1 Revision 1

² Title:

³ Pressure dependence of Si diffusion in γ -Fe

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20 Abstract

The pressure dependence of Si diffusion in γ -Fe was investigated at pressures of 5–15 GPa and 2122temperatures of 1473–1673 K using the Kawai-type multi-anvil apparatus to estimate the rate of mass transportation for the chemical homogenization of the Earth's inner core and those of small 23terrestrial planets and large satellites. The obtained diffusion coefficients D were fitted to the $\mathbf{24}$ equation $D = D_0 \exp\left(-\frac{E^* + PV^*}{RT}\right)$, where D_0 is a constant, E^* is the activation energy, P is the 25pressure, V^* is the activation volume, R is the gas constant and T is the absolute temperature. 26The least squares analysis yielded $D_0 = 10^{-1.17 \pm 0.54} \text{ m}^2/\text{s}$, $E^* = 336 \pm 16 \text{ kJ/mol}$, and $V^* = 4.3 \pm 0.2$ 27cm³/mol. Moreover, the pressure and temperature dependences of diffusion coefficients of Si in 28 γ -Fe can also be expressed well using homologous temperature scaling, which is expressed as D =29 $D_0 exp\left(-g\frac{T_m(P)}{T}\right)$ where g is a constant, $T_m(P)$ is the melting temperature at pressure P, and 30 D_0 and g are $10^{-1.0 \pm 0.3}$ m²/s and 22.0 ± 0.7 , respectively. The present study indicates that even for 311 billion years, the maximum diffusion length of Si under conditions in planetary and satellite 32cores is less than ~1.2 km. Additionally, the estimated strain of plastic deformation in the Earth's 33 inner core, caused by the Harper–Dorn creep, reaches more than 10³ at a stress level of 10³–10⁴ Pa, 34 although the inner core might be slightly deformed by other mechanisms. The chemical 35heterogeneity of the inner core can be reduced only via plastic deformation by the Harper-Dorn 36 37creep.

38

Introduction

39	The face-centered cubic (fcc) structure of iron (γ -Fe) is stable at relatively high temperature (>
40	700 K) and low pressure (< 100 GPa) conditions [e.g., Komabayashi and Fei, 2010] that have been
41	regarded as the dominant phase in the metallic cores of small terrestrial planets such as Mercury and
42	Mars and large satellites such as the Moon and Ganymede [e.g., Tsujino et al., 2013]. The cores of
43	terrestrial planets are primarily composed of iron alloys with certain amounts of light elements [e.g.,
44	Birch, 1952]. Because γ -Fe can contain 5–7 wt% of Si as a substitutional impurity at 10–40 GPa [e.g.,
45	Lin et al., 2002], Si can be incorporated in γ -Fe as a light element in the solid inner cores of small
46	planets and large satellites. On Earth, a high Mg/Si ratio in the fertile mantle compared to the cosmic
47	abundance of Si, the so-called "missing Si" [MacDonald and Knopoff, 1958], strongly suggests the
48	presence of Si in the core. Moreover, the ratio of heavier Si isotopes (²⁹ Si/ ²⁸ Si) in the bulk silicate being
49	higher than that in chondrites is interpreted to have been a result of the fractionation of metal silicate
50	[e.g., Georg et al. 2007]. Thus, Si has been regarded as an important light element in the Earth's core and
51	in those of small planets and satellites.
52	Seismological studies of the Earth's inner core have revealed that there are both spherical [e.g.,

Ishii and Dziewonski, 2002] and hemispherical [e.g., Tanaka and Hamaguchi, 1997] heterogeneities that
could be responsible for the formation of chemical heterogeneities during the growth of the inner core.
The maintenance or sustainability of these heterogeneities in the inner core on a geological time scale is

56	dependent on the degree of material movement directly from atomic diffusion. Another homogenizing
57	mechanism in the inner core is mechanical stirring and mixing accompanied by convection, which is
58	controlled by the rheological properties of Fe. It is known that under the conditions of high temperature
59	(> $0.6T_m$, where T_m is the melting temperature) and low stress (< $10^{-3}\mu$, where μ is shear modulus),
60	atomic diffusion is the rate-determining process of three dominant deformation mechanisms: the
61	dislocation creep controlled by dislocation climb; diffusion creep; and Harper-Dorn creep [e.g., Frost
62	and Ashby 1982]. Although the hexagonal close-packed (hcp) structure of iron (ɛ-Fe) would be stable at
63	conditions in the Earth's inner core [Tateno et al., 2010], the diffusion coefficient in ϵ -Fe could be
64	comparable with that in γ -Fe because both phases have the closest packed structure with, ideally, the
65	same interatomic distances [Reaman et al., 2012]. Diffusion data of γ -Fe is applicable to discuss the
66	Earth's inner core. Therefore, atomic diffusion in γ -Fe is key to understanding the evolution of planetary
67	and satellite cores. The self-diffusion of Fe and diffusion of substitutional elements in γ -Fe at ambient
68	pressure is well known [e.g., Buffington et al., 1961; Okinawa, 1982]. The diffusivity of substitutional
69	elements in γ -Fe is not significantly different from the self-diffusivity of Fe because both atoms diffuse
70	via point vacancies [Okinawa, 1982]. The effects of pressure on diffusivity for Au, Pd, and Re in Fe-Ni
71	alloy, which are substitutional elements, were determined up to 10 GPa by Watson et al. [2008], and the
72	pressure effect on inter-diffusion in Fe-Ni alloy has been reported up to 65 GPa by Reaman et al. [2012].
73	Nevertheless, the study of the pressure effect on the diffusivity of light elements, such as Si in γ -Fe, have

74 been quite limited.

75	In this study, we conducted diffusion experiments of Si in γ -Fe up to 1673 K and 15 GPa to
76	determine the pressure dependence of the diffusivity of Si. Based on the diffusion data obtained, we
77	estimated the rate of mass transportation to discuss the time scale of the chemical homogenization of the
78	Earth's inner core and those of small terrestrial planets and large satellites.
79	Experimental methods
80	High pressure (5–15 GPa) and high temperature (1473–1673 K) experiments were conducted to
81	determine the pressure and temperature dependence of the diffusion coefficient of Si in γ -Fe using the
82	Kawai-type multi-anvil apparatus at the Institute for Planetary Materials, Okayama University. An
83	assembly of cubic tungsten carbide second stage anvils (with a truncated edged length (TEL) of 7 mm)
84	compressed the octahedral pressure medium of 5 wt% Cr ₂ O ₃ -doped MgO (with an edge length of 14
85	mm), in which a cylindrical graphite or $TiB_2 + BN + AlN$ composite was used as a heater with a ZrO_2
86	thermal insulator. The temperature was monitored with a W97%Re3%-W75%Re25% thermocouple,
87	and its junction was set next to the sample across the MgO disk. To observe Si diffusion in γ -Fe, pure Fe
88	(99.99% purity, The Nilaco Corporation)—which consists of elongated grains approximately 10 μm \times
89	10 μ m × 200 μ m in size and 1 wt% Si-doped Fe with grains > 200 μ m in size (Rare Metallic Co., Ltd.)
90	were used for the diffusion couple, which was surrounded by a cylindrical MgO sleeve and disks to
91	prevent reactions with the heater and the thermocouple. The interfaces of both samples were finished by

92	careful polishing just before the experiments to minimize the formation of oxide film on them. The
93	metal couples were first compressed to the prescribed pressures at room temperature and heated to the
94	annealing temperatures (1473–1673 K) at the increasing rate of ~50 K/min. The temperature was kept
95	constant at the prescribed value within ± 2 K for 2–21 h.
96	After annealing, the recovered samples which transformed from an fcc structure to the
97	body-centered cubic structure after decompression were mounted in epoxy resin and polished with
98	diamond paste (1 μ m in grain size). The diffusion profiles on the polished cross section were obtained by
99	linear chemical analyses across the interface using an electron probe micro-analyzer (EPMA;
100	JEOL-8800) combined with wavelength dispersion spectroscopy (WDS) performed at the Institute for
101	Planetary Materials, Okayama University. An accelerating voltage of 15 kV and a beam current of 1.2 \times
102	10 ⁻⁸ A were applied in conjunction with counting times of 20 s for the peak and 10 s for the background
103	signals. Pure Fe and NiSi2 were used as the standards of Fe and Si, respectively, for quantitative
104	analyses.
105	Results and Discussion
106	The experimental conditions and diffusion coefficients of Si in γ -Fe obtained are summarized in
107	Table 1. Figures 1a and 1b show the typical secondary electron images of the cross section of the
108	recovered samples. In Figure 1c, a small number of very tiny SiO ₂ particles, which might have been

109 formed by the oxidized film after the samples were polished during their preparation and/or by reaction

110	with water adsorbed on them during the experiments, were sometimes observed near the interfaces. The
111	inhibitory effect of SiO ₂ particles on the diffusion process would have been negligibly small because of
112	the minor quantity of them present at the interface. As shown in Figure 1d, recovered samples show a
113	martensitic microstructure formed by back-transformation during quenching and/or decompression and
114	large domains (> 300 μ m) considered to be primary γ -Fe grains formed at a high pressure and
115	temperature. The effective diffusion coefficients for polycrystalline materials consist of lattice diffusion
116	and grain boundary diffusion. Yunker and Van Orman [2007] suggested that lattice diffusion became
117	dominant when grain size was larger than ~100 μ m for diffusion in fcc metals, including γ -Fe at the
118	P-T conditions similar to the present study. Therefore, lattice diffusion would be the dominant
119	mechanism in this study. Figures 2a and 2b show representative diffusion profiles, which are obviously
120	symmetrical with respect to the interface. Therefore, diffusion profiles obtained in the present study
121	were certainly formed by Si self-diffusion in γ -Fe. These profiles were analyzed using the 1D solution
122	to Fick's second law for a semi-infinite diffusion model with a constant diffusion coefficient D, [Crank,
123	1975] described as follows:

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$$C(x,t) = \frac{c_0}{2} erfc\left(\frac{x}{2\sqrt{Dt}}\right)$$
(1)

where C(x, t) is the Si concentration at distance x (x = 0 at the original interface) and time t, C_0 is the initial concentration of Si in Si-doped Fe, and *erfc* is the complementary error function. Pressure and temperature effects on the diffusion coefficient can be represented by the

128 Arrhenius-type relation as below:

 $H^*(P) = gRT_m(P)$

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129
$$D = D_0 \exp\left(-\frac{H^*(P)}{RT}\right)$$
(2)

130 where D_0 , R, T and $H^*(P)$ are a diffusion constant, the gas constant, the absolute temperature, and 131 the activation enthalpy, respectively. The activation enthalpy is expressed as follows:

132
$$H^*(P) = E^* + PV^*$$
 (3)

where E^* , P, and V^* are the activation energy, the pressure, and the activation volume, respectively. 133In equation (3), the activation enthalpy depends linearly on pressure. As shown in Figures 3a and 3b, 134diffusivity of Si in γ -Fe increases with increasing temperature while it decreases with increasing 135136pressure. The least squares fit of the obtained diffusion coefficients to Eqs. (2) and (3) yielded $D_0 =$ $10^{-1.17 \pm 0.54} \text{ m}^2/\text{s}$, $E^* = 336 \pm 16 \text{ kJ/mol}$, and $V^* = 4.3 \pm 0.2 \text{ cm}^3/\text{mol}$. In addition to the linear pressure 137dependency model, homologous temperature scaling, which is an Arrhenius-type plot, is frequently 138adopted to estimate the kinetic properties of materials [Yamazaki and Karato, 2001]. Homologous 139temperature scaling has also been found to provide a good description of experimental data for a broad 140range of metals and alloys at various conditions by Brown and Ashby [1980] and Sammis et al. [1981]. 141 142In this scaling, pressure and temperature dependences of the diffusivity are expressed through melting temperature, $T_m(P)$, at pressure, P, as below: 143

145 where g is a constant derived from Eq. (2). As shown in Figure 3c, D_0 and g are determined to be

(4)

 $10^{-1.0 \pm 0.3}$ m²/s and 22.0 ± 0.7, respectively, by using $T_m(P)$ determined by Komabayashi and Fei 146[2010]. 147

148	The activation energy for Si in γ -Fe of 336 \pm 16 kJ/mol at pressures of 5-15 GPa in this study is
149	larger than that at ambient pressure of 253 kJ/mol by Bergner et al. [1990]. Moreover, diffusion
150	coefficient of Si at 0 GPa extrapolated from the high pressure data in this study is slightly larger than
151	that of Si at ambient pressure determined by Bergner et al. [1990], as shown in Figure 3(a). Yamazaki
152	et al. [2004] suggested the elevated hydrogen pressure enhanced diffusion of Au in γ -Fe owing to
153	induction of vacancies. The diffusivity of Au at hydrogen pressure of 5 GPa is 2-3 times larger than it
154	is at ambient pressure. They also reported that the activation energy E^* of diffusion becomes larger
155	with the elevated hydrogen pressure. In preparation of the samples in the present study, we skipped the
156	drying process after polishing the surfaces to avoid the oxidation. In addition, hydrogen is
157	preferentially partitioned into Fe rather than silicate at a high pressure [Shibazaki et al., 2009], and the
158	water solubility of MgO surrounding the samples is very small (< 3.5 wt.ppm) [Joachim et al., 2013].
159	Therefore, some amount of hydrogen from adsorbed water may be absorbed into the samples and may
160	yield higher activation energy and diffusion coefficient measurements than those in the study by
161	Bergner et al. [1990], although such discrepancies in these values were often attributed in previous
162	studies to various experimental conditions and settings (e.g. the starting material's purity).
163	In the present study, the activation volume was determined to be 4.3 ± 0.2 cm ³ /mol from the fitting

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164	of Si diffusivity to Eqs. (2) and (3) over the experimental pressure range of 5–15 GPa. In comparison,
165	the activation volumes of diffusivity for Au, Pd, and Re in Fe-Ni alloy at up to 10 GPa were reported to
166	be 3-6 cm ³ /mol by Watson et al. [2008], in concordance with that for Si in the present study at a
167	similar pressure range. Additionally, the activation volumes of inter-diffusion in Fe-Ni alloy were
168	reported to be 6 cm ³ /mol at up to 4 GPa, 3.1 cm ³ /mol at 0–23 GPa, and 2.6 cm ³ /mol up to 63 GPa by
169	Goldstein et al. [1965], Yunker and Van Orman [2007] and Reaman et al. [2012], respectively.
170	Therefore, the previous studies suggest that the activation volume of inter-diffusion in Fe alloy
171	becomes smaller with increasing pressure. In this study, the homologous temperature scaling shown in
172	Eqs. (2) and (4) was also used to express the pressure effect on the diffusion coefficient of Si, as shown
173	in Figure 3c. The g-value of 22.0 ± 0.7 in Eq. (4) in this study is also consistent with the g-values of
174	20.4 and 19.3 \pm 2.7 for Fe-Ni alloy reported by Yunker and Van Orman [2007] and Reaman et al.
175	[2012], respectively. Therefore, the homologous temperature scaling could be adapted to various
176	pressure and temperature conditions for fcc metals. To extrapolate the Si diffusivity of the present
177	study to pressures in the Earth's core, homologous temperature scaling is more suitable than the
178	constant activation volume model.

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Implications for planetary and satellite cores

Diffusion is one of the important mechanisms that homogenized chemical heterogeneities that occurred during the formation and growth of the inner core. Figure 4 shows the typical diffusion length

182	of Si in γ -Fe on a geologic time scale (1 billion years) under the <i>P</i> - <i>T</i> conditions of the cores of satellites
183	and small terrestrial planets as estimated by Tsujino et al. [2013]. Despite the fact that the core sizes of
184	these satellites and small planets (> 100 km) are large, the maximum diffusion length for 1 billion years
185	is limited to be less than 1.2 km, which is more than two orders of magnitude smaller than the cores.
186	Both γ -Fe and ϵ -Fe structures are close-packed, ideally with the same interatomic distances, assuming
187	that the atoms are spherical. Therefore, the diffusion coefficients in ϵ -Fe would be close to those in γ -Fe
188	[Reaman et al., 2012]; consequently, the diffusion coefficient in γ -Fe can be applied to the Earth's inner
189	core, which is made of ε -Fe [Tateno et al. 2010]. Assuming $T/T_m = 0.9 - 1.0$ for the Earth's core, the
190	diffusion coefficient of Si is estimated to be 3×10^{-12} – 3×10^{-11} m ² /s. Therefore, the diffusion length of
191	Si is only 0.4–1.4 km for 1 billion years while the radii of the inner and innermost inner core of the Earth
192	are ~1200 km and 300–500 km [e.g., Ishii and Dziewonski, 2002], respectively. Therefore, the chemical
193	heterogeneity that formed during the growth of the inner core of terrestrial planets (including Earth) and
194	of large satellites would still be preserved only if the diffusion mechanism caused the transportation of
195	mass.

In general, the diffusivity of a substitutional solute atom in metal is similar to that of a solvent atom because both diffuse via point defects. Diffusivity by substituting Si in Fe [Bergner et al., 1990] is different from that of the self-diffusion of Fe [Buffington et al., 1961] by only half an order of magnitude, as shown in Figure 3a. The pressure effect on the diffusivity of Si in γ -Fe is consistent with 200those for Au, Pd, and Re in an Fe-Ni alloy under a similar pressure range [Watson et al., 2008]. Therefore, it is highly likely that the pressure and temperature dependence of Fe diffusivity in γ -Fe is 201similar to that of Si determined in the present study. The diffusion coefficient of Fe is estimated to be 3 202 $\times 10^{-12}$ m²/s, assuming that $T/T_m = 0.9$. Plastic deformation can mitigate the chemical heterogeneity of 203204the Earth's inner core via stirring and mixing processes accompanied with convection. At high temperatures, diffusion is the rate-limiting process for the deformation of three types of mechanisms 205[Frost and Ashby, 1982; Van Orman, 2004]. The first is dislocation creep, which is controlled by 206dislocation climb and is represented by the following equation: 207 $\dot{\gamma} = A\mu b \left(\frac{D}{kT}\right) \left(\frac{\sigma}{\mu}\right)^n$ 208(5) where $\dot{\gamma}$, A, μ , b, k, σ , and n are the shear strain rate, Dorn constant, shear modulus, length of 209 210Burgers' vector, Boltzmann constant, stress, and stress exponent, respectively. For γ -Fe, the Dorn constant and stress exponent are reported to be 4.3×10^5 and 4.5, respectively [Frost and Ashby, 1982]. 211212The stress at the Earth's inner core is assumed to be 10^3-10^4 Pa [Yoshida et al., 1996]. Therefore, the viscosity by dislocation creep was calculated to be $6 \times 10^{21} - 2 \times 10^{25}$ Pa·s; a high stress dependency is 213214expected due to the high stress exponent. The second mechanism is diffusion creep, in which materials deform as a Newtonian-viscous flow. The flow law of diffusion creep is shown as below: 215 $\dot{\gamma} = \frac{42\Omega}{d^2} \left(\frac{D}{kT}\right) \sigma$ 216(6)

217 where Ω is atomic volume and d is grain size of the inner core, which was estimated to be 1000–5000

m in conditions at the Earth's inner core conditions [Yamazaki et al., 2017]. Viscosity due to diffusion creep was calculated to be $1 \times 10^{26} - 2 \times 10^{27}$ Pa·s because of the large grain size. The third mechanism is Harper–Dorn creep, which becomes dominant at sufficiently low stress conditions (< $5 \times 10^{-6} \mu$), although it might be artificial [e.g., Kassner et al., 2007] because it is dominant at the limited condition of very low stress. This mechanism is expressed as follows:

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$$\dot{\gamma} = \rho \Omega \mu \left(\frac{D}{kT}\right) \left(\frac{\sigma}{\mu}\right)$$
 (7)

where ρ is the dislocation density. Data for the average dislocation spacing $\rho^{-0.5}$ in Al, NaCl, and LiF 224lies in the vicinity of $b\mu/\sigma$ in this dislocation creep [e.g., Streb and Reppich, 1972; Blum, 1991], while 225226the dislocation density ρ of deformed Al [Barrett et al., 1972] in the Harper–Dorn creep condition is $\sim 10^8$ /m² under various stress conditions. This density is consistent with the dislocation density of metal 227228after annealing without stress. Therefore, in the Harper-Dorn creep, dislocation density is almost constant and the material deforms in a Newtonian-viscous flow. The viscosity in the Harper–Dorn creep 229was calculated to be 5×10^{14} Pa·s. This is the lowest viscosity in the Earth's inner core conditions 230among the three mechanisms, suggesting that the Harper–Dorn creep would be the dominant one. This is 231supported by the stress level of 10^3-10^4 Pa reported in the Earth's inner core by Yoshida et al. [1996]; a 232shear modulus $\mu = 160$ GPa [Dziewonski and Anderson, 1981] is small enough for the Harper–Dorn 233234creep.

From geophysical observation based on seismic inferences of super-rotation of the inner core

236	[Buffett, 1997], viscosity of the Earth's inner core was estimated to be $< 3 \times 10^{16}$ Pa·s, or $> 1.5 \times 10^{20}$
237	Pa·s. The viscosity in Harper–Dorn creep is consistent with the observation of $< 3 \times 10^{16}$ Pa·s. Figure 5
238	shows the variation in estimated strains as functions of stress on a geologic timescale (100 My-1000
239	My) for the three deformation mechanisms. The strain on the inner core from the Harper–Dorn creep
240	could be greater than 10^3 at a stress of 10^3 – 10^4 Pa, indicating that the inner core would be well-stirred
241	due to the large strain $> 10^3$. In both Harper–Dorn and dislocation creep, strain would be controlled by
242	dislocation motion and result in observed seismic velocity anisotropies [e.g., Poupinet et al., 1983]
243	through crystallographic preferred orientation (CPO). The chemical heterogeneity can be reduced by
244	stirring and subsequent diffusion and the resultant CPO can be also formed by motion of dislocation.
245	However, recent studies suggested that Harper–Dorn creep might be artificial [e.g., Kassner et al., 2007].
246	If the Harper–Dorn creep was not realized, dislocation creep would preferentially dominate deformation
247	in the Earth's inner core. The viscosity of dislocation creep was also consistent with the geophysical
248	observation of > 1.5×10^{20} Pa·s [Buffett, 1997], and the inner core would be deformed slightly, as
249	shown in Figure 5. Using dislocation creep CPO could not be developed, owing to the small strain level
250	[Nishihara et al., 2019], to explain the seismic anisotropy in the inner core. Therefore, the conclusion is
251	that chemical heterogeneity can only be reduced via plastic deformation by the Harper–Dorn creep.

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261 **References**

- Barrett, C.R., Muehleisen, E.C., and Nix, W.D. (1972) High temperature-low stress creep of Al and Al +
 0.5% Fe. Materials Science and Engineering: A, 10, 33–41.
- Buffington, F.S., Hirano, K., and Cohen, M. (1961) Self diffusion in iron. Acta Metallurgica, 9, 434-439.
- Bergner, D., Khaddour, Y., and Lörx, S. (1990) Diffusion of Si in bcc- and fcc-Fe. Defect and Diffusion
 Forum, 66-69, 1407-1412.
- Birch, F. (1952) Elasticity and constitution of the Earth's interior. Journal of Geophysical Research, 57,
 227–286.
- Blum, W. (1991) Creep of aluminum and aluminum alloys. In: Langdon, T.G., Merchant, H.D., Morris,
 J.G., Zaidi, M.A. (Eds.), Creep of Aluminum and Aluminum Alloys, The Minerals. Metals and
 Materials Society, Warrendale, PA, pp. 181–209.
- Brown, A.M., and Ashby, M.F. (1980) Correlations for diffusion constants, Acta Metallurgica, 28,
 1085–1101
- Buffett, B.A., (1997) Geodynamic estimates of the viscosity of the Earth's inner core. Nature, 388, 571–
 573.
- 277 Crank, J. (1975) Mathematics of diffusion. Oxford University Press, New York.
- Dziewonski, A.M., and Anderson, D.L. (1981) Preliminary reference Earth model. Physics of the Earth
 and Planetary Interiors, 25, 297–356.
- Frost, H. J., and Ashby, M. F. (1982) Deformation-Mechanism Maps: The Plasticity and Creep of
 Metals and Ceramics, Pergamon, Oxford, U. K.
- Georg, R.B., Halliday, A.N., Schauble, E.A., and Reynolds, B.C. (2007) Silicon in the Earth's core.
 Nature, 447, 1102–1106.
- Goldstein, J.J., Hanneman, R.E., and Ogilvie, R.G., (1965) Diffusion in the Fe–Ni system at 1 atm and
 40 kbar pressure. Transactions of the Metallurgical society of AIME, 233, 812–820.
- Ishii, M., and Dziewonski, A. M. (2002) The innermost inner core of the Earth: Evidence for a change in
 anisotropic behavior at the radius of about 300 km, Proceedings of the National Academy of
 Sciences of the United States of America, 99, 14,026–14,030.
- Joachim B., Wohlers. A., Norberg, N., Garde's E., Petrishcheva, E., and Abart, R. (2013) Diffusion and solubility of hydrogen and water in periclase. Physics and Chemistry of Minerals, 40, 19-27.
- Kassner, M.E., Kumar, P., and Blum, W. (2007) Harper–Dorn creep. International Journal of Plasticity,
 23, 980–1000.
- Komabayashi, T., and Fei, Y.W. (2010) Internally consistent thermodynamic database for iron to the Earth's core conditions. Journal of Geophysical Research–Solid Earth, 115, B03202.

- Lin, J.F., Heins, D.L., Campbell, A.J., Devine, J.M., and Shen, G. (2002) Iron-silivin alloy in Earth's core?. Science, 295, 313-315.
- MacDonald, G.J.F., and Knopoff, L. (1958) On the chemical composition of the outer core. Geophysical
 Journal of the Royal Astronomical Society, 1, 284–297.
- Nishihara, Y., Ohuchi, T., Kawasoe, T., Seto, Y., Maruyama, G., Higo, Y., Funakoshi, K., Tange, Y.,
 and Irifune, T. (2019) Deformation-induced crystallographic-preferred-orientation of hcp-iron: An
 experimental study using a deformation-DIA apparatus, Earth and Planetary Science Letters, 490,
 151-160.
- 303 Oikawa, H. (1982) Lattice diffusion in iron A review. Tetsu-to-Hagané, 68,1489–1497.
- Poupinet, G., Pillet R., and A. Souriau A. (1983) Possible heterogeneity of the Earth's core deduced
 from PKIKP travel times, Nature, 305, 204-206.
- Reaman, M.D., Colijn, H.O., Yang, F., Hauser, A.J., and Panero, W.R. (2012) Interdiffusion of Earth's
 core materials to 65 GPa and 2200 K. Earth and Planetary Science Letters, 349-350, 8-14.
- Sammis, C.G., Smith, J.C., and Schubert. G. (1981) A critical assessment of estimation methods for
 activation volume, Journal of Geophysical Research, 86, 10707–10718.
- Shibazaki, Y., Ohtani, E., Terasaki, H., Suzuki, A., and Funakoshi, K. (2009) Hydrogen partitioning
 between iron and ringwoodite: Implications for water transport into the Martian core. Earth and
 Planetary Science Letters, 287, 463-470.
- Streb, G., and Reppich, B. (1972) Steady state deformation and dislocation structure of pure and
 Mg-doped LiF single crystals. Physica Status Solidi A, 16, 493-505.
- Tanaka S, and Hamaguchi H. (1997) Degree one heterogeneity and hemispherical variation of
 anisotropy in the inner core from PKP(BC)-PKP(DF) times. Journal of Geophysical Research,
 102(B2):2925–38.
- Tateno S, Hirose K, Ohishi Y, and Tatsumi Y. (2010) The structure of iron in Earth's inner core. Science,
 330:359–61.
- Tsujino, N., Nishihara, Y., Nakajima, Y., Takahashi, E., Funakoshi, K, and Higo, Y. (2013) Equation of
 state of γ-Fe: Reference density for planetary cores. Earth and Planetary Science Letters. 375,
 244-253.
- Van Orman, J.A. (2004) On the viscosity and creep mechanism of Earth's inner core. Geophysical
 Research Letters, 31, L20606.
- Watson, H.C., Watson, E.B., and Fei, T.W. (2008) Diffusion of Au, Pd, Re and P in FeNi alloys at high pressure. Geochimica et Cosmochimica Acta, 72, 3550-3561.
- Yamazaki, D., and S. Karato (2001), Some mineral physics constraints on the rheology and geothermal
 structure of Earth's lower mantle, American Mineralogist, 86, 385–391.
- 329 Yamazaki, Y., Iijima, Y., and Okada, M. (2004) Enhanced diffusion of Au in c-Fe by vacancies induced

- under elevated hydrogen pressure. Acta Materialia, 52, 1247-1254.
- Yamazaki, D., Tsujino, N., Yoneda, A., Ito, E., Yoshino. T., Tange, Y., and Higo, Y. (2017) Grain
 growth of ε-iron: Implications to grain size and its evolution in the Earth's inner core. Earth and
 Planetary Science Letters, 459, 238-243.
- Yoshida, S., I. Sumita, and M. Kumazawa (1996) Growth model of the inner core coupled with outer
 core dynamics and the resultant elastic anisotropy. Journal of Geophysical Research, 101,
 28085-28103.
- 337 Yunker, M.L., Van Orman, J.A. (2007) Interdiffusion of solid iron and nickel at high pressure. Earth and
- 338 Planetary Science Letters, 254, 203–213.

339 Figure captions

340	Figure 1. Secondary electron images of the whole recovered samples in (a) 1k2788 (1473 K, 5 GPa, 21
341	h) and (b) 1k2845 (1673 K, 10 GPa, 2 h). The upper and lower parts are 1 wt% Si-doped Fe and pure Fe,
342	respectively. (c) Expanded secondary electron image of the black square in (a). Tiny particles of SiO_2
343	near the interface between 1 wt% Si-doped Fe and pure Fe. (d) Backscattered electron image of the
344	etched recovered sample of (a) in 1k2788 (1473 K, 5 GPa, 21 h). The domain size, which represents the
345	grain size of γ -Fe at high pressure and temperature, is much larger than 300 μ m.
346	
347	Figure 2. The typical diffusion profiles of Si measured by linear chemical analyses using an electron
348	probe micro-analyzer in (a) 1k2788 (1473 K, 5 GPa, 21 h) and (b) 1k2845 (1673 K, 10 GPa, 2 h). Gray
349	symbols and black lines show the measurement data of normalized Si concentrations and the lines fitted
350	using Eq. (1), respectively.

351

Figure 3. Temperature and pressure dependence of the Si self-diffusion coefficient. The constant pressure dependency model is assumed in (a) and (b) and homologous temperature scaling is applied in (c). Fitting is shown by the solid lines. Red, green, and blue symbols represent diffusion data at 1673 K, 1573 K and 1473 K, respectively. Square, circle, and diamond symbols indicate diffusion data at 5 GPa, 10 GPa and 15 GPa, respectively. The broken and dotted lines in (a) show Si self-diffusion [Bergner et al., 1990] and Fe self-diffusion [Buffington et al., 1961], respectively, in γ-Fe at atmospheric pressure.

359	Figure 4. Estimated diffusion length of Si in γ -Fe on a timescale of 1000 My for the inner cores of
360	satellites and small planets, with conditions summarized by Tsujino et al. (2013). Purple, orange, green,
361	and blue regions show the diffusion lengths for Ganymede, the Moon, Mercury, and Mars, respectively.
362	
363	Figure 5. Estimated strains in the Earth's inner core for dislocation creep controlled by dislocation climb
364	(pink), diffusion creep (light blue), and the Harper-Dorn creep (green) as a function of stress on a
365	geologic timescale (100 My-1000 My). The gray area indicates the typical stress of the Earth's inner
366	core [Yoshida et al., 1996].

Table 1. Experimental conditions and the obtained diffusion coefficients of Si in γ -Fe.

Run No.	Pressure (GPa)	Temperature (K)	Duration (h)	$\log D_{\rm Si} ({\rm m^2/s})$
1K2788	5	1473	21	-13.86(1)
1K2794	5	1573	4	-13.01(2)
1K2786	5	1673	3	-12.36(1)
1K2846	10	1573	10	-13.83(2)
1K2845	10	1673	2	-13.06(1)
1K2852	15	1673	10	-13.64(2)











Figure 4



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