

**EXPERIMENTAL WEATHERING OF SILICATES AND SULFIDES IN CO<sub>2</sub> ATMOSPHERES: IMPLICATIONS FOR SULFATES VERSUS CARBONATES ON MARS.** E. Dehouck<sup>1</sup>, V. Chevrier<sup>2</sup>, A. Gaudin<sup>1</sup>, N. Mangold<sup>1</sup>, P.-E. Mathé<sup>3</sup>, P. Rochette<sup>3</sup>. <sup>1</sup>Laboratoire de Planétologie et Géodynamique de Nantes, UMR 6112 CNRS/Université de Nantes, BP 92208, 44322 Nantes cedex 3, France, [erwin.dehouck@univ-nantes.fr](mailto:erwin.dehouck@univ-nantes.fr), <sup>2</sup>Arkansas Center for Space and Planetary Science, MUSE 202, University of Arkansas, Fayetteville, AR 72701, USA, <sup>3</sup>Centre Européen de Recherche et d'Enseignement en Géosciences de l'Environnement, Europôle de l'Arbois, BP 80, 13545 Aix-en-Provence cedex 4, France.

**Introduction:** Orbital and landed missions to Mars have revealed complex sulfate-bearing deposits [1-4], which have been interpreted as the result of a late planet-wide acidic period linked to large volcanic emissions of SO<sub>2</sub>. Extraction of significant amounts of sulfur from the mantle by Fe-rich magmas is indeed expected on ancient Mars [5,6]. However, the balance between the oxidized (SO<sub>2</sub>) and reduced (H<sub>2</sub>S/sulfides) forms of magmatic S is still not clearly established for Martian magmas due to uncertainties about some key parameters (composition, pressure, temperature, oxygen fugacity, water content) [6]. The sulfide-bearing mineralogical assemblages and the low values of oxygen fugacity found in SNC meteorites suggest that SO<sub>2</sub>-dominated magmas must have been rare on Mars [7]. Therefore, sulfides (along with H<sub>2</sub>S) could be in fact the dominant form in which sulfur have reached the (near-)surface of Mars. Moreover, the scenario of a global acidic event is difficult to reconcile with the discovery of Noachian-to-Hesperian carbonates [8], because they should have been dissolved by the acidic conditions. Here, we present the results of a 4-year-long experiment designed to test a model first proposed by [9] in which Martian sulfates were formed at local or regional scale from the weathering of sulfide-rich basalts.

**Experimental protocol:** We used as initial material several primary silicates previously observed on Mars and in SNC meteorites : Mg-olivine (a dunite – O11, and monocrystals from Pakistan – O12), clinopyroxene from Vesuvium, Italy (CPx) and orthopyroxene from Ronda, Spain (OPx). Using an apparatus similar to the one described by [10], we exposed these minerals over 4 years – from 2005 to 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 15-20°C. O11, 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 elemental 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 quantity of this last mineral is strongly correlated with the chemistry of the initial silicate: it is only minor in the pyroxene samples, but is observed in larger quantities in the olivine samples, which have the 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 samples of pyroxene but not in any samples of olivine. Finally, we found goethite Fe<sup>3+</sup>O(OH) in all samples and hematite Fe<sup>3+</sup><sub>2</sub>O<sub>3</sub> in only one.

Without sulfide	O11		O12		CPx		OPx	
	H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>
Olivine	+++	+++	+++	+++				
Clinopx					+++	+++		
Orthopx	++	++					+++	+++
Amphibole							+	+
Nesquehonite		+	+	+				
With sulfide	O11-HPo		O12-HPo		CPx-HPo		OPx-HPo	
	H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>
Olivine	+++	+++						
Clinopx					+++	+++		
Orthopx	+	+	No corresponding sample	No corresponding sample			+++	+++
Amphibole	+	+			++	++	+	+
Talc+Mica	+						+	+
Pyrrhotite	+	+					+	+
El. sulfur	++	++			++	++	++	++
Gypsum	++	++			++	++	++	++
Hexahydrate	++	++			+	+	+	+
Jarosite					+	++		++
Goethite	++	++			++	++	++	++
Hematite		++						

**Table 1.** Summary of initial and secondary phases observed after 4 years of weathering, based on semi-quantitative XRD analyses. A distinction is made between minor (+), intermediate (++) and major phases (+++). H<sub>2</sub>O: atmosphere containing water vapor; H<sub>2</sub>O<sub>2</sub>: atmosphere containing water and hydrogen peroxide vapor.

**FTIR.** Near-infrared spectra of the final samples showed 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  $\sim 3.8\text{-}3.9\ \mu\text{m}$ , 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 [8]. 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, elemental 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 [11]. Furthermore, the near-infrared spectra obtained from our samples show a very good agreement with some data acquired by spaceborne imaging spectrometers (Fig. 1).

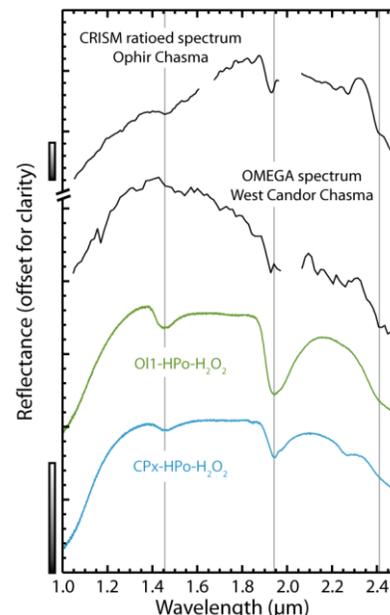
The presence of jarosite in three pyroxene/pyrrhotite mixtures shows that the weathering of pyrrhotite caused severe acidification, since jarosite is only stable at  $\text{pH} < 4$ . A possible explanation for its absence in the olivine/pyrrhotite mixtures is that the release of basic  $\text{Mg}^{2+}$  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. This process is expected to generate a Si-rich residue and, indeed, some areas enriched in Si whereas impoverished in other cations were found by SEM.

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 elemental sulfur (Table 1).

**Conclusion:** Both mineralogy and near-infrared spectra of our end-products give a good agreement with spaceborne and in situ observations of the Martian sulfate- and Fe-oxide-bearing terrains. Therefore, 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. and Fisher D. S. (1990) *JGR*, 95, 14169-14173. [6] Gaillard and Scaillet (2009) *EPSL*, 279, 34-43 [7] de Moor et al. (2011) *LPSC XLII*, Abstract #1238 [8] Ehlmann B. L. et al. (2008) *Science*, 322, 1828-1832. [9] Burns R. G. (1987) *JGR*, 92, E570-E574. [10] Chevrier V. et al. (2004) *Geology*, 32, 1033-1036. [11] Gooding J. L. (1978) *Icarus*, 33, 483-513. [12] Mangold N. et al. (2008) *Icarus*, 194, 519-543. [13] Wendt L. et al. (2010) *LPSC 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).