ATMOSPHERIC MASS AND THE GEOLOGIC RECORD OF WATER ON MARS.
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Introduction: Widespread evidence for the action of liquid water on early Mars includes dendritic valley networks [1,2], open-basin lakes [3], deltaic features [4], as well as other textural and mineralogical features. Most of these features, especially those requiring geomorphic work, which are hard to explain in the absence of surface runoff, appear to cluster in the late Noachian and early Hesperian (3.9–3.6 Ga) [1-4], when the Sun was less luminous than today. This clustering of aqueous activity coincides with a long maximum in volcanic activity, which includes the pre-Noachian emplacement of the Tharsis Montes [5], and the late Noachian–early Hesperian emplacement of extensive basaltic plains [6]. It has been widely suggested that an optically thicker atmospheric greenhouse, outgassed in association with the volcanic activity, compensated for the weaker solar flux and allowed warmer and wetter conditions on Mars' early surface. However, the latest global climate models cannot maintain near-melting mean annual surface temperatures (MAST), even with $p$$CO_2$ of several bar, and including the radiative effect of water vapor and CO_2 ice clouds [7,8].

The climate models do show, however, that whether with today's tenuous atmosphere or with a thicker atmosphere and lower solar luminosity, seasonal and diurnal maximum temperatures at latitudes of low zenith angle comfortably exceed 273 K [7,8]. For an obliquity near its present value, melting associated with all occurrences of surface temperature greater than 273 K is in apparent disagreement with observations. First, the integrated duration of low-latitude melting exceeds the time required to carve the valley networks (10^5–10^7 years [9]). Second, melting-related features are expected throughout Mars' history, in disagreement with the observed ages of most of these features.

Atmospheric Mass and the Location of Ice: To generate surface runoff, co-location of water ice and peak temperatures exceeding 273 K is required.

Low atmospheric mass, as on Mars today, leads to a distribution of water ice that is latitude-dependent—the high latitudes are the coldest regions on the planet and this is where ice accumulates. Above-melting temperatures, on the other hand, remain limited to latitudes of low zenith angle (low latitudes for the present obliquity), where the incident solar flux is high. Consequently, above-melting temperatures on the surface of present-day Mars do not lead to melting and geomorphic work, except in local microenvironments such as gullies [10].

High atmospheric mass leads to a distribution of water ice that depends on elevation as well as on latitude. Global climate models suggest that above a threshold $p$$CO_2$ of a few tenths of a bar, the southern highlands of Mars would be covered in ice [7]. Peak seasonal and diurnal temperatures could then lead to melting, runoff, the carving of valley networks and infilling of impact craters.

Atmospheric Stability: The maintainable atmospheric $p$$CO_2$ on Mars is limited by the stability of the atmosphere towards collapse by CO_2 condensation. Even with present-day solar luminosity, atmospheres not much more massive than the present atmosphere are unstable and condense on timescales of hundreds to thousands of years [11]. Therefore, even if early Mars possessed a larger reservoir of CO_2, much of this reservoir would be trapped as CO_2 ice. Atmospheric $p$$CO_2$ would remain low and the distribution of water ice would be such that peak temperatures could not lead to melting. Consequently, loss of the atmosphere to silicate weathering coupled to carbonate mineral precipitation—a process that requires liquid water—is expected to have been minor. Atmospheric escape, although relatively effective due to the absence of an active dynamo through the majority of Mars' history, is still slow enough that CO_2 can be replenished even by very slow volcanic emission (Table 1).

The emerging picture is that of a surface CO_2 reservoir slowly eroded by escape to space, but continuously replenished as long as active volcanism persisted. Only a small fraction of this reservoir, however, resided in the atmosphere, leading to accumulation of water ice at high latitudes, but to occurrence of above-melting temperatures at low latitudes (for near-present obliquity). Occasions of melting were, therefore, rare and limited to impact- or volcanism-related heat.

Volcanism Triggers Atmospheric Inflation: As mentioned above, generation of surface runoff requires $p$$CO_2$ to exceed a few tenths of a bar, so that the spatial distribution of water ice intersects that of above-melting peak temperatures. Such conditions would be possible, if a large enough reservoir of CO_2 were released, lead-

Loss/Gain	Lower limit	Upper limit
Escape (L)	~10^9 mol yr^{-1}	~10^{10} mol yr^{-1}
Outgassing (G)	~10^9 mol yr^{-1}	~10^{13} mol yr^{-1}

Table 1: Rates of early atmospheric loss by nonthermal escape [12] and gain by volcanic outgassing [13].

ing to atmospheric inflation, a substantial atmospheric temperature lapse rate and elevation-dependent distribution of water ice. As such atmospheres are inherently unstable, triggering mechanisms are required to release the condensed CO_2. Impacts could lead to local or regional release of CO_2. However, the majority of valley networks and crater lakes postdate times of high impact rates inferred from Mars' cratering record. A maximum in volcanic activity, however, appears coeval with the formation of the fluvial and lacustrine features [5].

Volcanic activity could trigger atmospheric inflation in two main ways. First, the release of SO_2 into a dusty martian atmosphere has been recently shown to lead to modest net warming, in excess of what can be maintained by an atmosphere containing only gaseous and condensed CO_2 and H_2O [13]. Second, the emplacement of some volcanic units, particularly the basaltic plains, is thought to have been accompanied by massive release of ash, the fine fraction of which would have been distributed globally [14]. Deposition of ash on CO_2 ice would decrease the albedo of the ice, and tilt the energy balance in favor of sublimation [15].

The warming and dispersion of ash associated with the volcanism is expected to be essentially instantaneous, and atmospheric inflation is expected to closely follow (Figure 1). Redistribution of water ice from the poles to the highlands may take several years [7], but limited melting is possible even during the transition. The elevation-dependent distribution, and associated melting, is expected to persist as long as the atmosphere remains inflated. Once pCO_2 declines below the threshold for elevation-dependent distribution of water ice, migration of ice to the polar cold traps over several years to a few decades will ultimately decouple the location of ice from the conditions suitable for melting. Overall, a strong eruption-inflation event could lead to several decades up to a few centuries of transient daytime melting during the summer months. As suggested by the McMurdo Dry Valleys (Antarctica), such conditions may lead to substantial geomorphic work.

At the beginning of volcanic eruptions, before atmospheric inflation leads to a redistribution of water ice and enables transient melting, atmospheric deposition of sulfate is expected. Such deposition is also expected for eruptions that are not strong enough to cause atmospheric inflation. This may explain the relatively uniform S enrichment of martian soils. Once melting commences, low-latitude sulfates are mobilized and redeposited in local topographic lows, as water evaporates or refreezes, but high-latitude sulfates remain uniformly distributed. The transition back to latitude-dependent ice distribution finally results in deposition of low-latitude sulfates until the next eruption strong enough to inflate the atmosphere.

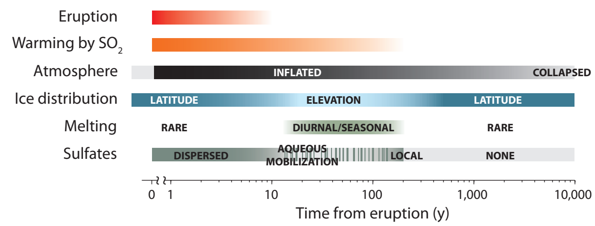

Figure 1: Sequence of events following a brief and voluminous volcanic eruption. Warming by SO_2 and ash deposition leads to atmospheric inflation, elevation-dependent water ice distribution, and melting whenever temperatures exceed 273 K. Dispersed atmospheric deposition of SO_2 and H_2SO_4 is followed by aqueous mobilization and redeposition of sulfate minerals in cycles of melting and refreezing, and ultimate deposition of sulfates in topographic lows.

A History of Atmospheric Mass and Climate: An initial surface reservoir of CO_2 was mostly trapped as CO_2 ice for the majority of the Noachian. Atmospheric pCO_2 was limited (by condensation) to less than ~100 mbar. Impacts and volcanic heat may have episodically released some of the CO_2, leading to a redistribution of water ice within a few decades. In the absence of volcanic S emissions, this redistribution led to erosion, but not to deposition of sulfate minerals.

Noachian and Hesperian volcanic activity added to the surface reservoir of CO_2, but more importantly, led to transient atmospheric inflation through the greenhouse effect of SO_2 and the darkening of the CO_2 ice by volcanic ash. The duration of warm periods was limited by the timescale for atmospheric collapse by condensation, which is 10^2–10^3 years. The S-bearing gases emitted by eruptions formed sulfate minerals, initially uniformly dispersed, then remobilized and locally redeposited at low latitudes.

As volcanic activity waned in the mid-Hesperian, the CO_2 was trapped as ice. Gradual atmospheric escape ultimately resulted in the remaining reservoir of CO_2—6 mbar of atmospheric CO_2, and a comparable amount trapped as CO_2 ice at the south pole.

[1] Fassett and Head (2008) *Icarus*, *195*, 61. [2] Hynek et al. (2010) *JGR*, *115*, E09008. [3] Fassett and Head (2008) *Icarus*, *198*, 37. [4] Di Achille and Hynek (2010) *Nature-Geosci*., *3*, 459. [5] Carr and Head (2010) *EPSL* , *294*, 185. [6] Head et al. (2002) *JGR*, *107*, E001445. [7] Wordsworth et al. (2013) *Icarus*, *222*, 1. [8] Forget et al. (2013) *Icarus*, *222*, 81. [9] Hoke et al. (2011) *EPSL 312*, 1. [10] Dickson and Head (2009) *Icarus*, *204*, 63 . [11] Soto et al. (2014) *Icarus*, *250*, 553. [12] Lammer et al. (2003) *Icarus*, *159*, 1. [13] Halevy and Head (2014) Nature-Geosci., 7. [14] Kerber et al. (2012) *Icarus*, *219*, 358. [15] Wilson and Head (2009), *J. Volcanol. Geotherm. Res.*, *185*, 290.