Unlocking Early Mars Redox Conditions: Evidence from Planetary-Scale Iron Oxide Deposits

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Introduction: While the composition of Mars' present-day atmosphere is well characterized through rover and orbiter missions, the composition and redox conditions of the ancient atmosphere remain poorly constrained and represent an active area of research [e.g. 1]. Early Mars likely experienced markedly different surface conditions possible with a thicker atmosphere, an atmosphere capable of supporting liquid water, along with distinctive geochemistry driven by more prevalent volcanism [2]. The early Martian atmosphere is hypothesized to have resembled that of ancient Earth, being rich in nitrogen, CO_2 , CH_4 and water vapor, with reactive species like oxygen present only in trace amounts—perhaps sufficient to form the small manganese oxide deposits observed at Gale Crater by the Curiosity rover [3,4].

These manganese deposits offer valuable insights into early Martian geochemical conditions [5], yet they are overshadowed by other more abundant oxidized phases across the planet. Mars' characteristic red hue results from extensive dust coverage containing up to ~30 wt.% ferrihydrite, an iron hydroxide mineral [6]. Ferrihydrite serves as a crucial recorder of aqueous and oxidizing surface conditions, making it an important proxy for reconstructing ancient geochemical and atmospheric environments.

The thickness of this ferrihydrite-rich dust coating varies widely across Mars. Coatings as thin as hundreds of microns create optically thick layers that obscure darker subsurface materials [12], as observed by rovers and landers. However, dust distribution shows remarkable regional variability: morphometric studies indicated dust layers 20-25 meters thick in the equatorial Arabia Terra region [9], radar analysis revealed 0.1 – 2 meter coverage in the low thermal inertia terrains of Elysium and Tharsis [8], and high-resolution imaging confirmed meter-thick dust accumulations in Tharsis [13].

While atmospheric transport and topographic dust trapping (investigated through GCMs) may explain dust settling patterns [14], they cannot explain the geological process that produced the dust in the first place. The enigmatic equatorial Medusa Fossae Formation (MFF) has been suggested as a potential primary dust source—complete erosion of this ~3.5 Ga unit could produce a global dust layer 2-12 meters thick [7]. Since the MFF formed during Mars' more habitable period, it may preserve critical information about the ancient atmosphere on Mars.

In this study we quantify the water and oxygen requirements for producing the iron hydroxide component in the dust and evaluate potential redox pathways responsible for these highly oxidized materials. In the conference we will present a new conceptual model describing the geological evolution of Martian surface based on its redox history.

Estimation of O_2 and H_2O in dust: In Table 1 we provide a simple yet insightful approximation of the primary compounds in the Martian dust. Our calculation of Mars' global dust inventory reveals a total mass of 5.0×10^{18} kg. The largest contribution comes from dust associated with the Medusae Fossae Formation (3.5×10^{18} kg), followed by regional deposits in Arabia Terra (5.3×10^{17} kg) and polar terrains (6.0×10^{17} kg). Low thermal inertia regions contribute an additional 1.8×10^{16} to 3.7×10^{17} kg of dust. Assuming ferrihydrite content of 30 wt% and hydration levels of 20 wt% H_2O in ferrihydrite across these dust reservoirs, the total water inventory is equivalent to a global layer thickness of approximately 2 meters if uniformly redistributed across the

Table 1. Estimation of total water and oxygen sequestered in Martian dust

Unit	Dust Thickness (m)	Volume (m^3)	Mass (kg)$^{\alpha}$	Ferrihydrite amount in dust (wt. %)$^{\beta}$	H_2O in ferrihydrite (wt. %)	Water GEL (m)	O_2 Pressure Equivalent (mbar)$^{\gamma}$	References
Medusa Fossae Formation	10^{*}	1.4×10^{15}	3.5×10^{18}	30	20	1.5	54	[7]
Low thermal inertia regions	0.1–2	5.3×10^{12}–1.1×10^{14}	1.8×10^{16} – 3.7×10^{17}	30	20	<0.2	5	[8]
Arabia Terra	20	2.1×10^{14}	5.3×10^{17}	30	20	0.2	8	[9]
Polar terrains	1.7^{*}	2.4×10^{14}	6.0×10^{17}	30	20	0.25	9	[10][11]
Total			5.0×10^{18}			~2	~80	

*If dispersed globally. $^{\alpha}$Assuming density of 2500 kg/m^3. $^{\beta}$Based on orbital and laboratory spectral analysis [6]. $^{\gamma}$Assuming ferrihydrite stoichiometry of Fe_5O_8H n H_2O.

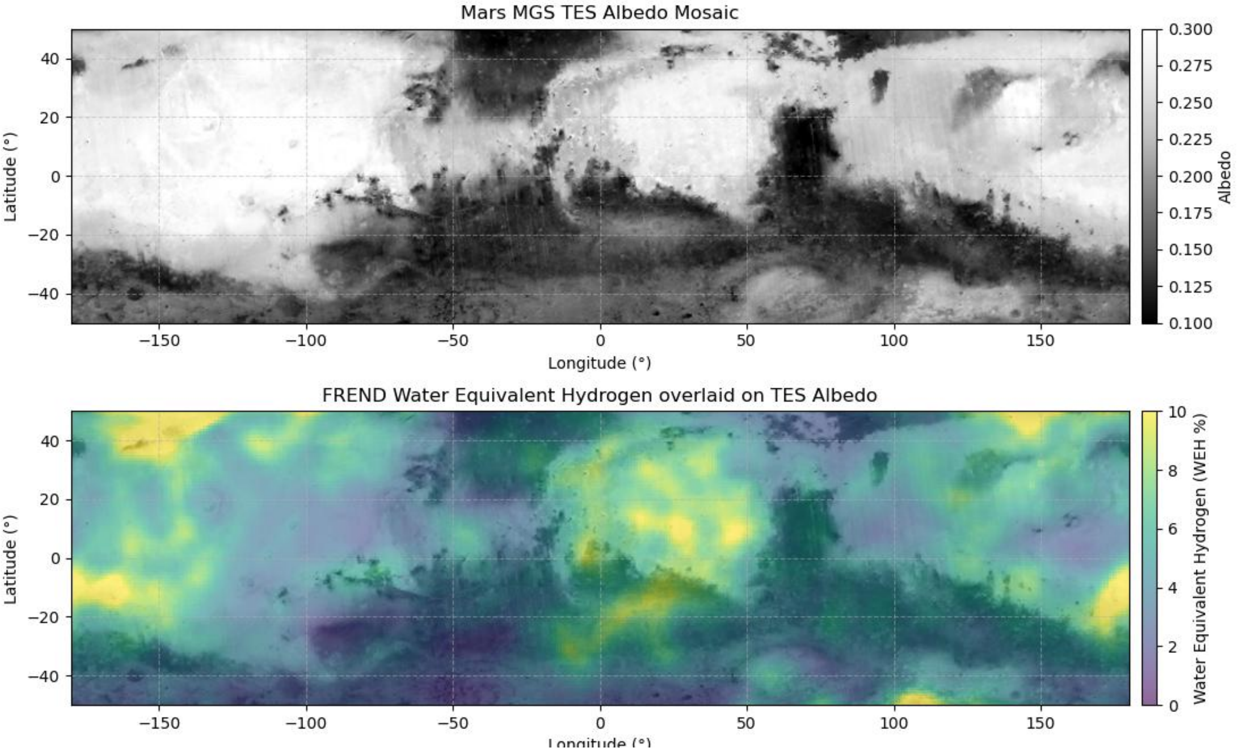

Figure 2. Distribution of dust and subsurface hydrogen on Mars. Top panel shows TES albedo data indicating dusty regions; bottom panel displays FREND neutron spectrometer data revealing subsurface hydrogen distribution. The correlation between high-albedo dust deposits and elevated hydrogen signals in equatorial regions suggests ferrihydrite-bearing dust and indurated duststone may be the primary water-bearing phases. FREND's detection of this hydration signal at ~1-meter depth provides evidence that these dust deposits are thick accumulations rather than thin surface veneers.

planet's surface. In addition, the ferrihydrite-rich dust may contain an equivalent of ~80 mbar oxygen atmosphere, calculated from the stoichiometric oxygen content in ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$) distributed across Mars' total dust/duststone inventory. This is several orders of magnitude larger than what is predicted from photochemical models [15]. We note that these estimates may provide minimum values because we did not include the rhythmite duststone deposits [16] that are also obscured by thick mantling of dust in Arabia Terra.

Hydration of Martian dusty terrains: Mars Odyssey's Gamma Ray Spectrometer (GRS) first revealed in 2001 that equatorial regions such as Arabia Terra exhibit elevated hydrogen abundance [17], potentially indicating the presence of hydrated minerals [18]. However, hydrated minerals subsequently detected by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) and Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité (OMEGA) spectrometers do not spatially correlate with the GRS hydrogen abundance maps [19]. Instead, these hydrogen detections correlate more strongly with Thermal Emission Spectrometer (TES) albedo maps, which are proxies for surface dust distribution [20]. We show this point here with the recently made public Fine Resolution Epithermal Neutron Detector on the Trace Gas Orbiter (FREND-TGO) Water Equivalent Hydrogen (WEH) maps [17] (Fig. 1). The WEH percentage equaling ~10% in Arabia generally agrees with our predicted H_2O amount in the dust resulting from ferrihydrite (~6%). Other minor hydrated phases such as sulfates may also be present in the dust particles and could carry the remaining hydration component.

Nature of the oxidant: The amount of dust and its components presented in the previous section poses a significant question regarding the nature of the oxidizing agent on early Mars. UV radiation has been proposed to directly oxidize magnetite in dry conditions into other ferric iron oxides such as hematite [21], but this mechanism cannot explain the existence of hydrated phases such as ferrihydrite. The dry photo-oxidation hypothesis has also been challenged by laboratory experiments where UV irradiation of magnetite particles showed no perceptible oxidation when measured by saturation magnetization [22]. Photolytic breakdown of water molecules by UV radiation to produce OH radicals or iron oxidation in aqueous phase by UV [23] presents a plausible scenario for Mars, but such a model would suggest that ferrihydrite formation should be restricted to areas where rocks were submerged under standing water bodies capable of precipitating iron hydroxide minerals. An alternative explanation involves thin films of water, but if so, erosion should be able to remove them and expose a mafic, less altered substrate, which is not observed at MFF.

Furthermore, the global distribution of duststones on Mars poses a difficulty for this water oxidation model. MFF is a high standing formation several hundred meters in height. Such emplacement suggests that oxidation occurred through processes involving atmospheric processes and precipitation, possibly, in the form of rain rather than standing bodies of water, favoring an ubiquitous atmospheric oxidant rather than localized aqueous conditions. MFF could alternatively represent mechanical accumulation of aeolian sediments rather than a site of aqueous chemical alteration processes but this idea is not supported by atmospheric circulation models [14], which predict dust accumulation over high topography rather than in low-lying regions like Amazonis or Elysium where the MFF is actually observed. In conclusion, the pervasive nature of ferrihydrite-rich dust across diverse geological settings may imply that the oxidizing agent was ubiquitous and capable of interacting with iron-rich surface materials during episodic wetting events.

***Volcanism*.** Volcanism and atmospheric photolysis may have produced free oxygen radicals sufficient to drive this oxidation. It was proposed [1] that such processes could lead to a transitional oxidizing atmosphere over time, switching from early reducing to later oxidizing conditions. However, quantitative modeling of whether photolytic oxygen production can account for the observed volume of oxidized dust deposits—potentially representing meters of global equivalent thickness—remains an open question. Further research integrating atmospheric photochemical models with the substantial mass balance constraints imposed by Mars' dust inventory is needed to resolve this issue.

Hydrogen peroxide (H_2O_2). On early Earth, hydrogen peroxide was hypothesized as an important photochemically produced atmospheric oxidizer [24]. Furthermore, it was shown that early Mars surface oxygen sink required H_2O_2, which could have oxidized ferrous iron [15]. Laboratory experiments have demonstrated that H_2O_2 is indeed a potent oxidant that can efficiently oxidize Fe^{2+}-bearing solutions [25,26], including green rust. In agreement with previous studies [25], our laboratory analysis (not published) indicates that oxidation of green rust by H_2O_2 leads to the formation of feroxyhyte, a distinct iron oxide mineral phase that is not present on Mars. Exposure of the green rust solution to air led to the precipitation of lepidocrocite, another phase that is not the dominant iron hydroxide mineral in the Martian dust. This result illustrates how different environmental conditions—including pH, temperature, and oxidizing potential—control which iron oxide phases form, providing unique formation pathways that can inform our understanding of ancient oxidation processes on Mars.

Other oxidants. Various alternative oxidants have been proposed for Mars, including bromine compounds for manganese oxide formation [27]. While such oxidants might explain localized deposits like those observed at Gale Crater, bromate and similar species (such as chlorate, perchlorate, or oxichlorine) are found to <1 wt. % trace levels on Mars and compared to ~30 wt. % ferrihydrite observed in Martian regolith and so thus may not be present on Mars in sufficient quantities to oxidize the estimated 10^{18} kg of Martian dust.

Life. Microbial life on Earth is fundamentally based on redox processes involving electron donors and acceptors. Some primitive microorganisms, such as iron-oxidizing bacteria (e.g., *Gallionella* and *Leptothrix* species), use ferrous iron as an electron donor during respiration, leading to Fe^{2+} oxidation and formation of ferrihydrite and other iron oxides [28]. Such biogeochemical processes can be observed in various modern environments on Earth, and we have identified possible iron-oxidizing microbial biosignatures in ferrihydrite samples from lava caves in the Azores.

Photosynthetic organisms can also contribute to iron oxidation by producing oxygen as a metabolic byproduct, which then serves as a powerful oxidant for iron-bearing surface materials. Earth's banded iron formations (BIFs) record the rise in atmospheric oxygen from cyanobacterial photosynthesis, as these organisms could produce sustained oxygen levels and continuously replenish the atmosphere. Oxygen is a particularly effective oxidant that can explain large-scale oxidation events due to its high redox potential and abundance.

However, oxygenic photosynthesis likely evolved later than iron respiration on early Earth and represents complex cellular machinery that required significant evolutionary time to develop. It remains unclear whether putative Martian life could have evolved such sophisticated metabolic pathways within the timeframe of early Mars habitability. Furthermore, any biotic explanation for Martian surface oxidation remains speculative without definitive evidence that life ever existed on Mars.

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