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Carbon Dioxide Hydrate and Floods on Mars

Abstract. *Ground ice on Mars probably consists largely of carbon dioxide hydrate, $CO_2 \cdot 6H_2O$. This hydrate dissociates upon release of pressure at temperatures between 0° and 10°C. The heat capacity of the ground would be sufficient to produce up to 4 percent (by volume) of water at a rate equal to that at which it can be drained away. Catastrophic dissociation of carbon dioxide hydrate during some past epoch when the near surface temperature was in this range would have produced chaotic terrain and flood channels.*

None of the features revealed by the 1971 Mariner 9 Mars orbiter has evoked more surprise than the huge channels in the equatorial zone, some as much as 40 km wide and hundreds of kilometers long. Accordant junctions, teardrop-shaped islands, braided reaches, and meandering courses indicate that these channels were shaped by running water (*1*). The widths and apparent depths of many channels indicate discharges much greater than that of the Amazon. Such discharges could only have been maintained for short periods. Indeed, the channels appear immature by comparison with river systems on Earth which evolved over geologic time and instead resemble catastrophic flood channels. The channeled scablands of Washington, a complex of deep channels carved in basalt in a few days or at most weeks by water released on the failure of an ice dam retaining glacial Lake Missoula

(*2*), offer a particularly close analog, and landforms that in the scablands indicate extraordinary volumes and velocities of flow can be recognized in narrow-angle frames of martian channels (*3*). The scablands are the one terrestrial feature that approaches the martian channel systems in magnitude. Although the Lake Missoula flood was an exceptional and perhaps unique event in the geologic record, comparable floods appear to have been normal phenomena in the history of Mars.

Two of the conditions listed below are implied by any fluvial activity; the third is required by its catastrophic nature:

1) Surface temperatures and atmospheric pressures allowed the stability or at least the persistence of water on or near the surface at one or more epochs in martian history.

2) A source for the water existed.

3) A mechanism for generating or releasing liquid water at a rate rarely if ever matched on Earth operated repeatedly.

Explanations for the first two conditions have been advanced; the third is the principal concern of this report.

The mean surface temperature of Mars is well below the melting point of ice, and, although midday temperatures in the equatorial region may reach 25°C, diurnal warming affects only a shallow near-surface layer (*4*). The total atmospheric pressure is insufficient or barely sufficient to prevent water from boiling, and the water content of the atmosphere is extremely low. Various hypotheses have been proposed, however, which indicate that more clement epochs have occurred in the past. Recent studies (*5*) suggest that advective instability in the atmosphere permits the martian climate to be driven by changes in the planetary obliquity, the solar luminosity, or the albedo of the polar caps from one to the other of two stable states, one close to present conditions and one with higher pressures and temperatures that would allow liquid water at the surface in the equatorial zone.

Although evidence for its existence is only inferential, ground ice is widely believed to exist on Mars (*6–8*) and its melting would be the obvious source of water. The decay of ground ice was proposed as the cause of the massively fractured and slumped "chaotic terrain" revealed in 1969 by the Mariner 6 Mars orbiter (*6*). Although alternative origins for chaotic terrain have been advanced, the decay of ground ice

Fig. 1. Chaotic terrain apparently drained northward by flood channels. The arrow points to the feature interpreted by Maxwell *et al.* (*11*) as an impact crater drained southeastward. Chryse region of Mars; frame center, 27.9°W, 3.4°N; frame width, 500 km. Mariner 9 photograph 7758698.

remains the leading hypothesis in contention [7]. Mariner 9 observations revealed that the largest channels head in areas of chaotic terrain (Fig. 1), thus suggesting that decay involved not merely evaporation but also melting and surface drainage of the water [1, 7, 9].

The magnitude of the floods may reflect either the rate of release of meltwater or the rate of melting. The physical storage of meltwater in underground reservoirs over centers of abnormally high internal heat flux and its sudden release by the bursting of an impervious cap rock have been tentatively proposed [9]. Investigation of the model has not been pursued, and the likelihood of the special conditions required, especially storage at a level that provides hydrostatic head on eventual release, remains to be evaluated. The alternative of sudden melting would seem to require the supply of unreasonably large quantities of heat over wide areas in very short periods of time [10, 11]. If, however, martian ground ice is not ordinary H_2O ice but rather the clathrate compound carbon dioxide hydrate, the heat problem disappears.

Miller and Smythe [12] have pointed out that $CO_2 \cdot 5\frac{3}{4}\ H_2O$ [or $CO_2 \cdot 6H_2O$ (the composition may vary)] is to be expected in the polar caps, but its existence in the subsurface at lower latitudes has not been considered previously. At standard martian surface pressure (6.1 mbar) the hydrate is not stable above $-120°C$ [12], but the dissociation curve (Fig. 2) indicates that at moderate pressures it is a stable phase at temperatures up to 10°C [13]. For any H_2O/CO_2 ratio above or below 6/1, the hydrate would coexist with either a water or a carbon dioxide phase, and the quantity of hydrate would depend on the origin and history of the ground ice. If martian ground ice formed by the trapping of juvenile volatiles, as suggested by several investigators [8], and if these outgassed in a ratio similar to that on Earth ($H_2O/CO_2 \sim 15/1$) [14], a third of the original ground ice would be the clathrate compound. Changes in the composition of ground ice with aging and thermal cycling and the composition of ground ice derived from descending meteoric volatiles are much more difficult to evaluate, but a high proportion of the hydrate seems probable [15].

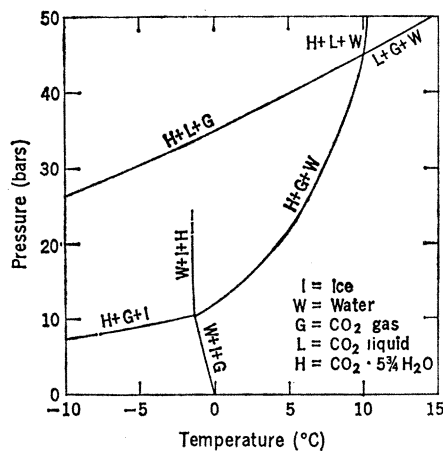The significant segment of the H_2O-CO_2 phase diagram (Fig. 2) is the

Fig. 2. Pressure-temperature projection of a part of the CO_2-H_2O system, after Takenouchi and Kennedy [13].

hydrate plus carbon dioxide gas plus water univariant curve $(H + G + W)$ between the quadruple points at 10°C, 45 bars and $-1.5°C$, 10 bars. If the pressure is reduced so as to cross or to follow this curve, as would occur if a fracture opened at depth, the hydrate would dissociate to 6 moles of liquid water (or, more precisely, a dilute carbonic acid solution) and 1 mole of carbon dioxide gas for each mole of hydrate. No such behavior is found in the pure water system, since pressure has a negligible effect on the melting of ordinary ice. Pressure increases with depth on Mars at a rate of about 1 bar per 10 m of depth for a lithostatic load and more gradually for a system with open or liquid-filled fissures or pores. The lower and upper quadruple point pressures are reached at depths of about a few hundred meters and 1 km, respectively.

Decomposition of the hydrate requires about 150 calories per gram of released water, compared to about 80 calories for the melting of 1 g of ordinary ice. But unlike a system with pure water, heat does not have to be transported from elsewhere but can be supplied by the cooling of the host rock and the released water. The amount of water that can be produced may be calculated from the approximate equation

$$150 = \left[c_{water} + c_{rock}\, d_{rock}\left(\frac{1-p}{p}\right)\right] \times \left(T - 0°C\right)$$

where c is the specific heat, d is the specific gravity, p is the fraction of hydrate (by volume), and T is the initial temperature (in degrees Celsius). For $c_{rock} = 0.2$, $d_{rock} = 2.75$, and $T = 10°C$, p is approximately 4 percent.

Each body of clathrate ice must gather heat from about 25 times its own volume of rock. The path lengths of heat transfer depend on the mode of occurrence of the ice, but for the probable case in which ice occupies the pore space of a particulate sediment typical path lengths would be millimeters or less. The maximum amount of water that can be produced by this mechanism is 4 percent, but, once collapse has been initiated, additional heat would be generated by the conversion of mechanical work as the material moves to a lower gravity potential.

The load of a column of water 270 m deep (at the lower quadruple point) would suppress the dissociation of the hydrate. Thus the sudden formation of a crevasse open only upward would cause dissociation only in its immediate vicinity. If, however, the crevasse opens to a steep slope so that the water can drain away, the sudden presence of the liquid and the evolution of the gas would weaken the rock so that fracturing, decompression, and hydrate dissociation would propagate into the slope. Physical separation from the rock mass of the water produced by dissociation and of any originally liquid water coexisting with the hydrate is to be expected, analogous to the dewatering and compaction of disturbed waterlogged sediments in terrestrial experience. Where drainage from a broad front is possible (as in the areas shown in Fig. 1), catastrophic dewatering would occur. Thus the formation of chaotic terrain and the formation of giant flood channels are complementary processes in a single event.

Thus, if the two generally held hypotheses of past climatic amelioration on Mars [16] and of the prevalence of ground ice are accepted, the fact that much of the ice would be the clathrate form provides a peculiarly martian explanation of a peculiarly martian feature, immense flood channels.

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15. I am attempting to develop models for the distribution of condensates in pore space in the martian subsurface, but the problem appears too complex for satisfactory solution even with an arbitrary choice of physical conditions. A feature common to many models, however, is that during a warming or a cooling cycle the solid phase with the highest melting temperature, carbon dioxide hydrate, forms at the expense of the other phases. The problem may best be attacked through a study of analogous occurrences on Earth. Clathrate hydrates of N_2 and O_2 form only at considerably higher pressures than that of carbon dioxide, so air hydrate is unimportant [S. L. Miller, *Science* **165**, 489 (1969)]. Gases of the paraffin series, however, form hydrates at conditions much like those for carbon dioxide, and large fields of solid natural gas hydrate have recently been discovered in the permafrost zone of Siberia [Yu. F. Makogon, F. A. Trebin, A. A. Trofimuk, V. P. Tsarev, N. V. Cherskiy, *Dokl. Akad. Nauk SSSR* **196**, 203 (1971)]. The process by which these form from dispersed gas-water systems has been considered by A. A. Trofimuk, N. V. Cherskiy, Yu. F. Makagon, and V. P. Tsarev [*Akad. Nauk SSR Sib. Otd. Geol. Geofiz. No. 8* (1972), p. 3] and G. D. Ginsburg [*Sb. Statei Gidrogeol. Geoterm. Vyp.* **1**, 109 (1969)]. It is even possible that hydrocarbon clathrates occur in martian permafrost if it originated by cold-trapping juvenile volatiles.
16. A less likely possibility, but one worth exploring, is that at least some flooding resulted from abnormal local internal heat flux under atmospheric conditions similar to that of the present, with water persisting at the surface because of kinetic effects or only local equilibrium. Models have been advanced in which water could persist long enough to form rivers under the far more rigorous conditions of the lunar surface [R. E. Lingenfelter, S. J. Peale, G. Schubert, *Science* **161**, 266 (1968); G. Schubert, R. E. Lingenfelter, S. J. Peale, *Rev. Geophys. Space Phys.* **8**, 199 (1970)] which, although not convincing, are not clearly impossible. With favorable underground temperatures, water production by the dissociation of carbon dioxide hydrate would proceed at a rate at which the nonequilibrium persistence of water is plausible.
17. Work done as part of the Mariner Mars 1971 Project, Jet Propulsion Laboratory, California Institute of Technology, under contract WO-8122.

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Cholera Toxin: Interaction of Subunits with Ganglioside G_{M1}

Abstract. *Vibrio cholerae* exotoxin is an aggregate of two different noninterconvertible subunits (molecular weights about 15,000 and about 25,000). Only the smaller subunit reacts with ganglioside G_{M1}, a possible biological receptor. The larger subunit, found only in active toxin molecules, can be eluted with 8 molar urea from insoluble complexes of toxin, ganglioside, and cerebroside.

The exotoxin of *Vibrio cholerae* has been purified and shown to be a protein of molecular weight about 84,000 (*1*). It has choleragenic and skin reactivity, and both of these activities are prevented if the protein is allowed to react with the monosialosyl ganglioside G_{M1} (a possible natural receptor for the toxin which is found in most tissues) at a molar ratio of ganglioside to protein of about 3.5 to 1 (*2*). Experiments suggesting that the ganglioside reacts with only one of two different types of subunit in the toxin molecule are now reported.

Electrophoresis of the native toxin in polyacrylamide gels in 6.25*M* urea at *p*H 3.2 (*3*) showed two bands (Fig. 1a): a fast band, fragment B; and a more weakly stained slower band, fragment A. If either of the two bands was eluted from the gels and subjected again to electrophoresis in the same system, the band ran true; there was no interconversion or breakdown.

The ganglioside that inactivates cholera toxin is soluble in water but can be made insoluble by forming a 1 : 9 (by weight) complex with cerebroside (*4*), and this product still reacts with the toxin. Brain ganglioside G_{M1} (1 mg) and brain cerebroside (9 mg) (supplied by N. Gascoyne) were dissolved in 2 ml of a mixture of chloroform and methanol (1 : 1, by volume) and dried in a vacuum. The residue was suspended in 1 ml of 0.1*M* tris-HCl buffer, *p*H 7.0, containing 1 mg of cholera toxin (from Dr. R. A. Finkelstein, lot No. 12.9.72), and incubated at 37°C for 45 minutes. More than 90 percent of the toxin was adsorbed to the ganglioside-cerebroside. The complex was removed by centrifugation, washed twice with buffer, suspended in 0.4 ml 8*M* urea, 0.25*M* tris-HCl, *p*H 7.0, and incubated at 37°C for 3 hours. Electrophoresis of the supernatant after this incubation showed that essentially only fragment A had been eluted (Fig. 1b). (There was a slight trace of fragment B, but the amount was not increased even after incubation for a total of 5 hours, although the elution of fragment A was complete after 3 hours.) The rest of the toxin molecule (entirely fragment B) was eluted after prolonged incubation at 37°C in 6*M* guanidine hydrochloride, *p*H 7.0, an observation compatible with a recent report that whole toxin could be eluted with "guanidine" from ganglioside insolubilized by covalent bonding to agarose gels (*5*).

If fragment A was dialyzed against 0.1*M* tris-HCl, *p*H 7.0, and treated again with ganglioside-cerebroside, it was not readsorbed. However, fragment B could be readsorbed after dialysis. These results suggest that binding of the whole toxin molecule to the ganglioside is through fragment B. Electrophoresis in the urea gels of choleragenoid (a "natural" cholera toxoid, also a gift from Dr. Finkelstein) showed that it contained material running with fragment B only (Fig. 1c). Fragment A was absent. Thus it seems that it is the protein of choleragenoid that reacts with ganglioside, an observation which could explain the observed blocking of cholera toxin by choleragenoid.

Fragment A (isolated after elution from ganglioside-cerebroside or by eluting directly from the polyacrylamide gels) has some skin reactivity (*6*), about 1 percent of that of native toxin. It is not possible to know what the reactivity would have been had it not been necessary to incubate the material first in 8*M* urea, under which conditions most proteins are denatured. Obviously it would also be desirable to test the activity of fragment A in the ligated intestinal loop, but it has not yet been possible to accumulate enough biologically active material (after treatment with 8*M* urea) to carry out such a test. What distinguishes the activity of fragment A in the skin from that of the native toxin is that it is not decreased at all by prior incubation with ganglioside G_{M1} even at a molar ratio of ganglioside to total protein of about 10,000 to 1.

Although the low *p*H gels in urea distinguish between the two fragments, they give no information about their size or nature. Thin-layer gel chromatography on Sephadex G-200 in 6*M* guanidine hydrochloride (*7*) can give such information. Native toxin was dissociated into two proteins visible after