

EUTECTOID-LIKE PHASE SEPARATION IN $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ ICES: MICROSTRUCTURAL OBSERVATIONS AND IMPLICATIONS FOR THE PHYSICAL PROPERTIES OF COMETS; 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.

As described previously¹⁻², we have modified an Electron Microscope to allow for the vapor deposition, thermal processing and *in situ* observation of mixed ices over the temperature range 12 - 200 K. We report here our observations of a simple mixed ice (2:1 $\text{H}_2\text{O}:\text{CH}_3\text{OH}$).

Two forms of amorphous water ice have been described through X-ray diffraction analysis,³ which we have identified by their diffraction patterns. The dense form, achieved by vapor deposition at about 10 K, is transformed to the less dense form at about 77 K. When amorphous water ice is heated above 125 K it irreversibly transforms into the cubic polymorph.^{4,5} The reaction is kinetically controlled and we observe the transformation at about 139 K. The transformation proceeds to completion relatively rapidly above this temperature yielding sub- μm randomly oriented crystallites. Upon further heating, a cubic to hexagonal phase change occurs at about 153 K which is irreversible^{4,5} and persists until the ice sublimates at about 160 K.

When pure methanol ice is vapor-deposited inside the microscope at 85 K, an amorphous solid results. At about 125 K, transformation into a crystalline phase which can be indexed as monoclinic⁶ occurs. Unlike cubic water ice, which persists as sub- μm crystals within its stability range, monoclinic methanol crystals quickly ripen into large sheets of single crystal material. The monoclinic phase persists in the microscope until the ice sublimates at about 160 K. A higher temperature orthorhombic phase has been reported⁶ but we have been unable to observe it, probably due to its high vapor pressure.

When a 2:1 $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ mixture is vapor-deposited on a thin carbon substrate held at 85 K inside the microscope, an amorphous solid is formed (Fig. 1). Diffraction patterns from this ice show two diffuse maxima similar to amorphous water ice (Fig. 2a). As the ice is warmed, a rapid and dramatic phase separation occurs at about 129 K (Fig. 3). Two phases, which have a grain size of 5-20 nm, can be characterized by electron diffraction. It is possible that additional amorphous material is also present but not observed. One of the phases appears to be cubic water ice, for which the {111}, {220} and {311} maxima are observed (marked by large arrows in Fig. 2b). The second phase has not been identified but has maxima at 0.39 nm (weak), 0.34 nm (strong), 0.297 nm (strong), and 0.206 nm (moderate), marked by small arrows in Fig. 2b. When this two phase assemblage is further warmed, the unidentified phase sublimates completely at about 150 K leaving a porous microstructure of hexagonal ice (Figs. 2c and 4).

Much additional work remains to be performed on this and other two component and multicomponent ices. However, two observations can be made which may have relevance to the mechanical and gas release properties of comets: First, sub-solidus phase separations ("eutectoid reactions") are capable of imparting a wide range of mechanical properties to solids. The most well known eutectoid reaction occurs the system Fe - C, in which small amounts of carbon and other alloying elements, along with thermal processing, produce the varied properties of steels. In like fashion, the mechanical hardness and physical integrity of cometary ice may be a specific (and predictable) function of composition and temperature history. Second, eutectoid phase separations produce a complex microstructure which upon further heating and sublimation of one of the phases, may result in a highly permeable microporous architecture. The presence of such microstructures within cometary ice may in part explain anomalous gas release.

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Fig. 1. TEM micrograph of 2:1 $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ ice deposited onto holey carbon film. Note the apparent absence of structure in the ice (28,000 X mag.). Fig. 2. Collage of diffraction patterns from Figs. 1,3 and 4. (a) Amorphous pattern from as-deposited ice, 85 K. Arrows mark diffuse maxima typical of amorphous ice. (b) Diffraction pattern from sub-solidus phase separation at 129 K. Large arrows mark maxima for cubic water ice, small arrows mark maxima for a second, unidentified phase. (c) Diffraction pattern from hexagonal water ice after apparent sublimation of the unidentified second phase, 150 K. Large arrows mark maxima for hexagonal water ice. Fig. 3. Bright field TEM micrograph of 2:1 $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ ice after eutectoid phase separation at 129 K. Fig. 4. Bright field TEM micrograph of 2:1 $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ ice after warming to 150 K. The ice appears to be a porous microstructure of single-phase hexagonal water ice.

