DIRECT DETERMINATION OF THE MORPHOLOGY, STRUCTURE AND COMPOSITION OF PLANETARY, COMETARY AND INTERSTELLAR ICE ANALOGS; D.F. Blake,1 L.J. Allamandola2 and Gary Palmer,3 1Planetary Biology Branch, MS 239-4 and 2Astrophysics Branch, 245-6, NASA/Ames Research Center, Moffett Field, CA 94035, and 3EM Engineering, 101 First St. Suite 109, Los Altos, CA 94022.

Ices of various kinds (H2O, CO, CO2, CH4, NH3, CH3OH, etc.) comprise a volumetrically significant proportion of objects in the solar system (comets, outer planets, planetary rings, satellites) as well as in interstellar space (astrophysical ices). Despite their widespread occurrence, few experimental data exist which address the phase equilibria and possible structural states of solar system and interstellar ices.1 A knowledge of the petrology of planetary, cometary and astrophysical ice analogs grown under controlled conditions in the laboratory will allow ground-based scientists to more confidently interpret remote IR observations of planetary surfaces, comets, cold molecular clouds and the like. The development and refinement of procedures for analyzing ices and other materials at cryogenic temperatures is critical to the successful study of materials returned from the proposed Rosetta comet nucleus and Mars sample return missions.

We have extensively modified an Hitachi H-500H Analytical Electron Microscope (AEM) to allow direct imaging and analysis of ices at temperatures from 15° to 273° K. An ion pump and massive LN2 cold finger maintain the objective pole-piece gap in the low 10^-7 Torr range. A video camera with image intensifier is interfaced to the column to allow routine low electron dose imaging. The video signal from the camera is input directly into a computer which digitizes the image at 30 frames/sec. Samples can be introduced into the AEM in two ways: Samples of ices collected or grown elsewhere can be introduced into the microscope in the frozen state using a cryotransfer device. Ices of selected compositions can be grown inside the AEM by bleeding pre-mixed gases from a sample bulb directly onto a cryogenically cooled sample substrate (usually a holey carbon film on an electron microscope grid). The same sample bulb is used for the introduction of gases into infrared spectrometers in the Low Temperature Spectroscopy Laboratory (LTSL) at Ames Research Center. Thus, experiments can be performed in which morphological and microstructural changes observed in ices via AEM can be correlated with the evolution of fine structure in the IR spectra of ices grown and processed in like fashion.

Although a great deal is already known about the microstructural characteristics and phase equilibria of pure water ice through the work of Dubochet et al.2 and others, little is known about multicomponent mixed molecular ices. Mixed ices comprise the bulk of celestial ices and their properties (spectral, vaporization, etc.) are substantially modified relative to pure ices.3 Our experiments to date have been carried out to characterize our instrument and to determine empirically under what conditions ices can be reliably analyzed and imaged without artifactual damage. With care, it is possible to observe pure water ice in the vitreous ("amorphous") state, IV, with a resolution of a few nanometers. Resolution is limited by mass loss (volatilization and/or lateral migration of water molecules) caused by radiolytic damage and local electron beam heating. Figure 1 shows IV grown on a holey carbon film substrate at 110° K. In diffraction mode, diffuse maxima characteristic of IV are observed (Figure 2, upper left). At lower magnifications (i.e. less electron dose per unit area), bright and dark field images can be obtained without sample damage (e.g., Figures 3 and 4). When IV is warmed inside the microscope, the sharp diffraction maxima of cubic ice, IC (Figure 2, upper right) begin to appear at 143 ±2° K, which is (within error) the reported temperature for this transition.2,4 Hexagonal ice, IH, is stable at temperatures between about 170° K and 273° K, although in the high vacuum of the microscope, volatilization occurs.
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The $I_c \rightarrow I_h$ transition temperature is difficult to measure because diffraction maxima from the two phases nearly coincide (Figure 2, upper right and bottom). We are presently limited to temperatures of 100° K or higher by our liquid N$_2$ sample holder. A liquid He sample holder is being fabricated which will allow operation to 15° K. This will allow us to extend out studies of ices from the temperature regime of the outer planets to the temperature regime of cold interstellar molecular clouds, and will permit ultrastructural, morphological and microchemical analysis of ice compositions for which a large body of IR data exist.5


Figure 1. Bright field electron micrograph of vitreous ice nucleated at 110° K onto a thin (~10 nm) holey carbon film substrate. Figure 2. Water ice diffraction patterns: Upper left, $I_v$, first and second diffuse maxima labelled. Upper right, $I_c$, major diffraction maxima indexed. Bottom, $I_h$, major diffraction maxima indexed. Figure 3. Bright field image of cubic ice, objective aperture in position labelled "b" in Figure 2. Figure 4. Dark field image of cubic ice, objective aperture in position labelled "d" in Figure 2.