THE METASTABLE PERSISTENCE OF VAPOR-DEPOSITED AMORPHOUS ICE AT ANOMALOUSLY HIGH TEMPERATURES. David F. Blake and Peter Jenniskens, Planetary Biology Branch, MS 239-4, NASA/Ames Research Center, Moffett Field, CA 94035-1000.

Studies of the gas release, vaporization behavior and infrared (IR) spectral properties of amorphous and crystalline water ice have direct application to cometary and planetary outgassing phenomena and contribute to an understanding of the physical properties of astrophysical ices. Several investigators report anomalous phenomena related to the warming of vapor-deposited astrophysical ice analogs (see, for example, 1-4). However gas release, ice volatilization and IR spectral features are secondary or tertiary manifestations of ice structure or morphology. These observations are useful in mimicking the bulk physical and chemical phenomena taking place in cometary and other extraterrestrial ices but do not directly reveal the structural changes which are their root cause. The phenomenological interpretation of spectral and gas release data is probably the cause of somewhat contradictory explanations invoked to account for differences in water ice behavior in similar temperature regimes. It is the microstructure, micromorphology and microchemical heterogeneity of astrophysical ices which must be characterized if the mechanisms underlying the observed phenomena are to be understood.

We have been using a modified Transmission Electron Microscope to characterize the structure of vapor-deposited astrophysical ice analogs as a function of their deposition, temperature history and composition (5,6). For the present experiments, pure water vapor is deposited at high vacuum onto a 15 K amorphous carbon film inside an Hitachi H-500H TEM. The resulting ice film (~0.05 μm thick) is warmed at the rate of 1 K per minute and diffraction patterns are collected at 1 K intervals. These patterns are converted into radial intensity distributions which are calibrated using patterns of crystalline gold deposited on a small part of the carbon substrate. The small intensity contributed by the amorphous substrate is removed by background subtraction. The proportions of amorphous and crystalline material in each pattern are determined by subtracting a percentage of crystalline component relative to amorphous and pure crystalline endmembers.

Vapor-deposited water ice undergoes two amorphous to amorphous structural transformations in the temperature range 15-130 K with important astrophysical implications (6). The onset of cubic crystallization occurs at 142-160 K (at 1 K per minute heating rates) during which the 220 and 311 diffraction maxima appear and 0.1 μm crystallites can be seen in bright field images. This transition is time dependent. Figure 1 shows our on-going work along with other published results (7,8) illustrating the time vs. temperature relationship derived for the onset and maturation of cubic crystallization from the amorphous state ("Full grown" refers to a point in time when the crystalline component no longer exhibits marked increases in diffracted intensity).

Within the time and temperature duration of these experiments (the most extreme of which was 16 hours @178 K), the ice does not fully crystallize, a phenomenon first reported by Dowell and Rinfret (7). The magnitudes of the cubic diffraction maxima become at best similar to those of the the amorphous component. The 0.1 μm cubic crystallites do not grow significantly in size even over extended time intervals but commonly show planar defects with spacings as small as 0.005 μm. We attribute these defects to local stacking disorder in which the normal ABCABC... sequence of the cubic polymorph is interrupted by ABAB... domains typical of the hexagonal polymorph. Evidence for this interpretation comes from selected area diffraction patterns which show weak diffraction maxima which can be indexed to the hexagonal polymorph. The inability of the stable cubic polymorph to grow at the expense of its highly metastable amorphous ice precursor is surprising and provides some insight into the nature of the structure and style of bonding of the amorphous ice (called "restrained amorphous ice," or "I_{ar}" (6)). We suggest that the precursor amorphous ice consists of small domains of cubic-like and hexgonal-like closest packing which extend no more than a few unit cells. Complete crystallization of the cubic polymorph would require breaking and reforming hydrogen bonds from hexagonally stacked domains which would have a higher energy barrier to crystallization than would randomly stacked amorphous water ice.

PERSISTENCE OF VAPOR-DEPOSITED AMORPHOUS ICE AT HIGH T: Blake, D.F.

The persistence of amorphous ice at temperatures in which crystalline ice is favored has important consequences for cometary outgassing behavior and the mechanical properties of cometary ice. It appears likely that in the vacuum of space, significant amounts of cometary water ice will vaporize directly from the amorphous state during transits through the inner solar system. Therefore, one would expect impurity gases to continue to be released long after the onset of crystallization (and even coincident with volatilization of the ice). The mechanical properties of cometary ice could also be affected. It is well known that hardness and toughness are imparted to engineering materials as a result of heat treatments, which (among other things) create heterogeneous microstructures of small crystallites. It may be that the icy surfaces of comets which are warmed during passage through the inner solar system are "heat treated" in similar fashion.

References:

1. Bar-Nun et al (1985), Icarus **63**, 317-322. 2. Laufer et al (1987), Phys. Rev. B **B36(17)**, 9219-9227. 3. Kouchi, A (1987), Nature **330**, 550-552. 4. Sandford and Allamandola (1988), Icarus **76**, 201-224. 5. Blake, D.F., et al (1991), Science **254**, 548-551. 6. Jenniskens, P. and D.F. Blake (1994), Science **265**, 753-756. 7. Dowell and Rinfret (1960), Nature **188**, 1144-1148. 8. Schmitt et al (1989), ESA SP-302, Physics and Mechanics of Cometary Materials, 65-69.

Figure 1. Crystallization of cubic ice from an amorphous precursor as a function of time.