High Pressure Kinetics Studies of Water Solidification in Dynamic-DAC

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Abstract. The phase diagram of water is both unusual and complex, exhibiting a wide range of polymorphs including proton-ordered or disordered forms. In addition, a variety of stable and metastable forms are observed. The richness of H$_2$O phases attests the versatility of hydrogen bonded network structures that include kinetically stable amorphous ices. In addition, natural gas hydrates are observed upon cooling and/or pressurization. The structures of gas hydrates are quite different from ices, yet guest molecules are enclathrated inside hydrogen bonded water cages. Hence, the presence of small impurity molecules can affect strongly the behaviours of hydrogen bonding and alter the phase diagram and phase boundaries of H$_2$O. In this paper, we report the effect of methane impurity on solidification and melting of H$_2$O under dynamic loading conditions. The presence of impurity mainly affects the growth rate of metastable ice VII, slowing down from 1.4 m/s in pure H$_2$O to 0.26 m/s in impure H$_2$O, neither the occurrence of metastable ice VII nor the melting of ice VI.

1. Introduction

Abundant in nature, water is a major constituent of planets and living organisms alike. The phase diagram of water exhibits a large number of polymorphs (Fig. 1) with great diversity in crystalline structures, chemical bonding, and collective interactions [1-3]. The hydrogen bond (OH-bond) angles and topology of relatively weak OH-bonds (with respect to covalent OH-bonds) are subject to large distortions, leading to proton and structural disorders and myriad phases—both stable and metastable (including amorphous). In addition to the fifteen known solid phases of H$_2$O, there are many metastable phases. These include several metastable phases of ice IV near the melt line [4] and VII observed in the stability field of ice VI [5], high- and low-density amorphous (HDA and LDA) at low temperatures [6-10], and high- and low-density water (HDW and LDW) [11]. Furthermore, liquid water under dynamic conditions is observed beyond the equilibrium phase boundaries. Therefore, the stability limit conjecture of liquid water [2], shown as the dotted broken line, is estimated from the homogeneous nucleation temperatures of the super-cooled liquid. Recently, HDA [12] ice is reported at room temperature under rapid compression, forming from metastable ice VII in the stability field of ice VI. This is in addition to a whole series of intermediate structures arising from amorphization, dipole ordering transitions, and symmetrization of hydrogen bonding [6,13]. The strength of OH-bonds varies in these metastable structures, as does the transition dynamics that is not well understood.

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Recent advances in dynamic-Diamond Anvil Cell (d-DAC) [5,12,14-16] enable the studies of metastable/intermediate states that are path-dependent and kinetically controlled. For example, dynamic pressure-induced dendrites have been observed and explained by Lee et al. In addition, metastable ice-VII, previously observed in the stability field of ice VI, is accounted for a lower interfacial surface energy between ice VII and super-compressed water [5]. Moreover, HDA ice [12] was observed at room temperatures under rapid compression. HDA is formed from metastable ice VII in the stability field of ice VI, well above the crystalline temperature of 150 K. It also arises from the structural similarity between HDA and ice VII. The kinetic data indicates that the formation follows an interfacial growth mechanism unlike the melting process. Nevertheless, the occurrence of HDA along the extrapolated melt line of ice VII (Fig. 1) resembles the ice Ih-to-HDA transition [6], indicating that the structural instabilities of parent ice VII and Ih drive the pressure-induced amorphization. The reported results strongly show that the d-DAC is a strong method to study the kinetics of materials and furthermore enables to study thermodynamics by varying pressures at different time scales.

**Figure 1.** The phase diagram of H$_2$O showing a wide range of metastable and disordered phases of water and ice. The present data signifies the appearance of metastable ice VII (hatched in baby blue) in the stability field of ice VI at room temperature – well before the equilibrium transition pressure. The blue dashed-dotted curves are the extrapolated melting lines of ice Ih and ice VII. The grey lines signify the proposed phase boundary of LDW and HDW[11] and the suggested crystallization line of amorphous ices[6-7,10-11]. The green curve is the calculated liquid metastable limit[2].

In the presence of small gaseous molecules, water form gas hydrate clathrates at low temperatures and low pressures, adding complexity in the phase diagram of water. Natural gas hydrates are made of hydrogen-bonded cages of water molecules containing a wide range of guest molecules (CH$_4$, H$_2$, CO$_2$, etc.). The existence of gas hydrates strongly show impurities play an important role on altering the phase diagram of H$_2$O via changing hydrogen bonding. Hence, the influence of impurity (methane) on the phase boundaries of metastable ice VII and ice VI under dynamic conditions is investigated in this study.
2. Experiments
Using a micro-syringe with a stainless steel needle, a drop of pure distilled water (< 10 nl) was loaded into a small (0.08-0.13 mm) hole of a pre-induced stainless steel gasket mounted between two opposed diamond anvils with 0.3 or 0.5 mm flats, together with a few small ruby chips for pressure calibrations. For dirty water samples, methane is used as the impurity. Highly pure methane gas (>99.999%, Advanced Specialty Gases) was used without future purification. A small bubble was then introduced in the sample chamber for the space of methane. Methane gas was then loaded into the sample chamber using a high-pressure gas loader developed at Washington State University. The confocal micro-Raman spectroscopy with a 0.8 cm⁻¹ spectral resolution is used to identify the status of water and ice phases. The Raman spectra were obtained in a back scattering geometry and using an Ar⁺ ion laser (Spectra Physics) at the 514.5 nm excitation wavelength. The formation of ice was recorded in-situ, using a high-speed camera (Photron FASTCAM APX RS). The sizes of growing or melting ices are measured in micro-photographic images by scaling to the known size of Ruby ball.

Our d-DAC incorporates three piezo-actuators (APC International, Ltd.) into a conventional DAC. The peak and modulating pressures and the compression rate of d-DAC are controlled by the shape and magnitude of the input electric signal to these actuators. We used a function generator and a power amplifier to tailor the input signal of the piezo-actuators. A digital delayed generator was used to synchronously operate all associated instrument, which includes a d-DAC, a CCD detector, a high-speed camera, and an oscilloscope. In this study, we typically used different time scales of symmetry trapezoidal waveforms. During these rise and fall periods, the images and pressures of the sample were measured in-situ using the high-speed camera and time-resolved Ruby luminescence, respectively. The Raman spectra were obtained before, at the top and after the waveforms. Figure 2 illustrates a 2-D image plate of time-resolved pressure measurement and the corresponding microphotographs as an example.

![Figure 2](image)

**Figure 2.** The time-resolved ruby luminescence recorded on a 2D CCD as a function of wavelength (or pressure) and time, shown together with the selected real-time micro-photographic images distinctive to different phases of water and ice.

3. Results and Discussions
The metastable ice VII with a “needle-like” morphology has been observed to form from super-compressed water at rapid compressions in the stability field of ice VI [5,12]. In addition, the pressure-induced amorphization of metastable ice VII at room temperature, HDA, is resulted from the structural instability of ice VII [12]. Interestingly, the metastable ice VII is also formed from super-compressed...
“dirty”-water. Surprisingly, the evolutions of metastable ice VII are different in the pure and dirty waters. Here, solidification of water, the evolutions of ices and melting of ice VI would be investigated in the pure and dirty water.

3.1. The water-to-metastable ice VII transition
At higher compression rate (> 0.1 GPa/s) to the final pressure above 1.3 GPa, the metastable ice VII is crystallized from super-compressed water. Figure 3 shows the representative micro-photographic images of the sample during rapid compression in pure (A) and dirty (B) water. The measured lengths of metastable ice VII as a function of time are also illustrated on the right. Firstly, pure water is solidified to metastable ice VII within one frame (less than 67 μs) and turns into HDA in couple of milliseconds. The detailed discussion regarding the Raman spectra of pure water, ice VII and HDA and the VII-HDA transition mechanism can be found in our recent paper [12]. The impure water sample shows well-separated regions of fluid methane (bubbles in Fig. 3B) and liquid water (featureless area in Fig. 3B). The metastable ice VII grows in one-dimensional direction, according to the real-time micro-photographic images. The Raman spectra of fluid methane and dirty water (including broad water Raman peaks and weak methane peak) are taken before the pressure modulation. The metastable ice VII with needle-like texture is proven at the peak pressure by ice VII Raman signature [12], not shown here.

Figure 3. High-speed microphotographic images of the sample during rapid compression showing (A) pure water solidification to ice VII and to HDA in comparison with (B) dirty water solidification to ice VII. The growth rates of metastable ice VII are illustrated on the right, ~ 1.4 m/s (black line) from pure water and ~ 0.35/0.40 m/s (red and blue lines) from dirty water.

At both pure and dirty water conditions, the metastable ice VII observed exhibits a needle-like texture. According to the images during ice VII forms in Fig. 3(B), it is reasonable to assume that needle-like ice VII grows one-dimensionally from nucleation sites. Thus, the growth rate can be obtained by directly measuring the length of ice VII in a sequence of images. Two representative lengths of metastable ice VII (red and blue dashed lines) are illustrated in the right panel of Fig. 3, which yield an average growth rate of ice VII, 0.26±0.14 m/sec, in the dirty water samples. Since the metastable ice VII in the pure water case forms so fast (< 67 μs across ~80 μm) that only one or two frames are caught by our high-speed camera even at the fastest recording rate of 30000 frames per second. Therefore, the growth rate of ice-VII in pure water samples of ~ 1.4±0.7 m/sec is only estimated with a large error bar (hatched area), based on the diameter of the entire sample, ~100-210 μm, and the one or two frame time of 70-140 μs. Furthermore, the growth rate of ice VII may also depend on the compression rate and other factors. Clearly, additional experimental data are needed for more meaningful discussions.

It is very interesting that metastable ice VII forms even in dirty water. First of all, impurities seem to make almost no contribution on changing the stability limit conjecture of liquid water, shown in Fig.
1. In other words, impurities would not influence homogeneous nucleation mechanisms of super-cooled or super-compressed liquid. This implies that the assumption regarding one-dimensional growth is suitable for this study. However, based on the observed growth rates of ice VII from pure and dirty waters, it is clear that the presence of impurity slows down the growth rate of metastable ice VII. The fact that metastable ice VII forms from super-compressed water indicates a similar local bcc-like structure between ice VII and super-compressed water. The observed slower growth rate in the dirty sample is then due to the perturbed local order by the impurity. In this regard, it would be interesting to find at which point (or level of impurities) the local order of ice VII and water become different.

Note that no HDA is observed in dirty water samples. In contrast, in pure water samples, metastable ice-VII converts into HDA, signifying the structure similarity between the two phases. This difference is either due to the higher transition pressure (close to the stability field of 2.1 GPa) to form ice VII in dirty water that that of pure (1.4-2.1 GPa) or to the formation of methane hydrates that can be formed in the water-methane mixtures [16].

3.2. The ice VI to water transition

Figure 4 shows the representative sequences of micro-photographic images of pure water (A) and dirty water (B), taken during pressure unloading. In pure water, HDA turns into ice VI and ice VI melts to liquid water upon decompression. In dirty water, ice VII transforms into ice VI and ice VI melts. In both cases, ice VI with a gland-like texture melts close to the equilibrium transition pressure, ~0.9 GPa, independent of the decompression rates. The time zero is defined by the frame right before water starts to appear. The measured area of ice VI directly from the images is scaled by the whole sample in order to compare among different samples. In dirty water, the interaction between H$_2$O and methane during ice VI melts is ignored.

In dirty water, ice VII directly transforms into ice VI, in contrast to HDA transforming into ice VI in pure water. The branches of ice VII grow wider and wider and turn into grand-like ice VI. In both cases, it is difficult to define the conversion rate to ice VI, either from HDA or ice VII. Nevertheless, we estimate the conversion rate based on the relative area changes of ice VI in pure (blue symbols) and dirty (red markers) water with time as plotted in Fig. 4 right. The different symbols signify the different decompression rates. Note that all melting behaviours of ice VI follow an exponential decay as illustrated in the well-fitted lines. Again, the melting of ice VI occurs always at the equilibrium...
transition pressure, regardless the initial pressure of ice VII. The melting time constants, $\tau$, extracted from the exponential fits (Fig. 4 Inset) indicate that the slower decompression results in the slower melting as well as that the impurity has no bearing on the melting process of ice VI in terms of the transition pressure or the dynamics of melting.

4. Conclusions

Using *dynamic*-DAC, we have demonstrated that metastable ice VII can be crystallized directly from super-compressed water in both pure and dirty water systems. This transition results from the similar bcc-like local structure between ice VII and super-compressed water. The presence of methane impurity seems to perturb the interfacial structure between the two, lowering the growth rate of ice VII from $1.4\pm0.7$ m/sec in pure water to $0.26\pm0.14$ m/sec in impure water. In pure water, HDA transforms from metastable ice VII in the pressure range of 1.4-2.1 GPa, again because of the similar local structure. This transition is absent in dirty water, either because the transition pressure to ice-VII is higher - close to the stability field or due to the formation of methane hydrates perturbing the local structure. Upon decompression, HDA or Ice VII converts to ice VI, which melts at the equilibrium transition pressure, *always*, independent of the impurity level. Thus, the result indicates little effect of impurity on melting. Ice VI melts faster at higher decompression rate, following an exponential rate dependence.

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References

[1] Hemley RJ, Jephcoat AP, Mao HK, Zha CS, Finger LW, and Cox DE 1987 *Nature* **330** 737
[2] Soper AK 2002 *Science* **297** 1288
[3] Nelmes RJ, Loveday JS, Strassle T, Bull CL, Guthrie M, Hamel G, and Klotz S 2006 *Nat. Phys.* **2** 414
[4] Chou IM, Blank JG, Goncharov AF, Mao H-K, and Hemley RJ 1998 *Science* **281** 809
[5] Lee GW, Evans WJ, and Yoo C-S 2006 *Phys. Rev. B* **74** 134112
[6] Mishima O, Calvert LD, and Whalley E 1984 *Nature* **310** 393; 1985 *Nature* **314** 76
[7] Klotz S, Hamel G, Loveday JS, Nelmes RJ, Guthrie M, and Soper AK 2002 *Phys. Rev. Lett.* **89** 285502
[8] Tse JS, Klug DD, Tulk CA, Swainson I, Svensson EC, Loong CK, Shpakov V, Belosludov VR, Belosludov RV, and Kawazoe Y *Nature* **400** 647
[9] Finney JL, Bowron DT, Soper AK, Loerting T, Mayer E, and Hallbrucker A 2002 *Phys. Rev. Lett.* **89** 205503
[10] Yoshimura Y, Mao H-k, and Hemley RJ 2006 *Chem Phys Lett* **420** 503
[11] Saitta AM and Datchi F 2003 *Phys. Rev. E* **67** 020201
[12] Chen J-Y and Yoo C-S 2011 *Proc. Natl. Acad. Sci. USA* **108** 7685
[13] Knight C, Singer SJ, Kuo J-L, Hirsch TK, Ojamae L, and Klein ML 2006 *Phys. Rev. E* **73** 056113
[14] Evans WJ, Yoo C-S, Lee GW, Cynn H, Lipp MJ, and Visbeck K 2007 *Rev. Sci. Instrum.* **78** 073904
[15] Lee GW, Evans WJ, and Yoo C-S 2007 *Proc. Natl. Acad. Sci. USA* **104** 9178
[16] Chen J-Y and Yoo C-S 2011 *MRS Proc.* **1262**-W04-03