# $CO_2$ PHASE CHANGES AND FLOW MECHANISMS FOR NON-AQUEOUS “FLOODS” ON MARS.

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**Introduction:** The surface of Mars is scarred by giant channels that have been ascribed by many authors to catastrophic outbursts of subterranean water [e.g. 1, 2]. However, most geochemical evidence suggests that Mars has always been relatively dry [3], and simple climate models would suggest that it has also been colder in the past [4]. The physical evidence of erosion is one of the main arguments for an extensive history of liquid water on Mars.

Alternate mechanisms for catastrophic erosion of the channels and emplacement of sediments merit analysis to see if they can avoid some of the paradoxical consequences of invoking liquid water flows on a cryogenic, arid, planet.

**Morphology:** The distinctive morphology of Outburst channels on Mars and their association with chaos zones has often been used as prima-facie evidence of subsurface outbursts and water flow, but a number of different mechanisms in different environments can potentially produce similar morphologies.

**Mechanisms:** Possible mechanisms on the scale required include:-

1) Water-rich subaerial flows [1, 2]
2) Dense slurries with water or other fluids [5, 6]
3) Dilute subaerial flows with other liquids [7, 8]
4) Dry avalanches and “rock rivers”
5) Intense channeled winds [9, 10]
6) Glaciers or ice sheets [11-13]
7) Lava channels [14, 15]
8) Volcanic pyroclastic flows [16]
9) Submarine turbidites [17, 18]
10) Cryogenic $CO_2$-supported density flows [16]

Many of these alternatives can quickly be ruled out because the context and appearance of the flows strongly suggests subaerial (9) and dilute flows with considerable fluidity (2, 4, 6). Volcanic flows (7, 8) can be excluded because the source areas of the flows – the distinctive chaos zones, do not have volcanic constructs.

We can rule out the involvement of intense but essentially normal winds (5) because metre-scale boulders at the Pathfinder Landing Site, show clear C-axis imbrication, implying deposition in situ from a dense, high energy transport system.

The involvement of non-aqueous liquids in surface flows (3) is difficult to support because the low vapour pressure of Mars (6.5 millibars at present day) is not compatible with even the minimum vapour pressure of liquid $CO_2$ [8] at surface (>5 bars at $-56.6\ ^{o}C$) or liquid SO2. Exotic alternatives such as liquid hydrocarbons [7] appear unlikely in the light of Viking surface chemistry.

This leaves two competing mechanisms: liquid water flows, or gaseous $CO_2$ density flows. Both mechanisms involve common volatiles and temperatures and pressures that are possible in the subsurface of Mars.

**Preferred model:** The details of chaos morphology, flow calculations, and thermal regimes tend to favour a $CO_2$ mechanism. In particular, water models require aquifer recharge while $CO_2$ models rely on large volumetric expansion from $CO_2$ liquifers [19] that are consumed in a one-time explosive outburst.

In addition, a number of long-standing paradoxes are solved instantly and automatically by invoking $CO_2$ as the active agent in the outburst “floods”.

Chief amongst these is the carbonate paradox. Although large amounts of orbiter time and payload budget have been expended on radiometers and surface scans, none have yet detected carbonate on the surface of Mars. A number of complex explanations have been attempted to explain why the expected carbonate is “invisible” but a simpler explanation is that it was never formed because Mars has always been cryogenic and water has been locked-up as water ice and $CO_2$-clathrate.

Another paradoxical issue is why the atmosphere of a putative warm and wet early Mars stopped being effective and is no longer present today (nor has been for the past 500Ma at least). Models of late atmospheric loss are not particularly successful in explaining the isotope ratios of the modern atmosphere.

The faint young Sun paradox further complicates this issue, since it is well-accepted by astrophysicists that the Early sun should have been significantly cooler than it is now. Only 70%-80% of the modern solar “constant” was available at ~4.5 Ga [20], with a steady increase over geologic time to the present value.

The “White Mars” model of volatiles on Mars [16] is simple, elegant, and fully self-consistent. It does not require different climatic conditions or atmospheres on Mars in the past. Indeed, the existing Mars climate models can be readily adapted to all past eras of Mars by simply reducing the solar forcing by an appropriate rate to reflect the faint young Sun [4].

**Flow Mechanisms:** Flows originate in chaos zones by collapse of fluid-saturated regolith, much as outbursts of water are envisaged. However there are a number of differences consequent on invoking liquid $CO_2$ as the active agent.

$CO_2$ is liquid down to –56.6 °C, therefore large sections of Mars subsurface are today at the ideal temperature for reservoirs of liquid $CO_2$ ("Liquifers" [19, 16] ). If Mars were at similar temperatures in the past, then this would also be the case. Liquid water, on the other hand is not encountered until zero Centigrade (or perhaps –10 °C for strong brines). zero centigrade is unusually warm for the subsurface of Mars, except in the close proximity to strong geothermal heat sources, or at considerable depth in the crust. The tendency of water to form a stable clathrate with $CO_2$ under pressure further reduces the availability of liquid water.

$CO_2$ exerts a significant vapour pressure. Even the solid has a vapour pressure of up to a few bars, depending on temperature. Liquid $CO_2$ varies from 5 bars at its liquidus to 35 bars at zero Centigrade. Each bar of pressure is sufficient to physically lift a layer of regolith 15 metres thick (density 2.0) in Mars gravity field., or to fracture through and disrupt a thicker layer. Liquid water at zero Centigrade can barely achieve 10 millibars, and even at 100 Centigrade only has a vapour pressure of 1 bar.

The collapse of terrain impregnated with liquid $CO_2$ would be an explosive runaway process (Figures 1, 2), with jets of debris blasting out of the walls of the chaos zone and regolith crumbling and disintegrating to a thickness of hundreds of metres, simply from the internal pressure of the $CO_2$. The result will be a huge cloud of gas and debris with a basal slurry of shattered regolith and liquid $CO_2$, boiling rapidly.

A $CO_2$-fuelled outburst flow would be a cryogenic density flow, supported by the pressure of $CO_2$ gas explosively subliming from reserves of dry ice, clathrate, and possibly liquid $CO_2$ transported in a dense basal layer of the flow. A fluidised bed of particles and gas would exhibit very low viscosity and flow rapidly downslope. The basal part of the flow would be strongly erosive, transporting metre-scale boulders and scouring deeply into the unconsolidated Martian regolith.

**Clathrates:** An alternative explanation has been proposed a number of times [e.g. 21-23]. In this, $CO_2$-Clathrate is the stored material and source for the flows. This is in many ways a compromise solution, seeking to invoke the expansive power of $CO_2$ vapour as an initiator for the flows, but generating liquid water as the flowing agent itself. Although superficially attractive, the kinetics and thermodynamics of clathrate decomposition do not support this mechanism for several reasons.

Clathrate can break down by two alternative pathways. If it is warmed at constant pressure, then it undergoes normal melting from a one-phase solid to a two-phase product (liquid water, plus $CO_2$ in either vapour or liquid phase, depending on the confining pressure). Even in intensely saline solutions, the breakdown of clathrate requires temperatures significantly higher than the melting point of pure ice, and has similar latent and specific heat demands. Thus, melting of clathrate is likely to be a slow process requiring significant hydrothermal or magmatic activity, for which we see no evidence at chaos zones.

The alternate breakdown mode of clathrate is when it is isothermally (or adiabatically) decompressed. Here, clathrate undergoes slow disequilibrium melting from solid clathrate to normal ice plus $CO_2$ vapour (or to 2 vapours if the ambient pressure is low enough). The breakdown process of equivalent methane hydrates on Earth is well-studied and involves slow decomposition over tens of minutes, even for hand-sized samples. The solid-state reactions are kinetically unfavourable and take considerable time to occur, allowing the vapour to readily disperse. Thus, although the energy budget for disequilibrium melting is low, the result is not explosive and therefore cannot significantly aid the breakdown of terrain.

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