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POSSIBLE SIGNIFICANCE OF CUBIC WATER-ICE, $H_2O$-Ic, IN THE ATMOSPHERIC WATER CYCLE OF MARS. J. L. Gooding, SN2/Planetary Materials Branch, NASA/Johnson Space Center, Houston, Texas 77058.

Introduction. Most discussions of water ice on Mars tacitly assume that common hexagonal ice, $H_2O$-Ih, is the appropriate phase. Although ice-Ih is the dominant polymorph of water-ice on Earth, a second low-pressure polymorph which crystallizes in the isometric (cubic) system, $H_2O$-Ic, can form in special ultracold environments. Indeed, the conditions that are known to favor formation of ice-Ic might be more prevalent on Mars than on Earth.

Occurrence of ice-Ic in the Mars water cycle would be significant for two reasons. First, the Ic/Ih phase transition might comprise a significant but previously unrecognized term in heat-balance equations that have been applied to evaporation or condensation in the water cycle in models for atmosphere/polar-cap or atmosphere/regolith interactions. Second, ice-Ic might possess distinctive properties as a nucleator of other condensates that could substantially affect the processing and distribution of volatiles in both the water and carbon dioxide cycles. Accordingly, it is important to assess prospects for the occurrence and probable behavior of ice-Ic on Mars.

Formation and Stability of Ice-Ic. As summarized by Hobbs [1], ice-Ic is known to form in at least three ways (Fig. 1). First, Ic can form by crystallization of noncrystalline ("amorphous") ice that was initially deposited onto an ultracold substrate (heterogeneous nucleation) from vapor but which subsequently experienced warming. Second, Ic can form directly by vapor deposition under similar (though slightly warmer) ultracold conditions. Third, Ic can form during heating of initially ultracold high-pressure polymorphs of ice (principally ices II, III, V, and IX; Fig. 2) from which confining pressure has been unloaded. A fourth, but still unconfirmed mechanism for production of ice-Ic, involves rapid "quench" solidification of liquid water containing dissolved ferrous or ferric ions. From all indications, it seems that the Ic/Ih transition is sluggish and irreversible. No experiments have succeeded in producing ice-Ic by cooling ice-Ih.

Thermodynamic and kinetic factors that govern ice-Ic are still imperfectly known. Stability of ice-Ic (relative to evaporation or transformation to ice-Ih) is influenced by various factors including nature of the substrate (for vapor-deposited ices), composition and pressure of surrounding gas, and heating rate [1]. Experiments that produced vapor-deposited ice under vacuum, followed by calorimetric measurements under 27 mbar of helium gave enthalpies of key transitions as follows: -1.64 kJ/mol ("amorphous" to Ic) and -0.16 kJ/mol (Ic to Ih) [2]. (For comparison, the enthalpy of the familiar transition of liquid water to ice-Ih is -6.0 kJ/mol).

STABILITY OF WATER-ICE Ic

Water Vapor
$< 135$ K ↓        135-160 K

Liquid Water with dissolved iron
?
77 K quench

Noncrystalline ("amorphous") Ice
↓ 135 K

Hi-P Ices II, III V, IX
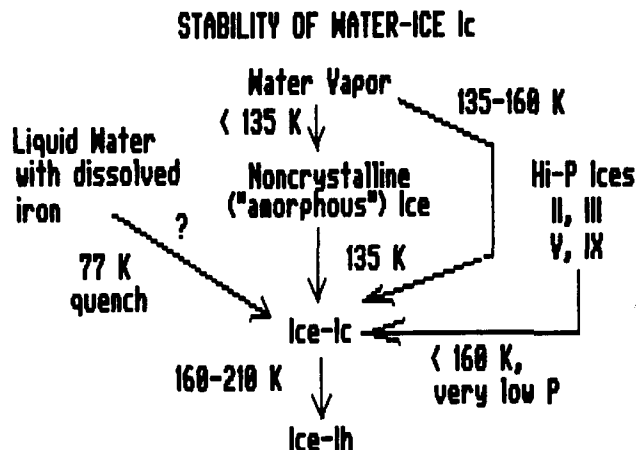
Ice-Ic
$< 160$ K, very low P

160-210 K ↓

Ice-Ih

Figure 1.

Schematic summary of processes that form ice-Ic under laboratory conditions. Transition temperatures vary with experimental conditions, including nature of the substrate in vapor-deposition modes. Temperatures suggested here are those derived from the calorimetric study by Sugisaki et al. [2]. Production of ice-Ic by the "77 K quench mode" was reported in one study but has not been confirmed [1].
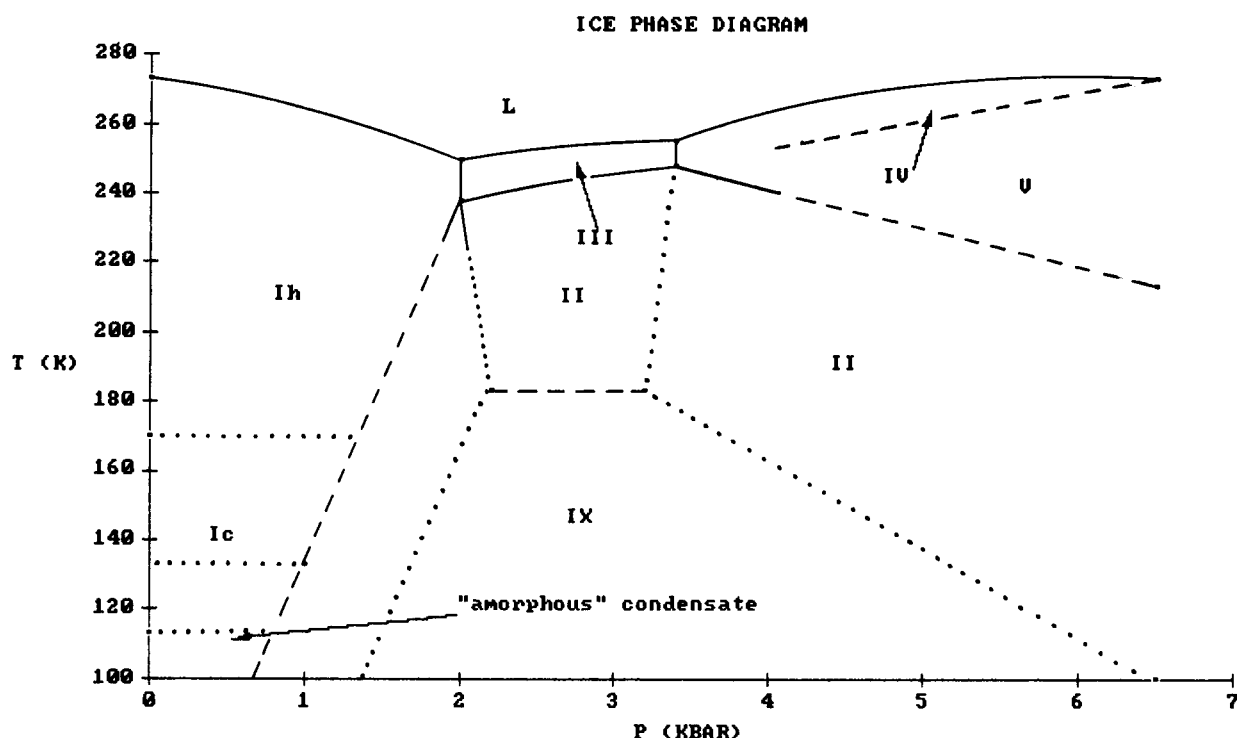
ICE PHASE DIAGRAM



Figure 2.

Phase diagram for water (neglecting vapor) in the pressure and temperature domains that support formation of ice-Ic. Phase demarcations include known equilibrium boundaries (solid lines), approximate metastable boundaries (dashed lines), and suspected metastable boundaries (dotted lines). The "amorphous condensate" field refers simply to the temperature fence below which noncrystalline ice is formed by vapor deposition (no reaction relationship between "amorphous" ice and ice-IX is implied). Below 113 K, vapor condensates tend to be noncrystalline whereas condensation at 113-135 K can produce mixtures of noncrystalline and Ic ices. The 170 K fence between Ic and Ih represents the extrapolated-onset of the Ic/Ih transition as determined by calorimetry [2]. Compiled from data summarized by Hobbs [1].

Prospects for Ice-Ic on Mars. On Mars, conditions that favor formation of ice-Ic might occur naturally whereas the necessary conditions on Earth are almost entirely restricted to laboratory experiments. Water vapor on Mars occurs mostly in the lower 20 km of the atmosphere where prevailing temperatures and pressures typically vary from 150 K/1 mbar at altitude to 250 K/10 mbar near the surface [3,4]. Condensate clouds near and above the summits of the Tharsis volcanoes (20-27 km elevation) have been interpreted as high-altitude water-ice clouds [5], indicating that atmospheric condensation on Mars does, in fact, occur under the ultracold, low-pressure conditions that should favor formation of ice-Ic by the vapor-deposition mode.

The Martian polar caps might be regarded as possible environments for formation of ice-Ic by the pressure-unloading mechanism. However, the conditions required to produce the high-pressure polymorphic precursors of ice-Ic might be unachievable in the Martian polar caps. A pressure of 1 kbar, which might represent a minimum value for producing ice-IX from ice-Ih (Fig. 2), would require on Mars a column of ice-Ih that was ≥ 30-km thick (11 km on

Earth). Although thicknesses of the Martian ice caps are not known, it is doubtful that they could ever have exceeded a few km. For example, transfer of a Martian global water budget of 10 m [6] to the north pole, with uniform deposition poleward of 80 N latitude, would produce a cap only 1.2-km thick. Of course, greater ice thicknesses could be invoked by appealing to much greater Martian water budgets.

Further pursuit of natural Martian conditions for achieving the ice-Ih/IX transformation at 1 kbar could invoke overburdens of either $\geq$ 17-km of solid carbon dioxide or $\geq$ 14 km of rocky regolith materials. However, seasonal accumulations of carbon dioxide frost at the Martian poles are probably < 1-m thick [7] and complete transfer of a Martian global carbon dioxide budget of 1060 g/sq cm [6] to the north pole would translate to a frost cap of only 0.8 km thickness. Therefore, overburdens of carbon dioxide appear inadequate whereas overburdens of rocky material are at least plausible. Ice-Ih deeply buried in the Martian regolith might transform to one or more high-pressure polymorphs although subequent transformation to ice-Ic would still require a mechanism for pressure (overburden) unloading. Deep exhumations might be accomplished by impact cratering although such catastrophic events could tend to favor melting or vaporization instead of solid-state phase changes of ice. It is at least conceivable, though, that unmelted blocks of ice excavated from great depth might transform to ice-Ic by the pressure-unloading mechanism.

Probable Behavior of Ice-Ic on Mars. Ice-Ic exposed at the Martian surface should tend to either evaporate or to transform to ice-Ih. However, if the ambient temperature was < 170 K, ice-Ic might persist metastably for extended periods of time. Regardless of the kinetics, though, transformation of ice-Ic to ice-Ih would be a modest but real heat source (i.e., transformation is exothermic). The vapor/solid transformation of carbon dioxide is the dominant phase transition in the Martian polar-cap heat balance and transitions involving water are considered negligible [7]. However, the ice-Ic/Ih transformation might be important to heat balance at the microphysical scale of processes that govern cloud and fog formation.

In a previous paper [8], calorimetric measurements of ice-Ih nucleation were combined with computations that relate to epitaxial overgrowth of water ice on foreign nuclei to emphasize the possible role of heterogeneous nucleation in the formation of condensates on Mars. One of the major results of that study was recognition of the potentially excellent properties of ice-Ic as a nucleator of other condensates. In theory, ice-Ic should be an outstanding nucleator of solid carbon dioxide and possibly carbon dioxide hydrate (clathrate) [8].

Paige and Ingersoll [7] ascribed the preferential accumulation of carbon dioxide frost at the Martian south pole to higher reflectivity (hence, lower heat absorption) of the southern cap relative to the northern cap. Lower reflectivities of the north polar cap were attributed to contamination of the frost deposits by admixed dust. Indeed, competing hypotheses involving ice-Ic and nucleation of frosts on dust particles are possible (Fig. 3). First, if ice-Ic was the earliest condensate to nucleate above the south polar cap, then carbon dioxide frost might have preferentially condensed on those nuclei. The net effect might have been to bury dust particles (as nuclei of ice-Ic) in optically thick layers of condensate that would have favored high reflectivity in the bulk deposits. If dust above the north pole favored a phase other than ice-Ic as the earliest condensate (e.g., ice-Ih), then overgrowth by carbon dioxide frost might have been much less favorable and subsequent growth might have led to particles with optically thin condensate layers. Alternatively, condensation of carbon dioxide, aided by ice-Ic, might have occurred equally at both poles but conditions at the north pole might have favored the exothermic transformation of ice-Ic to ice-Ih, thereby evaporating some of the condensed carbon dioxide. In that case, lower reflectivities would have

## NORTH/SOUTH DICHOTOMY OF SEASONAL $CO_2$ CAP

**HYPOTHESIS 1 FOR POSSIBLE ROLE OF ICE-Ic**

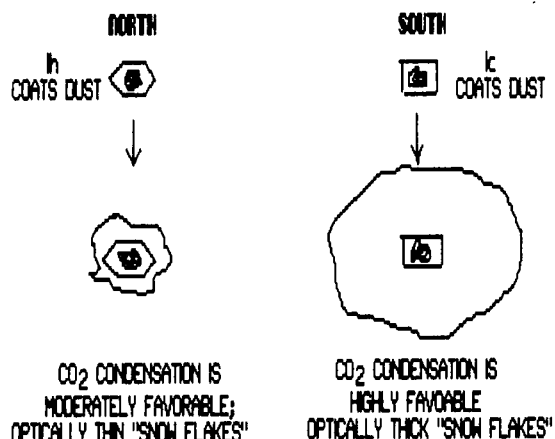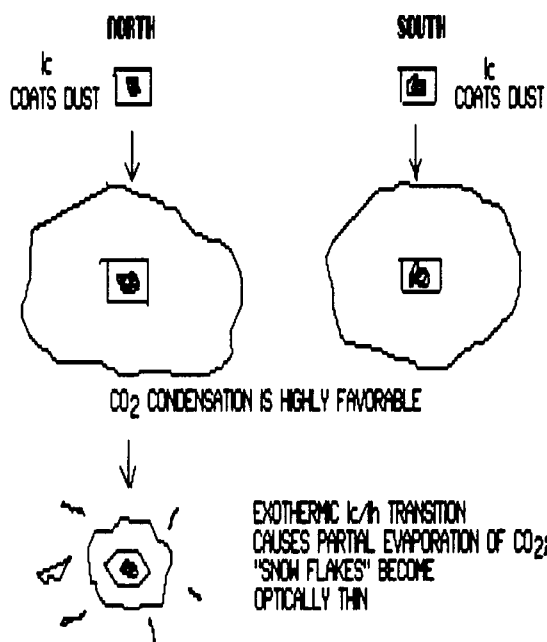SOUTH FAVORS Ic AS FIRST CONDENSATE,
NORTH FAVORS Ih

**HYPOTHESIS 2 FOR POSSIBLE ROLE OF ICE-Ic**

Ic IS FIRST CONDENSATE AT BOTH POLES,
BUT Ic/Ih TRANSITION IS IMPORTANT IN NORTH

**Figure 3.**

Schematic summaries of alternative hypotheses for possible role of ice-Ic in condensation of $CO_2$ at the Martian poles.

followed from partial loss of the carbon dioxide mantles on the ice particles. With the loss of favorable condensation nuclei, recondensation of the carbon dioxide might have been inhibited.

At present, existence of ice-Ic on Mars has not been demonstrated so that the possible role of ice-Ic on the atmospheric water and carbon dioxide cycles is only speculative. However, potential implications of ice-Ic on Mars are sufficiently meaningful that further work on the problem is warranted.

Experimental Tests for Ice-Ic on Mars. The infrared spectra of ice-Ih and ice-Ic are identical [1] so that it is doubtful that remote sensing will be able to either confirm or refute the existence of ice-Ic on Mars. Although near- and mid-infrared spectrophotometry might not be able to address the problem, there is a small chance that sufficiently sensitive thermal-infrared measurements of ice clouds and polar caps might provide some evidence for exothermic events that would be correlatable with the ice-Ic/Ih transformation. However, a preferred method of detecting ice-Ic would be by means of soft-landed spacecraft equipped with instrumentation for differential scanning calorimetry (DSC). The best detection strategy would probably rely on extended missions to the Martian poles to sample and analyze condensates as a function of location and season.

References:

[1] Hobbs P. V. (1974) Ice Physics, Oxford.
[2] Sugisaki M., Suga H., and Seki S. (1969) In Physics of Ice, N. Riehl, B. Bullemer, and H. Engelhardt (Eds.), 329-343, Plenum.
[3] Seiff A. and Kirk D. B. (1977) J. Geophys. Res., 82, 4364-4378.
[4] Davies D. W. (1979) J. Geophys. Res., 84, 8335-8340.
[5] Hunt G. E. and James P. B. (1985) Adv. Space Res., 5, 93-99.
[6] Anders E. and Owen T. (1977) Science, 198, 453-465.
[7] Paige D. A. and Ingersoll A. P. (1985) Science, 228, 1160-1168.
[8] Gooding J. L. (1986) Icarus, 66, 56-74.