. Our 224 K_D^0 can be well fitted with previous experimental data to a unified thermodynamic model (Asahara et al., 225 2007; Ozawa et al., 2008), except for the four data points reported by (Frost et al., 2010) (Text S3; Table 226 S3). At around 30-70 GPa and with similar oxygen contents in the liquid Fe, K_D^0 of (Frost et al., 2010) are 227 around half log unit higher than those of (Ozawa et al., 2008) and our extrapolated results. The source of 228 this discrepancy is unknown but may arise from the carbon contamination. K_D^0 reported by an early DFT 229 230 calculation (Davies et al., 2018) is around 0.3-0.6 log unit higher than those of (Ozawa et al., 2008) and our results at similar conditions. We note that Davies et al. (2018) calculated the chemical potential of FeO for 231 232 defect-free (Mg,Fe)O. Yet, both our simulations and previous studies (Karki and Khanduja, 2006; Van 233 Orman et al., 2003) support the existence of defects in ferropericlase at high temperatures, which may lower the free energy of the host mineral and enrich FeO in ferropericlase, leading to a reduced K_D^0 . 234



235

236 Figure 2. Mg (a) and O (b) exchange coefficients as a function of oxygen content in the iron (X_0) and 237 temperature at 140 GPa. Solid circles are the results from this study, and solid lines are the best-fit curves 238 (Supplementary Texts S2, S3). The color of curves and symbols represents the value of X_0 . Previous 239 calculations and experiments are also shown for comparison. (a) W23 denotes the DFT calculation result 240 by (Wilson et al., 2023) (upward triangle). B18 (dotted line), L19 (dashed line), and D19 (dotted-dashed 241 line) represents the Mg exchange coefficient between silicate melt and Fe liquid calibrated by (Badro et al., 242 2018), (Liu et al., 2019), and (Du et al., 2019), respectively. (b) Experimental studies include (Ozawa et al., 2008) (O08, downward triangle), (Asahara et al., 2007) (A07, diamond), (Frost et al., 2010) (F10, 243 244 upward triangle). DFT study includes (Davies et al., 2018) (D18, square). All previous results are 245 normalized to 140 GPa for a direct comparison using the best-fit pressure dependence, $\log_{10} K_D^0(140 \text{ GPa}) = \log_{10} K_D^0(\text{experiment}) - \frac{c_0(140-P)}{T}$, where P/T are experimental/calculation 246 pressure/temperature, and c_0 is a fitted constant (Table S3). L19 (dashed line) indicates the O exchange 247 248 coefficient of silicate-melt calibrated by (Liu et al., 2019). Uncertainties of the exchange coefficients of this 249 study are roughly represented by the symbol size.

251 4. Exsolution rate and geodynamo

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253 Earth's accretion and differentiation in its early history likely resulted in a core much hotter than it is today. 254 The precipitation of light elements due to the secular cooling of the core may have provided a vital energy 255 source to drive the geodynamo. The energetics of the exsolution-powered dynamo hinge on the cooling rate 256 and the exsolution rate. Here, we adopt a core thermal evolution model proposed by O'Rourke et al. (2017) 257 where the CMB temperature (T_{CMB}) drops from around 5000 K to around 4100 K over the first ~3.8 billion years (Gyr) with a cooling rate of ~230 K Gyr⁻¹. Given this thermal history of the core, the phase of 258 259 exsolution and the associated exsolution rate can be further determined using the element partitioning 260 models, along with knowledge of the initial core composition. All previous modeling of Mg exsolution 261 from the core assume that MgO exsolve as a component of silicate melts. However, our simulations show that MgO should exsolve as a component of crystalline ferropericlase, at least when light elements other 262 than Mg and O are absent (Badro et al., 2018; Du et al., 2019; Liu et al., 2019; Mittal et al., 2020). Here, 263 264 we first examine the Mg exsolution and its potential to drive the early geodynamo for an Mg- and O-bearing 265 core, and then we discuss the effects of additional light elements.

266

To model Mg exsolution from a core fluid with only Mg and O as light elements, we first determine the saturation conditions under which Mg precipitates. Previous N-body simulations and metal-silicate equilibrium experiments suggest that the Earth's core following its formation may contain 1.6-5 wt% O 270 (Fischer et al., 2017; Liu et al., 2019; Rubie et al., 2015). The corresponding saturation magnesium concentration in the core is 0.04-0.19 wt% at 140 GPa, as determined using the K_D^{Mg} between metal and 271 ferropericlase, which is significantly lower than that determined by K_D^{Mg} between metal and silicate melt 272 (Liu et al., 2019) (Figure 3a). This difference is expected, as the former K_D^{Mg} value is about one order of 273 274 magnitude smaller than the latter (Figure 2a). Hence, our work implies that a substantial amount of Mg may 275 have already been exsolved by the time the core cools to a $T_{\rm CMB}$ of 5000 K. Further cooling reduces the Mg 276 solubility in the core, with concentrations approaching 0.02-0.003 wt% at a $T_{\rm CMB}$ of 4000 K. This suggests a diminishingly small amount of Mg in the present-day outer core. We use these saturation magnesium 277 278 conditions as the initial core composition in our exsolution modeling.

279

280 Despite the contrasting Mg solubilities in the core, the compositions of the exsolutions are similar and 281 exhibit a comparable trend with temperature. Specifically, the exsolved phase in both models becomes 282 increasingly FeO-rich with cooling. At 4000 K, the exsolution contains up to 20 wt% FeO (Figure 3b). 283 Throughout the thermal history, T_{CMB} is lower than the solidus of exsolved ferropericlase (Deng et al., 2019), 284 indicating that exsolutions remain solid.

285

The resulting exsolution rates decrease with temperature, with the values dropping from $1.4-5.6 \times 10^{-6} \text{ K}^{-1}$ 286 at 5000 K to 0.2-1.0 $\times 10^{-6}$ K⁻¹ at 4000 K. Exsolution rates of ferropericlase are approximately one order of 287 288 magnitude smaller than those predicted for silicate melt exsolution (Figure 3c). Exsolutions are depleted in 289 iron and enriched in Mg. As a result, they are lighter than the outer core fluid and thus provide the buoyancy 290 flux that may sustain an exsolution-driven dynamo (O'Rourke and Stevenson, 2016). Converting the 291 exsolution rate to the magnetic field intensity is model dependent, however. The upper bound of the 292 exsolution rates $(1-5.6 \times 10^{-6} \text{ K}^{-1})$ derived here are similar to the previous reports (Badro et al., 2016; Du et 293 al., 2017). While Du et al. (2019) conclude that this exsolution rate is not sufficient to power the early 294 geodynamo alone, Badro et al. (2018) use a scaling law that relates the exsolution rate to dipolar magnetic field intensity $(B_{\text{surface}}^{\text{dipole}})$ and argue that MgO exsolution can well produce the dipolar magnetic field 295 intensity at Earth's surface consistent with observations. We follow (Badro et al., 2018) to convert the 296 exsolution rate to $B_{\text{surface}}^{\text{dipole}}$ (Figure 3d). The results show that $B_{\text{surface}}^{\text{dipole}}$ generated by the upper bound exsolution rate is broadly consistent with the paleo-intensities records dating back to 3.4 Gyr (Tarduno et 297 298 299 al., 2010), and that generated by the lower bound rate is overall smaller than the observations and thus may 300 not be sufficient (Tarduno et al., 2015). Overall, we find that MgO exsolution alone may be difficult to 301 power the early geodynamo, but it is nevertheless an important energy source. 302

303 While the exact composition of the core remains unknown, it may contain other light elements, such as S, 304 Si, C, and H (Hirose et al., 2021). As the core cools, the solubility of these light elements tends to decrease, 305 leading to their exsolution. For example, in a core composed solely of Si, O, and Fe, the exsolved phase 306 would likely be solid SiO₂ (Hirose et al., 2017; Zhang et al., 2022). The study by Helffrich et al. (2020) on the joint solubility of Mg. O, and Si in liquid Fe suggests that the presence of Si enhances the retention of 307 308 Mg in metal, thereby reducing the extent of MgO exsolution. It is crucial to note, however, that their 309 thermodynamic model is based on data from the silicate melt-Fe system and the SiO₂-Fe system without 310 considering ferropericlase. As a result, in their model, MgO is implicitly treated as a component of liquid 311 rather than as solid ferropericlase. Adding further complexity, instead of precipitating separate MgO and 312 SiO₂ solids, a Mg-Fe-Si-O system may yield exsolutions of MgSiO₃ bridgmanite or post-perovskite. Indeed, bridgmanite and post-perovskite with low iron content are quite refractory, with melting temperatures 313 exceeding the $T_{\rm CMB}$ assumed here and thus may form stable exsolution phases (Deng et al., 2023; Zerr and 314 Boehler, 1993). Whether bridgmanite, post-perovskite, solid SiO₂, B1 MgO, or liquid is the stable 315 316 exsolution phase depends on their free energies and is still open to question. Consequently, a comprehensive 317 re-evaluation of the phase relations in the Mg-Si-O-Fe system and more broadly, in the Mg-Si-O-C-H-S-318 Fe system, which considers exsolutions as solids, is warranted. This study marks a first attempt to

319 demonstrate the significance of solid exsolutions and the substantially different behaviors they exhibit 320 during exsolution.



Figure 3. MgO solubility (a), chemical composition of the exsolution (b), exsolution rate (c), intensity of the dipolar magnetic field at Earth's surface produced by exsolution-driven dynamo (d) based on the element partitioning models from this study with crystalline ferropericlase as the exsolved phase (solid lines) and those from a recent study with silicate melts as the exsolved phase (dashed lines) (Liu et al., 2019), respectively. Red and green denote initial oxygen concentration in the core of 5 wt% and 1.6 wt% at 5000 K, respectively.

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329

330 5. Conclusion

331 We developed a machine learning potential of *ab initio* quality for Mg-Fe-O system using the iterative 332 training scheme, which enables large-scale atomistic simulations of Mg exsolution processes at 4000-5500 333 K and 140 GPa without any *ad hoc* assumptions regarding the stable exsolution phase. The exsolved phase 334 is solid Fe-poor ferropericlase across all the thermodynamic conditions considered. Using the Gibbs 335 dividing surface method, we analyze simulation trajectories, obtain the chemical composition of exsolved phases and liquid phases, and determine Mg and O exchange coefficients. The results show that partitioning 336 337 of Mg into the exsolved phase is significantly enhanced when compared to scenarios where the exsolved 338 phase is assumed to be liquid, as in previous studies (Badro et al., 2018; Du et al., 2019; Liu et al., 2019; 339 Mittal et al., 2020). The resulting small Mg exchange coefficients suggest a reduced Mg solubility in the

- core. Assuming a reasonable initial core composition with 1.6-5 wt% oxygen, the MgO exsolution rate may
- be insufficient to generate the dipolar magnetic field at the Earth's surface with intensities that align with
- the paleomagnetic record.

Though not the focus of this study, it is noteworthy that our oxygen exchange coefficients are smaller than the previous *ab initio* results, indicating a reduced transport of FeO from ferropericlase into the core fluid (Davies et al., 2018), with implications for the dynamics of long-term core-mantle interaction. Moreover,

- solid exsolution may encapsulate distinctive core-characteristic signatures and transport them into the
- certain regions of the overlaying mantle (Helffrich et al., 2018), offering a valuable window to probe the
- 348 core-mantle interaction (Deng and Du, 2023).

349 Acknowledgments

350 This work was funded by the National Science Foundation under Grant EAR- 2242946. The simulations

- 351 presented in this article were performed on computational resources managed and supported by Princeton
- Research Computing, a consortium of groups including the Princeton Institute for Computational Science
- and Engineering (PICSciE) and the Office of Information Technology's High-Performance Computing
- **354** Center and Visualization Laboratory at Princeton University.

355 Data Availability Statement 356

357 All the data and source codes used in this study are stored at the Open Science Framework 358 (https://osf.io/msrv4/) via DOI 10.17605/OSF.IO/MSRV4 (Deng, 2024). For the software packages used 359 in this study, VASP is a commercial code available at https://www.vasp.at; DeePMD-kit is developed 360 at https://github.com/deepmodeling/deepmd-kit; LAMMPS is developed openly openly at 361 https://github.com/lammps/lammps; PLUMED 2 is developed openly at 362 https://github.com/plumed/plumed2; ASAP is developed openly at https:// github.com/BingqingCheng/ASAP; PYTIM is developed openly at https://github.com/Marcello-363 364 Sega/pytim.

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11 12 13 14 15 16 17	Contents of this file Texts S1, S2, S3 Figures S1, S2, S3, S4 Tables S1, S2
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19 Text S1 Construction of Machine learning potential

20 **1.1. DeePMD Approach**

21 The DeePMD approach adopts an end-to-end strategy (Wang et al., 2018; Zhang et al., 2018) and does not 22 make a priori assumptions about the form of the descriptor but rather uses a deep neural network to 23 determine its form based only on the spatial location, in a suitably defined coordinate frame, of the 24 neighboring atoms. Neural networks are widely used in the development of machine learning potentials 25 because they are, in principle, capable of approximating any continuous function to arbitrary accuracy 26 (Deng and Stixrude, 2021b; Hornik et al., 1989; Lorenz et al., 2004). With DeePMD, one uses a neural 27 network to find the functional form of the descriptor and a second neural network (fitting network) to 28 determine the form of the potential energy surface. The fitting network is composed of three layers with 29 240 nodes in each layer. A cutoff of 6 Å is employed to describe the atomic local environments. The loss 30 function is defined as

$$L(p_{\epsilon}, p_{f}, p_{\xi}) = p_{\epsilon} \Delta \epsilon^{2} + \frac{p_{f}}{3N} \sum_{i} |\Delta F_{i}| + \frac{p_{\xi}}{9} ||\Delta \xi||^{2},$$
(S1)

31 where $p_{\epsilon}, p_f, p_{\xi}$ are tunable prefactors for difference between the MLP prediction and training data. ϵ is

32 the energy per atom; F_i atomic force of atom i; ξ the virial tensor divided by N; N the number of atoms.

33 We adopt the conventional setting of increasing both p_{ϵ} and p_{ξ} from 0.02 to 1 while decreasing p_f from

34 1000 to 1 over the course of training.

35 1.2. *Ab initio* calculations

36 Ab initio calculations were performed using Vienna Ab Initio Simulation Package (VASP) (Kresse and 37 Furthmüller, 1996). We used the projector augmented wave (PAW) method (Kresse and Joubert, 1999) as 38 implemented in VASP (Kresse and Furthmüller, 1996) and PBEsol approximation (Perdew et al., 2008). 39 We use the PBEsol approximation as we have previously found that it yields good agreement with 40 experimental measurements of physical properties of silicates and oxides (Deng and Stixrude, 2021a; 41 Holmström and Stixrude, 2015; Scipioni et al., 2017). The core radii are O: 0.820 Å (2s²2p⁴), Mg: 1.058 Å 42 $(2p^63s^2)$, Fe: 1.164 Å $(3p^64d^74s^1)$. To construct the initial dataset, we perform *ab initio* molecular dynamics 43 (AIMD) simulations with relatively low precision settings: energy cutoff of 500 eV, energy cutoff of 10^{-4} 44 eV, and Gamma-point only k-mesh. AIMD simulations are performed in the NVT ensemble (constant 45 number of atoms, volume, and temperature) using the Nosé-Hoover thermostat (Hoover, 1985) and run for 46 5-20 ps with 1 fs time step. We assume thermal equilibrium between ions and electrons via the Mermin 47 functional (Mermin, 1965).

48

The major focus of this study is the exsolution process at the core-mantle boundary condition. Magnetic fluctuations no longer play a significant role for the liquid iron at this condition (Korell et al., 2019). In addition, (Mg,Fe)O, regardless of liquid or solid phase, will be of low-spin state and have zero net magnetic moment at the pressure and temperature considered (Badro, 2014; Karki et al., 2018). The influence of spin polarization on the MgO-Fe phase relation is likely to be small. Therefore, all the calculations are nonspin-polarized following previous studies (Wahl and Militzer, 2015; Wilson et al., 2023).

55

56 The configurations generated by these AIMD simulations as well as the multithermal and/or multibaric MD

57 simulations were then selected to construct the MLP. The energy, force, and stress of these selected

- 58 configurations were recalculated at much higher precision with: the energy cutoff that sets the size of the
- 59 basis set increased from 500 eV to 800 eV (Figure S1), the precision to which the self-consistent solution
- 60 to the Kohn-Sham equations is lowered from 10^{-4} eV to 10^{-6} eV, and sampling of the Brillouin zone

- 62 63 increased from the Gamma-point only to a $2 \times 2 \times 2$ Monkhorst-Pack mesh. We found this high precision recalculation to be important for optimizing the robustness of the MLP (Deng and Stixrude, 2021b).

66 Convergence tests of *ab initio* calculations



67 68 Figure S1. Convergence tests of total energy (a) and pressure (b) with varying energy cutoffs (ENCUT

- 69 flag in VASP) for a mixture of Mg₆₄O₆₄Fe₆₄ at the static condition. An energy cutoff of 800 eV is
- sufficient to obtain converged results for both energy and pressure. 70



Figure S2. Comparisons of energies (a), atomic forces (b), and stresses (c) between DFT and the machine
learning potential (MLP) for all the test data at temperatures up to 8000 K and pressures up to ~200
GPa. 15078 energies, 5988786 force components, and 135702 stress components are included in these





Figure S3. Comparisons of the total energy changes along molecular dynamics trajectories between the DFT (thick colored lines) and MLP potential (thin black lines) for liquid $Mg_{192}O_{192}$ (red), solid $Mg_{192}O_{192}$ (green), and liquid $Mg_{16}O_{16}Fe_{256}$ (green) at 140 GPa and 5000 K. The models used in this simulation contain 432 atoms, and none of the structures in the trajectories were included in the training set. The root mean square error of MLP is 4.9, 2.8, 4.6 meV/atom for liquid $Mg_{192}O_{192}$, solid $Mg_{192}O_{192}$, and liquid $Mg_{16}O_{16}Fe_{256}$, respectively.

89 Convergence with respect to system size



90

- 91 Figure S4. System size convergence test. Equilibrium atomic fractions of Mg (blue circle) and O (red star)
- 92 atoms in metallic phase as a function of system size (i.e., number of atoms in the system) at 5000 K and
- 93 140 GPa. The ratio of the numbers of Mg, O, and Fe are 2:2:3 for all the systems.

95 Text S2: Thermodynamic model for element partitioning

96 The exchange coefficients for Mg $(K_D^{Mg} = \frac{X_{Mg}^{met} X_0^{met}}{X_{Mg}^{ox}})$ and O $(K_D^{O} = \frac{X_{Fe}^{met} X_0^{met}}{X_{FeO}^{ox}})$ are functions of pressure,

97 temperature, and activity. Previous studies suggest that strongest non-ideality arise from interaction 98 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et 99 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et 99 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et 99 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et 99 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et 90 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et 91 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et 92 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et 93 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et 94 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et 94 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et 94 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et 94 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et 94 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et 94 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et 94 between light elements and Fe liquid, compared with silicate and oxide phase (Fischer et al., 2015; Liu et al., 2015; Liu

99 al., 2019). By considering the activity coefficients of light elements in the Fe liquid, one reaches,

$$\log_{10} K_D^{Mg} = \log_{10} K_{Mg} - \log_{10} \gamma_{Mg} - \log_{10} \gamma_{0}$$

$$\log_{10} K_D^0 = \log_{10} K_0 - \log_{10} \gamma_0$$

102 , where K_i is equilibrium constant, and γ_i is the activity coefficient (*i* is Mg or O). K_i is only a function of 103 pressure *P* and temperature *T* for a given system and can be written as

104
$$\log_{10}(K_i) = a_i + \frac{b_i}{T} + \frac{c_i P}{T}$$

105 , where parameters a, b and c are related to the changes of entropy, enthalpy and molar volume of the 106 dissociation reaction at reference state.

107 We use the formalism of (Ma, 2001) to describe γ_i

$$\log_{10} (\gamma_i) = -\frac{1}{2.303} \varepsilon_i^i \ln (1 - X_i) -\frac{1}{2.303} \sum_{i \neq j} \varepsilon_i^j X_j (1 + \frac{\ln (1 - X_j)}{X_j} - \frac{1}{1 - X_i}) +\frac{1}{2.303} \sum_{i \neq j} \varepsilon_i^j X_j^2 X_i \left(\frac{1}{1 - X_i} + \frac{1}{1 - X_j} + \frac{X_i}{2(1 - X_i)^2} - 1\right)$$

108

- 109 , where i and j are MgO, or O. X_i is the molar fraction of element *i* in the metallic phase. ε is the interaction
- 110 parameter with $\varepsilon_i^j = \varepsilon_j^i$. ε can be further expressed as $\varepsilon_i^j(T) = \frac{1873}{T} \varepsilon_i^j(T) = 1873 K$.

111

113 **Text S3 Regression**

114 We fit the exsolution simulation results and previous experiments on ferropericlase-Fe partitioning 115 simultaneously to resolve the thermodynamic parameters. We exclude the data with reported carbon 116 contamination (Du et al., 2019b). Early experiments do not report Mg contents in the liquid Fe and are 117 therefore only used to constrain O partitioning. We first explore fitting the oxygen partitioning independently using data from this study and experimental results from (Asahara et al., 2007; Frost et al., 118 119 2010; Ozawa et al., 2008). The goodness of fit (measured by R^2) dramatically drops from 0.93 to 0.74 as 120 long as the four data points reported by (Frost et al., 2010) are included. This is largely due to the conflicting results between (Frost et al., 2010) and (Ozawa et al., 2008) at around 30-70 GPa. We therefore reject the 121 122 data of (Frost et al., 2010) for fitting.

- We then fit both K_D^{Mg} and K_D^{O} simultaneously using the data of this study and (Asahara et al., 2007; Ozawa et al., 2008). Based on F-test, the model with or without a_{Mg} and ε_{Mg}^{Mg} fit the data equally well. As such, 123
- 124
- a_{Mg} and ε_{Mg}^{Mg} are set to be 0. The negligible roles of a_{Mg} and ε_{Mg}^{Mg} on partitioning are consistent with previous studies on metal-silicate systems (Badro et al., 2018; Du et al., 2019a; Liu et al., 2019). The 125
- 126
- 127 resulting fitted parameters are listed in Table S3.

Table S1 Summary of exsolution simulations at 140 GPa. N_{Mg} , N_{Fe} , and N_O are the numbers of Mg, Fe, O atoms, respectively. The difference between the composition of the bulk system and the sum of those of ferropericlase and metallic liquid yields the composition of the corresponding interface.

	Bulk system		Ferropericlase			Metallic			$\log_{10} K_D^{Mg}$	$\log_{10} K_D^0$	
T(K)						liquid					
	$N_{\rm Mg}$	$N_{\rm Fe}$	No	$N_{\rm Mg}$	$N_{\rm Fe}$	No	$N_{\rm Mg}$	$N_{\rm Fe}$	No	2	
5000	3136	4707	3136	1980.2	5.0	1986.6	8.4	2370.6	5.6	-5.09	-0.04
5000	738	4704	738	506.5	2.5	508.3	25.2	4313.3	23.7	-4.50	0.03
5500	738	4704	738	272.6	2.4	274.1	14.7	3819.0	68.1	-4.18	0.29
5500	1476	8364	2520	865.9	14.6	879.5	24.2	6819.2	616.5	-3.56	0.66
5000	1476	8364	2520	767.7	24.6	789.1	8.1	6444.8	502.0	-4.06	0.33
4500	1476	8364	2520	651.7	34.4	655.5	2.0	6108.0	360.8	-4.73	0.02
5000	1476	7525	3358	780.3	19.9	798.3	16.5	5561.3	1048.4	-3.39	0.73
4500	1476	7525	3358	577.0	30.9	602.4	8.5	4954.2	807.3	-3.66	0.37
4000	1476	7525	3358	511.0	57.4	570.4	1.1	4583.0	574.3	-4.57	-0.01
5500	2088	3456	2520	1755.8	47.2	1802.4	7.8	2511.7	161.8	-3.74	0.33
5000	2088	3456	2520	1202.8	29.9	1241.9	1.4	1612.9	33.2	-4.75	-0.09
5000	2088	3110	2866	1313.5	58.7	1364.2	1.8	1338.5	130.1	-3.94	0.28
5000	2088	3110	2866	1434.9	48.2	1478.3	2.7	1605.3	190.5	-3.79	0.46
5500	2304	3456	2304	1767.6	5.1	1771.9	23.7	2426.5	14.0	-4.26	0.29

- 135 136 Table S2 Summary of previous experimental results on ferropericlase-Fe element partitioning.Experiments with reported carbon and sulfur contamination are excluded. (see the content in a
- separate supplementary file)

Table S3. Fitted parameters of exchange coefficients. The pressure dependence of Mg is not resolved. 140

	а	b (K)	c (K/GPa)	$arepsilon_{Mg}^{i}$	ε_{O}^{i}
Mg	0	-24133±215	n.a.	0	-48.72±2.96
0	1.82±0.09	-6704±252	-11.53±1.63	-48.72±2.96	-9.17±0.87

n.a. Not applicable.

Reference

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- 213

P (GPa)	T (K)	X _{FeO}	Xo	X _{Fe}	$\log_{10} K_D^{O}$	Reference
3	2673	0.108	0.037	0.963	-0.4815957	Asahara et al., 2007
4	2373	0.217	0.029	0.971	-0.8868425	Asahara et al., 2007
5	2373	0.267	0.028	0.972	-0.991687	Asahara et al., 2007
5	2473	0.195	0.033	0.967	-0.7860942	Asahara et al., 2007
5	2833	0.105	0.061	0.939	-0.2631939	Asahara et al., 2007
7	2473	0.206	0.026	0.974	-0.9103349	Asahara et al., 2007
7	2573	0.169	0.041	0.959	-0.6332842	Asahara et al., 2007
9	2473	0.264	0.032	0.968	-0.9305786	Asahara et al., 2007
9	2673	0.161	0.069	0.931	-0.3990271	Asahara et al., 2007
9	2873	0.102	0.051	0.949	-0.3237638	Asahara et al., 2007
12	2873	0.115	0.059	0.941	-0.3162562	Asahara et al., 2007
15	2273	0.566	0.051	0.949	-1.06798	Asahara et al., 2007
15	2473	0.281	0.037	0.963	-0.8968783	Asahara et al., 2007
15	2473	0.318	0.056	0.944	-0.7792671	Asahara et al., 2007
15	2473	0.519	0.112	0.888	-0.7175364	Asahara et al., 2007
15	2873	0.18	0.109	0.891	-0.2679683	Asahara et al., 2007
15	2873	0.125	0.07	0.93	-0.283329	Asahara et al., 2007
15	2873	0.085	0.04	0.96	-0.3450877	Asahara et al., 2007
15	3073	0.091	0.059	0.941	-0.2145998	Asahara et al., 2007
15	3073	0.133	0.107	0.893	-0.1436164	Asahara et al., 2007
15	3123	0.159	0.12	0.88	-0.1777332	Asahara et al., 2007
15	3123	0.138	0.12	0.88	-0.1162152	Asahara et al., 2007
15	3123	0.138	0.121	0.879	-0.1131048	Asahara et al., 2007
20	3073	0.107	0.098	0.902	-0.0829512	Asahara et al., 2007
24.5	2273	0.71	0.061	0.939	-1.0932629	Asahara et al., 2007
24.5	2473	0.358	0.069	0.931	-0.7460843	Asahara et al., 2007
24.5	2473	0.521	0.215	0.785	-0.4895296	Asahara et al., 2007
24.5	2473	0.314	0.059	0.941	-0.752488	Asahara et al., 2007
24.5	2773	0.257	0.124	0.876	-0.3740073	Asahara et al., 2007
24.5	2773	0.232	0.077	0.923	-0.5137956	Asahara et al., 2007
24.5	3073	0.098	0.088	0.912	-0.0867486	Asahara et al., 2007
24.5	3073	0.145	0.128	0.872	-0.1136415	Asahara et al., 2007
24.5	3073	0.181	0.175	0.825	-0.0981866	Asahara et al., 2007
24.5	3173	0.133	0.195	0.805	0.07197885	Asahara et al., 2007
18	2900	0.196	0.109	0.891	-0.3049519	Ozawa et al., 2008
33	2900	0.222	0.076	0.924	-0.4998674	Ozawa et al., 2008
33	2900	0.227	0.064	0.936	-0.57857	Ozawa et al., 2008
38	2860	0.28	0.08	0.92	-0.5802802	Ozawa et al., 2008
74	3000	0.21	0.066	0.934	-0.5323285	Ozawa et al., 2008
94	3120	0.196	0.069	0.931	-0.4844573	Ozawa et al., 2008
134	3200	0.202	0.191	0.809	-0.1163695	Ozawa et al., 2008
124	3150	0.277	0.152	0.848	-0.3322403	Ozawa et al., 2008
72	3500	0.191	0.241	0.759	-0.0187745	Frost et al., 2010
70	3100	0.035	0.047	0.953	0.10712271	Frost et al., 2010
33	2800	0.059	0.045	0.955	-0.1376361	Frost et al., 2010
30	2800	0.076	0.063	0.937	-0.1097335	Frost et al., 2010

Table S2. Summary of previous experimental results on ferropericlase-Fe element partitioning. Experiments with reported carbon and sulfur contamination are excluded.

Note: X_{FeO} , X_{Fe} , X_{O} are the FeO content in ferropericlase, Fe content in metallic liquid, O content in metallic liquid, respectively.

Only data of Asahara et al., 2007 and Ozawa et al., 2008 are used for fitting.