

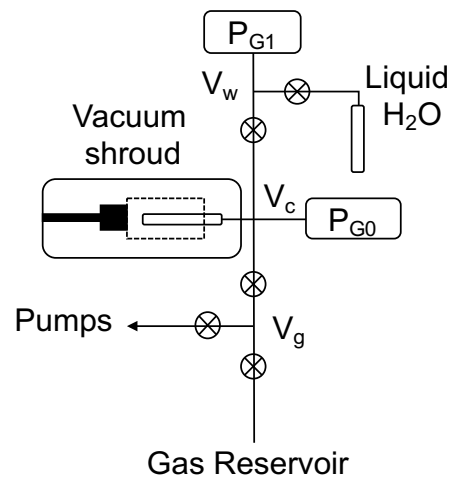
**Annealing of amorphous water at cryogenic temperature.** R. Yokochi<sup>1</sup>, <sup>1</sup> Department of the Geophysical Sciences, The University of Chicago (5734 S. Ellis Avenue, Chicago, IL 60637, USA, yokochi@uchicago.edu)

**Introduction:** Previous experimental studies reported that amorphous water can efficiently encapsulates ambient gases during its condensation at low temperature and high deposition rates [1,2], reflecting the physical and chemical conditions of the surrounding environment. It was suggested that the gas trapping may be understood as two stage process; gas adsorption onto ice surface and subsequent burial by added layer of ice, based on the pressure-dependent nature of the gas trapping at 77K [3]. In response to moderate heating, the trapped gas may be mobilized if significant change in physical properties of ice, which may affect the degassing profiles of comets if gas-rich amorphous water ice is one of building blocks of comets. Here we investigated the surface property change of amorphous water ice in response to moderate heating, via BET adsorption method using Ar.

**Methods:** The experimental system (Fig. 1) consists of a cryogenic chamber ( $V_c$ ), water vapor reservoir ( $V_w$ ), a gas reservoir ( $V_g$ ), and pumps, following the basic design of the setup presented in Yokochi et al. [3]. The  $V_c$  includes an MKS Baratron gauge ( $P_g$ ) and a vacuum shielded glass tube that can be cooled at desired temperatures above 12K using a closed-cycle He cryocooler. The tube is cooled by a copper heat conductor, and uncooled section of the tube is heated by a heating wire around 265K in order to minimize the moderately cooled surface area where ice condensation could occur at various intermediate temperatures. The  $V_w$  is equipped with a liquid water reservoir and another MKS Baratron gauge ( $P_w$ ) for determining the quantity of water deposited. A gas pipette is attached to  $V_g$  for introducing calibrated aliquots of gas reproducibly into  $V_c$ . All components outside the vacuum shroud are maintained at a constant temperature of 313 K. A Lakeshore cryogenic temperature controller controls the temperature of the glass tube using the temperature reading from silicon diode sensors attached to the copper heat exchanger. The temperature inside the glass tube was evaluated based on the vapor pressure of Ar [4]. The deviation of the internal temperature from the sensor reading was between 1.5-1.9 K for a temperature range between 35.1 and 64.3K.

Water vapor was introduced via the leak valve from  $V_w$  to  $V_c$  to form water ice in the cooled volume. The quantity of deposited water ice was deduced from the pressure before and after the deposition in  $V_w$ . Subsequently, calibrated aliquots of gas were introduced to  $V_c$  from  $V_g$ . The pressure was measured by

$P_g$  after each gas injection. The adsorption isotherm was determined via repeated gas injection and pressure measurements. The effect of annealing was also examined by heating the ice over several hours. The adsorption isotherm was always measured at a constant temperature of 50K after cooling from higher annealing or deposition temperature.



**Figure 1: Schematic diagram of the experimental system.**

**Results:** The BET plots of two sets of experiments are shown in Fig. 2a and 2b. The adsorption capacity of amorphous water ice significantly decreased at each 10 K increment heating step: The monolayer capacity decreased by about a factor of 2 after heating at 100K, and by a factor of 10 after heating at 160K where one expect the structural change of ice.

The amorphous ice deposited at different temperatures [50, 60, 70 and 80K] also show systematic difference in the surface adsorption capacity (Fig. 2b). The ice deposited at elevated temperature has lower gas adsorption capacity than the ice deposited at 50K and heated at the same elevated temperature.

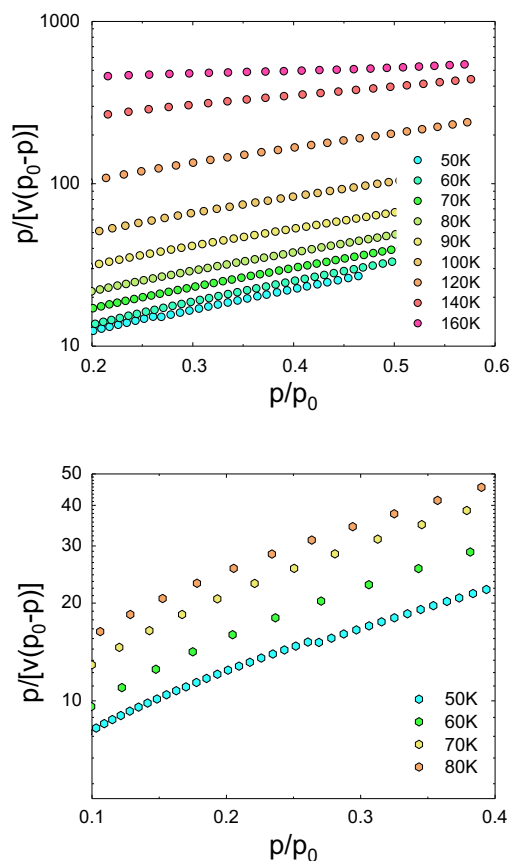
#### Discussions:

The higher adsorption capacity of ice formed at low temperature suggest that the amorphous water ice formed at different temperatures has different structures, and causes higher efficiency of gas trapping at

low temperature, in addition to the temperature effect on gas adsorptions.

Annealing of amorphous water occurs at low temperature, as low as 60 K, and it appears that any heating of ice causes change in surface (and probably structural) properties. It suggests that gas-loaded amorphous water ice, if present in the subsurface of comets, would start releasing gas in response to slight heating, and may cause gradual pore pressure increase. Such effect may have significant bearing on the degassing profiles of comets, and needs to be investigated. Another interesting finding of this work is that the ice formed at moderately temperatures has show relatively high adsorption capacity when cooled. Surface of cooled grains in cold region may host significant quantity of gas, which could subsequently be trapped by such processes as overgrowth.

**References:** [1] Bar-Nun A., Dror, J., Kochavi, E., Laufer, D. (1987) *Phys. Rev. B* 35, 2427-2435. [2] Nonesco, G., Bar-Nun, A., Owen, T. (2003) *Icarus* 162, 183-189. [3] Yokochi, R., Marboeuf, U., Quirico, E., & Schmitt, B. (2012). *Icarus*, 218(2), 760-770. [4] Fray, N., & Schmitt, B. (2009). *Planetary and Space Science*, 57(14-15), 2053-2080.



**Figure 2: BET plots of adsorption experiments. [Top] Effect of heating on ice deposited at 50K. The [Bottom] Amorphous ice deposited at different temperatures.**