

Introduction: The focus on liquid activity on Mars has been on water, but in fact the temperature and pressure conditions in the subsurface of Mars are ideal for liquid CO₂ over a wide range of latitudes and depths [1,2]. Potentially, that liquid CO₂ may be the major agent in erosion, diagenesis, and chemistry on Mars [2]. The key question is how much liquid CO₂ there may be and the balance between escape processes and resupply. Here we attempt to estimate the global inventory of liquid CO₂ and its supply to the deep regolith and use surface data to infer escape over geologic time.

The problem: Liquid CO₂ is a potent cryogenic volatile that has the potential to significantly modify subsurface conditions on Mars and to interact with H₂O in a variety of interesting ways. Clathrate formation extends the stability field of ice by about 10 K and deepens the H₂O cryosphere by ~ 1km (at realistic geotherms of 10 K/km). Excess CO₂ beyond the 1:5.75 stoichiometry of clathrate must be either retained in or expelled from the subsurface.

Due to its high vapour pressure and low viscosity, liquid CO₂ will rapidly exploit any pathway to lower pressure compartments and ultimately to the surface. In the process, non-polar solvent action of the liquid CO₂ will lead to diagenesis of the regolith in ways not encountered on Earth, and the formation of non-aqueous evaporate species.

However, without a mechanism for return of CO₂ to the deep regolith, this process will diminish exponentially over geologic time and at the present day one might expect to find only small and isolated pockets of liquid CO₂ in the subsurface [3]. This issue is comparable to that faced by water recycling models for the origin of chaos zones and many of the concepts used there can be applied to this issue, although the details of subsurface temperature and pressure appear to work more favourably with CO₂ as the volatile rather than H₂O.

CO₂ Inventory: The first question to be tackled is the total amount of CO₂ on modern Mars. This is a surprisingly poorly known value and at extremes of the possible range, very different situations may apply. The issue is also linked to the total H₂O volume on Mars and to the H₂O:CO₂ ratio. It is reasonable to suppose that Mars had a similar initial H₂O:CO₂ ratio as the other terrestrial planets – about 3:1. Over time, Mars has lost water to space, as attested by the D/H ratio of the atmosphere, but the denser CO₂ has been retained preferentially. Therefore at the present day the

ratio of H₂O to CO₂ should be around 1 or 1.5:1. This is an important constraint that we need to refer to.

Location: A small amount of CO₂ is present in the atmosphere and seasonal polecaps amounting to ~ 10 mbar. This is a minute fraction of the primordial inventory of 1 to 20 bars that Mars might have been endowed with (corresponding to an original global water supply equivalent to 50 m to 1 km). Where is the rest of Mars' CO₂?

On Earth, the majority of CO₂ is chemically bonded as carbonate rock. Searches for carbonate on Mars have been disappointing to say the least and a number of models suggest that it is present, but invisible to IR detection. However, each bar of CO₂ corresponds to about 20 metres global thickness of carbonate rock. We would expect to find carbonates preferentially in lowland basins, which cover ~1/4 of Mars surface at most. Therefore, the search for carbonates is a search for an average thickness of 80 to 1600 metres of carbonate rock and the higher the volatile inventory, the thicker the carbonate.

We can rule out the higher values since this would require the lowland plains to consist of over 50% carbonate, which would have been immediately detected by surface landers. The lower values are possible, so if Mars had a very limited initial inventory of both water and CO₂, we need look no further. (The small carbonate fraction in ALH84001 could account for a bar or two of CO₂, if large volumes of old igneous rocks share this chemistry).

The polecaps. All that we know of the permanent north polar cap is that it consists of H₂O-rich ice. It may be normal water ice or clathrate. Since deposition of solid CO₂ occurs every winter, one would expect clathrate as the H₂O-bearing phase. Therefore, the polecaps may contain up to 300 mbar of CO₂ (20 metres global equivalent of water). Thick polar permafrost represents a potential ice reservoir up to ten times the volume of the caps, so some 3 bars of CO₂ may be stored as clathrate in the polar regions, putting us well into the higher ranges of volatile inventory.

Given the expected ratio of CO₂ to H₂O, we have an excess of CO₂ to account for of about 3 times this value – i.e. 1 to 9 bars. If the permanent polecaps are not formed of clathrate, but of normal ice, the excess CO₂ amounts to 4 times the polar inventory – up to 12 bars.

So where are these ~10 bars of CO₂? We have already seen that it is highly unlikely that this much sedimentary carbonate could exist in the northern

plains. There are only two remaining reservoirs – CO₂ permafrost and liquid CO₂.

CO₂ permafrost may be present in distributed form or in layers or lenses in the sub-polar regions. It may also be present as occasional layers within the polecap itself. If CO₂ permafrost extends down to 45 degrees latitude, and has a mean thickness of 4 km and a saturation (or relative fraction) of 20% then this accounts for some 10 bars of CO₂ - the excess inventory we are seeking to account for. There is therefore an extensive polar and sub-polar reservoir of solid CO₂ is available for melting at depths of 2-6 km. The question then becomes one of the frequency and scale of thermal events that may occur over the sub-polar regions.

Evidence and mechanisms for melting

Past Melting Events: The acme of the outburst “floods”, at 3 to 3.5 Ga in the late Hesperian appears to represent an epoch of escape of potent volatiles from near-equatorial regions. White Mars models [2] propose that liquid CO₂ was generated by local thawing of a global CO₂ permafrost, leading to high local concentrations of energetic subsurface liquid CO₂. Subsequent to that time, no events on this scale are recorded, so the Hesperian is seen as a one-time melting of the equatorial regions.

Recent Melting Events: Small hills with summit craters have been noted around the north polar cap [4]. These may be large cryptovolcanoes and are exactly what would be expected if basal melts of CO₂ escaped to the surface and erupted as geysers or cryovolcanoes. Various tracts of “thumbprint” terrain can be interpreted as extensive fields of cryovolcanoes [5]. Thus many “volcanic” hills where lava flows are not seen may in fact be signs of cryogenic circulation of CO₂ from basal melts back to the atmosphere, where it will then redeposit in the permafrost and polecap.

Global melting events: At depths of 2 km or more, the base of the CO₂ cryosphere is protected from short & medium period orbital variations. Only events on a timescale of 10⁵ years or more will penetrate to these depths. On this timescale, orbital variations of 10° in obliquity and 0.02 in eccentricity are calculated [6]. Variations on this scale can lead to fluctuations of 20% in zonally-averaged insolation at higher latitudes (50-80°), leading to a 5% surface temperature variation i.e. 10-20 K. This would produce a change in the base of the CO₂ cryosphere by 1 to 2 km.

If the change is a warming, then this would lead to extensive generation of liquid CO₂ over a 1-2 km depth interval, beneath a thick seal of still-frozen CO₂. If the change is a cooling, then CO₂ will freeze-out. Calculations of recent change appear to suggest a recent obliquity increase of modest proportions, so per-

haps only a few hundred metres of newly melted CO₂ is available at the present day.

Local Geothermal events: Mars has a very focussed pattern of volcanism with large and long-lived stratovolcanoes, yet many smaller volcanic centres exist, some of which have relatively young ages. Just as one would expect intrusions of hot magma to melt ground ice and mobilise a hydrothermal circulation, so too would it melt clathrate and dry ice. Providing that the whole system were not so shallow and energetic as to break through to the surface (where it would form a cryptovolcano as discussed above), then the circulation would organise into a multi-layer “onion-shell” system. The hot magma would form the central core. Around this would be a modest-sized hydrothermal system (with carbonated water), and surrounding that would be a more extensive liquid CO₂ system.

An individual intrusion has enough thermal energy to melt 1-5 times its volume in ice, but around 2-10 times its volume in CO₂, at lower temperatures. Furthermore, as the intrusion cools the central wet core will freeze first while the outer CO₂ zone will contract inwards and replace the liquid water hydrothermal system, thus a senescent hydrothermal system will contain a very small watery core and a proportionally larger liquid CO₂ zone.

Implications for Mars: Any detected liquid water zone in the shallow regolith (< 2 km) is likely to be a local or temporary feature related to geothermal heating. In these circumstances, each occurrence of liquid water will be surrounded by a shell of liquid CO₂, which will represent a significant hazard to future attempts to drill into these pockets.

Due to recent orbital fluctuations, large areas of Mars have experienced modest surface warming over the past 10⁵ years or so, which means that regional liquifers of CO₂ are likely at the base of the CO₂ cryosphere in most high-latitude areas (above 50°). These liquifers will be a few hundred metres thick and are relatively young, therefore will not have had time to dissipate. The base of the CO₂ cryosphere ranges from ~2 km depth at 45° to 6-8 km depth in polar regions for realistic geotherms of 10 K/km.

References: [1] Vlassopoulos, D. (1997) *LPI Workshop on Early Mars*. Abstract 3008 [2] Hoffman, N. (1997) *Icarus*, **146**, 326-342. [3] Beatty, D.H. et al. (2001) '05 *Radar White Paper v11*. [4] Sakimoto, S.E.H. et al., LPS XXXII Abstract 1808 [5] Hoffman, N. LPS XXXII Abstract 1493. [6] Ward, W.R. in H.H. Kieffer et al., *Mars*.