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³ Pressure dependence of Si diffusion in γ-Fe

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20 Abstract

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The pressure dependence of Si diffusion in γ-Fe was investigated at pressures of 5–15 GPa and temperatures 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 terrestrial planets and large satellites. The obtained diffusion coefficients D were fitted to the 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 pressure, V^* is the activation volume, R is the gas constant and T is the absolute temperature. The least squares analysis yielded $D_0 = 10^{-1.17 \pm 0.54} \,\mathrm{m}^2/\mathrm{s}, \ E^* = 336 \pm 16 \,\mathrm{kJ/mol}, \ \mathrm{and} \ V^* = 4.3 \pm 0.2$ cm³/mol. Moreover, the pressure and temperature dependences of diffusion coefficients of Si in y-Fe can also be expressed well using homologous temperature scaling, which is expressed as $D = D_0 exp\left(-g\frac{T_m(P)}{T}\right)$ where g is a constant, $T_m(P)$ is the melting temperature at pressure P, and D_0 and g are $10^{-1.0 \pm 0.3}$ m²/s and 22.0 \pm 0.7, respectively. The present study indicates that even for 1 billion years, the maximum diffusion length of Si under conditions in planetary and satellite cores is less than ~1.2 km. Additionally, the estimated strain of plastic deformation in the Earth's inner core, caused by the Harper-Dorn creep, reaches more than 10³ at a stress level of 10³-10⁴ Pa, although the inner core might be slightly deformed by other mechanisms. The chemical heterogeneity of the inner core can be reduced only via plastic deformation by the Harper-Dorn creep.

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

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

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

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In this study, we conducted diffusion experiments of Si in γ -Fe up to 1673 K and 15 GPa to determine the pressure dependence of the diffusivity of Si. Based on the diffusion data obtained, we estimated the rate of mass transportation to discuss the time scale of the chemical homogenization of the Earth's inner core and those of small terrestrial planets and large satellites.

Experimental methods

High pressure (5–15 GPa) and high temperature (1473–1673 K) experiments were conducted to determine the pressure and temperature dependence of the diffusion coefficient of Si in γ -Fe using the Kawai-type multi-anvil apparatus at the Institute for Planetary Materials, Okayama University. An assembly of cubic tungsten carbide second stage anvils (with a truncated edged length (TEL) of 7 mm) compressed the octahedral pressure medium of 5 wt% Cr₂O₃-doped MgO (with an edge length of 14 mm), in which a cylindrical graphite or TiB₂ + BN + AlN composite was used as a heater with a ZrO₂ thermal insulator. The temperature was monitored with a W97%Re3%-W75%Re25% thermocouple, and its junction was set next to the sample across the MgO disk. To observe Si diffusion in γ -Fe, pure Fe (99.99% purity, The Nilaco Corporation)—which consists of elongated grains approximately 10 μm × 10 μm \times 200 μm in size and 1 wt% Si-doped Fe with grains \geq 200 μm in size (Rare Metallic Co., Ltd.) were used for the diffusion couple, which was surrounded by a cylindrical MgO sleeve and disks to prevent reactions with the heater and the thermocouple. The interfaces of both samples were finished by

careful polishing just before the experiments to minimize the formation of oxide film on them. The metal couples were first compressed to the prescribed pressures at room temperature and heated to the annealing temperatures (1473–1673 K) at the increasing rate of \sim 50 K/min. The temperature was kept constant at the prescribed value within \pm 2 K for 2–21 h.

After annealing, the recovered samples which transformed from an fcc structure to the body-centered cubic structure after decompression were mounted in epoxy resin and polished with diamond paste (1 μm in grain size). The diffusion profiles on the polished cross section were obtained by linear chemical analyses across the interface using an electron probe micro-analyzer (EPMA; JEOL-8800) combined with wavelength dispersion spectroscopy (WDS) performed at the Institute for Planetary Materials, Okayama University. An accelerating voltage of 15 kV and a beam current of 1.2 × 10⁻⁸ A were applied in conjunction with counting times of 20 s for the peak and 10 s for the background signals. Pure Fe and NiSi₂ were used as the standards of Fe and Si, respectively, for quantitative analyses.

Results and Discussion

The experimental conditions and diffusion coefficients of Si in γ -Fe obtained are summarized in Table 1. Figures 1a and 1b show the typical secondary electron images of the cross section of the recovered samples. In Figure 1c, a small number of very tiny SiO₂ particles, which might have been formed by the oxidized film after the samples were polished during their preparation and/or by reaction

with water adsorbed on them during the experiments, were sometimes observed near the interfaces. The inhibitory effect of SiO₂ particles on the diffusion process would have been negligibly small because of the minor quantity of them present at the interface. As shown in Figure 1d, recovered samples show a martensitic microstructure formed by back-transformation during quenching and/or decompression and large domains (> 300 μm) considered to be primary γ-Fe grains formed at a high pressure and temperature. The effective diffusion coefficients for polycrystalline materials consist of lattice diffusion and grain boundary diffusion. Yunker and Van Orman [2007] suggested that lattice diffusion became dominant when grain size was larger than $\sim 100 \mu m$ for diffusion in fcc metals, including γ -Fe at the P-T conditions similar to the present study. Therefore, lattice diffusion would be the dominant mechanism in this study. Figures 2a and 2b show representative diffusion profiles, which are obviously symmetrical with respect to the interface. Therefore, diffusion profiles obtained in the present study were certainly formed by Si self-diffusion in γ -Fe. These profiles were analyzed using the 1D solution to Fick's second law for a semi-infinite diffusion model with a constant diffusion coefficient D, [Crank, 1975] described as follows:

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

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:

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

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

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

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

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$$H^*(P) = gRT_m(P) \tag{4}$$

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

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

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

In the present study, the activation volume was determined to be 4.3 ± 0.2 cm³/mol from the fitting

of Si diffusivity to Eqs. (2) and (3) over the experimental pressure range of 5–15 GPa. In comparison, the activation volumes of diffusivity for Au, Pd, and Re in Fe-Ni alloy at up to 10 GPa were reported to be 3-6 cm³/mol by Watson et al. [2008], in concordance with that for Si in the present study at a similar pressure range. Additionally, the activation volumes of inter-diffusion in Fe-Ni alloy were reported to be 6 cm³/mol at up to 4 GPa, 3.1 cm³/mol at 0–23 GPa, and 2.6 cm³/mol up to 63 GPa by Goldstein et al. [1965], Yunker and Van Orman [2007] and Reaman et al. [2012], respectively. Therefore, the previous studies suggest that the activation volume of inter-diffusion in Fe alloy becomes smaller with increasing pressure. In this study, the homologous temperature scaling shown in Eqs. (2) and (4) was also used to express the pressure effect on the diffusion coefficient of Si, as shown 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 20.4 and 19.3 \pm 2.7 for Fe-Ni alloy reported by Yunker and Van Orman [2007] and Reaman et al. [2012], respectively. Therefore, the homologous temperature scaling could be adapted to various pressure and temperature conditions for fcc metals. To extrapolate the Si diffusivity of the present study to pressures in the Earth's core, homologous temperature scaling is more suitable than the 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

of Si in γ -Fe on a geologic time scale (1 billion years) under the P-T conditions of the cores of satellites and small terrestrial planets as estimated by Tsujino et al. [2013]. Despite the fact that the core sizes of these satellites and small planets (> 100 km) are large, the maximum diffusion length for 1 billion years is limited to be less than 1.2 km, which is more than two orders of magnitude smaller than the cores. Both γ -Fe and ϵ -Fe structures are close-packed, ideally with the same interatomic distances, assuming that the atoms are spherical. Therefore, the diffusion coefficients in ε -Fe would be close to those in γ -Fe [Reaman et al., 2012]; consequently, the diffusion coefficient in γ-Fe can be applied to the Earth's inner 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 diffusion coefficient of Si is estimated to be $3 \times 10^{-12} - 3 \times 10^{-11}$ m²/s. Therefore, the diffusion length of 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 are ~1200 km and 300-500 km [e.g., Ishii and Dziewonski, 2002], respectively. Therefore, the chemical heterogeneity that formed during the growth of the inner core of terrestrial planets (including Earth) and of large satellites would still be preserved only if the diffusion mechanism caused the transportation of mass.

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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

200 those 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 201 202 similar to that of Si determined in the present study. The diffusion coefficient of Fe is estimated to be 3 \times 10⁻¹² m²/s, assuming that $T/T_m = 0.9$. Plastic deformation can mitigate the chemical heterogeneity of 203 the Earth's inner core via stirring and mixing processes accompanied with convection. At high 204 205 temperatures, diffusion is the rate-limiting process for the deformation of three types of mechanisms [Frost and Ashby, 1982; Van Orman, 2004]. The first is dislocation creep, which is controlled by 206 207 dislocation climb and is represented by the following equation:

$$208 \qquad \dot{\gamma} = A\mu b \left(\frac{D}{kT}\right) \left(\frac{\sigma}{\mu}\right)^n \tag{5}$$

where $\dot{\gamma}$, A, μ , b, k, σ , and n are the shear strain rate, Dorn constant, shear modulus, length of Burgers' 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]. The 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 6×10^{21} – 2×10^{25} Pa·s; a high stress dependency is expected 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:

$$216 \qquad \dot{\gamma} = \frac{42\Omega}{d^2} \left(\frac{D}{kT}\right) \sigma \tag{6}$$

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:

$$223 \qquad \dot{\gamma} = \rho \Omega \mu \left(\frac{D}{kT}\right) \left(\frac{\sigma}{\mu}\right) \tag{7}$$

where ρ is the dislocation density. Data for the average dislocation spacing $\rho^{-0.5}$ in Al, NaCl, and LiF lies in the vicinity of $b\mu/\sigma$ in this dislocation creep [e.g., Streb and Reppich, 1972; Blum, 1991], while the dislocation density ρ of deformed Al [Barrett et al., 1972] in the Harper–Dorn creep condition is $\sim 10^8 \, / \text{m}^2$ under various stress conditions. This density is consistent with the dislocation density of metal after 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 was calculated to be $5 \times 10^{14} \, \text{Pa} \cdot \text{s}$. This is the lowest viscosity in the Earth's inner core conditions among the three mechanisms, suggesting that the Harper–Dorn creep would be the dominant one. This is supported by the stress level of $10^3 - 10^4 \, \text{Pa}$ reported in the Earth's inner core by Yoshida et al. [1996]; a shear modulus $\mu = 160 \, \text{GPa}$ [Dziewonski and Anderson, 1981] is small enough for the Harper–Dorn creep.

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

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

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Figure captions

Figure 1. Secondary electron images of the whole recovered samples in (a) 1k2788 (1473 K, 5 GPa, 21 h) and (b) 1k2845 (1673 K, 10 GPa, 2 h). The upper and lower parts are 1 wt% Si-doped Fe and pure Fe, respectively. (c) Expanded secondary electron image of the black square in (a). Tiny particles of SiO₂ near the interface between 1 wt% Si-doped Fe and pure Fe. (d) Backscattered electron image of the etched recovered sample of (a) in 1k2788 (1473 K, 5 GPa, 21 h). The domain size, which represents the grain size of γ-Fe at high pressure and temperature, is much larger than 300 μm.

Figure 2. The typical diffusion profiles of Si measured by linear chemical analyses using an electron probe micro-analyzer in (a) 1k2788 (1473 K, 5 GPa, 21 h) and (b) 1k2845 (1673 K, 10 GPa, 2 h). Gray symbols and black lines show the measurement data of normalized Si concentrations and the lines fitted using Eq. (1), respectively.

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.

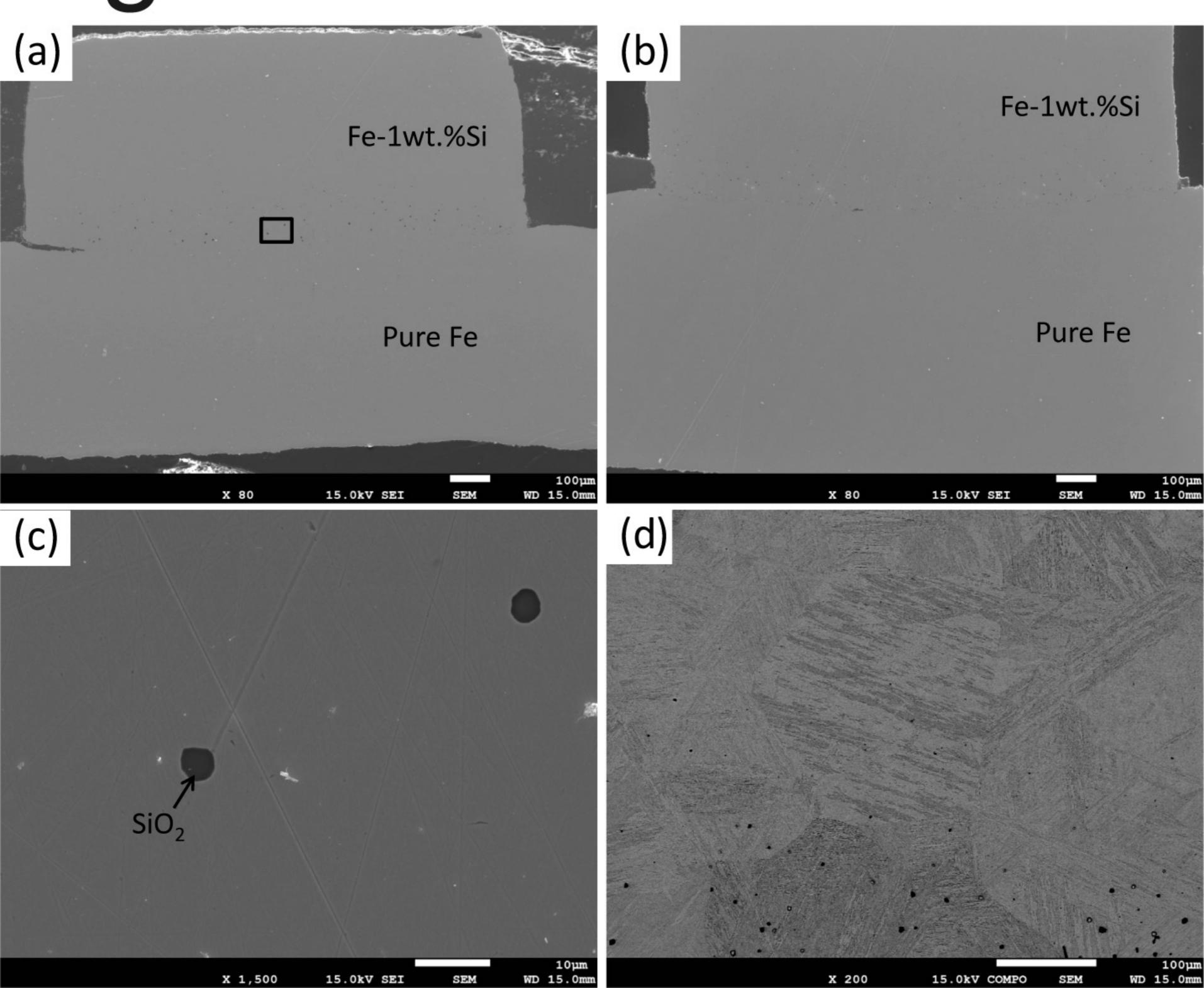
Figure 4. Estimated diffusion length of Si in γ -Fe on a timescale of 1000 My for the inner cores of satellites and small planets, with conditions summarized by Tsujino et al. (2013). Purple, orange, green, and blue regions show the diffusion lengths for Ganymede, the Moon, Mercury, and Mars, respectively.

Figure 5. Estimated strains in the Earth's inner core for dislocation creep controlled by dislocation climb (pink), diffusion creep (light blue), and the Harper–Dorn creep (green) as a function of stress on a geologic timescale (100 My–1000 My). The gray area indicates the typical stress of the Earth's inner

366 core [Yoshida et al., 1996].

 $\underline{\text{Table 1. Experimental conditions and the obtained diffusion coefficients of S}i \text{ in } \gamma\text{-Fe.}$

Run No.	Pressure (GPa)	Temperature (K)	Duration (h)	$\log D_{\rm Si} ({ m m}^2/{ m s})$
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)



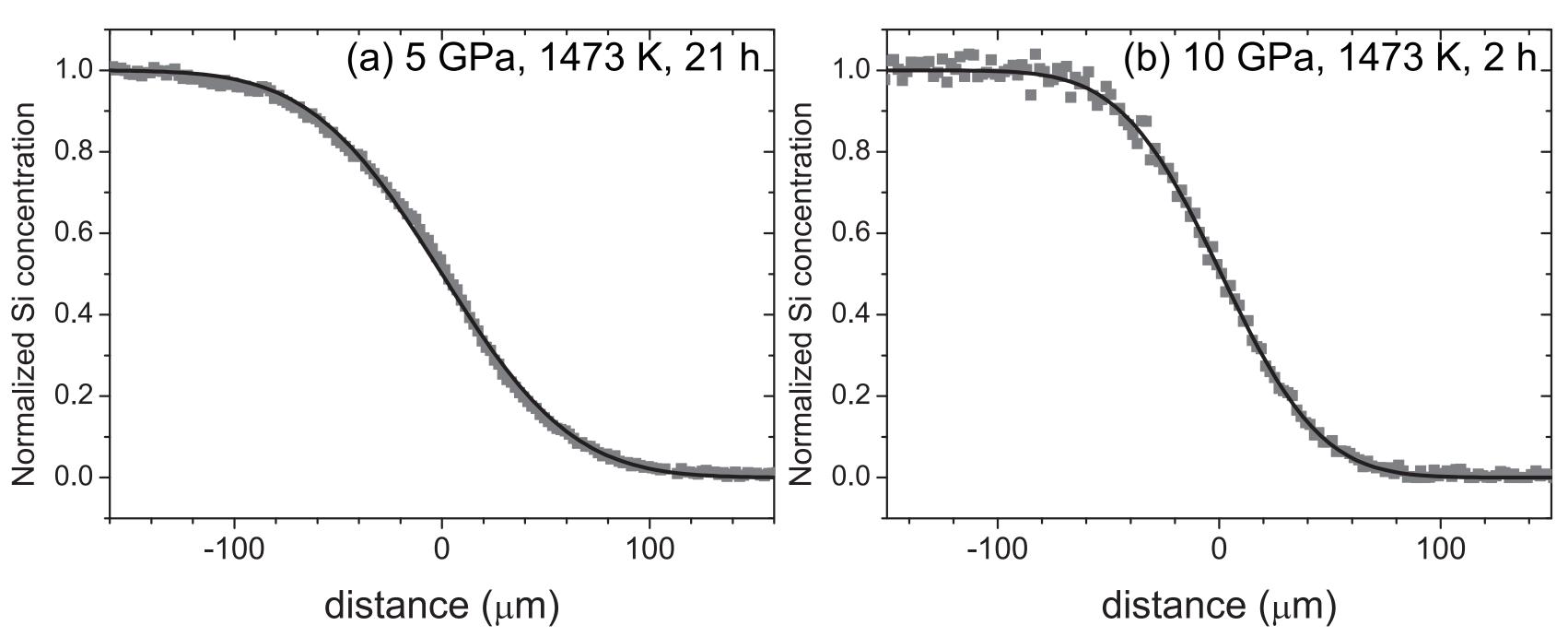


Figure 3

