Climate Transition and Atmospheric Redox evolution of Early Mars Revealed by Surface Iron Mobility

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Introduction: The modern-day Martian climate is characterized by extreme cold and aridity, with temperature varying according to latitude and water ice primarily accumulating in the polar regions. Conversely, geological records reveal strong aqueous activities on the surface of the early Mars, indicating a (episodically) warmer and wetter climate [1]. The modeling of early Martian climate suggests that temperature was predominantly elevation-dominant and water ice mainly accumulated in highlands and polar regions regardless of the mean annual temperature (MAT) [2]. There is significant climate mode change, but the timing and association of the climate and redox transitions remain inadequately understood [3, 4].

The coexistence of CO_2 and reducing gases (e.g., H_2) can generate a strong greenhouse effect (reducing greenhouse warming), which could have played a significant role in warming the early Martian climate [5] and diabatic cooling [6]. The intensity of greenhouse warming is closely tied to the concentration of reducing gases in the atmosphere. Therefore, the oxidation of the Martian atmosphere driven by the loss of reducing gases to space could theoretically result in the climate mode change.

Iron (Fe) mobility can be influenced by the redox, acidity, and temperature during the communication between atmosphere, hydrosphere, and lithosphere. We analyze the temporal and spatial distributions of Fe abundance on the surface of Mars to examine the effectiveness of reducing greenhouse and better understand the timing of and the relationships between the redox and climate transitions.

Evidence for a Chemically Reducing Atmosphere on Early Mars: Iron mobility is a good redox proxy because Fe is soluble and mobile as Fe(II) under anoxic conditions but insoluble and immobile as Fe(III) under oxidizing conditions. We identified several ancient chemical weathering sequences rich in clay minerals formed under warm climate and found strong Fe loss in these paleosols [5]. The intense top-down leaching of Fe suggests the high Fe mobility as Fe(II) under a warm climate on early Mars. The trend is the direct geological evidence for a reducing greenhouse on early Mars.

Widespread Fe Depletion at the Surface of Noachian-aged Terrains: The Mars Odyssey Gamma-ray spectroscopical (GRS) data reveal that surface Fe abundance in the Noachian terrains is generally low compared to the global surface average Fe abundance [7]. Planetary crustal evolution cannot explain the secular variation in Fe abundance, as there is no correlation with other elements that are expected to vary with Fe during normal igneous processes (such as the correlation between Fe and Si) [8]. Therefore, the low surface Fe abundance was highly likely caused leaching.

Fe can be leached downwards in chemical weathering sequences rich in clay minerals formed under temperatures above 0°C. However, there is no clear correlation between distributions of the Fe depletion zones identified through GRS and paleosols rich in clay minerals detected via CRISM [4]. The decoupling is possibly related to lack of areal coverage of CRISM data compared to the global coverage and larger footprint of GRS data. But it is more likely that the Fe depletion was caused by leaching under low-temperature conditions (<=0°C) without the formation of clay minerals.

Fe Depletion Promoted by Low-temperature Processes? We examine the spatiotemporal distribution of surface Fe abundance in the ancient Martian terrains, revealing that Fe abundance decreases with elevation in the older Noachian terrains but with latitude in the younger Noachian terrains (Fig. 1). We know that higher elevations or higher latitude experienced colder temperatures. The negative correlation between surface Fe abundance with elevation or latitude in the Noachian terrains, therefore, suggests that climate may have influenced the mobility of Fe. Low-temperature conditions in the high-elevation/latitude regions might have facilitated Fe depletion during the Noachian period.

Efficient Fe leaching under cooler conditions might have been related to elevated chemical weathering rate at cryogenic temperatures [9]. This is because freezing can increase the acidity of residual water, which counterintuitively accelerates the kinetics of chemical weathering to alter minerals at subfreezing temperatures. In addition to chemical weathering rate, the amount of water available and the duration of water-rock interaction can influence alteration degree. Freezing could create a closed system, which can sustain water-rock interaction for a longer time. Cryosauction of cold traps in high-elevation/latitude regions can attract more water molecule, which can be available for chemical weathering. All these three factors (kinetics, time and water availability) can promote more Fe release in a certain regions with low temperatures.

The release of Fe from rocks alone is insufficient to account for Fe depletion; top-down leaching driven by the penetration of liquid water is also required. In addition to freezing, the infiltration of meltwater during the thawing of ice is essential. Therefore, we propose that freeze-thaw cycles are crucial processes that promote Fe depletion on the surfaces of ancient terrains. In cold seasons, icy weathering can release Fe and form Fe-bearing salt. If ice-blocked pores can become interconnected owing of ice thaw during warm seasons, Fe-bearing salts would be dissolved by meltwater. Due to the infiltration of meltwater containing Fe(II), seasonal freeze-thaw can cause Fe leaching and therefore surface Fe depletion.

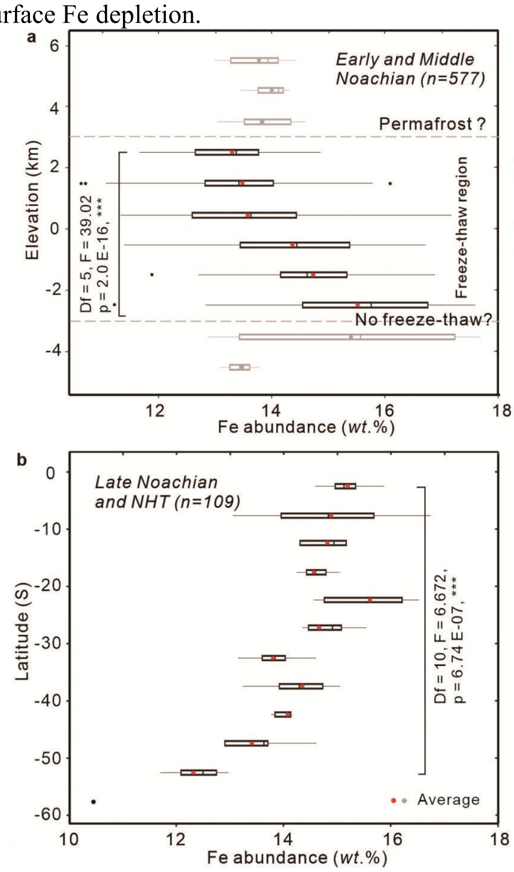

Figure 1. The spatial evolution of Fe abundance at the surface of ancient Martian terrains. a The gradual decrease in Fe abundance with increasing elevation (-3.0 km - +3.0 km) at the surface of the Early and Middle Noachian terrains. **b** The gradual decrease in Fe abundance with latitude at the surface of the Late Noachian terrains and the Noachian-Hesperian transition (NHT) terrains in the southern hemisphere.

Further analysis shows that the correlation coefficient (r) between elevation and Fe abundance decreases gradually over time during the Noachian period (Fig. 2b). In contrast, the correlation between Fe abundance and latitude becomes stronger over time from the Early Noachian to the Noachian-Hesperian transition epoch (Fig. 2b). If Fe depletion degree could be an good proxy for temperature, the patterns suggest that Mars has experienced a gradual climate mode transition from an elevation-dominant temperature to a latitude-dominant temperature distribution during the Noachian period.

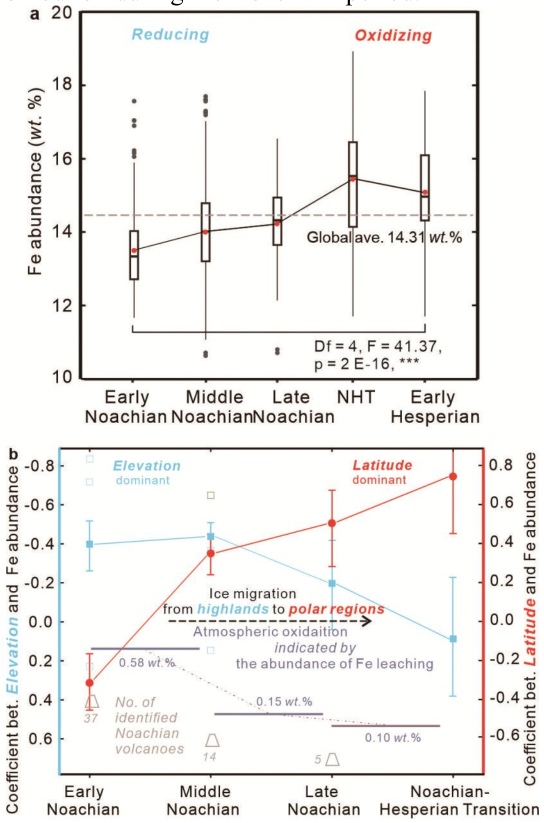

Figure 2. The temporal evolution of surface Fe abundance and atmospheric redox on early Mars. a The gradual increase in surface Fe abundance from the Early Noachian to the NHT terrains. **b** The gradual decorrelation between Fe abundance and elevation (solid squares) but a gradual increasing correlation between Fe abundance and latitude (solid cycles) on Mars over time. The climate transition is coupled with the gradual oxidation of the Martian atmosphere indicated by the Fe leaching intensity.

Atmospheric Oxidation on Noachian Mars: The surface average Fe abundance in the Early, Middle, and Late Noachian terrains are all below the global surface average but increases gradually (Fig. 2a). The Fe leaching intensity in each epoch increases during the Noachian period (Fig. 2b). The Fe abundance at the surface of the NHT terrains is remarkably high (~15.4 wt.%), which is ~1.2 wt.% higher than that of the Late Noachian terrains and ~1.1 wt.% higher than the global surface average (Fig. 2a).

The observation of less Fe at the surface of older Noachian Martian terrains is consistent with irreversible and progressive Fe leaching under a reducing atmosphere. Fe has been intensely leached during the Early Noachian epoch, suggesting its atmosphere was largely reducing. Fe leaching intensity decreases with time (Fig. 2b), suggesting that there is a decrease in the amount of atmospheric H_2 over time during the Noachian period. The Fe abundance jumps from the Late Noachian to NHT suggests a significant atmospheric redox shift from reducing to oxidizing (Fig. 2a). These observations suggest a global and broad trend of atmospheric oxidation.

Atmospheric Oxidation Led to Mars becoming Cold and Bipolar in its Early history: Recent result suggest that the greenhouse warming effect could play an important role in diabatic cooling [6]. Under the strong greenhouse, the surface is mainly heated by the atmosphere, which is controlled by advection and convection over the lowlands, resulting in the formation of cold traps associated with topography. Conversely, under the weak greenhouse, the surface is primarily heated by insolation and thus surface temperature decorrelates with elevation. In this case, the observed gradual decrease in diabatic cooling could be attributed to the gradual weakening of the atmospheric greenhouse effect.

Figure 2b shows that, from the Early to Late Noachian epoch, Fe leaching intensity decreases, covarying with coefficients of Fe abundance with latitude and elevation. The atmospheric oxidation is coupled with the Martian climate mode shift from elevation-dominant to latitude-dominant temperature distribution during the Noachian period. In conclusion, the surface Fe distribution suggests that atmospheric oxidation has contributed to not only climate cooling but also ice migration from southern highlands to polar regions on Noachian Mars.

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