

1 DOI:10.1016/j.icarus.2019.113401

2 **Rheological property of H₂O ice VI inferred from its self-diffusion:**
3 **implications for the mantle dynamics of large icy bodies**

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14

15 **ABSTRACT**

16 The volume diffusion coefficient of water in ice VI was determined in the
17 pressure-temperature range of 1.3 – 1.9 GPa and 300 – 320 K by in situ isotope tracer diffusion
18 experiments. We determined the activation energy of the volume diffusion to be
19 61.9 ± 9.5 kJ/mol. The viscosity of polycrystalline ice VI under diffusion creep was estimated
20 from the diffusion coefficients based on the theory of the diffusion creep. From a compilation of
21 viscosity values in the current diffusion creep regime and the viscosity previously determined by
22 plastic deformation experiments of ice VI in a high stress regime (Durham et al. 1996), here we
23 provide the relationships between viscosity, stress, and the average grain size of polycrystalline ice
24 VI. The most plausible deformation mechanism of the layers of ice VI underneath the internal
25 oceans in large icy bodies was inferred from the viscosity-stress-average grain size relationship. We
26 also discuss the critical thickness of the ice VI layer, which determines the onset of thermal
27 convection.

28

29 **Keywords:** Ices, Mechanical properties, Interiors, Ganymede, Titan

30 1. INTRODUCTION

31 The internal oceans of large icy bodies with diameters of more than 500 km are one of the
32 most important candidate zones for habitability in the solar system. The possibility of chemical
33 evolution occurring in these internal oceans is promoted by the chemical and physical interactions
34 between the oceans and the rocky mantles (Vance et al. 2007; Lammer et al. 2009). These
35 interactions include hydrothermal alteration of the mantles, the mass exchange between the
36 mantles and oceans, and the heat supply from the mantles. These internal oceans may resemble the
37 submarine hydrothermal system on Earth. The plausible pressure-temperature profiles in the
38 interiors of large icy bodies with diameters of more than 2000 km suggest the existence of layers of
39 high-pressure ice underneath the internal oceans (Noack et al. 2016; Vance et al. 2018). These
40 high-pressure ice layers may inhibit the above-described ocean-rock interactions. Many numerical
41 studies of interior planetary structures based on observations made by spacecraft have inferred the
42 existence of such high-pressure ice layers (e.g., Tobie et al. 2006; Lefèvre 2014; Choblet et al. 2017;
43 Kalousová et al. 2018). In particular, among the pressure-temperature phases of H₂O, ice VI has a
44 relatively wide stability region that can form thick layers over 100 km deep in the large icy bodies.
45 Thus, understanding the viscosity of polycrystalline ice VI is essential because it controls thermal
46 history and dynamics of these thick ice VI layers, thus affecting habitability in the interiors of the
47 large icy bodies. Furthermore, understanding the viscosity of polycrystalline ice VI is required for
48 undertaking the Jupiter Icy Moons Explorer mission (JUICE) scheduled for the 2030s. During the
49 mission, a tidal deformation measurement has been planned to prove the existence of an internal
50 ocean in Ganymede (Grasset et al. 2012). Assuming an interior structure without an internal ocean,
51 the tidal response will depend on the viscosity of ice VI (Kamata et al. 2016).

52 The viscosity of polycrystalline ice VI under low-stress conditions is the most important
53 parameter for understanding the dynamics of the ice VI layer, because the stress induced by the
54 buoyancy-driven thermal convection in large icy bodies was estimated to be below 0.1 MPa (Sotin
55 and Tobie 2004; McCarthy and Castillo-Rogez 2013; Choblet et al. 2017; Kalousová et al. 2018).
56 However, deformation experiments under such low-stress conditions are technically very difficult.
57 Durham et al. (1996) investigated the rheological properties of high-pressure ices V and VI using a
58 high-pressure gas medium deformation apparatus. They revealed viscosities and plastic deformation
59 mechanisms of polycrystalline ices V and VI in the range of 0.1 – 100 MPa. The viscosity of each
60 phase under high stress conditions is controlled by dislocation creep or the reduction of grain size
61 by recrystallization (Durham et al. 1996). The deformation rate of ice VI under this high-stress
62 creep regime is stress-dependent with the stress exponent of 4.5, and is insensitive to the average
63 grain size (Durham et al. 1996). The extrapolation of the plastic-flow law under this mechanism
64 into the lower stress conditions may give an overestimate for the viscosity, because the diffusion
65 creep can dominate under lower stress conditions of 0.1 MPa (Sotin and Tobie 2004; McCarthy and
66 Castillo-Rogez 2013). Under the diffusion creep regime, the viscosity of ice VI behaves as a
67 Newtonian fluid, which is sensitive to the grain size. Although the viscosity under the diffusion
68 creep regime cannot be measured directly, it can be quantitatively determined from the volume
69 diffusion coefficient of the molecules constituting the deforming material, as proposed by the
70 theories of diffusion creep (Frost and Ashby 1982). We therefore measured the diffusion coefficient
71 of ice VI in an isotope tracer diffusion experiment to determine its viscosity under the high-pressure
72 conditions of the large icy body interiors.

73 Conventional isotope diffusion methodology using mass spectrometers (e.g., Farver and

74 Yund 1991) cannot be applied for high-pressure conditions because it requires a high vacuum
75 environment. To address this problem, we used micro-Raman spectroscopy to develop an isotope
76 tracer diffusion method that has the potential to be an isotope probe for the high-pressure samples in
77 a diamond anvil cell (DAC). This method has been applied to diffusion studies for various hydrous
78 minerals (Noguchi and Shinoda 2010; Guo et al. 2013; Pilorgé et al. 2017; Ganzhorn et al. 2018).
79 First, to conduct the diffusion experiments for the high-pressure ices, an analytical method to
80 quantify isotope tracers using micro-Raman spectroscopy was developed (Noguchi and Shinoda
81 2010; Noguchi et al. 2016). We have successfully applied this method to tracer diffusion
82 experiments of ice VII using DAC, yielding the proton diffusion coefficient up to 17 GPa (Noguchi
83 and Okuchi 2016). In this study, we applied the technique to conduct hydrogen tracer diffusion
84 experiments for ice VI. We report the diffusion coefficients of water molecules of ice VI and its
85 viscosity under the diffusion creep regime. In addition, we discuss the condition required to trigger
86 convection in large icy bodies based on the temperature-dependence of viscosity.

87

88 **2. EXPERIMENTAL METHODS**

89 **2.1. Diffusion experiment**

90 A Mao-Bell type DAC was used to generate the pressure. The DAC was equipped with a
91 pair of type-IIa diamond anvils with a 600 μm diameter culet. A pre-indented Re foil with a sample
92 chamber of approximately 200 μm in diameter was used as a gasket. The thicknesses of the sample
93 chambers were in the range of 70 – 90 μm . Diffusion couples in each sample chamber were
94 prepared under low-humidity within a freezer cooled down to 252 K. A commercial isotope-tracer
95 reagent (D_2O ; 99.9 %, Wako Co. Ltd.) was used. The detailed methodology for preparing diffusion

96 couples was reported by Noguchi and Okuchi (2016). The schematic drawing of the diffusion
97 couple in the sample chamber is shown in **Fig. 1**. Firstly, D₂O ice was made in the sample chamber.
98 Several grains of ruby were also added to the chamber as the pressure marker (Mao et al. 1978). A
99 hole of approximately 100 μm in diameter was drilled in the isotope-tracer ice by using a hot
100 micro-pin. A micro ball of H₂O ice approximately 200 μm in diameter was prepared by freeze
101 spraying. The micro ball was dropped into the hole of the isotope-tracer ice. Finally, the diffusion
102 couple was pressurized to approximately 5 GPa at the temperature below the triple point for liquid,
103 ice I_h, and ice III. The diffusion couples of ice VII were transformed to ice VI by decreasing the
104 pressure. The grains in the polycrystalline ice VI were grown at approximately 1 GPa and at 293 K
105 which are the conditions near the melting point. Several grains with an average size range of 50 –
106 100 μm were released in the sample chamber (**Fig. 1**). In some cases, we succeeded in making a
107 diffusion couple composed of a single crystal, where grains of H₂O and D₂O ices were fused. The
108 DAC was then kept at 300 or 320 K in a constant temperature bath or a vacuum-oven to promote
109 self-diffusion. Pressure was repeatedly measured after keeping the sample for up to 10 h, and was
110 adjusted to maintain the pre-defined pressure through one diffusion experiment. Experimental
111 conditions are listed in **Table 1**.

112

113 **2.2. Raman spectroscopy**

114 A micro Raman spectroscope is composed of an optical microscope (Eclipse LV150,
115 Nikon Co. Ltd.) equipped with a motor-driven X-Y sample stage (SGSP20-35, Sigma Koki Co.
116 Ltd.), a 532 nm DPSS laser (100 mW, J100GS-1H-17-23, Showa Optronics Co. Ltd.), a notch filter,
117 and a polychromator (Spectra-Pro-300i, Acton Research Co. Ltd.) with a focal length of 30 cm. The

118 polychromator was equipped with a charge-coupled device (CCD) with an image resolution of 100
119 \times 1340 pixels (RS, Roper Co. Ltd). Diffractive grating of 1200 grooves/mm was selected for the
120 Raman measurement. The laser beam was focused through an objective lens with a \times 50
121 magnification (TPlan SLWD 50 \times , N.A. = 0.40, Nikon Co. Ltd.). The laser power at the focal point
122 was approximately 10 mW for the Raman measurements. At this laser power, we confirmed that
123 optical heating never melted the ice. The effective lateral and vertical resolutions of the
124 measurement in the DAC were 2.1 and 10.5 μm , respectively (Noguchi and Okuchi 2016). On the
125 tracer diffusion experiment, the spatial resolution of the probe is an important factor for estimating
126 the real tracer-diffusion coefficient (Ganguly et al. 1988).

127 The two-dimensional Raman mapping measurements of the diffusion couples in the DAC
128 were carried out using point-by-point illumination through sequential translation of the sample stage.
129 The position and shape of $\text{H}_2\text{O}/\text{D}_2\text{O}$ boundary could not be accurately established in the ice
130 diffusion couples. Visualizing the distribution of the concentration of the isotope tracers by the
131 mapping measurement was essential to be able to estimate the diffusion coefficient (**Fig. 1**). The
132 laser beam was focused on the middle plane of the sample chamber to exclude any interference
133 brought about by diffusion through the interface between the anvil surface and the diffusion couple.

134 The standard area dimension of Raman mapping was $80 \times 100 \mu\text{m}^2$, composed of grids of
135 $2 \times 2 \mu\text{m}^2$. The exposure time for each measurement point was 3–5 s, and the total time needed to
136 complete one Raman map was approximately 6 h. The diffusion of water in ice VI during the
137 Raman mapping was negligible, because the diffusion length at room temperature for 6 h estimated
138 from the diffusion coefficient and discussed in a later section, is less than 1 μm .

139

140 2.3. Quantitative analysis of deuterium concentration

141 A calibration curve was constructed to determine the molar concentration of
142 deuterium ($c_{OD} = D/(H+D)$) from the micro-Raman spectrum. Several Raman spectra of ice VI of
143 known c_{OD} values were measured at 1.4 GPa to construct the calibration curve (**Fig. 2a**). Raman
144 bands related to OD and OH stretching modes appeared in the ranges of 2120–2710 cm^{-1} and 2800–
145 3600 cm^{-1} , respectively. The OD stretching band overlapped with the multiphonon second-order
146 Raman band of diamond (**Fig. SA1a** in Noguchi and Okuchi 2016). The relative area ratio of the
147 OD stretching band to OH stretching band is expressed as:

$$148 A_{ratio} = \frac{A_{OD}}{A_{OD}+A_{OH}}, \quad (1)$$

149 where A_{OD} and A_{OH} are the areas under the Raman bands for OD and OH stretching modes,
150 respectively. The ratio was used as the index for determining c_{OD} . A correction due to the
151 overlapping of the Raman band of diamond on the estimate for A_{OD} was performed using the height
152 of the edge of the diamond Raman band at the high-wavenumber side, as reported by Noguchi and
153 Okuchi (2016). The c_{OD} was then plotted as a function of A_{ratio} in **Fig. 2b**. Although the shapes
154 of the Raman bands depend on the crystallographic orientation of the ice grain, we confirmed that
155 the relative area ratio (A_{ratio}) is independent of the orientation. Thus, the crystallographic
156 orientation did not affect the calibration line. However, another problem for the quantitative
157 analysis is the presence of a “dead zone” in the range of $0.65 < c_{OD} < 0.8$, where c_{OD} is not
158 very sensitive to A_{ratio} (**Fig. 2b**). Hence, a deuterium-rich water with a composition of
159 $(\text{H}_{0.4}, \text{D}_{0.6})_2\text{O}$ was prepared and used in all of the diffusion experiments. In so doing, we avoided the
160 problem of using that part of the calibration line within the dead zone. Expressed as a quartic
161 function, the calibrated relationship between the c_{OD} and the A_{ratio} when $c_{OD} < 0.65$ becomes:

162 $c_{OD} = 4.4192A_{ratio}^4 - 5.0012A_{ratio}^3 + 1.8429A_{ratio}^2 + 0.8603A_{ratio}$. (2)

163 The shapes and intensities of the Raman bands of the OH and OD stretching modes
164 depend on c_{OD} because of intermolecular coupling interactions (**Fig. 2a**), which are the cause of
165 the nonlinearity of the calibration curve. The molecular coupling interaction is induced where the
166 same molecular type adjoins in the crystal lattice, namely, H₂O...H₂O or D₂O...D₂O, and the
167 frequencies of the OH or OD stretching modes of these molecules are modulated slightly (Horning
168 et al. 1958; Bertie and Whally 1964; Noguchi and Okuchi 2016). Since the probability that
169 molecules of the same type adjoin in (H,D)₂O ice depends on c_{OD} , the shapes of the Raman bands
170 vary with c_{OD} .

171

172 **3. RESULTS**

173 The representative optical photographs of the diffusion couples are shown in **Fig. 3**. During
174 the diffusion experiments, the grain boundaries can reorder or migrate through recrystallization
175 processes that depend on the thermodynamic stability of grain shapes. However, such changes of
176 the polycrystalline textures were not observed during the diffusion experiments.

177 The two-dimensional c_{OD} distributions were determined from the area ratio of the OD
178 stretching mode to the OH stretching mode using the calibration curve (**Figs. 3a-c**). It is noteworthy
179 that signs of leakage of the tracer from grain boundaries to grain interiors appeared in the
180 two-dimensional c_{OD} distributions (**Figs. 3a and b**). Such leakage is an indication of fast
181 grain-boundary diffusivity. Although we currently acknowledge the difficulty of determining the
182 grain-boundary diffusion coefficient for the complex geometry of the grain boundaries, it may be
183 determined by numerical analysis in the future. The volume diffusion coefficient of hydrogen (D_V)

184 was determined from the two-dimensional c_{OD} distributions. We first selected a rectangular area 6
 185 μm wide and 80 μm in typical length, which was cut from each two-dimensional diffusion map to
 186 include the $\text{H}_2\text{O}/\text{D}_2\text{O}$ boundary perpendicular to the longer axis of the rectangle (dotted yellow
 187 rectangles in **Figs. 3a-c**). We then integrated the c_{OD} values within each rectangle in the direction
 188 parallel to the $\text{H}_2\text{O}/\text{D}_2\text{O}$ boundary (**Figs. 4a-c**). The ideal one-dimensional diffusion profile is
 189 expressed as the solution to the following diffusion equation:

$$190 \quad c_{OD}(x, t) = \frac{1}{l} \int_0^l f(x') dx' + \frac{2}{l} \sum_{n=1}^{\infty} \exp\left(-\frac{D_V n^2 \pi^2 t}{l^2}\right) \cos \frac{n\pi x}{l} \int_0^l f(x') \cos \frac{n\pi x'}{l} dx' ,$$

191 (3)

192 where $f(x)$ is the initial distribution, l is the length of a diffusion couple, and t is time (Crank 1956).
 193 The initial distribution was converted to $f(x)$ by fitting a Fourier series. The diameters of the sample
 194 chambers were used as the value of l . The measured diffusion profiles were affected by the spatial
 195 resolution. According to Ganguly et al. (1988), the resultant diffusion profile can be expressed as
 196 the convolution of the ideal diffusion profile and Gaussian function as follows:

$$197 \quad g(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{x^2}{2\sigma^2}\right) , \quad (4)$$

$$198 \quad c_{conv}(x, t) = \int_{-\infty}^{\infty} c_{OD}(x', t) \cdot g(x' - x) dx' , \quad (5)$$

199 where σ is a factor that accounts for the effective lateral resolution of the instrument. The value of σ
 200 was determined to be 2.1 μm from the result of the edge scan test using quartz (Noguchi and
 201 Okuchi 2016). The value of D_V for each run was determined by least-squares fitting of the
 202 one-dimensional diffusion profile with **Eq. 5 (Table 1)**.

203 The activation energy and frequency factor (pre-exponential factor) were determined
 204 from the slope and intercept of the Arrhenius plot of D_V (**Fig. 5**). Our measured Arrhenius equation

205 is:

$$206 \quad D_V = 2.1 \times 10^{-6} \exp\left[-\frac{61.9 \pm 9.5 \text{ kJ/mol}}{RT}\right] \text{ (m}^2\text{/s)}, \quad (6)$$

207 where R is the gas constant. The activation energy is relatively large compared to that of ice I_h (58
208 kJ/mol; Itagaki 1967; Ramseier 1967). In the pressure range of 1.3 – 1.9 GPa, pressure dependence
209 of D_V was not observed (**Table 1**).

210

211 **4. DISCUSSION**

212 **4.1. Viscosity of polycrystalline ice VI**

213 The convective vigor of the ice VI layers in large icy bodies depends on the deformation
214 mechanism of polycrystalline ice VI and the temperature dependence of its viscosity. To elucidate
215 the dominant deformation mechanism of plastic flow in the polycrystalline ice VI layer, we
216 estimated the viscosity as a function of deviatoric stress (σ) and average grain size (d). In a high
217 stress regime, viscosity can be derived from the plastic-flow law determined previously in a
218 deformation experiment (Durham et al. 1996); while in a low stress regime, the viscosity should be
219 derived from the plastic-flow law of the diffusion creep. The relationship between strain rate and
220 stress in the diffusion creep regime can be express as follows (Nabarro-Herring creep: Herring,
221 1950):

$$222 \quad \dot{\epsilon} = A \sigma/d^2, \quad (7a)$$

$$223 \quad A = 14\Omega D_V/RT, \quad (7b)$$

224 where $\dot{\epsilon}$, D_V , and Ω are the strain rate, the volume diffusion coefficient of the rate-controlling atom
225 or molecule, and the volume of one vacancy that can be approximated by the molar volume (Fortes
226 et al. 2012), respectively. The strain rate is controlled by the D_V of the slowest diffusion species in a

227 material. Estimating viscosity using **Eqs. 7a** and **b** requires understanding of the diffusion
228 mechanism of ice VI at the atomic level.

229 In the case of ice I_h , the free interstitial molecule mechanism is accepted as the dominant
230 diffusion mechanism (e.g., Onsager and Runnels 1963; Ikeda-Fukazawa et al. 2002). Moreover, the
231 similarity between the D_V values of ^3H and ^{18}O of ice I_h (Delibaltas et al., 1966) indicates that the
232 volume diffusion of the whole H_2O molecule is the deformation-controlling process. In the case of
233 ice VII, the dominant diffusion mechanism changes with increasing pressure. Below 10 GPa and at
234 300 K, the migration of the whole H_2O molecule is the dominant mechanism (Hernandez and
235 Caracas 2018); above 10 GPa, protonic diffusion becomes the dominant mechanism (Katoh et al.
236 2002; Noguchi and Okuchi 2016). Between the two, the protonic diffusion process is more complex,
237 with the formation of ionic defects, H_3O^+ and OH^- ; and the migration of rotational defects, D and L.
238 The oxygen atom in the H_2O molecule is the deformation-controlling species in the protonic
239 diffusion mechanism. In this case, the diffusion mechanism is affected by the hydrogen bond
240 distance and density (Hernandez and Caracas 2018). The hydrogen bond distance and density of ice
241 VI (Kuhs et al. 1984; Fortes et al. 2012) are intermediate between those of ice I_h at ambient pressure
242 and ice VII at 10 GPa. Thus, in the case of ice VI, the migration of the whole H_2O molecule must be
243 the dominant mechanism. We therefore consider the hydrogen diffusion coefficient determined by
244 this study (D_V) as the volume diffusion coefficient of the H_2O molecule.

245 The viscosity ($\eta = 2\sigma/\dot{\epsilon}$) of ice VI was calculated using **Eqs. 7a** and **b**. Grain-size
246 sensitive creep, which has been reported for ices I_h and II (Durham et al. 2001; Goldsby and
247 Kohlstedt 2001; Kubo et al. 2006), was not considered when the viscosity was estimated because it
248 was not reported in a previous deformation experiment on ice VI (Durham et al. 1996). The $\eta - \sigma -$

249 d relationships at 1.2 GPa, 270 K and at 1.2 GPa, 300 K are shown in **Fig. 6**. Their
250 pressure-temperature conditions are relevant in the middle part of the ice VI layer with thicknesses
251 of 200 and 500 km, which occur within Titan and Ganymede, respectively (Tobie et al. 2006;
252 Choblet et al. 2017; Kalousová et al. 2018).

253 As inferred from the **Fig. 6** constraining the two parameters controlling viscosity, σ and d ,
254 is key to elucidating the deformation mechanism in the ice VI layer. Plausible convective stresses in
255 the ice VI layers were previously estimated from the buoyancy, which range from 1 kPa to 0.1 MPa
256 (Sotin and Tobie 2004; McCarthy and Castillo-Rogez 2013; Choblet et al. 2017; Kalousová et al.
257 2018). On the other hand, the grain size is a kinetic parameter that must vary with time after the
258 initial planetary differentiation process. However, in the case of terrestrial ice I_h , the grain boundary
259 pinning by particles of impurities controls the final grain size (Barr and Mckinnon 2007a; Kubo et
260 al. 2009). Polycrystalline ices in sheets includes insoluble impurities of $\sim 5 \times 10^{-4}$ wt%, and their
261 grain sizes are typically within the range of 1 – 10 μm (e.g., Durand et al. 2006; Duval 2013).
262 Similar to this case, here we assume a huge quantity of particles of salt hydrates and silicates must
263 blend into the ice VI layer during the differentiation of the ice bodies. If this assumption is correct,
264 then the grain size of ice VI may be comparable to that of the terrestrial ice. Thus, the assumption
265 that the grain size does not exceed a few meters is very possible. Consequently, the most plausible
266 deformation mechanism inferred from the results in **Fig. 6** is diffusion creep.

267

268 **4.2. Convective criterion in the ice VI layer**

269 Here, we discuss the criterion for the onset of thermal convection in the ice VI layer
270 according to Newtonian rheology. The critical Rayleigh number for a Newtonian fluid is

271 $Ra_{cr} = 20.9\theta^4$, (8a)

272 $\theta = E\Delta T/RT_b^2$, (8b)

273 where T_b is the basal temperature of the ice VI layer, ΔT is the temperature difference across the
 274 layer, E is the activation energy for the plastic deformation, which is equal to the activation energy
 275 of the volume diffusion coefficient (Solomatov 1995). Using this critical Rayleigh number and the
 276 relationship between strain rate and stress, the critical layer thickness, D_{cr} , above which thermal
 277 convection can occur, is estimated as follows:

278
$$D_{cr} = \left(\frac{Ra_{cr} k d^2 \exp\left(\frac{E}{RT_b}\right)}{3A\rho g \alpha \Delta T} \right)^{1/3}, \quad (9)$$

279 where A is the pre-exponential constant of the plastic-flow law (**Eq. 7b**), k is the thermal diffusivity,
 280 ρ is the density, g is the local gravity acceleration, and α is the thermal expansivity (Barr and
 281 Pappalardo 2005; Solomatov and Barr 2006; Barr and Mckinnon 2007b). All parameters in **Eq. 9**
 282 except for the g and ΔT have been determined in previous and current experiments. The values for g
 283 and ΔT are constrained, based on the evolution models of Titan by Tobie et al. (2006) and
 284 Ganymede by Kalousová et al. (2018). The radii of the silicates mantles of Titan and Ganymede
 285 have been estimated to be about 1800 km. Furthermore, the valid value for g at the interface
 286 between the silicate mantles and the ice VI layers is 1.6 m/s^2 (Kalousová et al. 2018). Based on the
 287 thermal histories of Titan and Ganymede after differentiation (**Fig. 7**), the predicted ΔT is in the
 288 range of 15 to 30 K, while T_b falls within the range of 260 to 300 K. These parameters used for the
 289 calculation are shown in **Table 2**. D_{cr} as a function of d is shown in **Fig. 7**. During the evolution of
 290 large icy bodies, the onset of the convection of the ice VI layer occurred when its thickness
 291 exceeded a few km, as long as the final d was kept within the order of 10 mm as mentioned above

292 (Fig. 7). Thus, the heat from the silicate mantle was efficiently transported to the internal ocean.
293 Previous geophysical studies suggest that the current Titan and Ganymede have ice VI layers of at
294 least over 100 km thick (Tobie et al. 2006; Lefèvre 2014; Choblet et al. 2017; Kalousová et al.
295 2018). Therefore, thermal convection must currently be actively occurring in their ice VI layers.

296

297 5. CONCLUSIONS

298 We determined the volume diffusion coefficient of ice VI using a DAC and micro-Raman
299 spectroscopy. This method has been applied in diffusion studies of other high-pressure ice phases
300 such as ices II, III, V. Furthermore, the viscosity of polycrystalline ice VI was inferred from the
301 diffusion parameters determined here and the deformation parameters determined by a previous
302 deformation experiment (Durham et al. 1996). Assuming realistic values of convective stress and d
303 in the ice VI layer of large icy bodies, we conclude that diffusion creep is the mechanism currently
304 controlling plastic-flow. We also determined the critical thickness of the ice VI layer for convection
305 based on Newtonian rheology. Considering the uncertainty associated with estimates of d values
306 discussed within the context of deformation mechanisms, there is a need to conduct experiments on
307 the grain growth of polycrystalline ice VI in order to more reliably address the dynamics of large
308 icy bodies.

309

310 ACKNOWLEDGEMENTS

311 N. N. would like to thank Dr. S. Kamata of Hokkaido University for fruitful discussions.
312 This work was financially supported by the Grant-in-Aids (nos. 15K17795, 17K14422, 17H06456)
313 from the Japan Society for Promotion of Science.

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474 **TABLE**

475

TABLE I. Experimental conditions and hydrogen diffusion coefficients of ice VI (D_V).

Run No.	Isotope	T (K)	P (GPa)	Total t (h)	D_V (m ² /s)
1	D ₂ O ^a	300	1.30 ± 0.15	162.0	(4.3 ± 0.0) × 10 ⁻¹⁷
2	D ₂ O	300	1.55 ± 0.12	553.0	(3.5 ± 0.3) × 10 ⁻¹⁷
3	D ₂ O	300	1.88 ± 0.02	575.2	(2.1 ± 0.5) × 10 ⁻¹⁷
4	D ₂ O	300	1.90 ± 0.03	1171.2	(5.5 ± 1.1) × 10 ⁻¹⁷
5	D ₂ O	320	1.75 ± 0.12	250.0	(1.9 ± 0.9) × 10 ⁻¹⁶
6	D ₂ O	320	1.87 ± 0.02	222.3	(2.3 ± 0.8) × 10 ⁻¹⁶
7	D ₂ O	320	1.88 ± 0.02	202.2	(1.4 ± 0.1) × 10 ⁻¹⁶
8	D ₂ O	320	1.89 ± 0.03	343.3	(1.4 ± 0.5) × 10 ⁻¹⁶

^a True composition was (H_{0.4},D_{0.6})₂O (see text).

476

TABLE 2. List of parameters used in the calculation of the critical thickness (D_{cr}).

Symbol	Physical property	Value	Unit
T_b	Basal temperature of the ice VI layer ^a	260 – 290	K
ΔT	Temperature difference across the layer ^a	15 – 30	K
P	Pressure ^a	1.2	GPa
g	Gravity acceleration ^a	1.6	m/s ²
E	Activation energy of diffusion ^b	61.9	kJ/mol
α	Thermal expansivity ^c	1.9–2.1 × 10 ⁻⁴	1/K
k	Thermal diffusivity ^d	4.6–5.2 × 10 ⁻⁷	m/s ²
ρ	Density ^c	1370–1380	kg/m ³

^a See text.

^b This study.

^c Fortes et al. (2012)

^d Ros et al. (1978)

477

478

479 **FIGURE CAPTIONS**

480

481 **FIGURE 1.** Schematic drawing of the diffusion couple prepared within the sample chamber of the
482 diamond anvil cell (DAC).

483

484 **FIGURE 2.** Raman spectra of (H,D)₂O measured at 1.4 GPa and at room temperature (a). c_{OD}
485 indicates the molar deuterium concentration (D/(H+D)). (b) Correlation between A_{ratio} and c_{OD} for
486 (H,D)₂O ices. A_{ratio} indicates the relative area ratio of the OD stretching band to OH stretching band.
487 The dotted line shows the calibration line, which was determined by fitting a quartic function to the
488 averaged data with respect to pressure (**Eq. 2**).

489

490 **FIGURE 3.** Polarized-light optical photographs of the diffusion couples of polycrystalline ice VI
491 (the far-left column) and two-dimensional maps of c_{OD} (molar ratio of D₂O) of the diffusion
492 couples: a) Run. 4 (**Table 1**), b) Run. 6, c) Run. 7. Rectangles in the photographs show the
493 coverage of the Raman mapping measurements. Scale bars represent 50 μm . The black regions in a
494 and b, where the word “Ruby” is printed, are the regions where the intense fluorescence light from
495 the ruby interfered with Raman measurements.

496

497 **FIGURE 4.** One-dimensional hydrogen diffusion profiles (a – c) calculated from the data enclosed
498 by the yellow-dotted rectangular area in **Figs. 3a – c**, respectively. The solid lines, except for the
499 lines for 0 h, indicate the least squares fit of **Eq. 5** to the data. The lines for 0 h are $f(x)$, which was
500 determined by fitting a Fourier series to the initial distribution.

501

502 **FIGURE 5.** Arrhenius plot of D_V of ice VI (**Table 1**).

503

504 **FIGURE 6.** Viscosities of polycrystalline ice VI at 1.2 GPa, 270 K and at 1.2 GPa, 300 K. The
505 homologous temperatures at 270 K and 300 K correspond to 0.87 and 0.96, respectively
506 (Choukroun and Grasset 2010). The lines of the dislocation creep were calculated using the

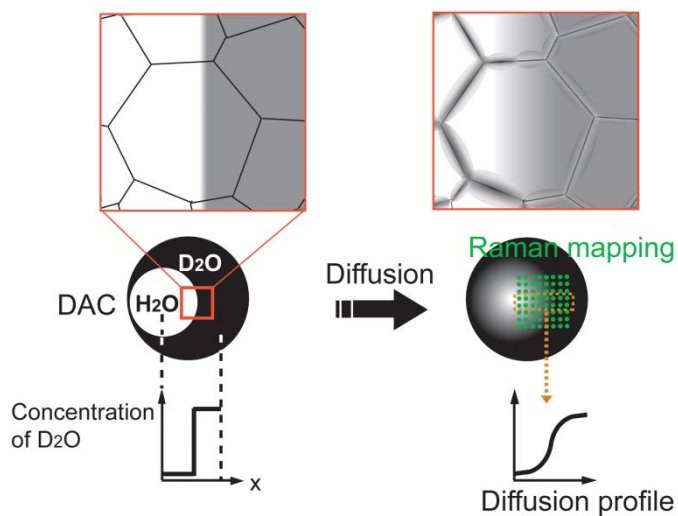
507 parameters taken from Durham et al. (1996). The gray and reddish bands of the dislocation creep
508 represent the error arising from the activation energy error of the dislocation creep.

509

510 **FIGURE 7.** Critical thickness of the ice VI layer in the large icy bodies for convection (D_{cr}).

511

512 Fig.1



513

514

515 **Fig. 2**

516

517

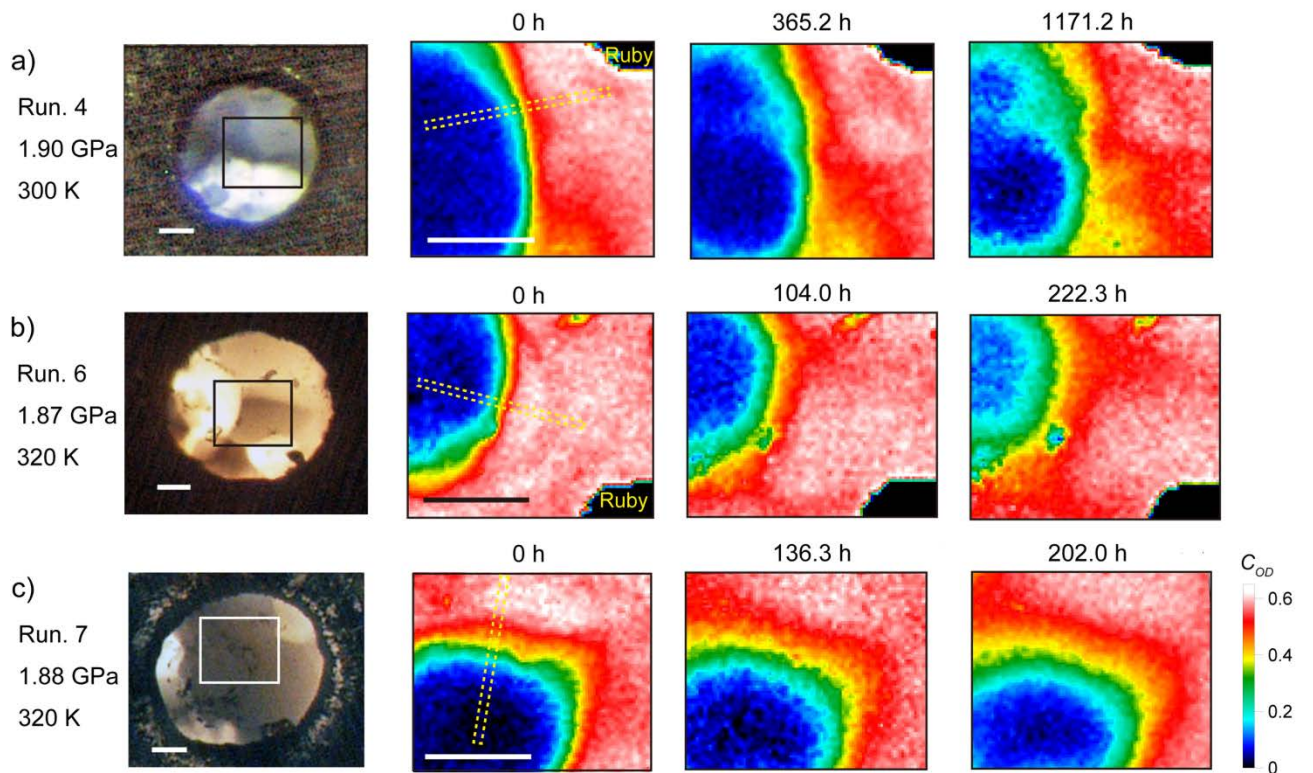
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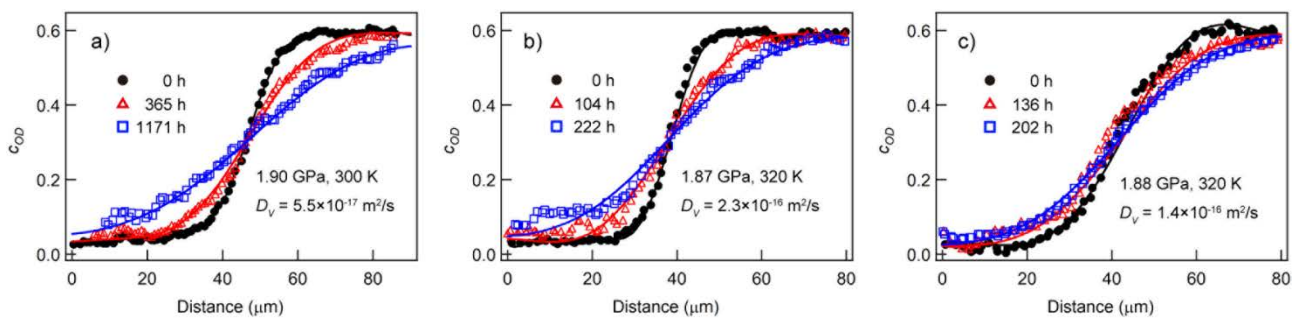
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522 **Fig.3**



523

524 **Fig.4**

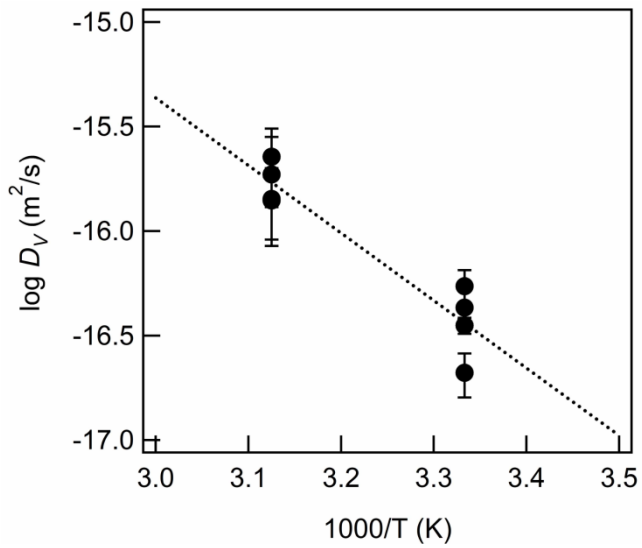


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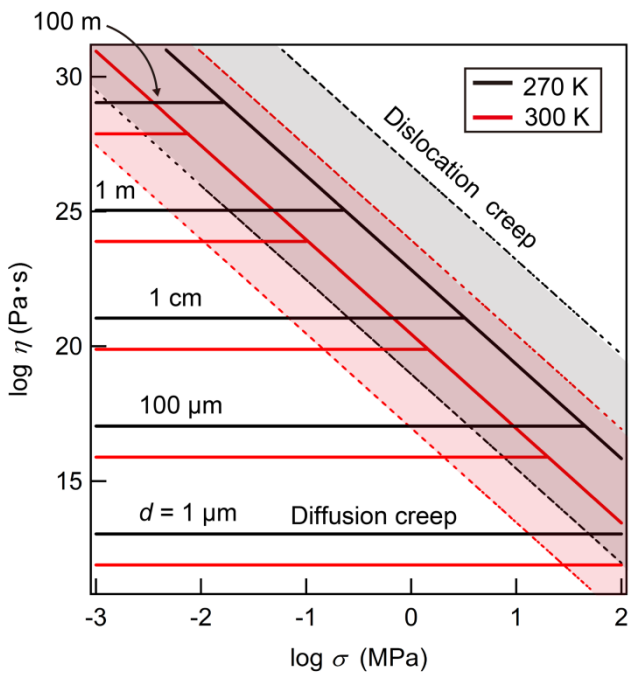
528 **Fig. 5**



529

530

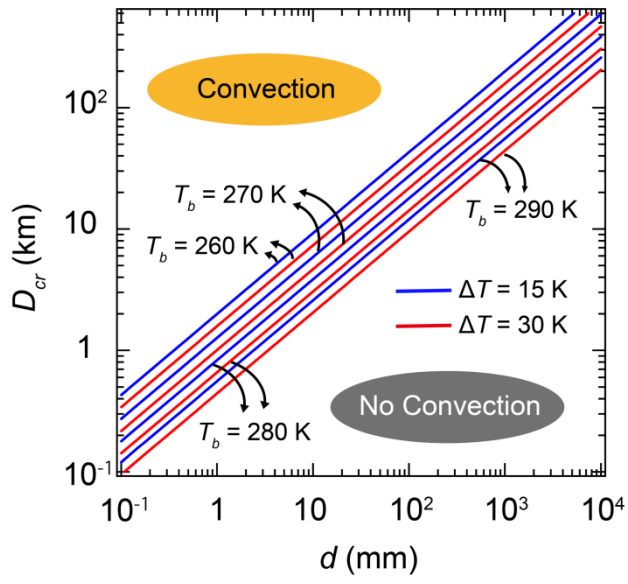
531 **Fig. 6**



532

533

534 **Fig. 7**



535