ATMOSPHERIC PRECIPITATION OF SULFURIC ACID: POTENTIAL ROLE ON EARLY MARS UNDER “COLD AND ICY HIGHLANDS” CLIMATE.

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Introduction: The nature of the early martian climate is a compelling scientific problem. Valley networks [e.g., 1], former lakes [2,3], and other morphological observations suggest that there was significant surface runoff and fluvial activity during the Late Noachian-Early Hesperian (LN-EH). This has led to suggestions that the early climate was “warm and wet”, with mean annual temperature above 273 K and abundant rainfall [e.g. 4]. In contrast, climate modeling suggests that the climate may have been “cold and icy”, with mean annual temperature of ~225 K and water ice covering a significant proportion of the surface in the highlands [5-6]. In this “cold and icy” scenario, fluvial activity would have occurred during periods of transient heating, ice melting, and water runoff [e.g. 7]. Many transient heating mechanisms can be envisioned. Under “cold and icy” conditions, Mars would have a global impermeable cryosphere separating water at the surface from groundwater beneath the cryosphere thus producing a horizontally stratified hydrologic system [8; their Fig. 1]. Ground ice was likely to be stable beneath the seasonal thermal skin over the entire planet, as it occurs today at high latitudes.

The LN-EH was a period of extensive volcanism [e.g., 9] dominated by flood basaltic eruptions. Volcanism was accompanied by emission of volcanic gases that brought sulfur species into the atmosphere [10-12]. In [13] we discussed the potential effects of sulfur species on geomorphologic processes under a cold martian climate. Here we elaborate specifically on the role that sulfuric acid (H_2SO_4) could have played in a LN-EH “cold and icy highlands” Mars climate.

Sulfuric acid cycle: *Sources.* Early Hesperian basaltic plains were emplaced by a series of brief voluminous eruptions separated by hiatuses thousands of years long [10]. Each eruption released some amount of sulfur in the form of gases (H_2S and/or SO_2). Degassing was more effective under lower atmospheric pressure [10-12]. A chain of photochemical reactions in the middle atmosphere quickly oxidized H_2S to SO_2, and more slowly, SO_2 to SO_3, which either precipitated or picked up water vapor (H_2O) and formed sulfuric acid (H_2SO_4), which also precipitated.

The characteristic lifetime of SO_2 in the atmosphere would depend on atmospheric temperature, pressure, H_2O abundance, the nature of atmospheric circulation, and UV flux from the Sun. It could vary from tens of days for a present-day atmosphere [14] to hundreds of years for a thick atmosphere [15]. This length of lifetime is long enough for global mixing, and potentially global SO_3 or H_2SO_4 precipitation. The lifetime was short enough to remove S from the atmosphere during the typical hiatus between eruptions. Latitudinal distribution of SO_3 or H_2SO_4 production and precipitation depended on Mars spin axis obliquity; for low to moderately high (~50°) obliquity precipitation prevails in low and midlatitudes due to higher UV flux, atmospheric temperature, and likely H_2O vapor abundance [16].

The nature of precipitation would strongly depend on temperature, atmospheric H_2O content, the presence of suspended dust, and nucleation microphysics. Precipitation might occur as a light snowfall of solid SO_3, or solid H_2SO_4, or its hydrated crystalline forms, or a mist of a concentrated aqueous solution of H_2SO_4, or fall of dust or tephra particles with H_2SO_4 coatings. The extreme abundance of fine tephra particles co-erupted in typical martian basaltic plinian eruptions will provide a huge number of nucleation sites [12,22]. Precipitated solid SO_3 would become H_2SO_4 upon contact with ice at the surface. Eventually, all degassed S would be delivered to the surface as H_2SO_4.

Runoff. Concentrated aqueous solutions of H_2SO_4 remain liquid at temperatures down to 211 K. If the surface temperature was higher than 211 K, H_2SO_4 would likely form aqueous solutions by melting ice or by deliquescence, unless the relative humidity is too low. On a ‘cold and icy’ Mars it is likely that the most dilute solution possible under the given temperatures is formed. Fig. 1 shows the amount of such a solution as a function of temperature calculated with FREZCHEM [e.g., 17].

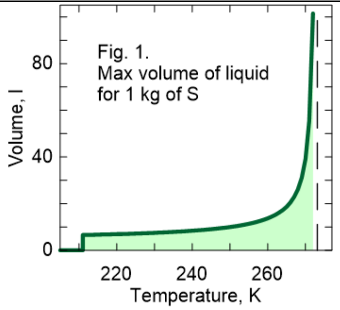

Fig. 1: Volume of liquid aqueous sulfuric acid as a function of atmospheric surface temperature.

If temperature dropped (at night or during the cold season), a part of water from the solution would freeze and form ice, and the solution concentration would increase. When the temperature rose back (days or warm seasons), melting recurred, and concentrations decreased. If the temperature dropped below 211 K, the remaining liquid would freeze to form a crystalline phase $H_2SO_4{\bullet}6.5H_2O$. Freezing of more concentrated solutions would produce a different hydrated crystal phase, $H_2SO_4{\bullet}4H_2O$.

In the 'icy highlands' scenario, H_2SO_4 solutions would drain in supraglacial streams. Minor streams would freeze during the nights and reactivate during the days. Larger streams might develop an ice cover and continue flowing through the night. As streams became pro-glacial, they would erode the regolith substrate, infiltrate into the ice-free thermal skin (the dry active layer), and generally flow along the top of the ice table [8], mechanically and thermally eroding the substrate [18] to produce valley networks. This process would be even more active during the warmer season, when the total amount of liquid phase was larger [19]. Due to the chemical reactivity of H_2SO_4 solid bedrock (and ice-cemented regolith) would be eroded at higher rates than due to simple mechanical erosion [18].

A conservative lower limit for the amount of liquid needed to erode the valley network is ~640 m global equivalent layer [20]. Assuming that this liquid is an H_2SO_4 solution in concentrations typical for 211 – 260 K (Fig. 1), this amount of liquid required $\sim 4\times10^{18}$ kg of S. A review [21] cited estimates of the total S degassing ranging from $\sim 5\times10^{16}$ to $\sim 2\times10^{19}$ kg; therefore, the amount we obtain is high, but plausible.

The liquid collected in open and closed basin lakes [2,3] might survive for a long time, being protected by a seasonal or perennial floating ice layer. H_2O evaporated from the solutions would be redeposited in the icy highlands replenishing the source. Evaporation of H_2SO_4 from its aqueous solutions at low temperatures is negligible, and no cycling of H_2SO_4 is possible.

Sinks. Aqueous solutions of H_2SO_4 can leach cations from associated co-erupted tephra [22] and/or silicate rocks [23] and deposit them as hydrated sulfates. For concentrated low-temperature solutions this process is much slower than for diluted high-temperature solutions, and concentrated acid could persist on the surface for a long time. However, S would ultimately leave the aqueous phase to form sulfates. The whole S cycle is actually a one-way process, from degassing through fluvial transport downhill to formation of sulfates [24].

Large meteoritic impacts would decompose sulfates and release S into the atmosphere, so that some S would make a second pass through surface runoff. This, however, is not an effective recycling mechanism, because in the Early Hesperian the flux of large impactors was already rather low, and large craters of that age are far from saturation.

Another potential sink for H_2SO_4 is infiltration into the frozen ground. The global cryosphere, being impermeable for pure water, is permeable for concentrated H_2SO_4 solutions: they could melt through ice-filled pore space, become diluted and warm and deposit sulphates there. However, this process is likely to be too slow to be an effective actual active sink in the EH.

Discussion: *Origin of Valley Networks*: In a LN-EH "cold and icy highlands" climate, the adiabatic cooing effect places perennial snow and ice distribution above a +1 km equilibrium line altitude [8], coincident with the primary areas of valley network formation and generally just above the distribution of open and closed basin lakes [8]. Broad precipitation and deposition of H_2SO_4 coincident with multiple volcanic episodes could readily cause significant melting of surface snow and ice, erosion of valley networks, and formation of open and closed-basin lakes.

Transient Warming Periods to Explain Valley Networks and Lakes in a Background Cold and Icy Highlands Climate: Proponents of a "cold and icy highlands" climate have searched for mechanisms to produce one or more transient atmospheric heating episodes to elevate mean annual temperature sufficiently to cause top-down melting and runoff to explain the fluvial and lacustrine features. The contemporary occurrence of H_2SO_4 solution may be sufficient to explain the correlation without resorting to climate extremes.

Origin of Sulfate Deposits: Sulfates are widely distributed in soils on Mars and in a variety of concentrated settings that vary in space and time [24]. LN-EH volcanism is clearly associated with the stratigraphic distribution of sulfate occurrences [25]. The formation and deposition of H_2SO_4 and the resulting formation of solutions with a range of pH provides an important link between the sources of sulfur, liquid water, and aqueous environments conducive to sulfate precipitation. Volcanic deposition of sulfur and H_2SO_4 provides a mechanism for the primary deposition in Valles Marineris Interior Layered Deposits [22] and efficient leaching and concentration of sulfur in Meridiani Planum-type sulfate deposits [24].

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