

FORMATION AND DISSOCIATION OF CLATHRATE HYDRATES ON MARS: POLAR CAPS, NORTHERN PLAINS, AND HIGHLANDS. J.S. Kargel¹, K.L. Tanaka¹, V.R. Baker², G. Komatsu³, and D.R. MacAyeal⁴, ¹U.S. Geological Survey, 2255 N. Gemini Dr., Flagstaff, AZ 86001, U.S.A. (first author: jkargel@usgs.gov), ²Dept. of Hydrology, U. of Arizona, Tucson, AZ 85721, U.S.A.; ³Int'l Research School of Planetary Sciences, U. d'Anunzio, Viale Pindaro 42, 65127 Pescara, Italy; ⁴Dept. Geophysics, U. of Chicago

Introduction: It has been recognized since 1970 that carbon dioxide clathrate hydrate is thermodynamically stable at the Martian poles (at least seasonally), in the interiors of both polar caps, and perhaps more widely [1-9]. Other nonpolar gases could form hydrates on Mars, including noble gases, nitrogen, sulfur dioxide, and methane [6,8,9]. We reexamine the possible global CO₂ inventory of Mars, the magnitude of possible regional outgassing events, possible mechanisms of formation of clathrates, and the stability of clathrate hydrates. Dissociation of clathrate hydrates may be an important link in the catastrophic formation of chaotic terrain, outflow channels, and northern plains deposits, and clathrates may influence the dynamic behavior of Martian polar caps and ice flows in the fretted canyons.

Mechanisms of clathrate formation on Mars: (1) Reaction of permafrost ice and groundwater with CO₂, CO, SO₂, noble gases, and other gases (possibly including biogenic CH₄) released from the mantle, lower crust, and magmatic intrusions. (2) Progressive freezing of an ocean and saturation of a clathrate phase due to enrichment of dissolved gases in residual water. (3) Direct reaction of atmospheric gas with an ocean or lakes to form clathrate if atmospheric CO₂ pressure was ever greater than about 9.6 bars and temperature decreased to 272 K or lower. (4) Polar precipitation and multi-year accumulation of ice and reaction with atmospheric CO₂ vapor or dry ice. (5) Basal melting of a CO₂ polar ice cap or other deposits of dry ice and reaction of liquid CO₂ with ground ice or ground water in the subsurface of the circumpolar northern plains. (6) Direct atmospheric precipitation and accumulation of CO₂ clathrate from a formerly denser, warmer CO₂ atmosphere. (7) Wintertime precipitation of ice at mid latitudes and night-time reaction with atmospheric CO₂ or dry ice frost. (8) Trapping and burial of Martian air in polar ice deposits and reaction with ice under pressure.

Some of these mechanisms may result in massive deposits of clathrates (mechanisms 1-6), whereas others result in negligible amounts (e.g., mechanism 8) or transient nightly winter frostings by clathrate (e.g., mechanism 7 [4]). Polar air hydrates are volumetrically insignificant but may hold valuable records of Martian climatic and atmospheric evolution [8]. Some of these mechanisms certainly occur in today's environment (polar and mid-latitude formation of clathrate reaction frosts and formation of polar air hydrates). Processes 1-6 would have large consequences but depend on theoretical details of geologic and geochemical models. Although Martian gas hydrates should con-

tain a mixture of guest molecules, CO₂ is expected to be by far the dominant Martian clathrate-forming gas.

We will consider in detail the formation of CO₂ clathrate in the upper crust at low latitudes. First we show that massive reservoirs of CO₂ could exist.

Global CO₂ inventory: The global inventory of CO₂ was calculated several ways. The inventory would be sufficient to generate between 2.6 and 16 bars atmospheric pressure if entirely in vapor form, or it could form a global mean layer thickness of CO₂ clathrate > 200 m and possibly > 1300 meters thick if all the CO₂ is present in hydrate form. The higher estimate is based on direct scaling (by planetary mass, surface area, and gravity) from the Venusian atmosphere; it is not an upper limit, since Mars is probably more volatile-rich than Venus. The lower estimate is based on a model of crust formation (40 km global mean crust thickness) and attendant outgassing (0.06 wt. % CO₂ outgassed from the crust). Some outgassed CO₂ could exist as carbonates, some as dry ice, and some may have escaped Mars or may have been reduced to graphite. More recent outgassing, e.g., due to Tharsis magmatism, may have added more than 50 m of additional clathrate to rocks overlying the magmatic activity. Regardless of details, the potential is for large masses of CO₂ clathrate and CO₂-saturated water (in equilibrium beneath a clathrate bearing layer) to exist in the upper crust and polar deposits of Mars.

Phase stability of pure CO₂ in the Martian crust at low latitudes: The pressure-temperature conditions within the Martian upper crust encompass a large zone at all latitudes where liquid CO₂ is stable (Figure 1). Slowly ascending CO₂-rich gas coming from the mantle, lower crust, or deep magmatic plutons starts in the supercritical region and, for any reasonable geotherm, the gas then passes gradually to a liquid phase. As it ascends further, with attendant depressurization and cooling, liquid CO₂ eventually reaches either a stable dry-ice zone (in regions where the mean surface temperature is < 215 K) or the gas stability zone, meaning that it boils (if the mean annual surface temperature is > 215 K).

The widespread stability of dry ice in the shallow subsurface of Mars may seem surprising but, with important caveats, it is inevitable for the conditions cited. These caveats are that (i) the subsurface must be sealed from the atmosphere and (ii) H₂O is not abundant, is less abundant than needed to react with all CO₂ present in the system, or is prevented from reacting fully.

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Since ice is probably the most common sealant (salts also being effective) and since ground water is widely present at depth, more relevant equilibria might be the clathrate-forming system $\text{CO}_2\text{-H}_2\text{O}$.

Stability and formation of CO_2 clathrate in Martian crust at low latitudes: CO_2 clathrate is stable within a large volume of the Martian upper crust at all latitudes for all reasonable present-day mean annual surface temperatures (Figure 2). The caveat that the interior is sealed from the atmosphere still applies. The thickness of the stable zone of CO_2 clathrate is a factor of several greater than in major clathrate environments on Earth. On Mars, the stable zone is very thick and extends to the equator, whereas on Earth the clathrate stable zone is comparatively thin and exists only in permafrost regions (or near-permafrost regions) and parts of the seafloor. (On Earth the commonest clathrate-forming gas is CH_4 , but in some cases CO_2 is important.) CO_2 rising from the Martian mantle, magmatic intrusions, or the lower crust starts out in the supercritical region but becomes liquid before finally intersecting the clathrate stability curve in a region where liquid water also is stable. In regions of elevated heat flow, such as Tharsis, the deeper limit of clathrate stability may occur at a depth of 1.6 km, below which ground water and liquid CO_2 should coexist immiscibly. The ground-water zone generally should exist above a liquid- CO_2 zone (or, if the water is extremely salty, the liquid CO_2 may float on the groundwater beneath the clathrate). Any groundwater in equilibrium with Martian CO_2 clathrate at high pressure is saturated with about 7 weight percent CO_2 .

In regions of average global heat flow, CO_2 clathrate will remain stable to a depth of about 10 km. Thus, the CO_2 storage capacity of the crust is very large and could easily accommodate the amounts of clathrate calculated above from model inventories.

Dissociation of gas hydrates could occur by long-term geothermal heating and elevation of geotherms or by sudden depressurization due to faulting or impacts. Venting of gas-rich groundwaters and liquid CO_2 so produced might explain chaotic terrains and outflow channels [3-5], and the floods or debris flows unleashed could contribute to lacustrine/marine sedimentary deposits in the northern plains. The rheologic behavior [11], low thermal conductivity [10], and volatile releases of clathrates and dry ice may strongly influence the dynamic behavior of Martian polar caps and ice flows in the fretted canyons.

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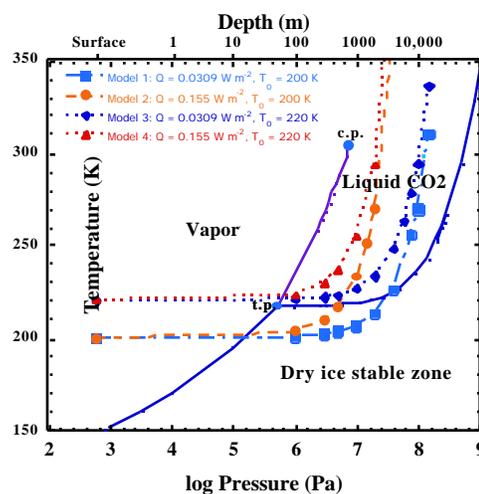


Figure 1. Martian geotherms and CO_2 phase stability (pure system CO_2). The geotherms represent mean annual surface temperatures = 200 and 220 K, and heat flows = current global average heat flow or five times the average. The higher heat flow is consistent with the global average Martian heat flow about 3 billion years ago or may represent current heat flow in volcanically active regions.

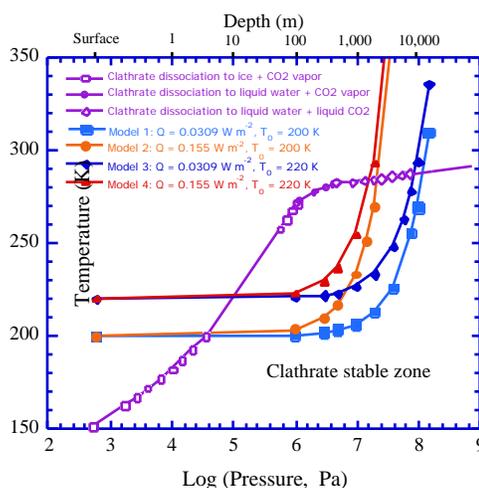


Fig. 2. Martian geotherms and the CO_2 -clathrate dissociation/formation curve. Geotherms same as in Fig. 1.