

Redox conditions and alteration pathways on early Mars

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Abstract

Laboratory experiments under CO₂ atmospheres show that strong oxidants would have inhibited the formation of Fe/Mg-smectites on early Mars.

1. Introduction: oxidation on Mars

Sulfates and Fe-oxides detected by orbital and in situ missions [e.g., 1,2] indicate that oxidizing conditions existed on early Mars, at least locally and/or episodically. In the context of rock alteration and weathering, redox conditions are especially critical for the behavior of iron, which is soluble in his divalent state but insoluble in his trivalent state. Abiotic oxidation of ferrous iron under a primitive, CO₂-rich atmosphere can take place through different mechanisms: (1) alteration of Fe²⁺-bearing minerals into Fe³⁺-bearing products by reduction of H₂O during rock-water interactions (e.g., serpentinization); (2) direct photo-oxidation of aqueous Fe²⁺ by ultraviolet irradiation; or (3) chemical oxidation by reaction between Fe²⁺-bearing minerals or aqueous Fe²⁺ and an oxidant produced by the UV photolysis of H₂O (e.g., O₂, H₂O₂). All these mechanisms involve directly or indirectly the reduction of H₂O to H₂, and therefore require H₂ loss into space to prevent back reactions and obtain net oxidation at a global scale.

Among these three mechanisms, oxidation by photolysis-derived oxidants is the most efficient in low-temperature, surficial conditions, because: (1) it is very rapid and thus overcomes gel/mineral precipitation [3] and (2) it has the potential to create oxidizing conditions in environments protected from direct UV exposure, through diffusion or percolation.

2. Effects of redox conditions on alteration pathways

In the past years, we have reported in several publications [4-7] the results of laboratory experiments studying the alteration of various primary

materials in conditions relevant for early Mars (Table 1). Among other parameters, these experiments tested the influence of highly-oxidizing (H₂O₂-bearing) vs poorly-oxidizing (H₂O₂-free) conditions on the secondary mineralogy of early Mars.

2.1 Sulfides and silicate+sulfide mixtures

Results from [4-6] show that the alteration of Fe-sulfides (pyrrhotite) and silicate+sulfide mixtures under H₂O₂-bearing and H₂O₂-free conditions produce assemblages similar in nature (elemental sulfur, sulfates and Fe-oxides). However, in silicate+sulfide mixtures, the relative abundances of Mg- and Ca-sulfates were controlled by the composition of the silicate component, demonstrating that the acidification induced by the alteration of pyrrhotite promoted the alteration of silicates in both conditions. In addition, H₂O₂ do favor the formation of sulfates (especially jarosite) at the expense of elemental sulfur.

2.2 Primary silicates

Here we present new analyses of samples of olivine and orthopyroxene (“O11” and “OPx” in [6]) weathered for 4 years under CO₂. Although these samples were much less modified than the corresponding mixtures with pyrrhotite, a careful study of their near-infrared spectra reveals absorption bands at 2.31 and 2.39 μm associated with Mg-rich smectite clays (Fig. 1). In the case of olivine, these bands are present for the sample weathered in poorly-oxidizing conditions (i.e., without H₂O₂, named “H₂O” in Fig. 1), while they are absent for the initial sample and for the sample weathered with H₂O₂. In the case of orthopyroxene, the initial sample displays shallow bands at these positions due to pre-experiment alteration. However, the band depths clearly increased for the sample weathered without H₂O₂, whereas they remained stable for the one weathered with H₂O₂.

The formation of smectite clays (or precursors) is further confirmed in the O11-H₂O and OPx-H₂O samples by the observation by SEM of “filaments”

similar in size and morphology to those observed in [7]. These filaments are absent from the initial samples and from the samples weathered with H₂O₂.

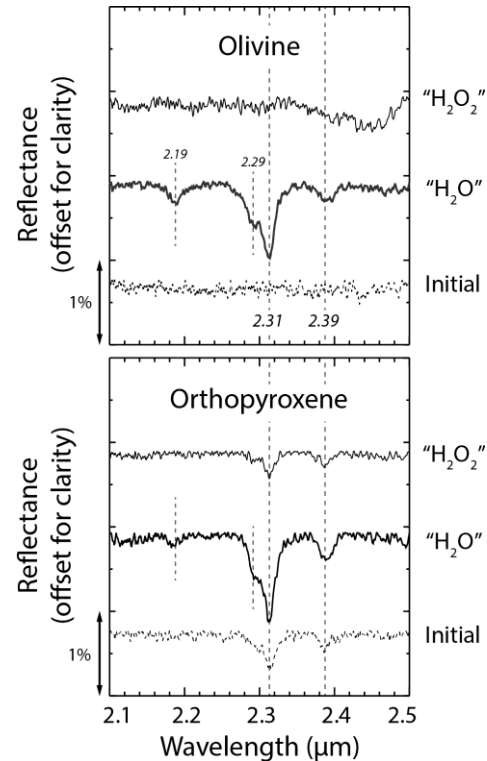
3. Implications

Our experimental results show that highly-oxidizing conditions on early Mars (e.g., due to H₂O₂ deposition on the surface) would have strongly inhibited the formation of Fe/Mg-smectites from alteration of igneous ferromagnesian minerals. This is due to the fact that purely Mg-smectites are not stable at the relatively low pH associated with a CO₂ atmosphere, and thus that Fe²⁺ is required, at least transiently, to form the smectites [7]. In turn, this suggests that volcanic release of reduced gases was high enough to overcome photochemical production of oxidants and thus prevent effective oxidation of the surface during the Noachian era. Nonetheless, strong oxidants were found to enhance the production of sulfates – especially jarosite – during alteration of Fe-sulfides and silicate+sulfide mixtures, which suggests that their influence on the secondary mineralogy may have progressively increased later in Mars history.

Table 1: Summary of primary materials studied in our alteration experiments under simulated early Mars conditions. Po = pyrrhotite; L/R = liquid-to-rock ratio.

Primary materials	Magnetite α-Fe Pyrrhotite	Olivine OPx CPx Ol+Po OPx+Po CPx+Po	Olivine
Atmospheres and oxidants	CO ₂ CO ₂ +H ₂ O ₂	CO ₂ CO ₂ +H ₂ O ₂	CO ₂ CO ₂ +H ₂ O ₂ Air Air+H ₂ O ₂
Experimental parameters	T=15-20°C P=0.8 bar Low L/R	T=15-20°C P=0.8 bar Low L/R	T=45°C P=1.5 bar L/R=10
Duration	1.4 year	4 years	3 months
References	[3,4]	[6], this study	[7]

Figure 1: Continuum-removed spectra of olivine and orthopyroxene samples before and after alteration under CO₂ atmospheres. Absorptions bands at 2.31 and 2.39 μm are typical of Mg-rich smectites.



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