

# Redox conditions and alteration pathways on early Mars

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## Abstract

Laboratory experiments under CO<sub>2</sub> 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, CO<sub>2</sub>-rich atmosphere can take place through different mechanisms: (1) alteration of Fe<sup>2+</sup>-bearing minerals into Fe<sup>3+</sup>-bearing products by reduction of H<sub>2</sub>O during rock-water interactions (e.g., serpentinization); (2) direct photo-oxidation of aqueous Fe<sup>2+</sup> by ultraviolet irradiation; or (3) chemical oxidation by reaction between Fe<sup>2+</sup>-bearing minerals or aqueous Fe<sup>2+</sup> and an oxidant produced by the UV photolysis of H<sub>2</sub>O (e.g., O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>). All these mechanisms involve directly or indirectly the reduction of H<sub>2</sub>O to H<sub>2</sub>, and therefore require H<sub>2</sub> 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 (H<sub>2</sub>O<sub>2</sub>-bearing) vs poorly-oxidizing (H<sub>2</sub>O<sub>2</sub>-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 H<sub>2</sub>O<sub>2</sub>-bearing and H<sub>2</sub>O<sub>2</sub>-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, H<sub>2</sub>O<sub>2</sub> 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 CO<sub>2</sub>. 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 H<sub>2</sub>O<sub>2</sub>, named “H<sub>2</sub>O” in Fig. 1), while they are absent for the initial sample and for the sample weathered with H<sub>2</sub>O<sub>2</sub>. 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 H<sub>2</sub>O<sub>2</sub>, whereas they remained stable for the one weathered with H<sub>2</sub>O<sub>2</sub>.

The formation of smectite clays (or precursors) is further confirmed in the O11-H<sub>2</sub>O and OPx-H<sub>2</sub>O 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 H<sub>2</sub>O<sub>2</sub>.

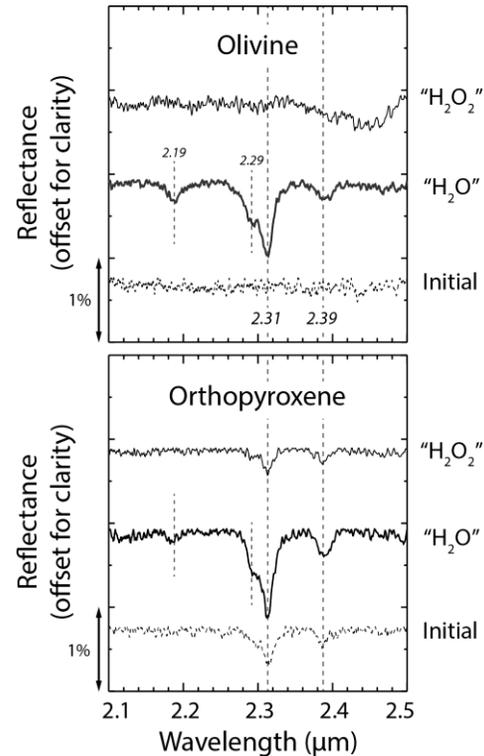
### 3. Implications

Our experimental results show that highly-oxidizing conditions on early Mars (e.g., due to H<sub>2</sub>O<sub>2</sub> 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 CO<sub>2</sub> atmosphere, and thus that Fe<sup>2+</sup> 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 <sub>2</sub> CO <sub>2</sub> +H <sub>2</sub> O <sub>2</sub>	CO <sub>2</sub> CO <sub>2</sub> +H <sub>2</sub> O <sub>2</sub>	CO <sub>2</sub> CO <sub>2</sub> +H <sub>2</sub> O <sub>2</sub> Air Air+H <sub>2</sub> O <sub>2</sub>
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 CO<sub>2</sub> atmospheres. Absorptions bands at 2.31 and 2.39 μm are typical of Mg-rich smectites.



### References

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