Low- and High-Density Unknown Waters at Interfaces between Water and Ices Grown/Melted by Pressure

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Non-equilibrium phenomena at crystal-melt interfaces during melt growth hold keys to understand elementary processes in crystal growth. The formation of ice from water belongs to melt growth and its interfacial phenomena are also important. Numerical analyses based on molecular dynamics (MD) simulation have been actively performed to understand ice-water interfacial phenomena so far. These analyses have provided the widely accepted picture that the structural order and density of ice continuously change to those of water within a few nm of a transient interfacial layer at the interface. However, the actual picture of the non-equilibrium interface still remains unclear because of the lack of experimental investigations. Here, we unexpectedly discovered, by simple *in-situ* optical microscopy, the existence of macroscopic unknown water layers separated from bulk water at the non-equilibrium interface between water and ices grown/melted by applying pressure [1, 2].

Ice I_h, III and VI were crystallized in ultrapure water by attaining two-phase coexist conditions using a sapphire anvil cell (SEED; Syntek Co. Ltd) in low temperature room ((-10^{o}C, 107 MPa), (-20^{o}C, 248 MPa) and (25^{o}C, 954 MPa) for ice I_h, III and VI, respectively.). The growth and melting of the ices driven by (de)pressurization were visualized by polarized light, differential interference contrast and interferometric optical microscopy.

Figure 1 A, B and C show time-lapse micrographs of the *in-situ* observations for ice I_h, III and VI, respectively. The observation revealed that unknown waters immiscible to the surrounding bulk water appear at the interface in various forms. The immiscibility probably originates from the difference in the local structure and density. Analyses of wetting angles suggested that densities of the unknown waters are similar to those of ices supporting the unknown waters than bulk water. This suggests that two kinds of, low- and high-density, unknown waters exist because densities of ice I_h and high-pressure ices are lower and higher than bulk water, respectively. Our observation provides insights not only on the crystal-melt interface but also on the non-classical crystallization of ice and the second critical point hypothesis of supercooled water to explain mysterious properties of water.

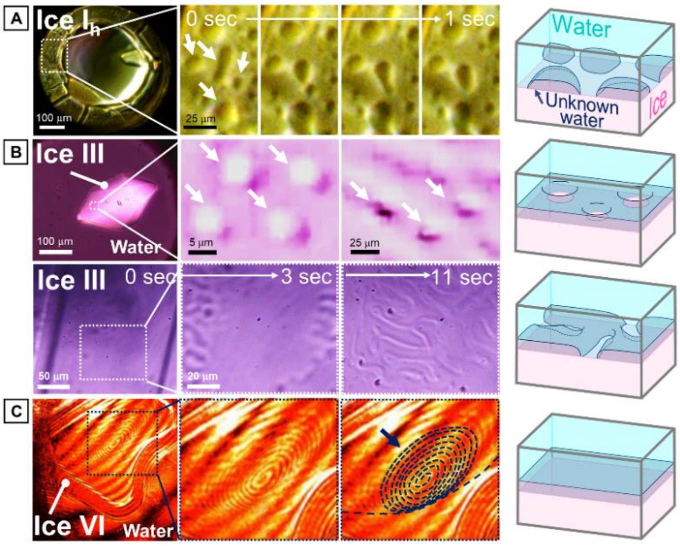

Fig. 1 Time-lapse micrographs of the *in-situ* observation on water-ice interfaces. Left A: Ice I_h, B: Ice III, C: Ice VI. Right: schematics showing the forms of the unknown waters.

References

[1] Niinomi H et al. High-density liquid water at a water–ice interface. J. Phys. Chem. Lett. 2020;11(16):6779-6784.

[2] Niinomi H et al. Low-and High-Density Unknown Waters at Ice–Water Interfaces. J. Phys. Chem. Lett. 2022;13(19):4251-4256.