

Grain boundary diffusion of ferropericlase: Implications for the core-mantle interaction

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Abstract

Geophysical observations indicate that iron enrichment of various spatial scales may be present in the lowermost mantle. Various mechanisms have been proposed to explain the process of iron infiltration from the core to the mantle, though each with its own inherent limitations. Grain boundary (GB) diffusion significantly outpaces bulk diffusion within crystal interiors, and may facilitate iron transport across the core-mantle boundary (CMB). In this study, we investigate diffusion in two symmetric tilt GBs in ferropericlase using large-scale molecular dynamics simulations. The GB diffusivities of Mg and O of periclase as well as their temperature dependence agree well with previous studies. In addition, we study the GB diffusion of Fe in (Mg,Fe)O GBs for the first time. The results suggest that GB diffusion of Fe is likely to be sluggish near the CMB, and thus may not be an effective mechanism to transport iron from the core to the mantle.

1 **Grain boundary diffusion of ferropericlase: Implications for the**
2 **core-mantle interaction**

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6 **Key Points:**

- 7 • The grain boundary diffusivities of Mg, Fe, and O in ferropericlase are calculated from
8 molecular dynamics simulations
9 • The grain boundary diffusivity first increases and then converges to a constant with increasing
10 vacancy concentration
11 • Grain boundary diffusion is unlikely to be efficient enough for iron transport across the
12 core-mantle boundary

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13 **Abstract**

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16 infiltration from the core to the mantle, though each with its own inherent limitations. Grain boundary
17 (GB) diffusion significantly outpaces bulk diffusion within crystal interiors, and may facilitate iron
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19 symmetric tilt GBs in ferropericlase using large-scale molecular dynamics simulations. The GB
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21 previous studies. In addition, we study the GB diffusion of Fe in (Mg,Fe)O GBs for the first time.
22 The results suggest that GB diffusion of Fe is likely to be sluggish near the CMB, and thus may not
23 be an effective mechanism to transport iron from the core to the mantle.

24 **Plain Language Summary**

25 Seismic observations suggest the existence of regions rich in iron of scales from a few hundred
26 meters to thousands of kilometers above the Earth's core-mantle boundary. The Earth's core, com-
27 posed primarily of liquid iron, may interact with the mantle rocks and transport iron into the mantle.
28 The diffusion of atoms along the boundaries of different grains of mantle rocks has been proposed as
29 a possible mechanism for the core-mantle interaction. We performed atomistic simulations of one of
30 the dominant mineral phases at the core-mantle boundary, (Mg,Fe)O ferropericlase to calculate the
31 diffusion rates of magnesium, iron, and oxygen within grain boundary regions. The results suggest
32 that, on the time scale of the Earth's history, the distance of the grain boundary diffusion of iron is
33 likely to be very limited and insufficient to explain any iron enrichment phenomena at the bottom of
34 the lower mantle.

35 **1 Introduction**

36 As the sharpest compositional discontinuity in the Earth's interior, the core-mantle boundary
37 (CMB) at the depth of 2889 km exhibits strong complexity and has a significant impact on the
38 chemical evolution of the Earth (Young & Lay, 1987). The interaction between the solid silicate
39 mantle and the liquid iron core may cause extensive enrichment of iron at the lowermost mantle,
40 which is supported by multiple geophysical observations. First, two continent-sized large low shear
41 velocity provinces (LLSVPs) extend up to 1200 km above the CMB (Garnero et al., 2016) and can be
42 explained by iron-enriched materials (Vilella et al., 2021; Yuan et al., 2023). They exhibit electrical
43 conductivity anomalies (Nagao et al., 2003; Ohta et al., 2010) which may also be associated with
44 iron. Second, the 5–40 km thick patches right above the core with unusually low seismic velocities,
45 known as ultralow-velocity zones (ULVZs) (Williams & Garnero, 1996), may be attributed to local
46 iron enrichment (Wicks et al., 2010). Third, a ~200-m-thick high conductance layer above the core
47 has been inferred from Earth's nutations (Buffett, 1992; Buffett et al., 2002) and may comprise
48 metallic FeO (Knittle & Jeanloz, 1986; Sherman, 1989).

49 Various hypotheses have been proposed to explain this putative iron enrichment above the CMB.
50 The thickness of the iron-enriched layer caused by capillary rise is only < 20 m (Poirier et al., 1998).
51 Alternative hypotheses suggest that pressure gradients caused by the dynamic topography at the
52 CMB may drive iron upwards into the lower mantle (Kanda & Stevenson, 2006). Additionally, iron
53 infiltration can be caused by the sedimentation of the liquid outer core (Buffett et al., 2000). However,
54 both of them are sensitive to the viscosity of the lowermost mantle, which is subject to considerable
55 uncertainty (Rudolph et al., 2015). Otsuka and Karato (2012) proposed that the penetration of iron
56 into the mantle can be caused by a morphological instability, which is a mechanism independent of
57 viscosity, but the effective diffusivity used to calculate iron infiltration thickness is extrapolated from
58 low-pressure experimental data and remains controversial (J. Deng et al., 2019; Yoshino, 2019).

59 Grain boundaries (GBs) are regions that separate different grains in a polycrystalline material.
60 Due to the more disordered atomistic structure at the interface compared to the crystalline lattice,

61 atomic diffusion along GBs is typically orders of magnitude faster than its lattice counterpart (Joesten,
62 1991; Dohmen & Milke, 2010). Therefore, GB diffusion strongly affects physical properties in
63 the Earth's materials, including the viscosity (Mantisi et al., 2017), electrical conductivity (ten
64 Grotenhuis et al., 2004), and seismic attenuation (Jackson et al., 2002). It is suggested that GB
65 diffusion provides an efficient mechanism to exchange carbon and siderophile elements between the
66 mantle and the core (Hayden & Watson, 2007, 2008), and may effectively modify the tungsten and
67 helium isotopic compositions of the plume-source mantle (Yoshino et al., 2020; Ferrick & Korenaga,
68 2023). The diffusion of iron along GBs may be another potential mechanism for iron infiltration
69 from the outer core to the lower mantle.

70 Previous experimental and theoretical studies have explored the GB diffusion in MgO periclase
71 (McKenzie et al., 1971; Van Orman et al., 2003; Karki et al., 2015; Landuzzi et al., 2015; Riet et
72 al., 2021). However, most of these results do not account explicitly for pressure and temperature
73 conditions near the CMB, and the GB diffusion in (Mg,Fe)O, one of the most abundant phases at
74 the CMB (X. Deng et al., 2023), remains poorly understood. In addition, recent results have shown
75 that the structure of a GB is far from unique, and is not simply determined by the misorientation
76 between the grains. In particular, GB structures evolve when interacting with vacancy complexes,
77 resulting in significant changes in GB properties Hirel et al. (2022). In this study, we investigate the
78 GB diffusion of Mg, Fe, and O along GB in (Mg,Fe)O bicrystals under the CMB conditions using
79 large-scale molecular dynamics (MD) simulations. Bicrystals of high compaction, expected to be
80 most favourable in high-pressure conditions of the CMB, are constructed (Hirel et al., 2019). We
81 explore the dependence of the GB diffusion coefficient on defect concentration and temperature. The
82 results are used to examine the efficiency of transporting iron from the core to the mantle through
83 GB diffusion of (Mg,Fe)O ferropericlase.

84 **2 Methods**

85 **2.1 Interatomic potential**

86 There are two main methods to describe the interaction of atoms in MD simulations: *ab*
87 *initio* method based on density functional theory and the force field approach. The *ab initio*
88 method is considered more accurate because it calculates the electronic structure of material quantum
89 mechanically, in principle, without relying on empirical parameters. However, this method is
90 computationally demanding, limiting simulations to smaller systems and shorter times. On the
91 other hand, the force field approach uses simplified force parameters, allowing for less intensive
92 computations and enabling longer simulations of larger systems, which is crucial for simulating
93 polycrystalline systems and reducing statistical error. Therefore, in this study, we choose the force
94 field approach and use a new rigid-ion potential developed by Pedone et al. (2006). This approach
95 incorporates long-range Coulomb interactions, a Morse function for short-range interactions, and
96 a repulsive term similar to the Lennard-Jones function. The parameters were calibrated using
97 experimental measurements, including lattice dimensions, elasticity values, both high-frequency and
98 static dielectric constants, lattice energies, piezoelectric constants, and phonon frequencies observed
99 in binary oxides. This potential demonstrates high reliability and applicability in modeling lattice
100 defects, diffusion, and GBs in forsterite (Hirel et al., 2021; Furstoss et al., 2022). Hirel et al. (2021)
101 highlight its ability to accurately reproduce various properties across a pressure range of 0 to 12
102 GPa, while Furstoss et al. (2022) further confirm its effectiveness through its good agreement with
103 *ab initio* calculations in terms of GB atomistic structures, energies, and excess volumes in forsterite.
104 To further verify the reliability of this potential for simulating (Mg,Fe)O GBs, we calculated the
105 formation enthalpy of MgO GBs across pressure conditions of nearly the entire mantle (Figure
106 S1). The results are in good agreement with Hirel et al. (2019), supporting the applicability of this
107 potential to the periclase system at elevated pressures.

108 **2.2 Molecular Dynamics Simulations**

109 The GBs used in this study are symmetric tilt GBs where grains are rotated by opposite
110 angles around the same [001] axis. Our focus is on structures with high-angle GBs as they are

111 more common in polycrystalline MgO (Saylor et al., 2003), likely more pertinent to understanding
 112 GB diffusion within the Earth’s interior, and also more convenient to study (Riet et al., 2021).
 113 Bicrystals are constructed with AtomsK (Hirel, 2015). Two crystals of MgO are rotated by opposite
 114 angles ($\pm\alpha/2$), cut and then stacked together. We apply translation to one of the two symmetrical
 115 single crystals along the GB, and compute relative energies of different configurations, which yields
 116 several energy minima. Configurations corresponding to these minima can be called “complexions”.
 117 As demonstrated earlier, at the high pressures reigning in the Earth’s mantle, the most compact
 118 complexions are energetically most favourable (Hirel et al., 2019), and is used as a starting point.
 119 Such a compact complexion can interact with vacancy complexes, thus transforming its atomic
 120 configuration further (Hirel et al., 2022). In the following two symmetric tilt GB are modelled,
 121 corresponding to two different misorientation angles: $\alpha = 36.8^\circ$ where the two crystals meet with
 122 $\{310\}$ planes, and $\alpha = 29.5^\circ$ where the GB plane does not correspond to any high-symmetry crystal
 123 plane. Mg-O vacancy pairs are randomly introduced within a region approximately 1 nm wide
 124 adjacent to the GB of the complexion to obtain the initial configuration of MgO bicrystals for the
 125 following MD simulations. The vacancy concentration C_{vac} is defined as the ratio between the
 126 number of MgO units removed and the number of MgO units in the 1-nm GB region. Following
 127 Ammann et al. (2010), the vacancy concentrations considered in this study range from 0.4 at% to
 128 8.0 at%, which are estimated from experimental results (Holzapfel et al., 2003; Yamazaki & Irifune,
 129 2003). The structure of (Mg,Fe)O is generated by the random substitution of Mg with different
 130 contents of Fe in the aforementioned MgO structure.

131 To ensure a genuine depiction of real material, (Mg,Fe)O single crystal must be of adequate
 132 size so that its inner structure mimics that of large grains (Glišović et al., 2015) in the lower mantle.
 133 We construct bicrystal systems containing over 50,000 atoms, resulting in an average distance of
 134 over 20 nm between the centers of adjacent grains. Each GB operates independently from others,
 135 ensuring that atoms involved in one boundary do not interact with any other boundaries throughout
 136 the simulation. A supercell with larger GB area has also been simulated and yields similar GB
 137 diffusion coefficients, confirming the size convergence of our systems (Figure S3).

138 All MD simulations are conducted using LAMMPS (Plimpton, 1995) under periodic boundary
 139 conditions. The systems are first equilibrated in isothermal-isobaric conditions (NPT) for 100 ps
 140 at a series of temperatures, under two pressures of 0 GPa and 140 GPa for MgO and (Mg,Fe)O,
 141 respectively. The resulting structures are then used as the initial configurations to set up the MD
 142 simulations for 5 ns under an canonical ensemble (NVT) with the Nosé-Hoover thermostat (Hoover,
 143 1985), in order to evolve the GB structure to reach a steady state. Subsequently, we perform long
 144 NVT simulations for 5 to 10 ns, from which the GB diffusion is investigated. The timestep of all
 145 simulations is 1 fs.

146 2.3 Trajectory analysis

147 Due to the spatially heterogeneous diffusion in polycrystalline systems, a direct analysis of the
 148 MD trajectory of the entire system would mask the distinct characteristics of the crystal interiors and
 149 GBs. Following Riet et al. (2021), we employed an advanced local ionic environment analysis to
 150 extract the atomic properties within the GB regions from the bulk system. The first post-processing
 151 step is an energy minimization to map instantaneous MD configurations (sampling at 1-ns intervals)
 152 to their nearest local energy minima. Through this, we remove the thermal vibrational displacement
 153 of atoms and thereby obtain a more distinct representation of the GBs. Subsequently, we examine
 154 the distribution of nearest neighbors of all atoms at the energy minima to identify which atoms have
 155 complete coordination with the six nearest neighbors and which ones are undercoordinated. The
 156 undercoordinated atoms are associated with the GB regions (Riet et al., 2018). This analysis is
 157 realized through the nearest neighbor search using the MDAnalysis package (Michaud-Agrawal et
 158 al., 2011). Consistent with Riet et al. (2018) and Riet et al. (2021), the fraction of undercoordinated
 159 atoms at the GBs, denoted as g , remains relatively constant through a single MD trajectory. This
 160 insight allowed us to apply the modified Hart equation (Hart, 1957; Dohmen & Milke, 2010; Riet et
 161 al., 2021) to compute the GB diffusion coefficient:

$$162 \quad D_{\text{total}} = gD_{\text{GB}} + (1 - g)D_{\text{vol}}, \quad (1)$$

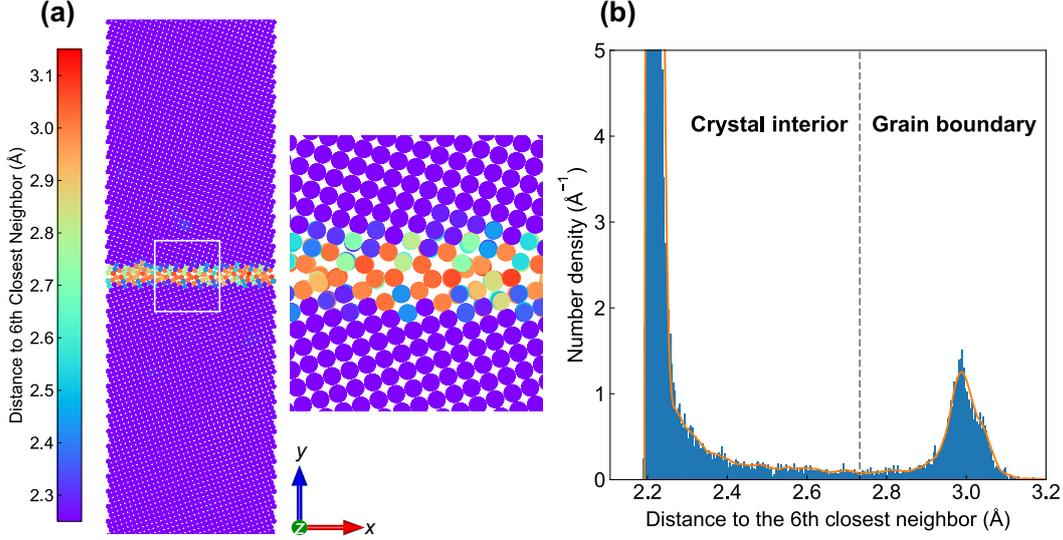


Figure 1. The local ionic environment analysis of MgO at 0 GPa and 2000 K. The results are derived from a snapshot of the MD simulation at 6 ns. The energy minimization is applied to remove the thermal vibration of atoms. (a) The color mapping of the distances from a central ion to its 6th closest neighbor. The view is perpendicular to the rotation angle of the grain boundaries. The atoms enclosed by the white frame are zoomed in to show details. (b) Distributions of distances from a central ion to its 6th closest neighbor. The orange curve is the smoothed histogram using the Savitzky-Golay filter (Savitzky & Golay, 1964), and its minimum value between the two peaks is used to determine the cutoff distance.

163 where D_{total} , D_{GB} , and D_{vol} are the overall diffusion coefficient, GB diffusion coefficient, and
 164 volume diffusion coefficient within the single crystal interiors, respectively. Since our analysis of
 165 atoms within crystal interiors showed negligible diffusion, we assume $D_{\text{vol}} \approx 0$. Thus, the GB
 166 diffusion coefficient is approximated by:

$$167 \quad D_{\text{GB}} = \frac{D_{\text{total}}}{g} \quad (2)$$

168 D_{total} can be easily derived as the slope of mean square displacement (MSD) using the Einstein
 169 diffusion relation

$$170 \quad D_{\text{total}} = \lim_{t \rightarrow \infty} \frac{\text{MSD}}{6t} = \lim_{t \rightarrow \infty} \frac{\langle [\vec{r}(t+t_0) - \vec{r}(t_0)]^2 \rangle_{\alpha}}{6t}, \quad (3)$$

171 where $\vec{r}(t)$ is the particle trajectories continuous in Cartesian space, and $\langle \cdot \cdot \rangle_{\alpha}$ represents an average
 172 over atoms of species α (Mg, Fe, O) and over time with different origins (Karki, 2015). Only when
 173 the MSD is a linear function of time do we intercept the segment of MSD and calculate the diffusion
 174 coefficient by linear fitting. The temperature-dependent diffusion coefficient can be fitted using the
 175 Arrhenius equation,

$$176 \quad D = D_0 e^{-\frac{\Delta H}{RT}}, \quad (4)$$

177 where D_0 is the pre-exponential factor, R is the ideal gas constant, and ΔH is the activation enthalpy.

178 3 Results and Discussion

179 3.1 Identification of grain boundary atoms

180 In this study, we analyze the structure of the GB and identify the GB atoms by examining the
 181 local ionic environments following Riet et al. (2021). In the ferropericlase or magnesiowüstite phase

182 of (Mg,Fe)O, ions within the grain typically have six equidistant nearest neighbors. In contrast, ions
 183 at the GB exhibit a non-crystalline local environment with varying distances to neighboring ions
 184 and often less than six nearest neighbors. Figure 1a shows the color mapping of the distances from
 185 a central ion to its sixth-closest neighbor in a snapshot of the MD trajectory of MgO at 0 GPa and
 186 2000 K, in which the atoms associated with the GB region are clearly presented (i.e., atoms that are
 187 not colored purple). The distribution of distances from a central ion to its sixth-closest ion at energy
 188 minima structures is shown in Figure 1b, which exhibits a bimodal pattern. The first peak in this
 189 distribution indicates ions with six neighbors, characteristic of atoms within a single crystal, not in a
 190 GB. The adjacent shoulder on this peak represents atoms near the GB, where relaxation can lead to
 191 slightly longer bond distances compared to the crystal interior. The second peak signifies ions that
 192 are undercoordinated, typically having five or fewer neighbors, and are located in the GB region. We
 193 set the minimum point between the first and second peaks as the cutoff distance for each system to
 194 differentiate between internal and GB ions following Riet et al. (2021).

195 **3.2 Grain boundary diffusivity**

196 In this section, we discuss the GB diffusion coefficients in MgO at ambient pressure, and in
 197 (Mg,Fe)O at 140 GPa, calculated using Equation 2 and Equation 3. The MSD data from all the
 198 simulations in this study can be found in Figure S4 in Supporting Information. Taking pure MgO as
 199 an example, we explore how the GB diffusion coefficients of Mg and O vary with C_{vac} , system size,
 200 and the misorientation angle of the GB (see Text S1 in Supporting Information). This preliminary
 201 study allowed us to determine that fully converged results are obtained when C_{vac} reaches 3.2 at% or
 202 above, hence, only the diffusivity data at this concentration are presented in the following.

203 **3.2.1 MgO at 0 GPa**

204 Figure 2 summarizes the GB diffusion coefficients of MgO as a function of temperature at
 205 ambient pressure. To ensure convergence, we adopt a defect concentration of 3.2 at% to constrain
 206 the upper bound of the diffusivity (see Text S1 in Supporting Information). Our results generally
 207 agree well with previous theoretical studies using molecular dynamics simulations, and fall between
 208 the results of Riet et al. (2021) and Landuzzi et al. (2015) for both Mg and O. McKenzie et al. (1971)
 209 experimentally obtained $\frac{\delta D_{\text{GB}}}{\sqrt{D_{\text{vol}}}}$ for oxygen diffusion in periclase at around 2000 K, where δ is the
 210 GB width. However, since the value of D_{vol} in MgO remains poorly constrained, it is difficult to
 211 directly compare experimentally inferred GB diffusivity with our simulation outcomes. Riet et al.
 212 (2021) estimated that δD_{GB} of oxygen lies between $4 \times 10^{-23} \text{ m}^3 \text{ s}^{-1}$ and $2 \times 10^{-21} \text{ m}^3 \text{ s}^{-1}$, based
 213 on the highest and lowest D_{vol} values reported in the literature (Oishi & Kingery, 1960; Yang &
 214 Flynn, 1994) and experimental measurements (McKenzie et al., 1971). Our result for $C_{\text{vac}} = 3.2$
 215 at% is $\sim 4 \times 10^{-21} \text{ m}^3 \text{ s}^{-1}$, slightly higher than this range. However, the C_{vac} in pure MgO is
 216 significantly lower compared to (Mg,Fe)O due to the absence of multivalent ions (Van Orman et
 217 al., 2003; Ammann et al., 2010). Considering lower vacancy concentrations of $C_{\text{vac}} < 0.8$ at%, our
 218 simulation results fall within the range of experimental estimates.

219 The GB diffusion coefficients increase significantly with temperature, and can be well fitted by
 220 Equation 4 (dashed lines in Fig. 2). The activation enthalpies for Mg and O are $229(\pm 10) \text{ kJ mol}^{-1}$
 221 and $217(\pm 64) \text{ kJ mol}^{-1}$, respectively. The only experimental results of the activation enthalpy
 222 for GB diffusion of O is 230 kJ mol^{-1} (measured at 1380–1800 K, Passmore et al., 1966), which
 223 our simulations match closely. Karki et al. (2015) reported the activation enthalpies for Mg (221
 224 kJ mol^{-1}) and O (212 kJ mol^{-1}) migration along the {410} symmetric boundaries of MgO bicrystals
 225 at 0 GPa using *ab initio* calculations. Similar results were obtained by Harris et al. (1997) using
 226 MD simulations with empirical potentials. Our simulation results also align very well with these
 227 theoretical predictions that assumed *ad hoc* diffusion pathways. It is noteworthy that in the bulk
 228 crystal of periclase, the diffusion activation enthalpy of Mg is smaller than that of O (Ammann et
 229 al., 2010), while in the GB, they are quite similar and the activation enthalpy of O is slightly smaller.
 230 This may be related to the markedly different chemical environments at the GBs compared to the
 231 interior of the crystal. In summary, the GB diffusion properties of MgO at ambient pressure obtained
 232 from this study are consistent with previous theoretical and experimental data.

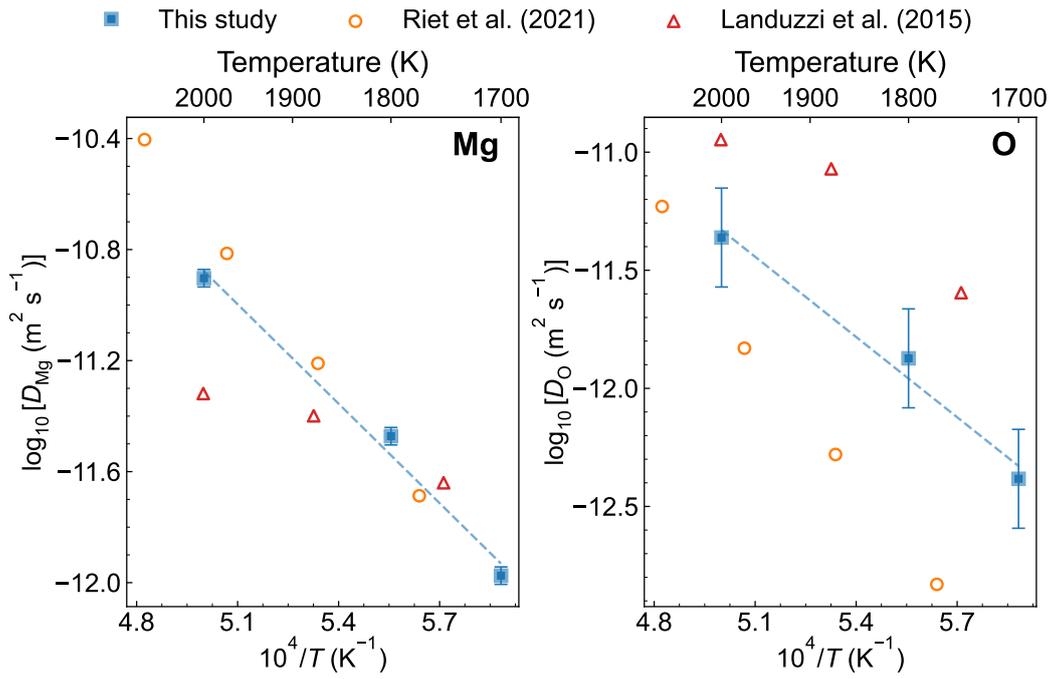


Figure 2. Grain boundary diffusion coefficients of Mg (left) and O (right) as a function of reciprocal temperature (1700 K, 1800 K, and 2000 K) in MgO with a C_{vac} of 3.2 at% at ambient pressure. The error bars are estimated from the error bars in Figure S2, assuming the same relative standard deviation for each element. Results from previous theoretical studies are plotted in open symbols for comparison (Riet et al., 2021; Landuzzi et al., 2015). Dashed lines are fitted Arrhenius functions (Equation 4).

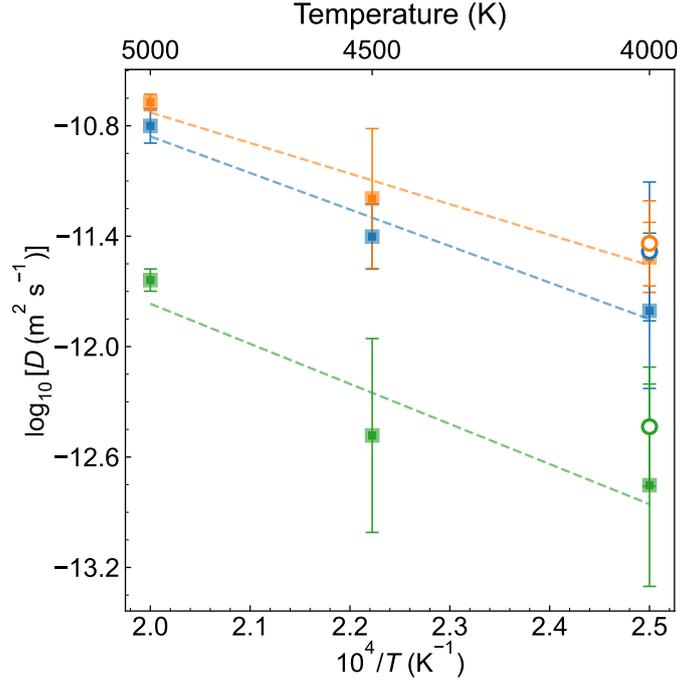


Figure 3. Grain boundary diffusion coefficients as a function of reciprocal temperature (4000 K, 4500 K, and 5000 K) in (Mg_{0.9}Fe_{0.1})O (solid squares) and (Mg_{0.16}Fe_{0.84})O (open circles) with a C_{vac} of 3.2 at% at 140 GPa. The diffusivity of Mg, Fe, and O are shown in blue, orange, and green, respectively. The error bars represent 2SD of the diffusion coefficients calculated from four 5-ns-long MD trajectories. Dashed lines are fitted Arrhenius functions (Equation 4).

233 3.2.2 (Mg,Fe)O at 140 GPa

234 The high-pressure diffusion coefficients of Mg, Fe, and O in (Mg,Fe)O with two different iron
 235 contents are shown in Figure 3. For (Mg_{0.9}Fe_{0.1})O ferropericlase, the simulation temperatures are
 236 set between 4000 to 5000 K, corresponding to the upper bounds of the estimated CMB temperatures
 237 throughout the Earth’s thermal evolution (Andraut et al., 2016). (Mg_{0.16}Fe_{0.84})O magnesiowüstite
 238 is taken as a prototype Fe-rich material that has been suggested to be the main constituent of ULVZs
 239 (Wicks et al., 2010, 2017) and the high conductance layer (Buffett, 1992; Knittle & Jeanloz, 1986),
 240 and consequently it may serve as an important medium for the iron transport from the outer core
 241 to the lower mantle. Recent studies suggest that the melting point of FeO wüstite under CMB
 242 pressure conditions reaches up to 4140 K (Dobrosavljevic et al., 2023), indicating that our simulation
 243 temperature of 4000 K for (Mg_{0.16}Fe_{0.84})O is below its solidus. Overall, the diffusion coefficients
 244 slightly increase with iron content, and the order of diffusion coefficients for the three elements follows
 245 $D_{GB}^{Fe} \approx D_{GB}^{Mg} > D_{GB}^O$. We find that the diffusion coefficient of Mg is about an order of magnitude
 246 larger than that of O, closely aligning with the results of Riet et al. (2021). Furthermore, Fe and Mg
 247 have similar diffusion coefficients, both significantly larger than O, which is consistent with the MD
 248 data for GB diffusion in olivine (Mantisi et al., 2017). This suggests that the relative magnitudes
 249 of GB diffusion coefficients for different elements are, to a large extent, controlled by ionic radii,
 250 considering that the ionic radii of Fe²⁺, Mg²⁺, and O²⁻ are 75, 86, and 126 pm, respectively (Slater,
 251 1964). Due to the steric effect (Nalwa, 2001), smaller ions are better suited to move through available
 252 space to facilitate diffusion. We find that the uncertainty of the diffusion coefficients at 5000 K is
 253 much smaller than at lower temperatures, which may be due to the more stable premelting state of
 254 the GBs at higher temperatures, reducing the variation in diffusivity. Regarding the temperature
 255 dependence, the diffusion activation enthalpies for Mg, Fe, and O are 448(±63) kJ mol⁻¹, 328(±37)

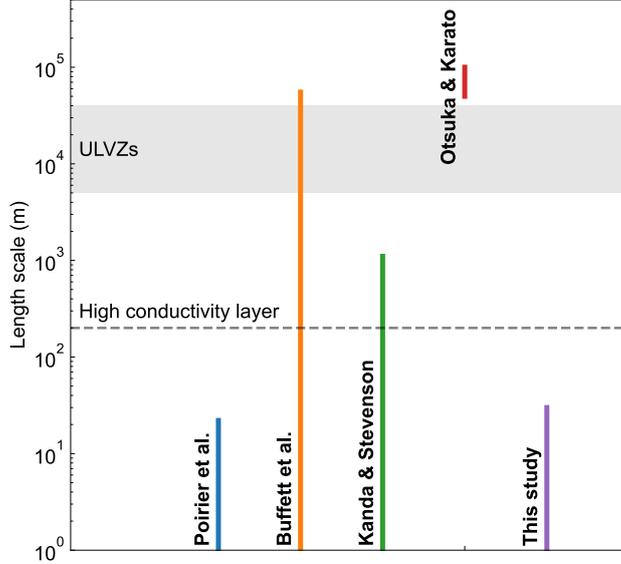


Figure 4. Length scale of iron transport from the core to the mantle compared to length scales of high conductance layer and ULVZs. Different iron infiltration mechanisms are shown for comparison (Poirier et al., 1998; Buffett et al., 2000; Kanda & Stevenson, 2006; Otsuka & Karato, 2012).

256 kJ mol⁻¹, and 479(±97) kJ mol⁻¹, respectively. Due to the pressure effect on diffusion, they are
 257 significantly higher than the activation enthalpies for MgO under ambient pressure.

258 4 Implications

259 To explore the upper limit of the efficiency of iron transport via the GB diffusion mechanism,
 260 we consider the maximum diffusivity of iron in Figure 3 ($2.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$) for the subsequent
 261 calculations. The effective diffusion coefficient for a polycrystalline material can be estimated using
 262 this equation (Balluffi et al., 2005):

$$263 \quad D_{\text{eff}}^{\text{Fe}} = D_{\text{vol}}^{\text{Fe}} + \frac{3\delta}{d} D_{\text{GB}}^{\text{Fe}}, \quad (5)$$

264 where δ is the GB width (~1 nm) and d is the grain size (0.01–10 mm, Glišović et al., 2015) in the
 265 lower mantle. For pure MgO periclase, the D_{vol} values of Mg and O under the CMB conditions
 266 are very small and can be negligible (less than $10^{-20} \text{ m}^2 \text{ s}^{-1}$, Ita & Cohen, 1998), while in the
 267 presence of Fe, higher vacancy concentrations might lead to faster lattice diffusion of Mg, O, and Fe
 268 (Ammann et al., 2010). We extract the actual contribution of GB diffusion to the effective diffusion
 269 coefficient by setting $D_{\text{vol}}^{\text{Fe}} = 0$, and obtain the characteristic length scale of the iron transport through
 270 GB diffusion:

$$271 \quad L_{\text{GB}}^{\text{eff}} = \sqrt{\frac{3\delta}{d} D_{\text{GB}}^{\text{Fe}} t}, \quad (6)$$

272 where the time scale t is set to the age of the Earth (4.54 Gyr, Dalrymple, 2001). The result of $L_{\text{GB}}^{\text{eff}}$
 273 does not exceed 30 m, as shown in Figure 4. Other iron infiltration mechanisms proposed by previous
 274 studies, including capillary rise (Poirier et al., 1998), suction (Kanda & Stevenson, 2006), upward
 275 sedimentation of outer core alloys (Buffett et al., 2000), and morphological instability (Otsuka &
 276 Karato, 2012) are also plotted for comparison. The results indicate that the effective transport
 277 distance of Fe through GB diffusion in (Mg,Fe)O is likely to be quite small, considering the transport
 278 distances of other mechanisms and the spatial scales of ULVZs and the high conductance layer. To
 279 further validate this finding, we solve Fick's second law of diffusion to calculate the concentration

280 profile of iron in the mantle:

$$281 \quad \frac{\partial C}{\partial t} = -\frac{3\delta}{d} D_{\text{GB}}^{\text{Fe}} \nabla^2 C \quad (7)$$

282 Assuming that the core always maintains a composition of pure iron, and considering an initial
 283 condition of zero Fe concentration in the mantle, we obtained the concentration distribution of iron
 284 in the mantle after the GB diffusion of 4.54 Gyr. The total mass of Fe that has been transported
 285 to the mantle is 5.1×10^{19} kg, which can only account for less than 20 wt% of the ~200-m-high
 286 conductance layer.

287 At the CMB, not only (Mg,Fe)O but also silicate minerals such as bridgmanite and post-
 288 perovskite are present. Given that lattice diffusion of elements in silicate perovskite is much slower
 289 than in ferroperricite (Ammann et al., 2010; Holzapfel et al., 2003, 2005), we argue that GB diffusion
 290 is unlikely to be an effective mechanism to transport Fe from the core to the lower mantle. Considering
 291 that some siderophile elements (e.g., W) have larger atomic radii and mass than Fe, we speculate
 292 that their GB diffusion coefficients in (Mg,Fe)O might be even smaller than that of Fe. So far the
 293 only data available for comparison are experimental results under relatively low pressures (Hayden
 294 & Watson, 2007; Yoshino et al., 2020). Therefore, more studies are needed to accurately quantify
 295 the efficiency of GB diffusion in exchanging siderophile elements across the CMB to elucidate the
 296 scale and extent of the core-mantle interaction.

297 **5 Open Research**

298 Data used in this study are available at Peng and Deng (2024). The software LAMMPS used in
 299 this study is developed openly at <https://github.com/lammps/lammps> and available at Plimpton
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1 **Grain boundary diffusion of ferropericlase: Implications for the**
2 **core-mantle interaction**

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6 **Key Points:**

- 7 • The grain boundary diffusivities of Mg, Fe, and O in ferropericlase are calculated from
8 molecular dynamics simulations
9 • The grain boundary diffusivity first increases and then converges to a constant with increasing
10 vacancy concentration
11 • Grain boundary diffusion is unlikely to be efficient enough for iron transport across the
12 core-mantle boundary

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13 **Abstract**

14 Geophysical observations indicate that iron enrichment of various spatial scales may be present
15 in the lowermost mantle. Various mechanisms have been proposed to explain the process of iron
16 infiltration from the core to the mantle, though each with its own inherent limitations. Grain boundary
17 (GB) diffusion significantly outpaces bulk diffusion within crystal interiors, and may facilitate iron
18 transport across the core-mantle boundary (CMB). In this study, we investigate diffusion in two
19 symmetric tilt GBs in ferropericlase using large-scale molecular dynamics simulations. The GB
20 diffusivities of Mg and O of periclase as well as their temperature dependence agree well with
21 previous studies. In addition, we study the GB diffusion of Fe in (Mg,Fe)O GBs for the first time.
22 The results suggest that GB diffusion of Fe is likely to be sluggish near the CMB, and thus may not
23 be an effective mechanism to transport iron from the core to the mantle.

24 **Plain Language Summary**

25 Seismic observations suggest the existence of regions rich in iron of scales from a few hundred
26 meters to thousands of kilometers above the Earth's core-mantle boundary. The Earth's core, com-
27 posed primarily of liquid iron, may interact with the mantle rocks and transport iron into the mantle.
28 The diffusion of atoms along the boundaries of different grains of mantle rocks has been proposed as
29 a possible mechanism for the core-mantle interaction. We performed atomistic simulations of one of
30 the dominant mineral phases at the core-mantle boundary, (Mg,Fe)O ferropericlase to calculate the
31 diffusion rates of magnesium, iron, and oxygen within grain boundary regions. The results suggest
32 that, on the time scale of the Earth's history, the distance of the grain boundary diffusion of iron is
33 likely to be very limited and insufficient to explain any iron enrichment phenomena at the bottom of
34 the lower mantle.

35 **1 Introduction**

36 As the sharpest compositional discontinuity in the Earth's interior, the core-mantle boundary
37 (CMB) at the depth of 2889 km exhibits strong complexity and has a significant impact on the
38 chemical evolution of the Earth (Young & Lay, 1987). The interaction between the solid silicate
39 mantle and the liquid iron core may cause extensive enrichment of iron at the lowermost mantle,
40 which is supported by multiple geophysical observations. First, two continent-sized large low shear
41 velocity provinces (LLSVPs) extend up to 1200 km above the CMB (Garnero et al., 2016) and can be
42 explained by iron-enriched materials (Vilella et al., 2021; Yuan et al., 2023). They exhibit electrical
43 conductivity anomalies (Nagao et al., 2003; Ohta et al., 2010) which may also be associated with
44 iron. Second, the 5–40 km thick patches right above the core with unusually low seismic velocities,
45 known as ultralow-velocity zones (ULVZs) (Williams & Garnero, 1996), may be attributed to local
46 iron enrichment (Wicks et al., 2010). Third, a ~200-m-thick high conductance layer above the core
47 has been inferred from Earth's nutations (Buffett, 1992; Buffett et al., 2002) and may comprise
48 metallic FeO (Knittle & Jeanloz, 1986; Sherman, 1989).

49 Various hypotheses have been proposed to explain this putative iron enrichment above the CMB.
50 The thickness of the iron-enriched layer caused by capillary rise is only < 20 m (Poirier et al., 1998).
51 Alternative hypotheses suggest that pressure gradients caused by the dynamic topography at the
52 CMB may drive iron upwards into the lower mantle (Kanda & Stevenson, 2006). Additionally, iron
53 infiltration can be caused by the sedimentation of the liquid outer core (Buffett et al., 2000). However,
54 both of them are sensitive to the viscosity of the lowermost mantle, which is subject to considerable
55 uncertainty (Rudolph et al., 2015). Otsuka and Karato (2012) proposed that the penetration of iron
56 into the mantle can be caused by a morphological instability, which is a mechanism independent of
57 viscosity, but the effective diffusivity used to calculate iron infiltration thickness is extrapolated from
58 low-pressure experimental data and remains controversial (J. Deng et al., 2019; Yoshino, 2019).

59 Grain boundaries (GBs) are regions that separate different grains in a polycrystalline material.
60 Due to the more disordered atomistic structure at the interface compared to the crystalline lattice,

61 atomic diffusion along GBs is typically orders of magnitude faster than its lattice counterpart (Joesten,
62 1991; Dohmen & Milke, 2010). Therefore, GB diffusion strongly affects physical properties in
63 the Earth's materials, including the viscosity (Mantisi et al., 2017), electrical conductivity (ten
64 Grotenhuis et al., 2004), and seismic attenuation (Jackson et al., 2002). It is suggested that GB
65 diffusion provides an efficient mechanism to exchange carbon and siderophile elements between the
66 mantle and the core (Hayden & Watson, 2007, 2008), and may effectively modify the tungsten and
67 helium isotopic compositions of the plume-source mantle (Yoshino et al., 2020; Ferrick & Korenaga,
68 2023). The diffusion of iron along GBs may be another potential mechanism for iron infiltration
69 from the outer core to the lower mantle.

70 Previous experimental and theoretical studies have explored the GB diffusion in MgO periclase
71 (McKenzie et al., 1971; Van Orman et al., 2003; Karki et al., 2015; Landuzzi et al., 2015; Riet et
72 al., 2021). However, most of these results do not account explicitly for pressure and temperature
73 conditions near the CMB, and the GB diffusion in (Mg,Fe)O, one of the most abundant phases at
74 the CMB (X. Deng et al., 2023), remains poorly understood. In addition, recent results have shown
75 that the structure of a GB is far from unique, and is not simply determined by the misorientation
76 between the grains. In particular, GB structures evolve when interacting with vacancy complexes,
77 resulting in significant changes in GB properties Hirel et al. (2022). In this study, we investigate the
78 GB diffusion of Mg, Fe, and O along GB in (Mg,Fe)O bicrystals under the CMB conditions using
79 large-scale molecular dynamics (MD) simulations. Bicrystals of high compaction, expected to be
80 most favourable in high-pressure conditions of the CMB, are constructed (Hirel et al., 2019). We
81 explore the dependence of the GB diffusion coefficient on defect concentration and temperature. The
82 results are used to examine the efficiency of transporting iron from the core to the mantle through
83 GB diffusion of (Mg,Fe)O ferropericlase.

84 **2 Methods**

85 **2.1 Interatomic potential**

86 There are two main methods to describe the interaction of atoms in MD simulations: *ab*
87 *initio* method based on density functional theory and the force field approach. The *ab initio*
88 method is considered more accurate because it calculates the electronic structure of material quantum
89 mechanically, in principle, without relying on empirical parameters. However, this method is
90 computationally demanding, limiting simulations to smaller systems and shorter times. On the
91 other hand, the force field approach uses simplified force parameters, allowing for less intensive
92 computations and enabling longer simulations of larger systems, which is crucial for simulating
93 polycrystalline systems and reducing statistical error. Therefore, in this study, we choose the force
94 field approach and use a new rigid-ion potential developed by Pedone et al. (2006). This approach
95 incorporates long-range Coulomb interactions, a Morse function for short-range interactions, and
96 a repulsive term similar to the Lennard-Jones function. The parameters were calibrated using
97 experimental measurements, including lattice dimensions, elasticity values, both high-frequency and
98 static dielectric constants, lattice energies, piezoelectric constants, and phonon frequencies observed
99 in binary oxides. This potential demonstrates high reliability and applicability in modeling lattice
100 defects, diffusion, and GBs in forsterite (Hirel et al., 2021; Furstoss et al., 2022). Hirel et al. (2021)
101 highlight its ability to accurately reproduce various properties across a pressure range of 0 to 12
102 GPa, while Furstoss et al. (2022) further confirm its effectiveness through its good agreement with
103 *ab initio* calculations in terms of GB atomistic structures, energies, and excess volumes in forsterite.
104 To further verify the reliability of this potential for simulating (Mg,Fe)O GBs, we calculated the
105 formation enthalpy of MgO GBs across pressure conditions of nearly the entire mantle (Figure
106 S1). The results are in good agreement with Hirel et al. (2019), supporting the applicability of this
107 potential to the periclase system at elevated pressures.

108 **2.2 Molecular Dynamics Simulations**

109 The GBs used in this study are symmetric tilt GBs where grains are rotated by opposite
110 angles around the same [001] axis. Our focus is on structures with high-angle GBs as they are

111 more common in polycrystalline MgO (Saylor et al., 2003), likely more pertinent to understanding
 112 GB diffusion within the Earth’s interior, and also more convenient to study (Riet et al., 2021).
 113 Bicrystals are constructed with AtomsK (Hirel, 2015). Two crystals of MgO are rotated by opposite
 114 angles ($\pm\alpha/2$), cut and then stacked together. We apply translation to one of the two symmetrical
 115 single crystals along the GB, and compute relative energies of different configurations, which yields
 116 several energy minima. Configurations corresponding to these minima can be called “complexions”.
 117 As demonstrated earlier, at the high pressures reigning in the Earth’s mantle, the most compact
 118 complexions are energetically most favourable (Hirel et al., 2019), and is used as a starting point.
 119 Such a compact complexion can interact with vacancy complexes, thus transforming its atomic
 120 configuration further (Hirel et al., 2022). In the following two symmetric tilt GB are modelled,
 121 corresponding to two different misorientation angles: $\alpha = 36.8^\circ$ where the two crystals meet with
 122 $\{310\}$ planes, and $\alpha = 29.5^\circ$ where the GB plane does not correspond to any high-symmetry crystal
 123 plane. Mg-O vacancy pairs are randomly introduced within a region approximately 1 nm wide
 124 adjacent to the GB of the complexion to obtain the initial configuration of MgO bicrystals for the
 125 following MD simulations. The vacancy concentration C_{vac} is defined as the ratio between the
 126 number of MgO units removed and the number of MgO units in the 1-nm GB region. Following
 127 Ammann et al. (2010), the vacancy concentrations considered in this study range from 0.4 at% to
 128 8.0 at%, which are estimated from experimental results (Holzapfel et al., 2003; Yamazaki & Irifune,
 129 2003). The structure of (Mg,Fe)O is generated by the random substitution of Mg with different
 130 contents of Fe in the aforementioned MgO structure.

131 To ensure a genuine depiction of real material, (Mg,Fe)O single crystal must be of adequate
 132 size so that its inner structure mimics that of large grains (Glišović et al., 2015) in the lower mantle.
 133 We construct bicrystal systems containing over 50,000 atoms, resulting in an average distance of
 134 over 20 nm between the centers of adjacent grains. Each GB operates independently from others,
 135 ensuring that atoms involved in one boundary do not interact with any other boundaries throughout
 136 the simulation. A supercell with larger GB area has also been simulated and yields similar GB
 137 diffusion coefficients, confirming the size convergence of our systems (Figure S3).

138 All MD simulations are conducted using LAMMPS (Plimpton, 1995) under periodic boundary
 139 conditions. The systems are first equilibrated in isothermal-isobaric conditions (NPT) for 100 ps
 140 at a series of temperatures, under two pressures of 0 GPa and 140 GPa for MgO and (Mg,Fe)O,
 141 respectively. The resulting structures are then used as the initial configurations to set up the MD
 142 simulations for 5 ns under an canonical ensemble (NVT) with the Nosé-Hoover thermostat (Hoover,
 143 1985), in order to evolve the GB structure to reach a steady state. Subsequently, we perform long
 144 NVT simulations for 5 to 10 ns, from which the GB diffusion is investigated. The timestep of all
 145 simulations is 1 fs.

146 2.3 Trajectory analysis

147 Due to the spatially heterogeneous diffusion in polycrystalline systems, a direct analysis of the
 148 MD trajectory of the entire system would mask the distinct characteristics of the crystal interiors and
 149 GBs. Following Riet et al. (2021), we employed an advanced local ionic environment analysis to
 150 extract the atomic properties within the GB regions from the bulk system. The first post-processing
 151 step is an energy minimization to map instantaneous MD configurations (sampling at 1-ns intervals)
 152 to their nearest local energy minima. Through this, we remove the thermal vibrational displacement
 153 of atoms and thereby obtain a more distinct representation of the GBs. Subsequently, we examine
 154 the distribution of nearest neighbors of all atoms at the energy minima to identify which atoms have
 155 complete coordination with the six nearest neighbors and which ones are undercoordinated. The
 156 undercoordinated atoms are associated with the GB regions (Riet et al., 2018). This analysis is
 157 realized through the nearest neighbor search using the MDAnalysis package (Michaud-Agrawal et
 158 al., 2011). Consistent with Riet et al. (2018) and Riet et al. (2021), the fraction of undercoordinated
 159 atoms at the GBs, denoted as g , remains relatively constant through a single MD trajectory. This
 160 insight allowed us to apply the modified Hart equation (Hart, 1957; Dohmen & Milke, 2010; Riet et
 161 al., 2021) to compute the GB diffusion coefficient:

$$162 \quad D_{\text{total}} = gD_{\text{GB}} + (1 - g)D_{\text{vol}}, \quad (1)$$

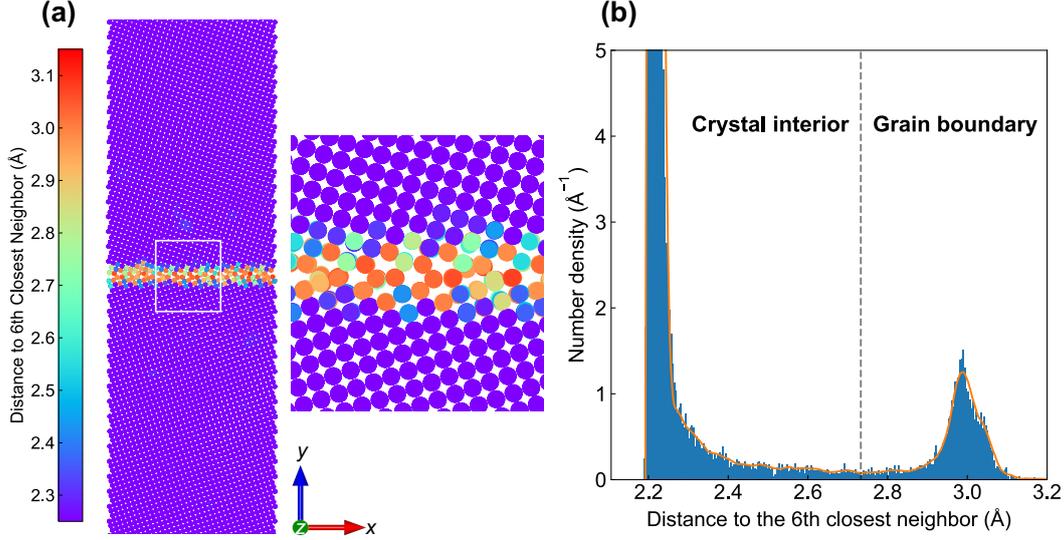


Figure 1. The local ionic environment analysis of MgO at 0 GPa and 2000 K. The results are derived from a snapshot of the MD simulation at 6 ns. The energy minimization is applied to remove the thermal vibration of atoms. (a) The color mapping of the distances from a central ion to its 6th closest neighbor. The view is perpendicular to the rotation angle of the grain boundaries. The atoms enclosed by the white frame are zoomed in to show details. (b) Distributions of distances from a central ion to its 6th closest neighbor. The orange curve is the smoothed histogram using the Savitzky-Golay filter (Savitzky & Golay, 1964), and its minimum value between the two peaks is used to determine the cutoff distance.

163 where D_{total} , D_{GB} , and D_{vol} are the overall diffusion coefficient, GB diffusion coefficient, and
 164 volume diffusion coefficient within the single crystal interiors, respectively. Since our analysis of
 165 atoms within crystal interiors showed negligible diffusion, we assume $D_{\text{vol}} \approx 0$. Thus, the GB
 166 diffusion coefficient is approximated by:

$$167 \quad D_{\text{GB}} = \frac{D_{\text{total}}}{g} \quad (2)$$

168 D_{total} can be easily derived as the slope of mean square displacement (MSD) using the Einstein
 169 diffusion relation

$$170 \quad D_{\text{total}} = \lim_{t \rightarrow \infty} \frac{\text{MSD}}{6t} = \lim_{t \rightarrow \infty} \frac{\langle [\vec{r}(t + t_0) - \vec{r}(t_0)]^2 \rangle_{\alpha}}{6t}, \quad (3)$$

171 where $\vec{r}(t)$ is the particle trajectories continuous in Cartesian space, and $\langle \cdot \cdot \rangle_{\alpha}$ represents an average
 172 over atoms of species α (Mg, Fe, O) and over time with different origins (Karki, 2015). Only when
 173 the MSD is a linear function of time do we intercept the segment of MSD and calculate the diffusion
 174 coefficient by linear fitting. The temperature-dependent diffusion coefficient can be fitted using the
 175 Arrhenius equation,

$$176 \quad D = D_0 e^{-\frac{\Delta H}{RT}}, \quad (4)$$

177 where D_0 is the pre-exponential factor, R is the ideal gas constant, and ΔH is the activation enthalpy.

178 3 Results and Discussion

179 3.1 Identification of grain boundary atoms

180 In this study, we analyze the structure of the GB and identify the GB atoms by examining the
 181 local ionic environments following Riet et al. (2021). In the ferropericlase or magnesiowüstite phase

182 of (Mg,Fe)O, ions within the grain typically have six equidistant nearest neighbors. In contrast, ions
 183 at the GB exhibit a non-crystalline local environment with varying distances to neighboring ions
 184 and often less than six nearest neighbors. Figure 1a shows the color mapping of the distances from
 185 a central ion to its sixth-closest neighbor in a snapshot of the MD trajectory of MgO at 0 GPa and
 186 2000 K, in which the atoms associated with the GB region are clearly presented (i.e., atoms that are
 187 not colored purple). The distribution of distances from a central ion to its sixth-closest ion at energy
 188 minima structures is shown in Figure 1b, which exhibits a bimodal pattern. The first peak in this
 189 distribution indicates ions with six neighbors, characteristic of atoms within a single crystal, not in a
 190 GB. The adjacent shoulder on this peak represents atoms near the GB, where relaxation can lead to
 191 slightly longer bond distances compared to the crystal interior. The second peak signifies ions that
 192 are undercoordinated, typically having five or fewer neighbors, and are located in the GB region. We
 193 set the minimum point between the first and second peaks as the cutoff distance for each system to
 194 differentiate between internal and GB ions following Riet et al. (2021).

195 **3.2 Grain boundary diffusivity**

196 In this section, we discuss the GB diffusion coefficients in MgO at ambient pressure, and in
 197 (Mg,Fe)O at 140 GPa, calculated using Equation 2 and Equation 3. The MSD data from all the
 198 simulations in this study can be found in Figure S4 in Supporting Information. Taking pure MgO as
 199 an example, we explore how the GB diffusion coefficients of Mg and O vary with C_{vac} , system size,
 200 and the misorientation angle of the GB (see Text S1 in Supporting Information). This preliminary
 201 study allowed us to determine that fully converged results are obtained when C_{vac} reaches 3.2 at% or
 202 above, hence, only the diffusivity data at this concentration are presented in the following.

203 **3.2.1 MgO at 0 GPa**

204 Figure 2 summarizes the GB diffusion coefficients of MgO as a function of temperature at
 205 ambient pressure. To ensure convergence, we adopt a defect concentration of 3.2 at% to constrain
 206 the upper bound of the diffusivity (see Text S1 in Supporting Information). Our results generally
 207 agree well with previous theoretical studies using molecular dynamics simulations, and fall between
 208 the results of Riet et al. (2021) and Landuzzi et al. (2015) for both Mg and O. McKenzie et al. (1971)
 209 experimentally obtained $\frac{\delta D_{\text{GB}}}{\sqrt{D_{\text{vol}}}}$ for oxygen diffusion in periclase at around 2000 K, where δ is the
 210 GB width. However, since the value of D_{vol} in MgO remains poorly constrained, it is difficult to
 211 directly compare experimentally inferred GB diffusivity with our simulation outcomes. Riet et al.
 212 (2021) estimated that δD_{GB} of oxygen lies between $4 \times 10^{-23} \text{ m}^3 \text{ s}^{-1}$ and $2 \times 10^{-21} \text{ m}^3 \text{ s}^{-1}$, based
 213 on the highest and lowest D_{vol} values reported in the literature (Oishi & Kingery, 1960; Yang &
 214 Flynn, 1994) and experimental measurements (McKenzie et al., 1971). Our result for $C_{\text{vac}} = 3.2$
 215 at% is $\sim 4 \times 10^{-21} \text{ m}^3 \text{ s}^{-1}$, slightly higher than this range. However, the C_{vac} in pure MgO is
 216 significantly lower compared to (Mg,Fe)O due to the absence of multivalent ions (Van Orman et
 217 al., 2003; Ammann et al., 2010). Considering lower vacancy concentrations of $C_{\text{vac}} < 0.8$ at%, our
 218 simulation results fall within the range of experimental estimates.

219 The GB diffusion coefficients increase significantly with temperature, and can be well fitted by
 220 Equation 4 (dashed lines in Fig. 2). The activation enthalpies for Mg and O are $229(\pm 10) \text{ kJ mol}^{-1}$
 221 and $217(\pm 64) \text{ kJ mol}^{-1}$, respectively. The only experimental results of the activation enthalpy
 222 for GB diffusion of O is 230 kJ mol^{-1} (measured at 1380–1800 K, Passmore et al., 1966), which
 223 our simulations match closely. Karki et al. (2015) reported the activation enthalpies for Mg (221
 224 kJ mol^{-1}) and O (212 kJ mol^{-1}) migration along the {410} symmetric boundaries of MgO bicrystals
 225 at 0 GPa using *ab initio* calculations. Similar results were obtained by Harris et al. (1997) using
 226 MD simulations with empirical potentials. Our simulation results also align very well with these
 227 theoretical predictions that assumed *ad hoc* diffusion pathways. It is noteworthy that in the bulk
 228 crystal of periclase, the diffusion activation enthalpy of Mg is smaller than that of O (Ammann et
 229 al., 2010), while in the GB, they are quite similar and the activation enthalpy of O is slightly smaller.
 230 This may be related to the markedly different chemical environments at the GBs compared to the
 231 interior of the crystal. In summary, the GB diffusion properties of MgO at ambient pressure obtained
 232 from this study are consistent with previous theoretical and experimental data.

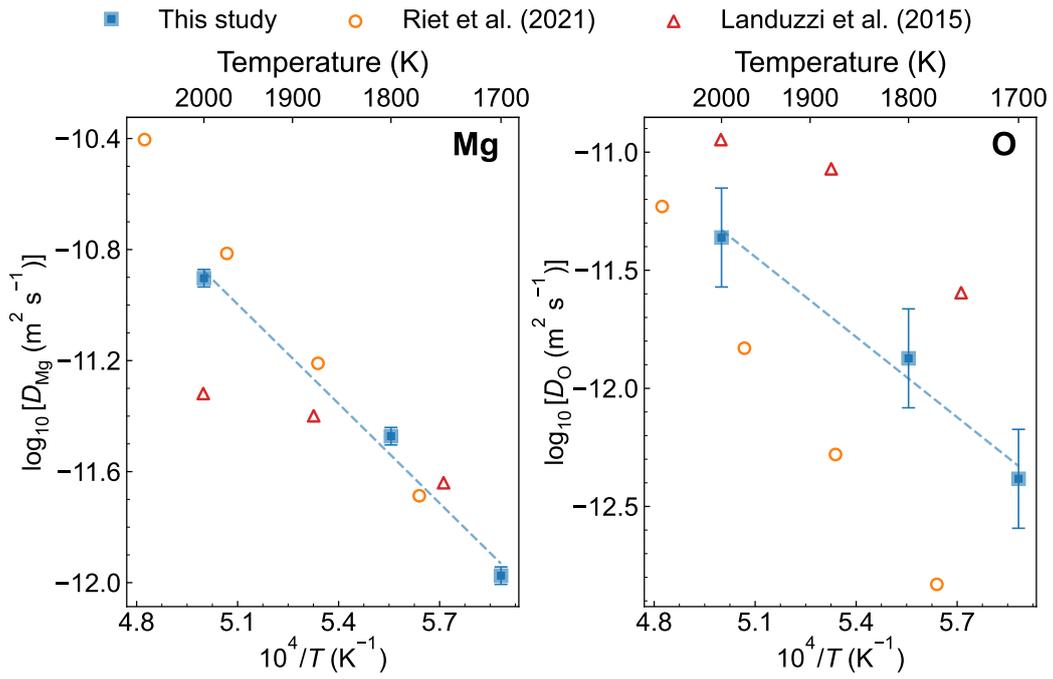


Figure 2. Grain boundary diffusion coefficients of Mg (left) and O (right) as a function of reciprocal temperature (1700 K, 1800 K, and 2000 K) in MgO with a C_{vac} of 3.2 at% at ambient pressure. The error bars are estimated from the error bars in Figure S2, assuming the same relative standard deviation for each element. Results from previous theoretical studies are plotted in open symbols for comparison (Riet et al., 2021; Landuzzi et al., 2015). Dashed lines are fitted Arrhenius functions (Equation 4).

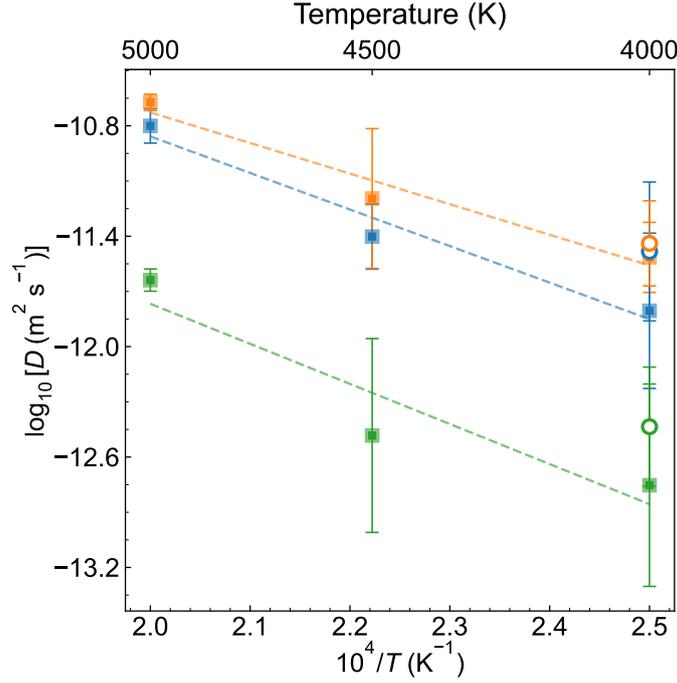


Figure 3. Grain boundary diffusion coefficients as a function of reciprocal temperature (4000 K, 4500 K, and 5000 K) in (Mg_{0.9}Fe_{0.1})O (solid squares) and (Mg_{0.16}Fe_{0.84})O (open circles) with a C_{vac} of 3.2 at% at 140 GPa. The diffusivity of Mg, Fe, and O are shown in blue, orange, and green, respectively. The error bars represent 2SD of the diffusion coefficients calculated from four 5-ns-long MD trajectories. Dashed lines are fitted Arrhenius functions (Equation 4).

233 3.2.2 (Mg,Fe)O at 140 GPa

234 The high-pressure diffusion coefficients of Mg, Fe, and O in (Mg,Fe)O with two different iron
 235 contents are shown in Figure 3. For (Mg_{0.9}Fe_{0.1})O ferropericlase, the simulation temperatures are
 236 set between 4000 to 5000 K, corresponding to the upper bounds of the estimated CMB temperatures
 237 throughout the Earth’s thermal evolution (Andraut et al., 2016). (Mg_{0.16}Fe_{0.84})O magnesiowüstite
 238 is taken as a prototype Fe-rich material that has been suggested to be the main constituent of ULVZs
 239 (Wicks et al., 2010, 2017) and the high conductance layer (Buffett, 1992; Knittle & Jeanloz, 1986),
 240 and consequently it may serve as an important medium for the iron transport from the outer core
 241 to the lower mantle. Recent studies suggest that the melting point of FeO wüstite under CMB
 242 pressure conditions reaches up to 4140 K (Dobrosavljevic et al., 2023), indicating that our simulation
 243 temperature of 4000 K for (Mg_{0.16}Fe_{0.84})O is below its solidus. Overall, the diffusion coefficients
 244 slightly increase with iron content, and the order of diffusion coefficients for the three elements follows
 245 $D_{GB}^{Fe} \approx D_{GB}^{Mg} > D_{GB}^O$. We find that the diffusion coefficient of Mg is about an order of magnitude
 246 larger than that of O, closely aligning with the results of Riet et al. (2021). Furthermore, Fe and Mg
 247 have similar diffusion coefficients, both significantly larger than O, which is consistent with the MD
 248 data for GB diffusion in olivine (Mantisi et al., 2017). This suggests that the relative magnitudes
 249 of GB diffusion coefficients for different elements are, to a large extent, controlled by ionic radii,
 250 considering that the ionic radii of Fe²⁺, Mg²⁺, and O²⁻ are 75, 86, and 126 pm, respectively (Slater,
 251 1964). Due to the steric effect (Nalwa, 2001), smaller ions are better suited to move through available
 252 space to facilitate diffusion. We find that the uncertainty of the diffusion coefficients at 5000 K is
 253 much smaller than at lower temperatures, which may be due to the more stable premelting state of
 254 the GBs at higher temperatures, reducing the variation in diffusivity. Regarding the temperature
 255 dependence, the diffusion activation enthalpies for Mg, Fe, and O are 448(±63) kJ mol⁻¹, 328(±37)

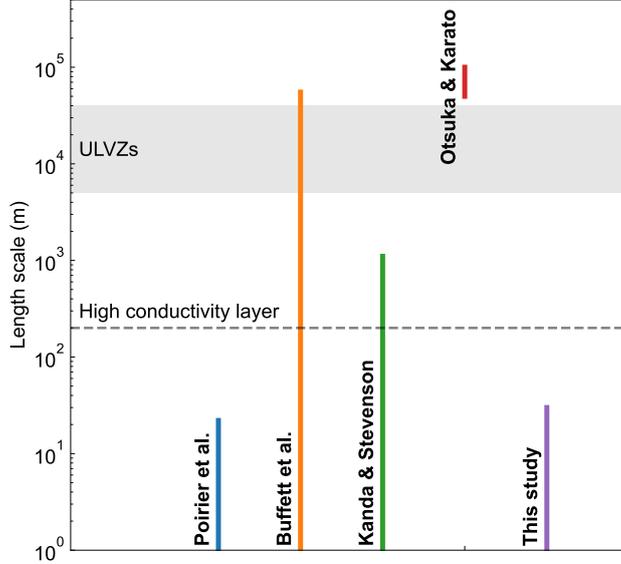


Figure 4. Length scale of iron transport from the core to the mantle compared to length scales of high conductance layer and ULVZs. Different iron infiltration mechanisms are shown for comparison (Poirier et al., 1998; Buffett et al., 2000; Kanda & Stevenson, 2006; Otsuka & Karato, 2012).

256 kJ mol⁻¹, and 479(±97) kJ mol⁻¹, respectively. Due to the pressure effect on diffusion, they are
 257 significantly higher than the activation enthalpies for MgO under ambient pressure.

258 4 Implications

259 To explore the upper limit of the efficiency of iron transport via the GB diffusion mechanism,
 260 we consider the maximum diffusivity of iron in Figure 3 ($2.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$) for the subsequent
 261 calculations. The effective diffusion coefficient for a polycrystalline material can be estimated using
 262 this equation (Balluffi et al., 2005):

$$263 \quad D_{\text{eff}}^{\text{Fe}} = D_{\text{vol}}^{\text{Fe}} + \frac{3\delta}{d} D_{\text{GB}}^{\text{Fe}}, \quad (5)$$

264 where δ is the GB width (~1 nm) and d is the grain size (0.01–10 mm, Glišović et al., 2015) in the
 265 lower mantle. For pure MgO periclase, the D_{vol} values of Mg and O under the CMB conditions
 266 are very small and can be negligible (less than $10^{-20} \text{ m}^2 \text{ s}^{-1}$, Ita & Cohen, 1998), while in the
 267 presence of Fe, higher vacancy concentrations might lead to faster lattice diffusion of Mg, O, and Fe
 268 (Ammann et al., 2010). We extract the actual contribution of GB diffusion to the effective diffusion
 269 coefficient by setting $D_{\text{vol}}^{\text{Fe}} = 0$, and obtain the characteristic length scale of the iron transport through
 270 GB diffusion:

$$271 \quad L_{\text{GB}}^{\text{eff}} = \sqrt{\frac{3\delta}{d} D_{\text{GB}}^{\text{Fe}} t}, \quad (6)$$

272 where the time scale t is set to the age of the Earth (4.54 Gyr, Dalrymple, 2001). The result of $L_{\text{GB}}^{\text{eff}}$
 273 does not exceed 30 m, as shown in Figure 4. Other iron infiltration mechanisms proposed by previous
 274 studies, including capillary rise (Poirier et al., 1998), suction (Kanda & Stevenson, 2006), upward
 275 sedimentation of outer core alloys (Buffett et al., 2000), and morphological instability (Otsuka &
 276 Karato, 2012) are also plotted for comparison. The results indicate that the effective transport
 277 distance of Fe through GB diffusion in (Mg,Fe)O is likely to be quite small, considering the transport
 278 distances of other mechanisms and the spatial scales of ULVZs and the high conductance layer. To
 279 further validate this finding, we solve Fick's second law of diffusion to calculate the concentration

280 profile of iron in the mantle:

$$281 \quad \frac{\partial C}{\partial t} = -\frac{3\delta}{d} D_{\text{GB}}^{\text{Fe}} \nabla^2 C \quad (7)$$

282 Assuming that the core always maintains a composition of pure iron, and considering an initial
 283 condition of zero Fe concentration in the mantle, we obtained the concentration distribution of iron
 284 in the mantle after the GB diffusion of 4.54 Gyr. The total mass of Fe that has been transported
 285 to the mantle is 5.1×10^{19} kg, which can only account for less than 20 wt% of the ~200-m-high
 286 conductance layer.

287 At the CMB, not only (Mg,Fe)O but also silicate minerals such as bridgmanite and post-
 288 perovskite are present. Given that lattice diffusion of elements in silicate perovskite is much slower
 289 than in ferroperricite (Ammann et al., 2010; Holzapfel et al., 2003, 2005), we argue that GB diffusion
 290 is unlikely to be an effective mechanism to transport Fe from the core to the lower mantle. Considering
 291 that some siderophile elements (e.g., W) have larger atomic radii and mass than Fe, we speculate
 292 that their GB diffusion coefficients in (Mg,Fe)O might be even smaller than that of Fe. So far the
 293 only data available for comparison are experimental results under relatively low pressures (Hayden
 294 & Watson, 2007; Yoshino et al., 2020). Therefore, more studies are needed to accurately quantify
 295 the efficiency of GB diffusion in exchanging siderophile elements across the CMB to elucidate the
 296 scale and extent of the core-mantle interaction.

297 **5 Open Research**

298 Data used in this study are available at Peng and Deng (2024). The software LAMMPS used in
 299 this study is developed openly at <https://github.com/lammps/lammps> and available at Plimpton
 300 et al. (2021).

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1 **Supporting Information for “Grain boundary diffusion of**
2 **ferropericlase: Implications for the core-mantle interaction”**

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5 **Contents of this file**

- 6 1. Text S1
7 2. Figures S1 to S7

8 Text S1.

9 We take pure MgO as an example to explore how the grain boundary (GB) diffusion coeffi-
10 cients vary with vacancy concentration (C_{vac}), system size, and the misorientation angle of the
11 GB.

12 At ambient pressure with $C_{\text{vac}} \geq 3.2$ at%, the GB diffusivities in MgO for different C_{vac} show
13 similar values within the error bars (Figure S2). Moreover, the misorientation angle likely only
14 marginally affects the GB diffusivity (Figure S2), and the diffusivities are not sensitive to the
15 size of the simulation system (Figure S3). We note that the present results are based on only
16 two high-symmetry tilt GBs and other types of GB, like twist GB remain to be investigated.
17 The diffusivity as a function of C_{vac} at high pressure is presented in Figure S5. Similar to the
18 diffusion of Mg and O in MgO single crystals (e.g., Ammann et al., 2010), the diffusion coeffi-
19 cient shows a near-linear positive correlation with C_{vac} when C_{vac} is relatively low ($C_{\text{vac}} \leq 1.6$
20 at%). However, for $C_{\text{vac}} \geq 3.2$ at%, its facilitation effect on diffusion tends to saturate, resulting
21 in the nearly constant GB diffusivity. Additionally, we observed that in all the systems studied,
22 atomic diffusion occurs only within a GB region approximately 1 nm wide. Over the simulation
23 timescale of 10–20 ns, these vacancies do not migrate into the crystal interior, thereby demon-
24 strating strong anisotropy aligning with the findings of Riet, Van Orman, and Lacks (2018).
25 Specifically, diffusion parallel to the GB direction (x - z plane) is the most significant (Figure
26 S5b). Figure S6 shows the MD trajectories of Mg in the MgO GB at 4000 K and 140 GPa.
27 It can be observed that within the 1-nm-wide GB region, some atoms no longer occupy spe-
28 cific crystallographic sites but show liquid-like motion. The GB transitions into a liquid-like,
29 thermodynamically stable nanoscale film, even though the simulation temperature is below the

30 melting point. This order-disorder transition is termed GB premelting (Torabi Rad et al., 2020)
31 and has been observed in many materials (e.g., Glicksman & Vold, 1972; Dillon & Harmer,
32 2007; Frolov et al., 2013). Similar to the findings of Riet, Van Orman, and Lacks (2021) and
33 Mantsi, Sator, and Guillot (2017), the GB in this quasi-liquid state exhibits considerable disorder
34 nature and transport properties close to those of a supercooled liquid. To further investigate
35 the evolution of the atomic structure of GBs with C_{vac} , we compare snapshots of MgO GBs
36 at various C_{vac} values during MD simulations (Figure S7). We capture the transition of the GB
37 structure from ordered to disordered as C_{vac} increased. The disorder upon reaching the limit may
38 correspond to the saturation effect observed in the GB diffusivity. This indicates that vacancies
39 within the crystal can influence the structure (Hirel et al., 2022) and diffusion characteristics of
40 the GB. However, once the GB structure stabilizes, diffusion becomes almost independent of
41 the number of vacancies in the single crystal.

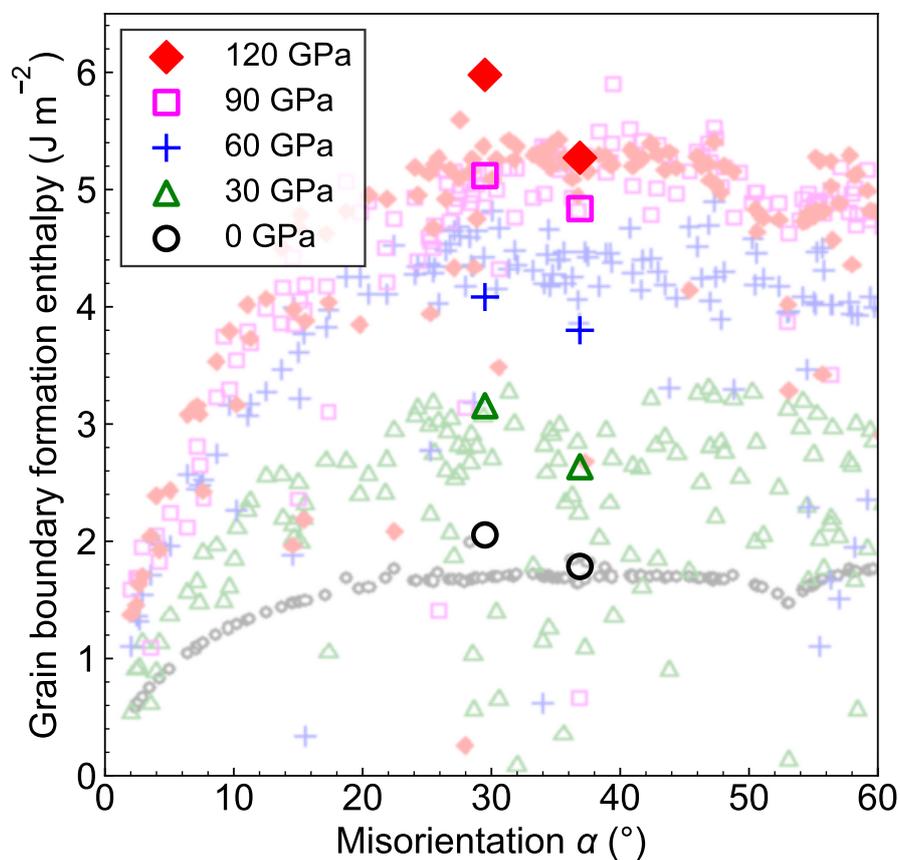


Figure S1. The formation enthalpy of [001] symmetric tilt grain boundaries in MgO as a function of the misorientation angle at 0 GPa (black open circles), 30 GPa (green open triangles), 60 GPa (blue crosses), 90 GPa (magenta open squares), and 120 GPa (red diamonds). The data from Hirel et al. (2019) are shown in light symbols for comparison.

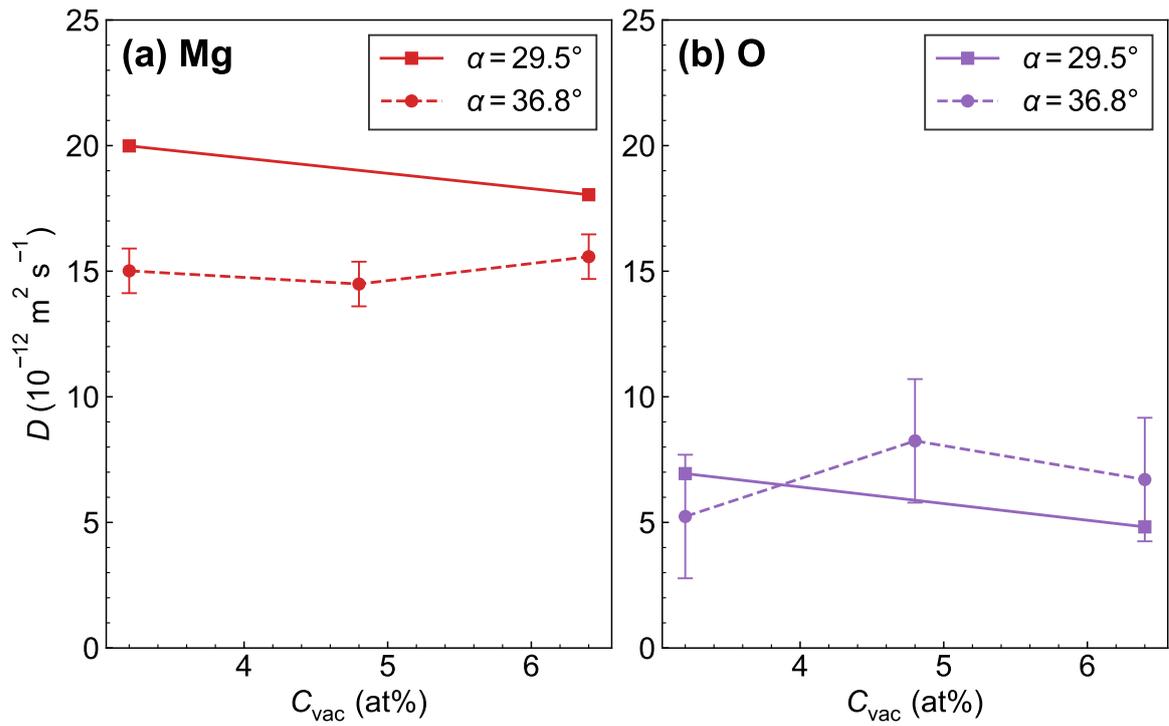


Figure S2. Grain boundary diffusion coefficients of Mg (a) and O (b) as a function of vacancy concentration for two different misorientation angles (α) at 2000 K and 0 GPa. The error bars for $\alpha = 36.8^\circ$ are the 2SD values for the diffusivity data with different vacancy concentrations.

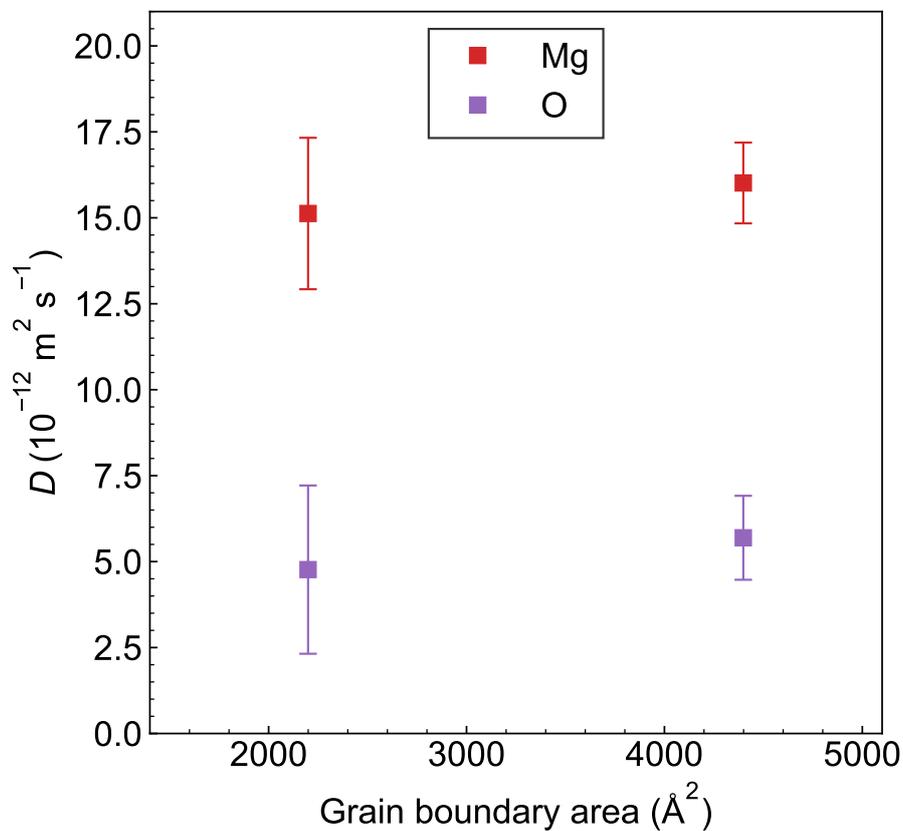


Figure S3. Grain boundary diffusion coefficients of Mg (red) and O (purple) as a function of the area of the grain boundary in the simulation box at 2000 K and 0 GPa. The larger supercell (grain boundary area: 4398.5 \AA^2) is obtained by duplicating the smaller supercell (grain boundary area: 2199.3 \AA^2) along the z-axis twice. The error bars are given by the differences of the results from two 5-ns trajectories.

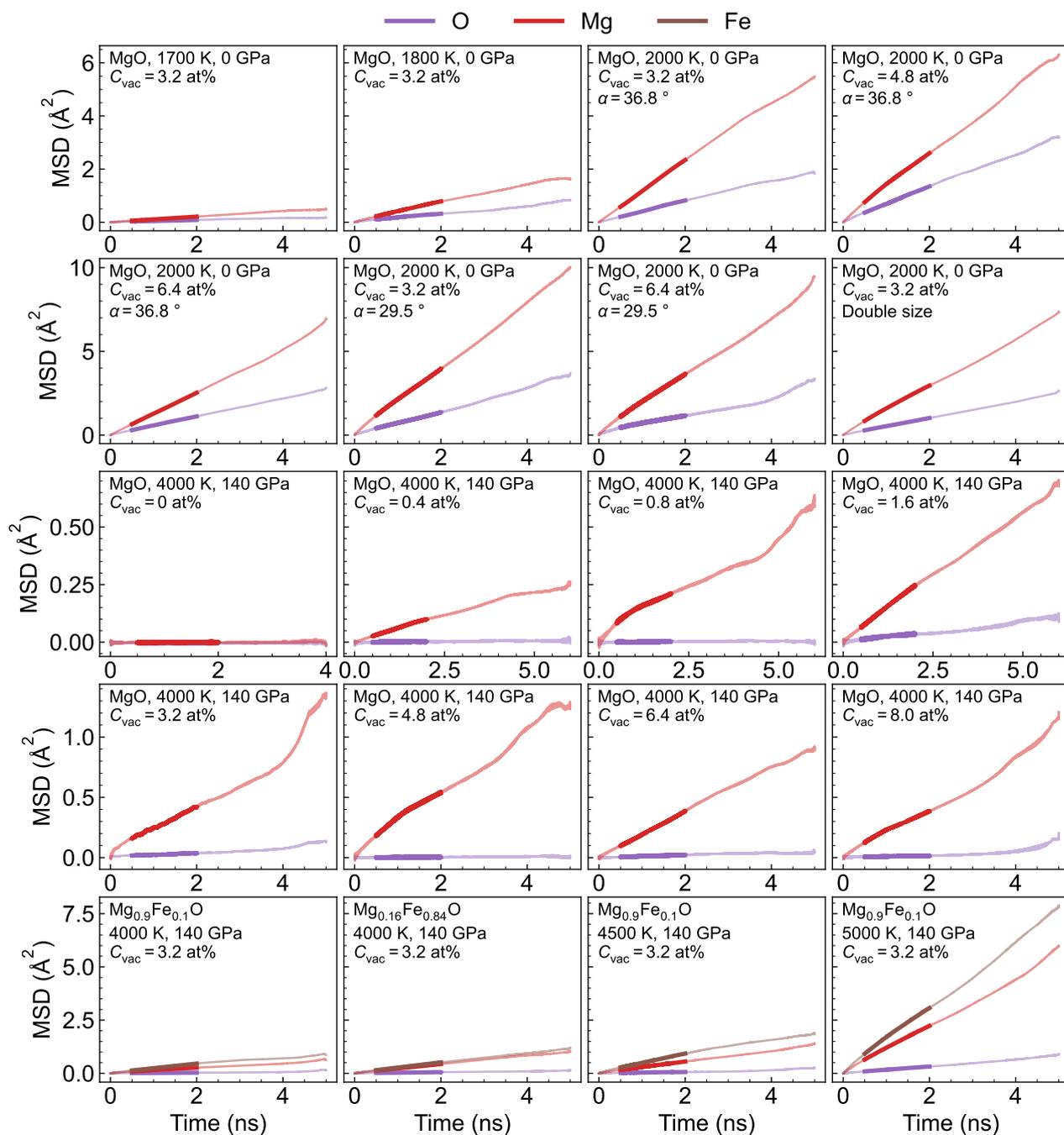


Figure S4. The mean square displacements (MSDs) as a function of simulation time for all diffusion coefficients calculated in this study. The chemical composition, temperature (T), pressure (P), and vacancy concentration (C_{vac}) are listed for all systems. The misorientation angle (α) is listed for systems in Figure S2. Average MSDs are shown for systems with multiple trajectories. Thick lines represent the sections used for linear fitting.

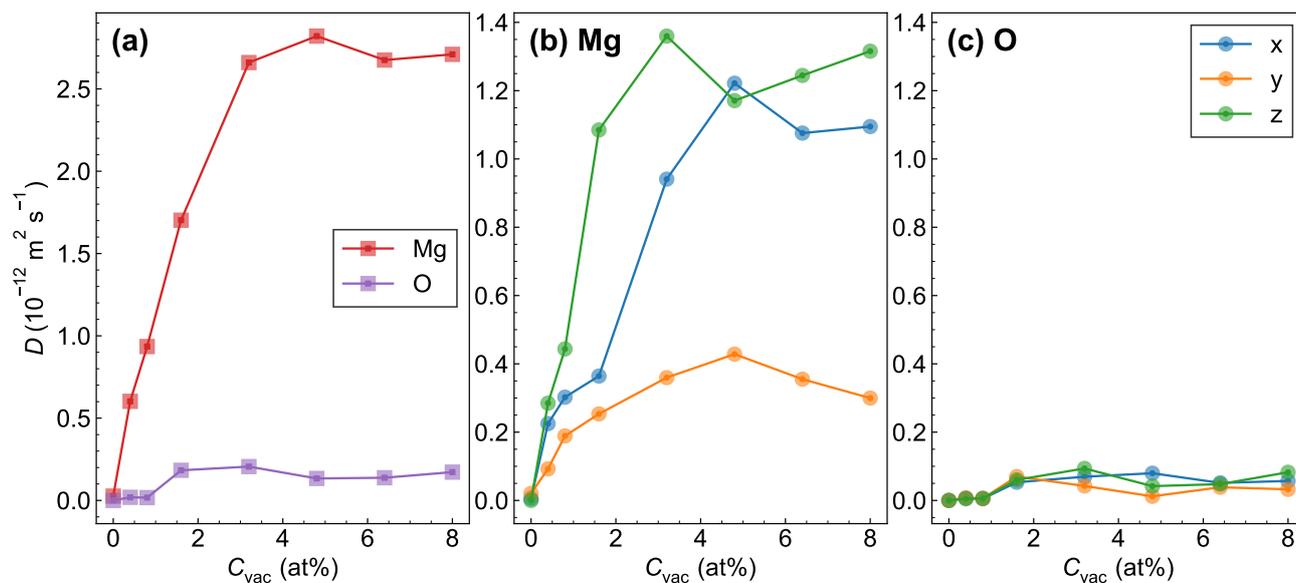


Figure S5. (a) The grain boundary diffusion coefficients of Mg (red) and O (purple) as a function of vacancy concentration for MgO at 140 GPa and 4000 K. (b, c) The anisotropy of grain boundary diffusion of Mg (b) and O (c) shown by plotting diffusion coefficients along three axes, x (blue), y (orange), and z (green).

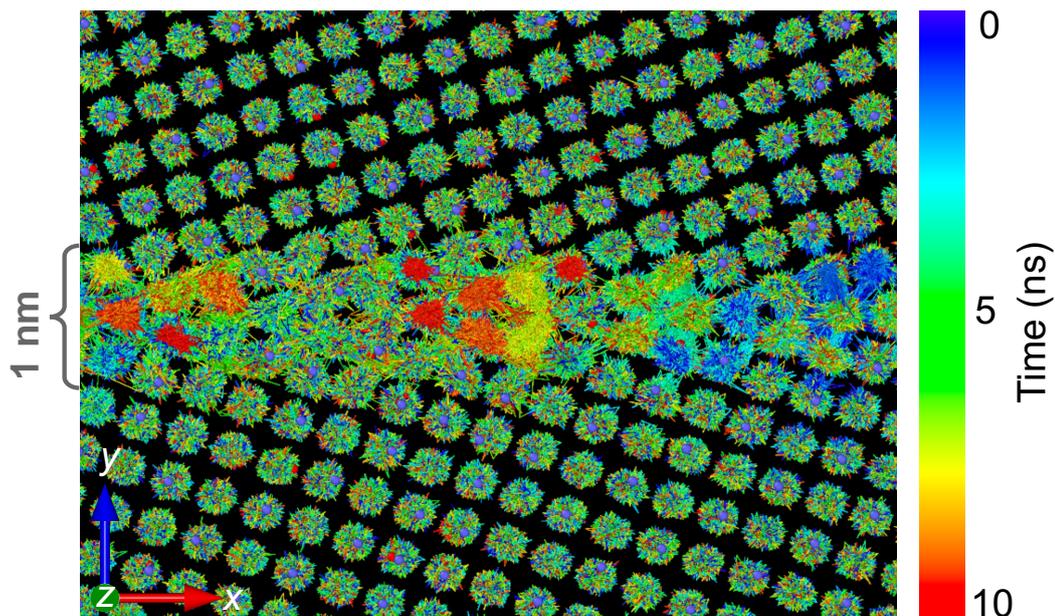


Figure S6. Color mapping of the trajectories of Mg over time in polycrystalline MgO ($C_{\text{vac}} = 3.2 \text{ at\%}$) at 4000 K and 140 GPa. As the simulation time increases from 0 ns to 10 ns, the color of the trajectory changes along the visible spectrum.

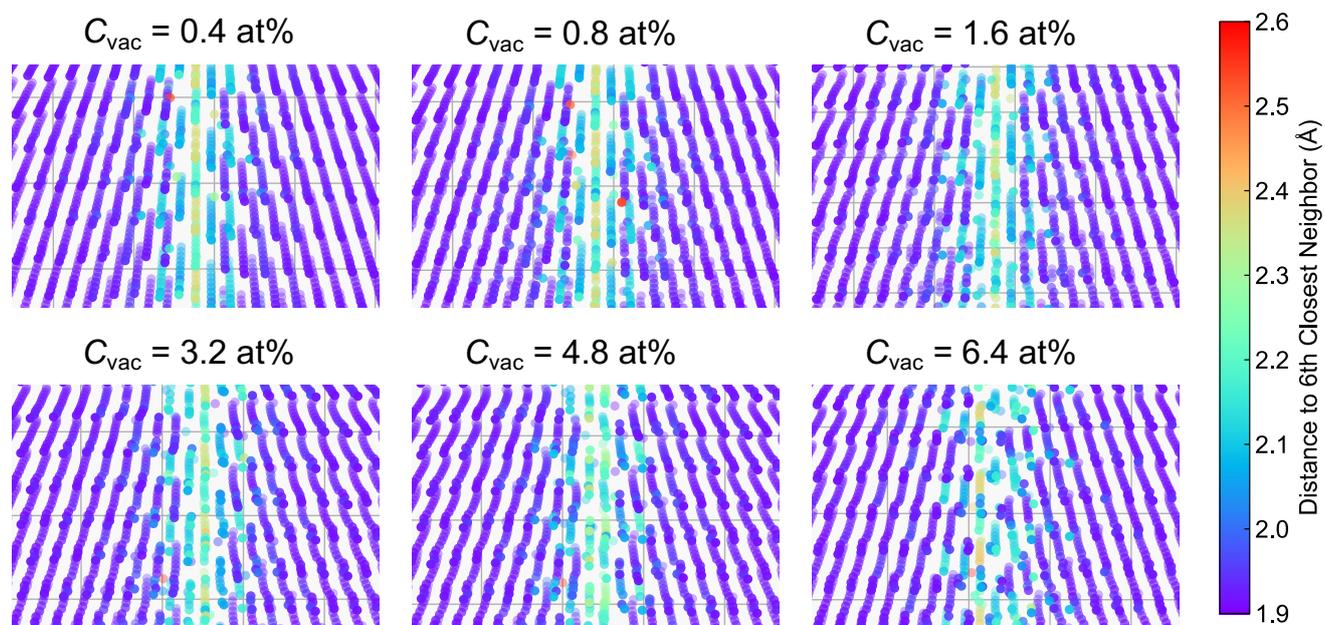


Figure S7. The evolution of grain boundary structure of MgO as a function of vacancy concentration at 4000 K and 140 GPa. The colors of atoms are obtained by mapping the distance from each atom to its 6th nearest neighbor. All snapshots are taken at 1 ns of the MD simulations and relaxed by energy minimization.

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