

CO₂-H₂O PHASE EQUILIBRIA: RESIDUAL ICE LAYERS AND BASAL MELTING OF THE MARTIAN POLAR ICE CAPS. J. Longhi, Lamont-Doherty Earth Observatory, Palisades, NY 10964 (longhi@lamont.ldeo.columbia.edu)

Shifts in the gas+ice saturation surfaces with pressure favor formation of residual layers of solid CO₂ at the martian south pole and water-ice at the north pole. Preferential melting of CO₂ ice and clathrate layers within polar ice caps during periods of low obliquity may lead to sequestration of liquid CO₂ in the Martian crust.

Fig. 1 is an update of the P-T projection of the CO₂-H₂O phase diagram [1] showing the approximate location of the solid-state breakdown of CO₂ clathrate (H) to water ice (I) and solid CO₂ (S). Because of extremely limited solubility of H₂O in CO₂ liquid and gas at low temperatures, binary equilibria 1 and 5 are virtually equivalent to the sublimation and boiling curves for pure CO₂, respectively.

Few solubility data are available with which to draw temperature composition diagrams at the low temperatures and pressures appropriate to Mars' surface, but it is possible to combine the temperatures and stoichiometry of univariant equilibria in Fig. 1 with some observational data to construct approximate temperature-composition diagrams.

For example, it is widely noted that ground ice is stable poleward of ~ 40° latitude and that night frosts occur even where no ice is present [2]. This implies that the martian atmosphere is on average saturated with water-ice (or close to it), and that the atmospheric composition (0.031 mole% H₂O) and frost point (195° K) [2] can be employed to construct a T-X diagram for the average martian surface pressure of 5.6 mbar [3] as illustrated in Fig 2. The diagram predicts that water ice will be the first phase to precipitate upon cooling, that another 40° cooling is needed before the precipitate changes to clathrate (hydrate), and that an additional 10° cooling is needed before solid-CO₂ and clathrate precipitate together. Two other curves are also shown for the extremes of surface pressure (10 mb for the north polar regions and 2 mb for the south polar region and the higher portions of Tharsis). These curves are repeated in Fig. 3 where the ranges of measured atmospheric water contents [4] are also shown. For north polar conditions the atmospheric composition is almost always more H₂O-rich than the gas-eutectic (heavy arrow). This means that pure water-ice is first to precipitate, but also last to sublimate (relative to clathrate and eutectic mixtures). At the south pole, however, the atmospheric composition lies to the

CO₂-rich side of the gas eutectic for much of the year. This means that pure solid-CO₂ precipitates first and sublimates last. Thus water-ice will tend to form a residual layer in the north, whereas solid-CO₂ is more likely in the south

Basal melting has been suggested for both ice caps [5,6,7]. Fig 4 illustrates a schematic polybaric section along the temperature gradients calculated by [6]. Depths are given in km. Because ice is a much better conductor than solid-CO₂ or clathrate [6], greater thicknesses are possible for water-rich ice caps before basal melting ensues. It is believed that in periods of low obliquity the polar ice caps tend to thicken with the addition of solid-CO₂ [8]. Because the solid-CO₂ and clathrate are much better insulators than water ice, the thermal gradient would have increased as a CO₂-rich ice cap thickened until melting began. The diagram predicts that mixtures of solid-CO₂ and clathrate melt at much lower temperature than water ice + clathrate. Therefore, generation of CO₂-rich melts is to be expected during low obliquity cycles, and because liquid CO₂ is denser than water or water ice, it is likely to percolate into the crust. Temperature increases more rapidly along calculated temperature-depth profiles [5] than along the melting curve, so liquid CO₂ will be stable at depth. This process, which sequesters CO₂ in the crust, may be a major agent of atmospheric evolution. Migrating subsurface liquid-CO₂ will flow below and equilibrate with subsurface water, and on those occasions when water rises to the surface, CO₂ rising behind the water will change to gas first and act as a propellant.

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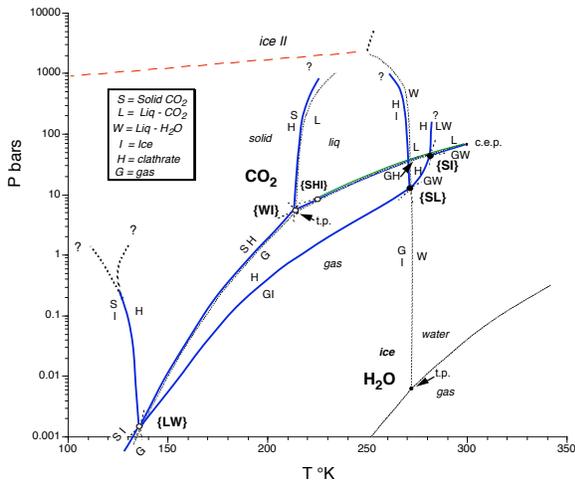


Fig. 1. Low-temperature portion of CO₂-H₂O phase diagram after [1]. Proposed binary invariant points indicated by open circles. Position of low-T stability limit of clathrate (H = S + Ice) is calculated.

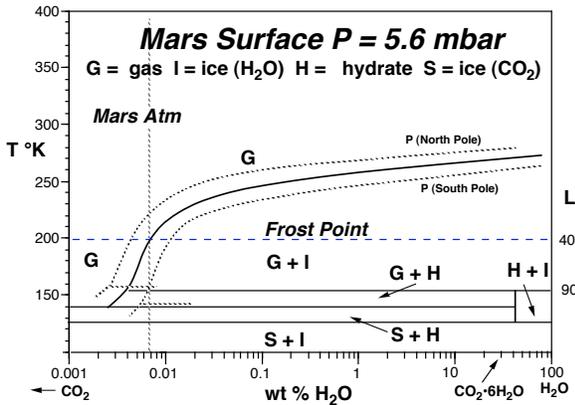


Fig. 2 Schematic isobaric sections based on frost point and atmospheric composition.

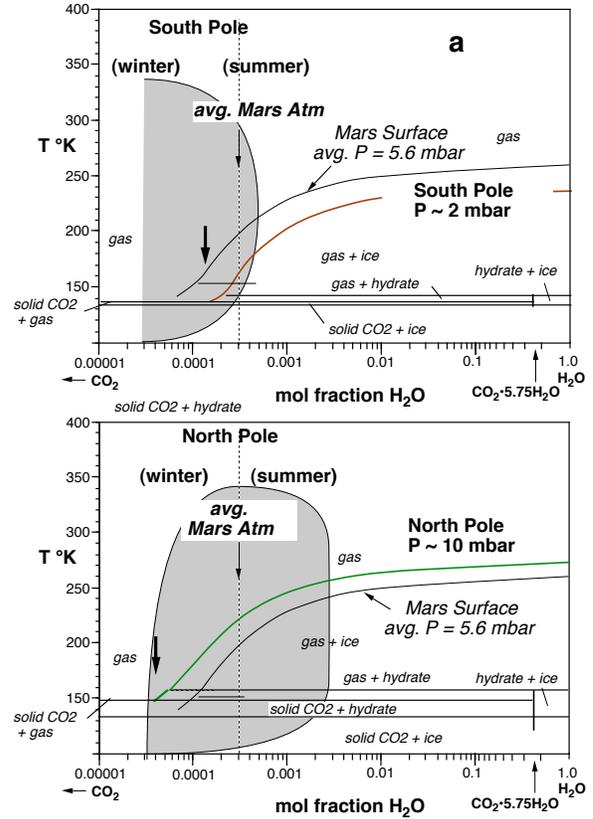


Fig. 3 T-X sections at pressures appropriate to south and north polar regions.

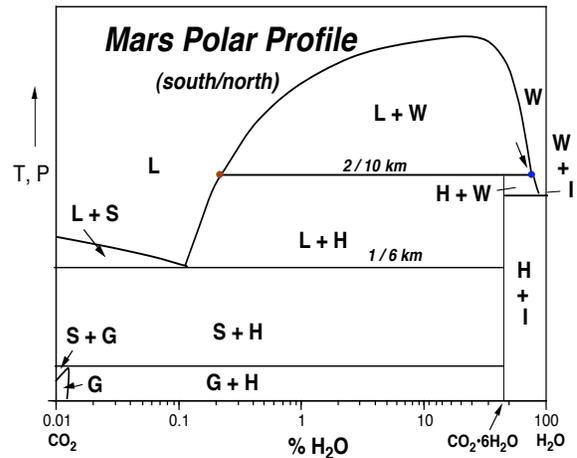


Fig. 4 Schematic profile along polar P-T profiles after [6]. Numbers are depths in km along thermal profiles calculated by [6]: S = solid-CO₂.