

SUBSURFACE FORMATION OF OXIDANTS ON MARS AND IMPLICATIONS FOR THE PRESERVATION OF ORGANIC BIOSIGNATURES

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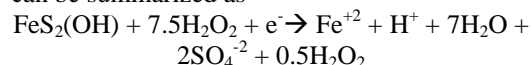
Introduction: Global and *in situ* mineralogical mapping of the Martian surface has revealed late Noachian to early Hesperian Ca-, Mg-, and Fe-sulfates deposits with imbedded hematite spherules, which formed as the result of episodic inundations by surface water [1]. The same suit of minerals has been identified in massive layered deposits within Valles Marineris, and in Margaritifer Terra [2] suggesting a common origin associated to aqueous alteration over a relatively large portion of the Martian surface.

The presence of jarosite and the absence of carbonates, indicates that the ambient waters where the deposits formed had a low pH. The oxidation state of iron, mostly present as Fe³⁺, is evidence of highly oxidizing conditions [3]. The estimated thickness of the deposits (≥ 1 km) [4] also requires a large source of sulfur. We propose a geochemical model for the aqueous formation of oxidants and sulfate-rich groundwater in the subsurface of Mars. The model reconciles the inferred geochemistry of ancient aqueous solutions on Mars, with the observed mineralogy in Meridinae Planum, Margaritifer Terra and Valles Marineris and with current hydrological models. We also discuss its implications for the preservation of organic compounds.

Model for the aqueous formation of oxidants on Mars: Using aqueous equilibrium computations, we have modeled the interaction of pyrite with anoxic, oxidizing, and circumneutral water for different water/rock ratios (Figure 1). Upon contact of water and pyrite, H₂O₂ is produced instantaneously [5]. The concentration of H₂O₂ is lower at high W/R ratios but increases exponentially as the amount of water decreases. The pH decreases slightly at high W/R ratios, but the solution becomes very acidic and reaches a minimum pH of 3.4 at very low W/R. The redox potential reaches maximum values between 600-1100 mV at low W/R. Molecular oxygen is also produced due to the spontaneous decomposition of H₂O₂ to water and oxygen gas.

The presence of H₂O₂ and O₂ induces the oxidation of pyrite to sulfate (Figure 1). The amount of H₂O₂ produced depends on the surface area of the pyrite, and the presence and number of Fe³⁺ reactive sites on the pyrite surface. As H₂O₂ is generated, the number of

reactive sites diminishes due to the reduction of the Fe³⁺ to Fe²⁺. Reactivation of the Fe³⁺ occurs through the oxidation of the pyrite surface by H₂O₂ and O₂. The overall autocatalytic reaction can be summarized as



where H₂O₂ acts both as a reactant and a product. Therefore the pyrite-induced H₂O₂ formation will occur until all the pyrite has been completely oxidized, or the liquid water has been exhausted. The reaction is independent of light as an energy source [5], and yields relatively large concentrations of H₂O₂ ($>10^{-3}$ mol L⁻¹) at low W/R ratios (Figure 1), several orders of magnitude larger than those derived from the diffusion of atmospheric oxidants [6]. Evaporation and/or sublimation of pyrite-derived H₂O₂-H₂O solutions increases the concentration of H₂O₂, with a resultant decrease of pH (<4), an increase of the oxidative potential (>900mV), and the precipitation of Ca- and Fe- sulfates. Goethite precipitates almost instantaneously at low H₂O₂ concentrations, but becomes unstable as evaporation/sublimation proceeds (Figure 1).

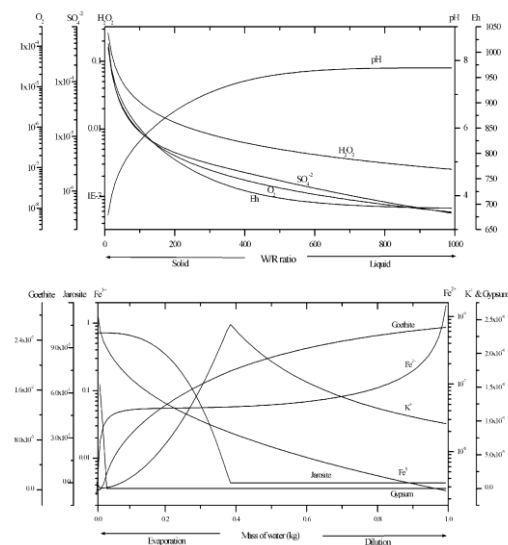


Figure 1. *Top:* Aqueous formation of oxidants through the interaction of anoxic water and pyrite for different W/R ratios. *Bottom:* Evaporation/sublimation of the oxidant-rich groundwater results in Ca- and Fe-sulfates and Fe-oxides precipitation. Dissolved and solid species in mol(kgH₂O)⁻¹; Eh in mV.

The subsurface formation of oxidants on Mars: Upon contact of groundwater with iron-sulfides, relatively high concentrations of oxidants would have formed in the Martian crust. Once exposed to atmospheric conditions, the concentration of H_2O_2 in solution could have risen through photochemical reactions and freezing, evaporation and/or sublimation of water. As water was removed from the system, Mg-, Ca- and Fe- sulfates and iron-oxides precipitated. This model is independent of photochemical reactions in the atmosphere and consistent with the formation of massive layered sulfate deposits in relatively localized areas such as Meridiani Planum, despite the low levels of atmospheric oxidants and the prevailing arid conditions. The large amounts of sulfur could have been stored in Massive Volcanogenic Sulfide deposits (MVS), similar to those found on Earth, which would have been emplaced within the crust during the formation of Tharsis. The geographical distribution of the sulfates and iron oxides deposits and their thickness, coupled to their proximity to the Tharsis volcanic province supports this interpretation.

Implications for the preservation of organic compounds on Mars: The pyrite-induced formation of H_2O_2 could have been responsible for the intense oxidation of large portions of the crust and the Martian surface, including any accumulated organic molecules. The depth of the oxidation front would be determined by the thickness of the pyrite deposits, the porosity of the host rock, and the diffusivity of the H_2O_2 - H_2O solution in the regolith. Some of the VMS deposits on Earth have thicknesses of several hundred meters. Lateral and vertical diffusion of H_2O_2 - H_2O solutions could have driven the oxidation front close to the surface and deep into the regolith through extended regions of the Martian crust (Figure 2). Therefore, large portions of the upper crust may be depleted in organics as molecular biomarkers are oxidized by groundwater-rock interactions. This conclusion contradicts the traditional “follow-the-water” paradigm for the search of evidence for life on Mars. The oxidation potential of water was greatly enhanced due to water-rock interactions within the crust, which may have effectively erased any organic biomarkers associated with aqueous processes, down to depths inaccessible with present day technological capabilities. Conversely, the ice-rich permafrost of the Southern Highlands may be the best place for the search of biomolecular traces of life on Mars [9]. These terrains still hold a remnant magnetization from the primeval Martian magnetic field, and represent very ancient

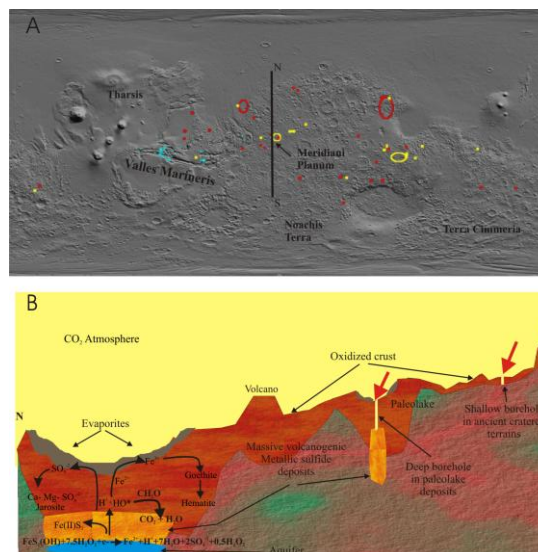


Figure 2. **A.** Global distribution of hydrated minerals on Mars. data from the OMEGA instrument onboard Mars Express superimposed on a MOLA topography map. Red dots: phyllosilicates; blue dots: sulfates; yellow dots: other hydrated minerals. Solid line: North-South transect from the sulfate deposits in Meridiani Planum to the ancient cratered and magnetized terrains in Noachis Terra. Modified from [8] **B.** Cross section of the Martian crust along the N-S transect in A, with possible target environments for the search of extinct life (red arrows). The pyrite-induced H_2O_2 formation may have oxidized the surface and subsurface of the Martian crust down to depth of tens to hundreds of meters. In the Southern Highlands, where liquid water was likely present at depth and scarcely in the surface, the oxidation layer may be only a few meters deep, due to the diffusion of atmospheric oxidants into the crust.

environments where significant aqueous oxidation never took place. These terrains could have been the niches for a putative biosphere composed of psychrophilic microorganisms in the Martian past, similar to those that inhabit Arctic and Antarctic permafrost [9]. Here, the prevailing low temperatures, the limited aqueous chemistry and the low diffusivity of atmospheric oxidants in the permafrost-rich regions, may have favored the preservation of organic biomarkers that may be reachable at depths of only a few meters.

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