

A COUPLED MODEL OF EPISODIC WARMING, OXIDATION AND GEOCHEMICAL TRANSITIONS ON EARLY MARS

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Introduction: Extensive geologic evidence indicates that 3–4 Ga, surface conditions on Mars were dramatically different, with multiple episodes of fluvial erosion, aqueous alteration and sediment deposition [1]. The most plausible explanation for this is greenhouse warming from a thicker early atmosphere, although the details continue to be debated [2,3]. Various analyses suggest that in total, between 10^4 and 10^7 years of warm conditions were required to erode observed valley networks, deposit sediment in craters and form weathering sequences [4–7]. In addition, abundant ancient exposures of unaltered igneous minerals such as olivine and the relative absence of surface carbonates on Mars indicate that large bodies of surface liquid water were likely not present over periods much longer than a few million years [8,9]. Today Mars' surface is highly oxidized, but its mantle appears more reduced than Earth's, and some Mars meteorites preserve non-zero sulfur mass-independent fractionation (MIF) signatures [10], suggesting anoxic atmospheric intervals. Rover observations at both Meridiani Planum and Gale Crater have also shown strong variability in mineral redox chemistry [11], with oxidizing surface conditions around the Noachian-Hesperian boundary ca. 3.5 Gya (Figure 1) suggested by the presence of concentrated hematite and manganese oxide [11–13]. The manganese deposits in particular appear to require the simultaneous presence of liquid water and strong oxidants such as O_2 , ultraviolet radiation or possibly chlorates [12,14].

Stochastic atmospheric evolution model. To investigate these diverse strands of geologic evidence, we have developed a stochastically forced atmospheric evolution and climate model (Fig. 1). We represent the release of reducing gases to the atmosphere due to volcanism [15], meteorite impacts [16,17] and crustal alteration [17,18] in a generalized way by randomly sampling from a power law distribution. Escape of hydrogen and oxygen to space via diffusion-limited and non-thermal escape processes is also included, as is oxidative weathering of the crust. Water loss to space is constrained via D/H data. Changes in surface temperature over time due to greenhouse warming by CO_2 and reducing gases are also taken into account. We find that the model produces rapid and repeated fluctuations between warmer, more reducing and

colder, more oxidizing conditions during Mars' early history (Fig. 1–2), with integrated warm periods sufficient to match geomorphic observations for mean rates of reducing gas input in the range of upper limits from volcanism, impacts and crustal processes.

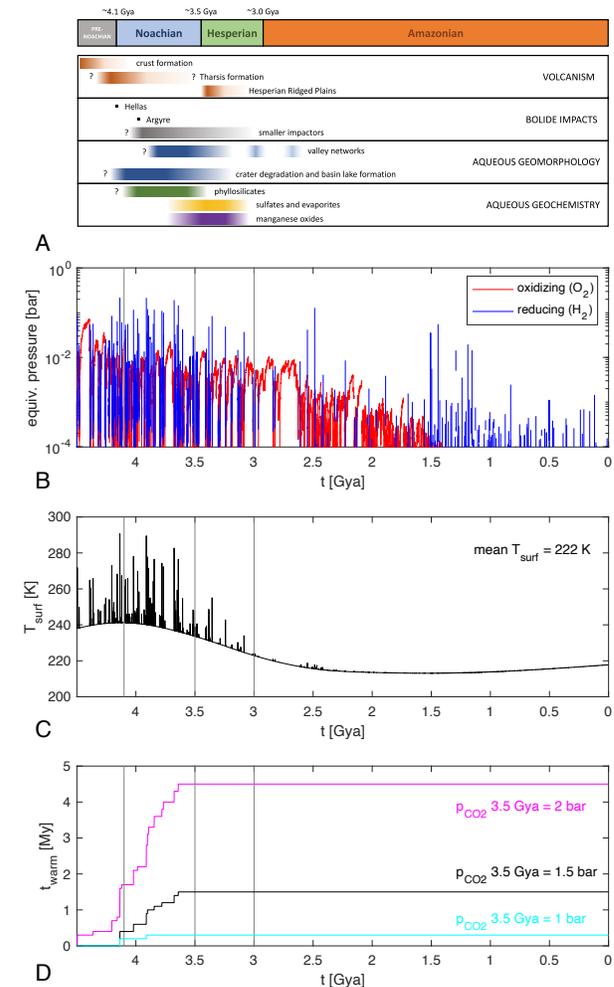


Figure 1: Observations vs. stochastic evolution model predictions over Mars' history. A) Timeline of major events on the martian surface from geologic observations. B) Changes in the net redox state of the atmosphere vs. time due to the competing effects of episodic release of reducing gases, atmospheric escape and surface weathering. C) Corresponding surface temperature evolution and D) cumulative integral of time spent with surface temperature >273 K.

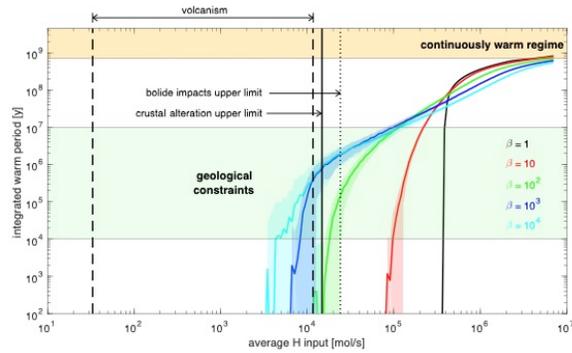


Figure 2: Integrated duration of warm intervals as a function of H fluxes into the martian atmosphere. Colored lines show the integrated warm period from 4.1 Gya onwards as a function of the average rate of reducing gas input to the atmosphere over the entire 4.5 Gy simulation interval. Colors indicate the assumed variability ratio (specifically, the maximum possible input rate in a 0.1 My interval relative to the time-varying mean value).

Sulfate, Hematite and Manganese Chemistry. We hypothesize that the increase in sulfate deposition from the Noachian into the Hesperian was also linked to changes the planet's redox state through time, for three reasons. First, oxidation of the upper martian mantle could potentially have moderately increased the fraction of S outgassed by the Hesperian [19]. Second, preservation of evaporite deposits against later remobilization would have only been favored toward the waning stages of the Noachian, from 3.5 Ga onward [20]. Third, sulfate minerals can be converted to reduced minerals like pyrite or pyrrhotite when dissolved under reducing conditions, particularly during high temperature post-impact conditions that would have occurred frequently during the early to mid-Noachian. Redox fluctuations can also help explain the appearance of sedimentary hematite and manganese oxide deposits. Our model predicts intervals of elevated atmospheric oxygen throughout the Noachian and Hesperian. In these intervals, upper layers of the regolith would slowly oxidize via dry weathering reactions, formation of oxychlorine species and adsorption of volatile species like H_2O_2 . During warming intervals, some of this regolith would have been transported as sediment to standing bodies of water. The extremely slow rate of reaction of $\text{H}_2(\text{aq})$ with oxidized species like $\text{Fe}^{3+}(\text{aq})$ [13,21] mean these sediments would have remained out of chemical equilibrium with the atmosphere, plausibly leading to the local formation within the sediments of oxidized minerals such as hematite over time. Warming of early Mars on 10^4 - 10^7 year timescales under O_2 -rich atmospheric conditions is not currently predicted in state-of-the-art climate models, but if it did occur, it could also have led to the formation of diagenetic hematite and manganese in Hesperian sediments. In

any case, shorter periods of warming (up to a few years) would still have occurred episodically when the atmosphere was O_2 -rich, via the mobilization of surface ice deposits by redox-neutral bolide impacts [22]. This would have provided additional routes for the formation, transport and deposition of highly oxidizing minerals, providing a plausible explanation for the Mn-rich fracture-filling materials in the Kimberley Formation at Gale Crater [12].

Conclusions and Outlook. An episodically fluctuating scenario for Mars' chemical and climate evolution appears consistent with several key features of the planet's geological record. It also predicts formation scenarios for various aqueous minerals that can be tested further by upcoming rover missions and eventually by investigation of returned samples.

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