

## Reply to the comment on “Pressure-induced phase transition of ice in aqueous KOH solution”

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The conclusions that have been drawn in the previous papers [1–4] regarding the pressure-induced phase transition of ice in aqueous electrolyte salt solutions were drawn on the basis of the compressions of quick pre-cooled samples. I suppose that the main difference in the results between Yoshimura and Handle et al. lies in the (initial) cooling rate of the sample, *i.e.* path (1) in Figure 1 in the original paper [3]. Supporting evidence for this is that if I cooled the sample solution at a slower cooling rate (*e.g.* 5 K/min), I found that the samples show a “normal” transition behavior (*i.e.*  $I_h$ -HDA-VII) at the reported pressures, as stated in the previous papers [2–4]. This is probably because the cooling rate should influence the morphology, the dimension and the distribution of ice crystals. In actual fact, methods reported for the rapid quenching of aqueous solutions were developed for the purpose of achieving small ice crystals [5]. The transition of the ice crystal size from macroscopic to nanometer dimensions occurs discontinuously at a critical cooling rate (and also over a very limited temperature range) [6]. I propose that most of the salt segregates at grain boundaries, and such segregation would lead to very small particles of ice in the sample and reduce the size of the ice crystals. It is possible that, this effect could cause the unexpected transition.

In the measurements, I used a specially designed cooling apparatus (flow-type liquid N<sub>2</sub> cryostat) as shown in Figure 1. First, the whole of a small-size diamond anvil cell (DAC) (SR-DAC-KYO-3-1, Kyowa Co. Ltd; screw-type diamond anvil cell, o.d. = 25 mm, height = 55 mm) with the sample solution was directly immersed into liquid nitrogen. In doing so, the overall cooling rate of ~150 K/min was achieved. The samples were milky in appearance either because of the inclusions of salts or because of the concentrated salt solution. In this procedure, small transient clusters (seeds) may exist in the sample before the transition upon compression. On the other hand, generally if we cool the sample slowly, the solutes are largely rejected into the liquid and do not make the solid solution upon freezing of aqueous solutions. It should be, however, noted that Klotz et al. [7] recently reported that it is possible for salts to enter the ice lattice structure and form the salty ice under high pressure at lower temperatures. Then, the sample was compressed isothermally keeping liquid nitrogen temperature during the *in situ* Raman measurements

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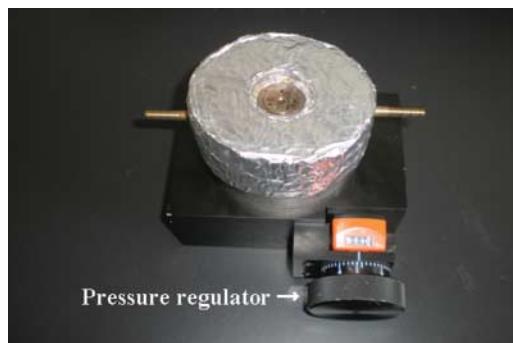


Figure 1. A schematic picture of the cooling system employed in the *in situ* Raman measurements. The screw-type DAC holding the sample in a phosphor bronze gasket of 0.15 mm thickness, with an opening of 0.4 mm in diameter, was set in the container filled with liquid nitrogen. The spectra were obtained by the back-scattering method from the sample in the DAC.

(*i.e.* path (2) in Figure 1 in reference [3]). The temperatures of the sample during the measurements were monitored by differential thermocouples (alumel–chromel thermocouple) with one junction mounted on the gasket and the other in ice.

As has been pointed out by Handle and Loerting in their comment, there may be a chance of unwanted shock-wave heating, because the sample pressures were regulated manually, but, nonetheless, the fact that the obtained results show differences depending on the salts highlights the present results. I think that the solutes can serve as nucleation sites for high pressure ice phases and this nucleation is enhanced by the application of pressure. Therefore, it is most likely that one can selectively form ice phases by choosing the suitable salt as an impurity in the rapid-quenched ice. The conditions such as those found in the present work may exist on the icy mantles of several satellites of the outer planets throughout the solar system.

## References

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