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1 Low- and High-Density Unknown Waters
2 at Ice–Water Interfaces
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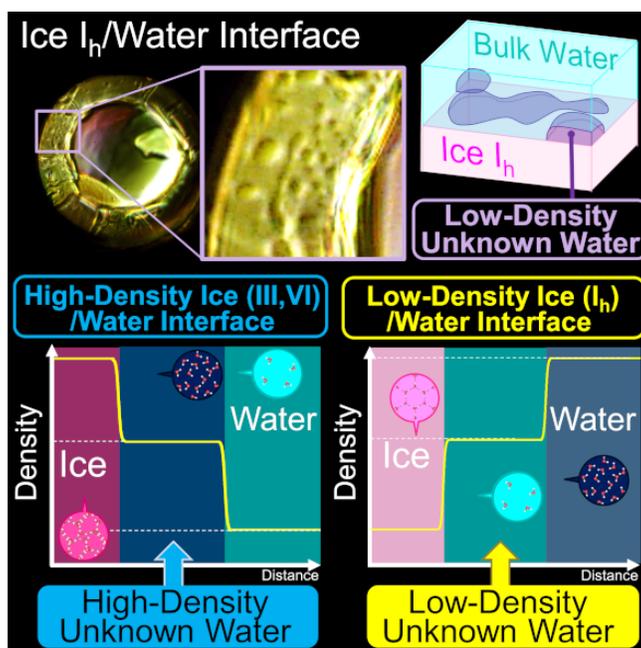
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25 **ABSTRACT**

26 Experimental confirmation of liquid polymorphs of water, high-density liquid (HDL) and low-
27 density liquid (LDL), is desired not only for understanding the liquid state of matters but also for
28 the origin of the mysterious properties of water. However, this remains challenging because the
29 liquid-liquid critical point of water lies in experimentally inaccessible supercooling conditions
30 known as ‘no-man’s land’. Here, we show by *in situ* optical microscopy that droplets and layers
31 of a low- and high-density unknown waters (LDUW and HDUW) appear macroscopically
32 depending on ice polymorphs at non-equilibrium interfaces between water and ices under
33 experimentally accessible (de)pressurization conditions. These unknown waters were found to
34 have characteristic velocities (about 20 m/s and 100 m/s for LDUW and HDUW, respectively)
35 different from water (about 40 m/s) and quasi-liquid layers (QLLs) (about 2 m/s and 0.2 m/s for
36 droplet and layer forms of QLL, respectively.). Our discoveries provide insight on liquid
37 polymorphism of water.

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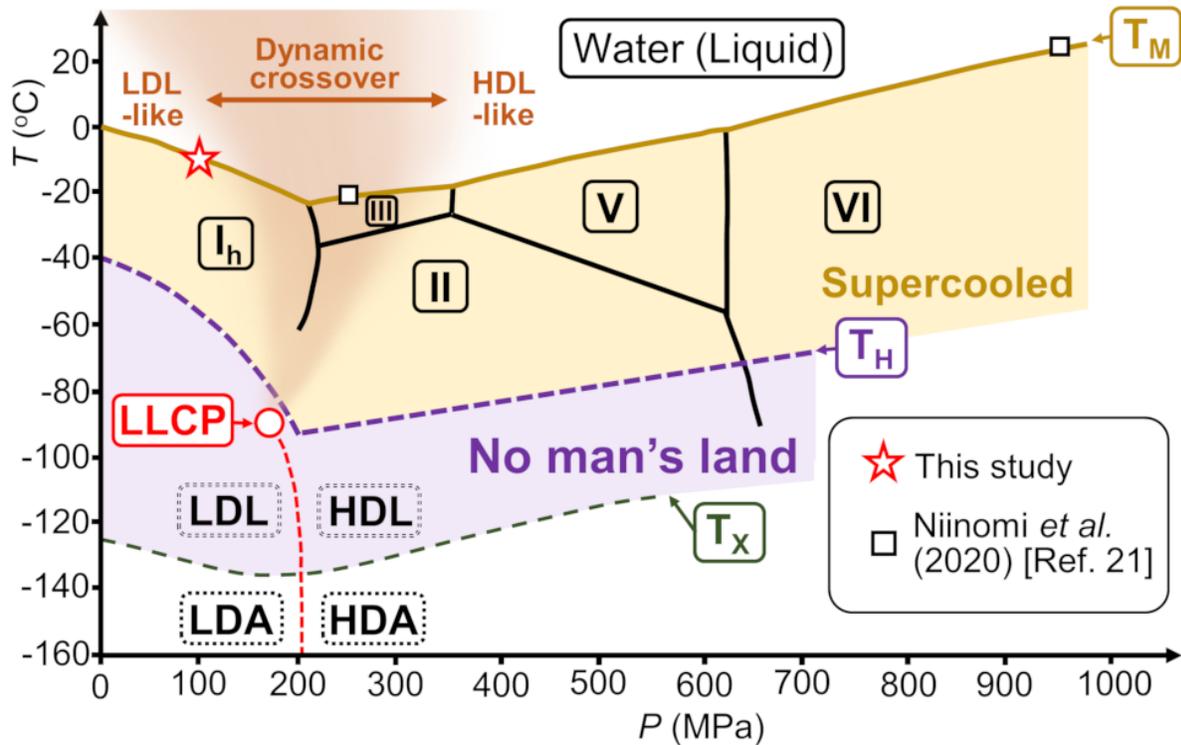
41 Experimental confirmation of polymorphism in single-component liquids is a key to
42 understanding the liquid state of matter¹⁻³. Unlike crystalline-state polymorphs, whose which can
43 be well characterized by reciprocal-space analysis because of their long-range ordering, the variety
44 of disordered liquid states is obscured by the lack of clear expressions to characterize their
45 structural signatures. Recent studies have suggested that single-component substances can exist in
46 two or more liquid phases characterized by differences in their density and local ordering; this
47 phenomenon is referred to as liquid polymorphism^{3,4}. Phase transformation between liquid
48 polymorphs, i.e. liquid-liquid phase separation (LLPS) or liquid-liquid phase transition (LLPT),
49 has been theoretically predicted in various pure substances including silicon⁵, carbon⁶, hydrogen⁷,
50 and nitrogen⁸. However, experimental confirmation of the phenomenon is exceedingly rare, and a
51 liquid–liquid critical point at which LLPS takes place has not been experimentally confirmed,
52 except in the case of sulphur¹. This situation is mainly because such LLPTs occur under
53 experimentally difficult conditions involving high temperatures and pressures, or they occur in
54 supercooled regions with inevitable contamination by crystal formation⁹. Such experimental
55 constraints have seriously hindered the progress of research into liquid polymorphism.

56 Water, which is such an abundant material on the Earth that its phase transitions governs
57 various natural and biological phenomena, is also considered to be a candidate for showing liquid
58 polymorphism as a consequence of the second-critical-point hypothesis¹⁰, which attempts to
59 explain the origins of the various unique properties of water¹¹, such as its maximum density at
60 4 °C. In this hypothesis, water is considered to exist as a supercritical state formed from two types
61 of liquid with different densities and local structures: a low-density liquid (LDL) and a high-
62 density liquid (HDL). LLPS of water into LDL and HDL is considered to arise at a liquid–liquid
63 critical point that occurs at a low temperature and a high pressure (Figure 1)¹². This is because the

64 unique properties of water can be elegantly explained by hypothesizing the existence of this liquid–
65 liquid critical point: the second-critical-point hypothesis^{10,13}. This hypothesis has motivated
66 numerous studies on local structure of water at a molecular scale by spectroscopic^{14,15}, X-ray^{16,17},
67 and neutron-scattering experiments^{18,19} in the supercritical regime. These studies have supported
68 the hypothesis by suggesting that two structural classes of water fluctuate and change their
69 correlation lengths in supercooled water depending on the conditions near the liquid–liquid critical
70 point²⁰. However, no experimental confirmation of a macroscopic LLPS or a LLPT of water has
71 been found. This is because the liquid–liquid critical point of water lies in experimentally
72 inaccessible conditions known as ‘no-man’s land’, where supercooling of liquid is obstructed by
73 rapid crystallization beyond the experimentally accessible time scale^{16,17}. Studies on liquid
74 polymorphism in water have been seriously hampered by the constraint imposed by this
75 supercooling limit.

76 We have previously discovered by *in situ* optical microscopy that macroscopic droplets and
77 layers of high-density unknown water (HDUW) separated from bulk water by a clear interface
78 appear at the interface between water and high-density ices (ices III and VI) grown or melted by
79 depressurization or pressurization in a sapphire anvil cell²¹. In the present work, we found that
80 macroscopic droplets and layers of low-density unknown water (LDUW) separated from bulk
81 appear at the interface between water and low-density ice (ice I_h) grown or melted by
82 depressurization or pressurization in an electrically-regulated sapphire anvil cell (see Experimental
83 Methods and Supporting Information (SI) Text S1)²². In addition, we determined the ratio between
84 the interfacial tension and the viscosity—the so-called characteristic velocity. The results confirmed

85 that LDUW and HDUW differ from previously observed waters, including the quasi-liquid layer
 86 observed at air–ice interfaces^{23,24}.

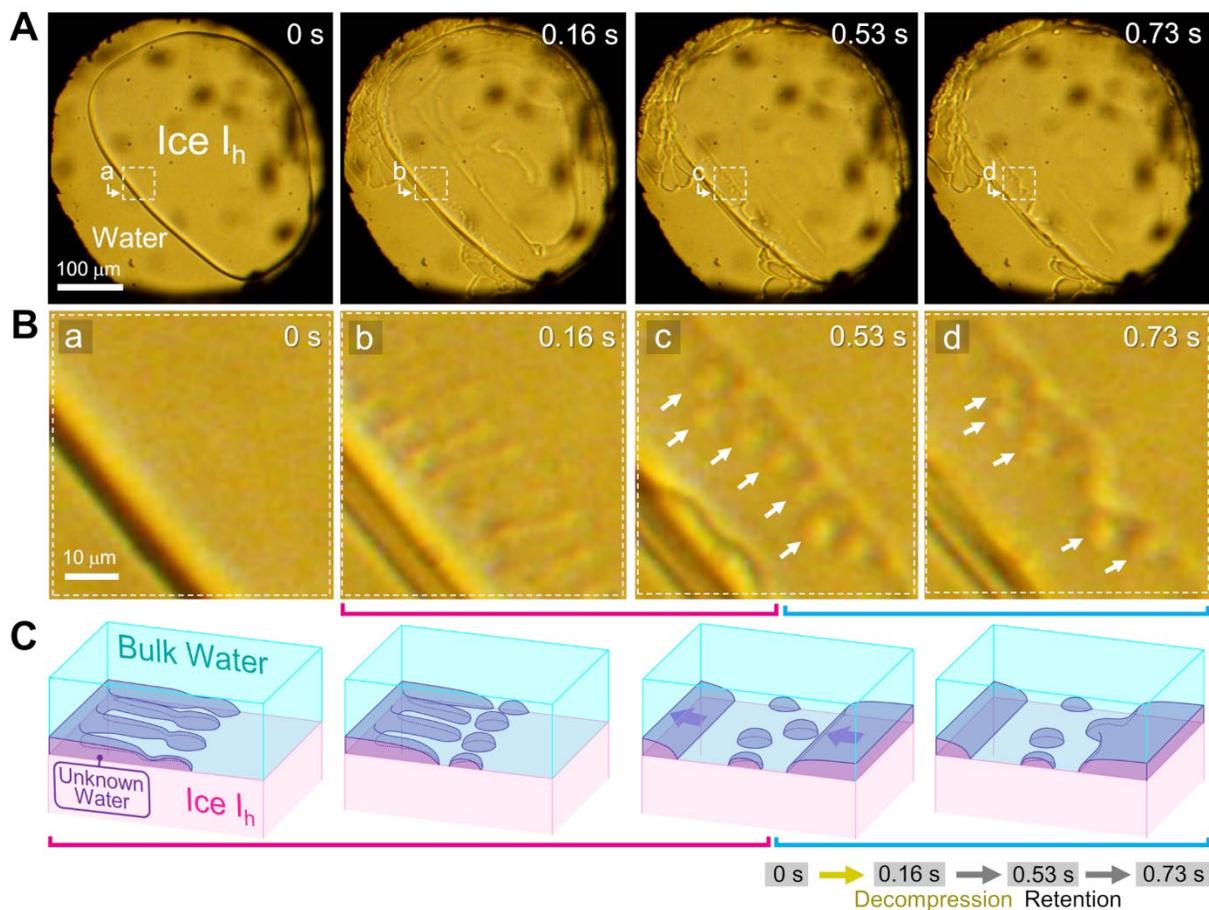


87 **Figure 1. Phase relations of water, and the experimental conditions for the in situ**
 88 **observations of the water–ice interfaces.** Phase relations of water and our observation
 89 conditions. The red star indicates the conditions for the observations of the water–ice I_h interface
 90 in this study. The black squares indicate the conditions for observations of water–high-pressure
 91 ice III or ice VI interfaces in a previous study²¹. The solid brown line indicated by T_M shows the
 92 melting temperatures of the ices. The liquid water below T_M is metastable supercooled water. The
 93 region where supercooled water can exist is highlighted in yellow. The purple dashed line indicated
 94 by T_H is the temperature at which homogeneous nucleation inevitably occurs and supercooled
 95 water cannot exist because of the supercooling limit; the temperature region below T_H is therefore
 96 the so-called ‘no-man’s land’, highlighted in purple. The dashed green line indicated by T_X is the
 97 amorphous ice crystallization line. The red circle indicates the liquid–liquid critical point (LLCP).
 98 The red dashed line emanating from the liquid–liquid critical point is the expected first-order
 99 transition line between LDL (low-density amorphous ice, LDA) and HDL (high-density
 100 amorphous ice, HDA) above (below) T_X . The region highlighted in the brownish colour emanating
 101 from the liquid–liquid critical point is the region that contains the dynamic crossover lines between
 102 LDL-like and HDL-like water, as suggested by previous studies and summarized by Taschin *et al.*
 103 ¹² The range of this region was depicted by reference to Ref. 12. Stable, metastable, and predicted
 104 metastable phases are indicated by the rectangles surrounded black solid, dotted, and dotted
 105 double lines, respectively.

106

107 Figure 2 shows *in situ* bright-field optical micrographs of the interface between bulk water and
108 ice grown in water by depressurization (see also SI Movie S1). Liquid droplets separated from the
109 bulk water with a clear interface between the water and the growing ice I_h when effective
110 overdepressure of about 2.3 GPa to drive crystal growth was applied at the interface²⁵ in the
111 electrically-regulated anvil cell (Figure 2, SI Text S2). This overdepressure corresponds to a
112 thermodynamic driving force for crystallization of about 8.6×10^{-21} J. The water–ice interface
113 exhibited a macroscopically smooth morphology before depressurization (Figures 2 **A** 0 s and **B** 0
114 s) but upon depressurization, it exhibited wavelike pattern (Figures 2 **A** 0.16 s and **B** 0.16 s),
115 resulting in the formation of droplets through breakaway of the tips of the waves (Figures 2 **A** 0.53
116 s and **B** 0.53 s). This indicated that the substance that exhibited the wavelike pattern was also liquid.
117 The resulting liquid coalesced when a droplet reached a step-like contrast, indicating that this step-
118 like contrast arose from the existence of a thin layer of liquid (Figures 2 **A** 0.73 s and **B** 0.73 s).
119 We confirmed the existence of the thin layer of liquid by *in situ* observation with an optical

120 microscope equipped with a Fizeau-type laser interferometer (See Materials and Methods and SI
 121 Movie S2).



122 **Figure 2. Time-lapse micrographs showing the appearance of LDUW at the interface**
 123 **between water and ice grown by decompression.** (A) Time-lapse micrographs captured by the
 124 *in situ* observations. (B) Magnified images of the regions indicated by the white dashed squares
 125 denoted by a–d. The white arrows indicate droplets of LDUW. A 0 s shows the initial state before
 126 decompression. A 0.16 s–0.73 s show time-lapse micrographs after decompression. The pressure
 127 was maintained in A 0.16 s–0.73 s. (C) Schematics showing the temporal evolution of the
 128 morphology of LDUW. The magenta and cyan solid lines indicate the corresponding schematic
 129 for the temporal evolution of the morphology shown in micrographs B 0.16 s–0.73 s underlined
 130 with magenta and cyan solid lines. The yellow and grey arrows in the right-hand bottom corner
 131 show the operations of decompression and retention, respectively. See also SI Movie S1.

132

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134 Observations by interferometric microscopy showed that the wetting liquid layer spread over a
135 wide area of the ice surface, suggesting that its wetting angle was less than 90° . If the wetting angle
136 θ was in the range $90\text{--}180^\circ$ the thickness of the liquid layer (h) would have been unrealistically
137 large on the basis of the following equation for wetting of a substrate by a spherical droplet of
138 radius r :

$$139 \quad h = r(1 - \cos\theta) \quad (1)$$

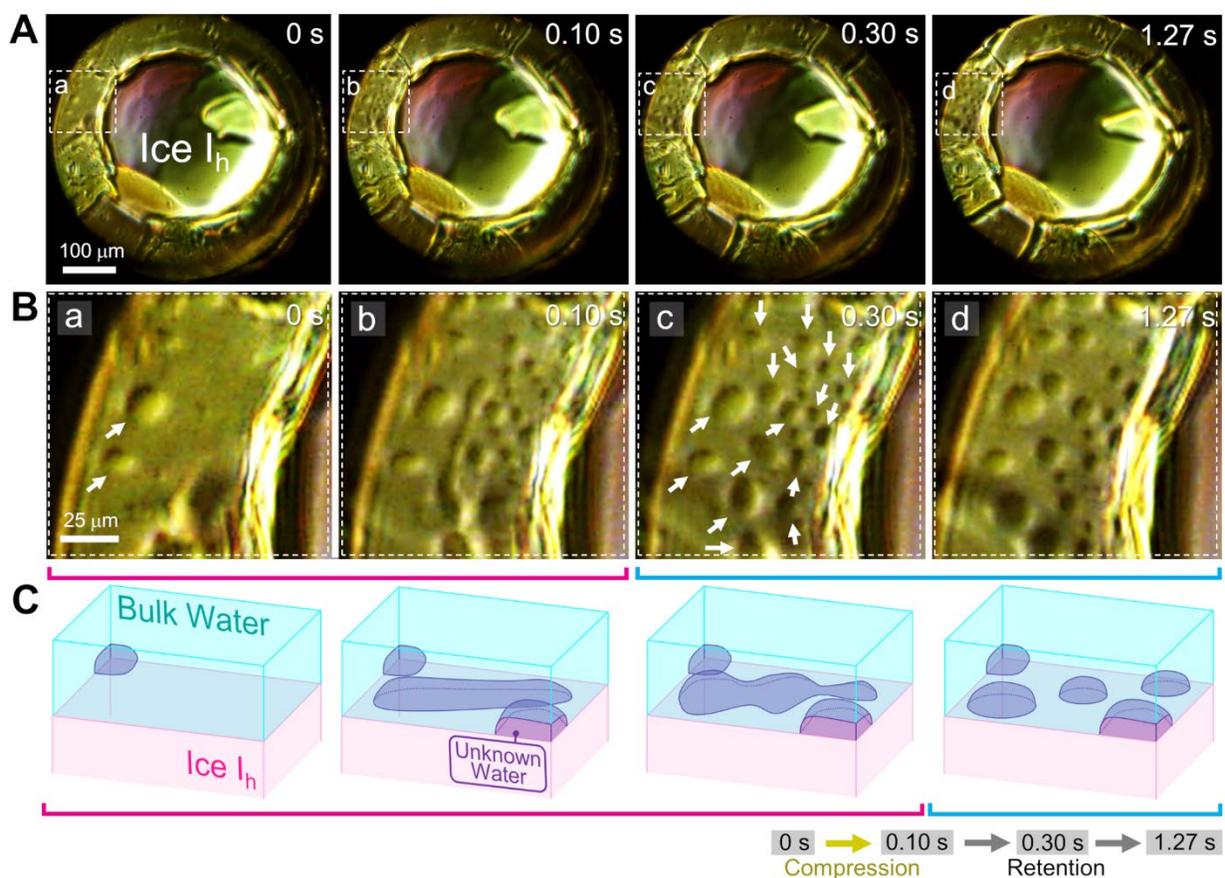
140 Equation (1) suggests that the thickness t is in the range $r < t < 2r$ for $90^\circ < \theta < 180^\circ$. Because
141 $2r$ corresponds to the in-plane size of the liquid layer and this size was $100\text{--}200 \mu\text{m}$ (SI Movie
142 S2), the thickness must have been at least $150\text{--}100 \mu\text{m}$ if the wetting angle is assumed to be more
143 than 90° . This thickness is comparable with the thickness of the sample chamber determined from
144 the thickness of a hole in the gasket after the experiment. However, the observations clearly
145 showed that the thickness of the thin layer was markedly smaller than that of the sample chamber.
146 Therefore, the wetting angle must have been less than 90° . This allowed us to estimate whether
147 the density of the liquid comprising the thin layer was lower than that of bulk water by using
148 Young's equation²⁶:

$$149 \quad \gamma_{IW} = \gamma_{IL} + \gamma_{LW}\cos\theta \quad (2)$$

149 where γ_{IW} , γ_{IL} , and γ_{LW} are the ice–bulk water, ice–newly discovered liquid, and newly
150 discovered liquid–bulk water interfacial free energies, respectively. From this equation, the
151 constraint $\theta < 90^\circ$ leads to $\gamma_{IW} > \gamma_{IL}$, implying that the structure of the liquid thin layer is more
152 similar to that of ice I_h , (with a lower density than that of bulk water) compared with that of bulk

153 water. Therefore, the density of the thin layer is probably lower than that of bulk water. Hereinafter,
 154 we refer to this unknown liquid at the water–ice I_h interface as ‘LDUW’.

155 Droplets of LDUW were also observed on melting ice I_h (Figures 3 and SI Movie S3). Upon
 156 pressurization corresponding to 8.6×10^{-21} J of thermodynamic driving force for melting, droplets
 157 separated from the bulk water and a clear interface appeared (Figures 3 **A** 0.10 s and **B** 0.10 s).
 158 Initially, some of these droplets had a non-hemispherical elongated shape that changed into a
 159 hemispherical shape through splitting into smaller droplets within one second (Figures 3 **A** 0.30 s
 160 and **B** 0.30 s). We also observed that moving droplets coalesced within one second, clearly
 161 demonstrating their fluid nature. Observations by interferometric microscopy confirmed the
 162 existence of a thin layer of liquid when the ice was melted by pressurization (SI Movie S2).

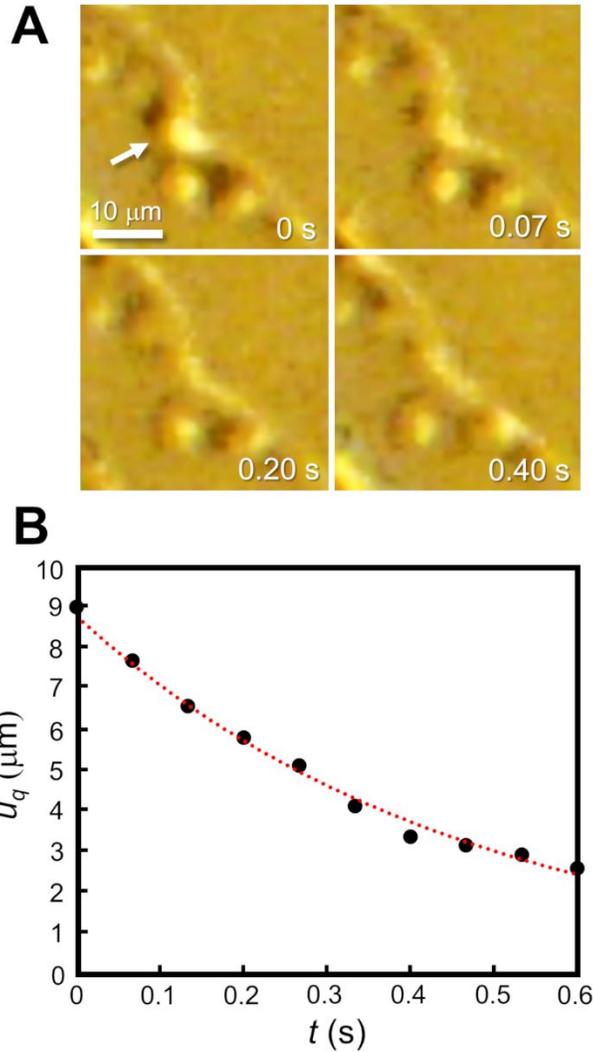


163 **Figure 3. Time-lapse micrographs showing the appearance of LDUW at the interface**
 164 **between water and ice melted by compression.** (A) Time-lapse micrographs captured by the *in*
 165 *situ* observations. The ice crystal had a ring-like shape because the edge of the disk-like single
 166 crystal in contact with the thermally conducting copper gasket tended to grow faster than the
 167 central region distant from the gasket. (B) Magnified images of the regions indicated by the white
 168 dashed squares denoted by a–d. The white arrows indicate droplets of LDUW. A 0 s shows the
 169 initial state before compression. A 0.10 s–1.27 s show time-lapse micrographs after compression.
 170 The pressure was maintained in A 0.10 s–1.27 s. (C) Schematic showing the temporal evolution
 171 of the morphology of LDUW. The magenta and cyan solid lines indicate the corresponding
 172 schematic of the temporal evolution of the morphology shown in micrographs B underlined by
 173 magenta and cyan solid lines. The yellow and grey arrows in the right-hand bottom corner indicate
 174 the operations of compression and retention, respectively. See also SI Movie S3.
 175

176 We also succeeded in determining the characteristic velocity of LDUW by analysing the
 177 dynamics of coalescence of a small liquid droplet with a liquid thin layer (Figures 4 A and SI
 178 Movie S4). It is known that the process of coalescence of a small droplet with a large one can be
 179 regarded as a weak perturbation of the contact line for the larger droplet. When the contact angle
 180 of the droplet is small enough to validate the lubrication approximation ($\theta \ll 1$ rad)²⁷, the temporal
 181 evolution of the relaxation of the amplitude of the contact lines perturbed by a mode with wave
 182 vector q is described by the following equation^{28,29}:

$$u_q = u_q(0) \exp\left(-\frac{V^* \theta^3 q}{3l} t\right) \quad (3)$$

183 where $V^* = \gamma/\eta$ is the characteristic velocity (where γ and η are the interfacial tension and
 184 shear viscosity of LDUW, respectively), and $u_q(0)$ is the initial value of the amplitude. The
 185 logarithmic factor $l = \ln(L/a)$ is a cutoff parameter to eliminate a singularity at the contact line
 186 and at infinite distance; here, a is the molecular size (3.7 Å for water) and L is the approximate
 187 size of the larger liquid droplet. From Eq. (3), the relaxation time is given by $\tau_q = 3l/(V^* \theta^3 q)$.



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Figure 4. Temporal evolution of the pattern of the contact line during the coalescence of a droplet and a thin layer of LDUW. (A) Time-lapse micrographs showing the temporal change in the pattern of the contact line during the coalescence of the droplet and the thin layer of LDUW. The white arrow indicates the droplet coalescing with the thin layer. (B) Temporal evolution of the amplitude u_q . The black dots are measured data. The data are fitted well by Eq. (3) (the red dotted line). See also SI Movie S4.

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198 We can regard the thin layer as a large droplet that absorbs the small droplet in the relaxation
199 process. An analysis of the *in situ* microinterferogram showed that the wetting angle was in the
200 range $1.76\text{--}1.82^\circ$ (~ 0.03 rad), ensuring that the lubrication approximation is valid (See SI Text S3).
201 Figures 4 **B** shows the measured temporal evolution of the amplitude of the contact line in the
202 observation shown in Figures 4 **A**. The measured value was well fitted by Eq. (3), allowing us to
203 calculate the relaxation time to be 0.467 s and $q^{-1} \sim u_q(0)$ to be 8.78 μm . Therefore, V^* is
204 estimated to be in the range 19.3 to 21.2 m/s. This value is one order of magnitude larger than that
205 of a quasi-liquid droplet (~ 2 m/s) and two orders of magnitude larger than that of a layer on the
206 air–ice interface (~ 0.2 m/s)²⁸. Note that the values for the quasi-liquid layer are based on the
207 interfacial tension for air, whereas that of LDUW is based on that for water. The interfacial tension
208 between liquids with the same composition should generally be smaller than that for air. This leads
209 to the estimation that the characteristic velocity of LDUW should be much smaller than that of the
210 quasi-liquid layer if their viscosities are similar. Nevertheless, the characteristic velocity of LDUW
211 is much larger than that of the quasi-liquid layer, meaning that the viscosity of LDUW must be
212 less than that of the quasi-liquid layer. Therefore, LDUW is distinguishable from the quasi-liquid
213 layer. In addition, the maximum value of the viscosity of LDUW can be estimated to be about
214 1.6×10^{-3} Pa·s (See SI Text S4), which confirms that LDUW is liquid, because the value is much
215 smaller than that at the glass-transition temperature (10^{12} Pa·s)³⁰. This estimated value is also
216 smaller than that of bulk water ($\sim 2.3 \times 10^{-3}$ Pa·s)^{31,32} under the conditions of our observations
217 (-10 °C and 107 MPa), (See SI Text S5). These comparisons confirmed that LDUW is
218 distinguishable from previously observed forms of water.

219 *In situ* optical microscopy has previously shown that macroscopic droplets and layers of
220 HDUW appear at the interface between water and high-pressure ices III and VI grown or melted

221 in bulk water²¹. Thus, the observations in this study showed that both low- and high-density
222 unknown waters can be observed macroscopically at interfaces of water with various ice
223 polymorphs in analogy with the LDL–HDL pair even under conditions far from those of the so-
224 called ‘no-man’s land’ (Figure 1). Although the observation of the low- and high-density unknown
225 waters does not directly show the existence of LDL, HDL and their critical point, signs of
226 transitions between an LDL and HDL have been suggested not only for supercooled water but also
227 for water at temperature above the melting temperature as a dynamic crossover between LDL-like
228 and HDL-like water¹³. Although a dynamic crossover is not a first-order transition, its line is
229 characterized by a change in the slope of the dependency of the physical and structural properties
230 of water, such as its viscosity, spectroscopic stretching band, or rotational correlation time, with
231 pressure or temperature. The pressure region where the dynamic crossover has been suggested to
232 occur ranges from about 150 to 300 MPa¹³, where high-pressure ice III is stable if the temperature
233 is below the melting temperature (Figure 1). The structures of ice I_h and ice VI are similar to the
234 local structures of LDL and HDL, respectively, whereas ice III has an intermediate structure^{20,33-}
235 ³⁶ (Figure S7). These relationships imply a relationship between the region of dynamic crossover
236 and the stable regions of ices, leading to a relationship between the pair of LDL-like and HDL-
237 like waters above the melting temperature and the LDUW–HDUW pair. This relationship can be
238 inferred not only from the local structure, but also from the physical properties. Our analysis of
239 the dewetting dynamics of HDUW at the water–ice III interface showed that its characteristic
240 velocity is about 100 m/s (See SI Text S6 and SI Movie S5). This value is roughly an order of
241 magnitude larger than that for LDUW, suggesting that LDUW is much more viscous than HDUW.
242 This is consistent with the relationship between the LDL and HDL forms predicted by a molecular-
243 dynamics simulation, which suggested that the viscosity of LDL is an order of magnitude larger

244 than that of HDL near the estimated conditions for the LDL–HDL first-order transition (-65.15°C ,
245 50 MPa)³⁷. A detailed comparison of LDUW and HDUW might provide further insights into their
246 relationships with LDL and HDL.

247 In summary, we have discovered, by *in situ* optical microscopic observations, that a
248 macroscopic layer and droplets of an unknown form of water with a lower density than that of bulk
249 water can appear at a nonequilibrium water–ice I_h interface. We also succeeded in determining the
250 characteristic velocities of LDUW and HDUW to be about 20 m/s and 100 m/s , respectively. These
251 results suggest that LDUW and HDUW have different local structures from previously observed
252 forms of water, including the quasi-liquid layer at the air–ice I_h interface. Taken in conjunction
253 with our previous observations, which showed macroscopic separation of HDUW from bulk water
254 at the interfaces between water and high-pressure ices III and VI, we have therefore shown that
255 LDUW and HDUW can be observed at nonequilibrium interfaces between water and various forms
256 of ice, in an analogous manner to LDL and HDL, under the conditions far from ‘no-man’s land’.
257 The macroscopic appearance of LDUW and HDUW with a lifetime observable by conventional
258 optical microscopy is possibly significant for the development of research, not only on the origin
259 of the unique properties of water hidden in the “no-man’s land” region, but also the liquid
260 polymorphisms of single-component systems in regions where there are experimental constraints,
261 such as supercooling limits of the pure liquid.

262

263 A dynamic sapphire anvil cell electrically-regulated by piezo actuators (d-SAC) was used for
264 the high-pressure experiment (See SI Text S1 for details)²². Ultrapure water from an ultrapure-
265 water-producing apparatus (Simplicity UV; Merck Millipore, Burlington, MA, USA) fed with

266 distilled water (Kyoei Seiyaku Co., Tokyo, Japan) was used as the mother liquid for crystallization
267 of ice I_h . A single crystal of ice I_h in water was repeatedly melted and grown by compression and
268 decompression using the d-SAC in the low-temperature room kept at -10°C . The interface between
269 the water and the ice I_h crystal repeatedly grown and melted in synchronization with
270 (de)compression was observed *in situ* by bright-field microscopy, differential-interference phase-
271 contrast microscopy, and Fizeau-type laser interferometric microscopy using an inverted optical
272 microscope (IX71; Olympus Corp., Tokyo, Japan) located in the low-temperature room.

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278 **SUPPORTING INFORMATION (SI)**

279 The Supporting Information is available free of charge on the ACS Publications website at XXXX.

280 SI Text S1. The details of experimental methods., SI Text S2. Thermodynamic driving
281 force for crystallization by d-SAC., SI Text S3. Estimation of the wetting angle of LDUW
282 at the water–growing ice interface., SI Text S4. Estimation of the maximum possible
283 value for the viscosity of LDUW., SI Text S5. Estimation of the viscosity of bulk water
284 at -10°C and 107 MPa. SI Text S6. Determination of the characteristic velocity of
285 HDUW at the water–ice III interface., SI Figure S1. Electrically regulated anvil cell with
286 piezo actuator, dynamic sapphire anvil cell (d-SAC). SI Figure S2. Experimental setup of
287 the microinterferometer and *in situ* observation of the thin layer of LDUW at the water–

288 growing ice interface with the microinterferometer., SI Figure S3. Estimation of the
289 effective overpressure at the water–ice I_h interface and the thermodynamic driving
290 force for crystallization produced by the actuating d-SAC., Figure S4. Schematic showing
291 the relationship of the wetting angle of LDUW at the water–ice I_h interface, based on the
292 interval of the interference fringes in the in situ microinterferograms., Figure S5. Pressure
293 dependence of the refractive index of bulk water at 643.847 nm and the temperature
294 dependence of the increment of the refractive index per 0.1 MPa of pressure increment.,
295 Figure S6. Dependence of the viscosity of bulk water on the pressure and temperature.,
296 Figure S7. Comparison of oxygen–oxygen two-body distribution functions (TBDFs) for
297 LDL, HDL, Ice I_h , Ice III, Ice VI, and supercooled waters under a high pressure., Figure
298 S8. Analysis of nucleation-and-growth-type dewetting dynamics of HDUW at the water–
299 ice III interface., Figure S9. *In situ* microinterferogram of the hole in the HDUW thin
300 layer at the water–ice III interface., Legends for SI Movies S1-S5, SI References (PDF),
301 SI Movie S1. Appearance of Low-Density Unknown Water at the Interface between
302 Water and Ice I_h Grown by Decompression (MPEG), SI Movie S2. *In situ* Laser-
303 Interferometric Observation of Low-Density Unknown Water at the Interface between
304 Water and Ice I_h Grown/Melted by De/Compression. (MPEG), SI Movie S3. Appearance
305 of Low-Density Unknown Water at the Interface between Water and Ice I_h Melted by
306 Compression. (MPEG), SI Movie S4. Coalescence Dynamics of a Low-Density Unknown
307 Water Droplet with Its Thin Layer. (MPEG), SI Movie S5. Nucleation-and-Growth-Type
308 Dewetting Dynamics of High-Density Unknown Water at Water–Ice III Interface.
309 (MPEG).

310 **Notes**

311 The authors declare no competing financial interest.

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