

## ROLE OF SULFIDE-WEATHERING IN THE FORMATION OF SULFATES OR CARBONATES ON MARS.

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**Introduction:** Spaceborne imaging spectrometers have discovered hydrated sulfates in different regions of Mars, including Valles Marineris and Terra Meridiani [1,2]. In this last region, the Mars Exploration Rover (MER) Opportunity has observed Ca-, Mg-sulfates and jarosite [3,4]. That's why the MER team nicknamed the superficial rock units "Burns formation" to honor Roger Burns, who predicted that ferric sulfates should occur on Mars [5]. However, the model suggested by R. Burns, which involved the weathering of Fe-sulfides [6], has not subsequently been considered as a formation process for the Meridiani paragenesis.

Imaging spectrometers have also been used to look for carbonate rocks. Although data have not shown any evidence of large-scale carbonate-rich units [1], several carbonate-bearing outcrops have been discovered in the Nili Fossae region [7].

The chemical contexts required for the formation of sulfates and carbonates are clearly incompatible, because acidic conditions in which most sulfates are formed preclude the formation or the preservation of carbonates [8]. This suggests that the distribution of sulfates and carbonates is driven by local and/or regional processes rather than global ones. On the basis of the original model of R. Burns, we developed an experimental study designed to test the role of Fe-sulfides in the formation of sulfates or carbonates through weathering of silicate bedrock on Mars.

**Experimental protocol:** We used as initial material several primary silicates previously observed on Mars and in SNC meteorites: olivine–forsterite (a dunite – OI1, and monocrystals from Pakistan – OI2), clinopyroxene–diopside from Vesuvium, Italy (CPx) and orthopyroxene–enstatite from Ronda, Spain (OPx). Using an apparatus similar to the one described by [9], we exposed these minerals over 4 years – from September 2005 to September 2009 – to a ~0.8-bar, CO<sub>2</sub>-rich atmosphere containing either H<sub>2</sub>O or H<sub>2</sub>O+H<sub>2</sub>O<sub>2</sub> vapor at saturation at ~20°C. OI1, CPx and OPx samples were also weathered in the same conditions, but as 50 wt% mixtures with hexagonal pyrrhotite Fe<sub>0.9</sub>S (HPo) from Ducktown Mine, Tennessee. We characterized the weathered samples by X-Ray

diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

**Results and interpretations:** Initial and secondary phases found by XRD in the silicate-only and silicate/sulfide samples at the end of the experiment are summarized in Table 1.

**XRD.** Despite the 4-year duration of the experiment, the samples without sulfide underwent only minor alteration. Both pyroxenes appeared unaffected in the XRD data. The only secondary phase found was the Mg-carbonate nesquehonite Mg(HCO<sub>3</sub>)(OH)·2H<sub>2</sub>O, detected in small quantities in three olivine samples.

In contrast, mixtures with pyrrhotite showed extensive weathering: all samples produced several secondary phases, including elementary sulfur, hydrated sulfates and Fe-(oxy)hydroxides. No carbonate was formed here. Sulfur S<sup>0</sup>, directly derived from pyrrhotite [9], appeared in all samples, as did gypsum CaSO<sub>4</sub>·2H<sub>2</sub>O and hexahydrate MgSO<sub>4</sub>·6H<sub>2</sub>O. The quantities of these two minerals correlated with the chemistry of the initial silicate: gypsum was only a minor component in the olivine samples, whose Ca content was low, but it was more abundant in the clinopyroxene samples, because clinopyroxene contains Ca; and hexahydrate was observed in larger quantities in the olivine samples, because of their higher Mg content. Jarosite (K, Na, H<sub>3</sub>O)<sup>+</sup>Fe<sup>3+</sup><sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>3</sub> was observed in three sam-

Scale 0 5 10 15 30 50 vol%	Initial assemblage						Sulfur and sulfates			Fe-oxides		Carb.	
	Olivine	Clinopyroxene	Orthopyroxene	Amphibole	Talc	Pyrrhotite	Sulfur	Gypsum	Hexahydrate	Jarosite	Goethite		Hematite
Identified minerals →													
Samples ↓													
OI1-H <sub>2</sub> O	•••••		••										
OI1-H <sub>2</sub> O <sub>2</sub>	•••••		••										•
OI1-HPo-H <sub>2</sub> O	•••••		•	•	•	•	••	•	••		••		
OI1-HPo-H <sub>2</sub> O <sub>2</sub>	•••••		••	•	•	•	••	•	••		••	••	
OI2-H <sub>2</sub> O	•••••												•
OI2-H <sub>2</sub> O <sub>2</sub>	•••••												•
CPx-H <sub>2</sub> O		•••••											
CPx-H <sub>2</sub> O <sub>2</sub>		•••••											
CPx-HPo-H <sub>2</sub> O		•••••		••	•	•	••	••	•	•	••		
CPx-HPo-H <sub>2</sub> O <sub>2</sub>		•••••		••	••	••	••	••	•	••	••		
OPx-H <sub>2</sub> O			•••••	•									
OPx-H <sub>2</sub> O <sub>2</sub>			•••••	•									
OPx-HPo-H <sub>2</sub> O			•••••	•	•	•	••	••	•	•	••		
OPx-HPo-H <sub>2</sub> O <sub>2</sub>			•••••	•	•	•	••	••	•	••	••		

**Table 1.** Summary of initial and secondary phases observed after 4 years of weathering, based on XRD analyses. Ol: olivine; CPx: diopside; OPx: enstatite; HPo: pyrrhotite; H<sub>2</sub>O: atmosphere containing water vapor; H<sub>2</sub>O<sub>2</sub>: atmosphere containing water and hydrogen peroxide vapor.

ples of pyroxene but not in any samples of olivine. Finally, we found goethite  $\text{Fe}^{3+}\text{O}(\text{OH})$  in all samples and hematite  $\text{Fe}^{3+}_2\text{O}_3$  in only one (O11-HPo- $\text{H}_2\text{O}_2$ ).

**FTIR.** Near-infrared spectra of the final samples showed very good agreement with the XRD results. As expected, spectra of the samples without sulfide were very similar before and after weathering. However, for the samples where nesquehonite was detected by XRD, small absorption bands appeared in the corresponding spectra at  $\sim 3.8$ - $3.9 \mu\text{m}$ , consistent with bicarbonate ions in the mineral structure. Spectra of silicate/sulfide mixtures showed more extensive modifications (Fig. 1). The spectral signature of silicates, that was still discernible in the unaltered 50wt% mixtures with pyrrhotite, had completely disappeared after weathering despite the high quantity of remaining silicates ( $>30 \text{ vol}\%$ , Table 1). Instead, absorption features of goethite and hydrated sulfates became dominant.

**Weathering processes.** On Earth, nesquehonite tends to transform into more stable magnesite  $\text{MgCO}_3$  via progressive dehydration. On Mars, the few carbonate-bearing outcrops discovered so far are uniquely associated with olivine-bearing units and are composed of mainly (hydro)magnesite [7]. Our results show that these outcrops could derive from weathering of olivine-bearing rocks under a  $\text{CO}_2$  and  $\text{H}_2\text{O}$ -bearing atmosphere. In contrast, the formation of Ca-carbonates could have been precluded by slower kinetics.

The weathering of silicate/sulfide mixtures produced complex parageneses composed of unaltered silicates, traces of remaining pyrrhotite, elementary sulfur, hydrated sulfates and Fe-(oxy)hydroxides. These last two secondary phases closely match some mineralogical assemblages observed on Mars, especially since goethite is known to evolve to hematite with decreasing water vapor activity [10]. Furthermore, the near-infrared spectra obtained from our samples show a very good agreement with some data acquired by spaceborne imaging spectrometers (Fig. 1).

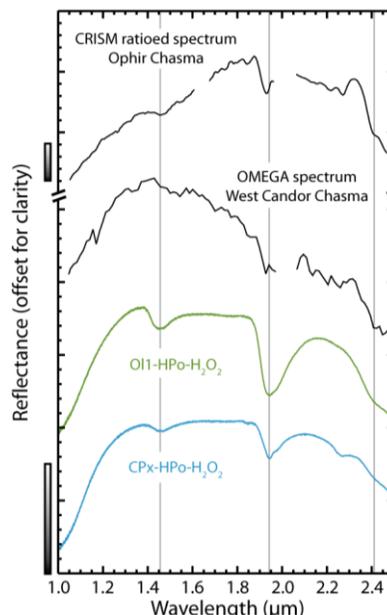
The presence of jarosite in three pyroxene/pyrrhotite mixtures shows that the weathering of pyrrhotite caused severe acidification, since jarosite is only stable at  $\text{pH} < 3$  [11]. A possible explanation for its absence in the olivine/pyrrhotite mixtures is that the release of basic  $\text{Mg}^{2+}$  cations by olivine caused a buffering effect in these samples. The formation of Ca- and Mg-sulfates shows that silicates were altered along with pyrrhotite, because silicates were the only source of these cations in our closed chemical system. Therefore, the acidification induced by the weathering of pyrrhotite appears to promote the weathering of silicates.

Our study demonstrates that the formation of sulfates on Mars could have occurred under  $\text{CO}_2$ -rich atmosphere similar to today's, but with a higher  $\text{H}_2\text{O}$

content. High partial pressures of  $\text{O}_2$  or  $\text{SO}_2$  are not required. The presence of  $\text{H}_2\text{O}_2$  is not required either; however, the higher oxidizing power of  $\text{H}_2\text{O}_2$  favors the precipitation of sulfates – and particularly jarosite – at the expense of elementary sulfur (Table 1).

**Conclusion:** Our experimental results strongly support the idea that sulfides have played a major role in the formation of sulfates on Mars [5]. They show that regional bedrock enrichment in sulfides is sufficient to explain the formation of sulfates locally. This explains the preservation of carbonates and phyllosilicates that otherwise would have been destroyed by global acidic conditions.

**References:** [1] Bibring J.-P. et al. (2005) *Science*, 307, 1576-1581. [2] Gendrin A. et al. (2005) *Science*, 307, 1587-1591. [3] Christensen P. R. et al. (2004) *Science*, 306, 1733-1739. [4] Klingelhöfer G. et al. (2004) *Science* 306, 1740-1745. [5] Burns R. G. (1987) *JGR*, 92, E570-E574. [6] Burns R. G. and Fisher D. S. (1990) *JGR*, 95, 14169-14173. [7] Ehlmann B. L. et al. (2008) *Science*, 322, 1828-1832. [8] Fairen A. G. et al. (2004) *Nature*, 431, 423-42. [9] Chevrier V. et al. (2004) *Geology*, 32, 1033-1036. [10] Gooding J. L. (1978) *Icarus*, 33, 483-513. [11] Zolotov M. Y. and Shock E. L. (2005) *GRL*, 32, L21203. [12] Mangold N. et al. (2008) *Icarus*, 194, 519-543. [13] Wendt L. et al. (2010) *LPS XLI*, Abstract #1699.



**Fig. 1.** Near-infrared spectra of two silicate/sulfide weathered samples (bottom). Two spectra obtained by Mars orbiters are shown for comparison [12,13] (top).