

**EFFECTS OF SO<sub>2</sub> VS SULFIDES AS A SOURCE OF SULFUR ON THE WEATHERING OF FORSTERITIC OLIVINE.** E. Dehouck<sup>1</sup>, V. Chevrier<sup>2</sup>, T. S. Altheide<sup>2</sup> and C. G. Lozano<sup>2</sup>. <sup>1</sup>Department of Geosciences, Stony Brook University, NY, USA ([erwin.dehouck@stonybrook.edu](mailto:erwin.dehouck@stonybrook.edu)); <sup>2</sup>Arkansas Center for Space and Planetary Science, University of Arkansas, Fayetteville, AR, USA.

**Introduction:** Various sulfate minerals have been identified on Mars by both orbital and in situ missions, including Ca- (e.g., gypsum), Mg- (e.g., kieserite), and Fe-bearing species (e.g., jarosite) [1-6]. Based on early results from the OMEGA spectrometer, Bibring et al. [7] proposed that sulfates were the dominant alteration products of the “Theiikian” era, which roughly coincides with the Hesperian geologic era. Accordingly, one of the main goals of the ongoing Mars Science Laboratory mission is to characterize the stratigraphy of Aeolis Mons, the central mound of Gale crater, which is thought to record an environmental shift between a phyllosilicate-dominated era to a sulfate-dominated one [8].

There are two main possible sources of sulfur to produce sulfates on Mars, both of which have been tested experimentally: gaseous SO<sub>2</sub> injected into the martian atmosphere by volcanic eruptions [9-11], or (Fe-)sulfides emplaced along with basalts [12-13]. Here, we present the preliminary results of a low-temperature weathering experiment of silicate minerals under SO<sub>2</sub> atmospheres (either with H<sub>2</sub>O alone or with H<sub>2</sub>O+H<sub>2</sub>O<sub>2</sub>). The advantage of this study is that it used a setup and protocols similar to those of a previous work dealing with the alteration of silicate/pyrrhotite mixtures [13]. This allows a direct comparison of the effects of the sulfur source (SO<sub>2</sub> vs Fe-sulfides) on the weathering of silicate minerals.

**Methods:** The experimental setup and protocols are similar to those described in [12] and [13]: powdered samples were placed in the middle of vacuum desiccators, the bottom of which was filled with 0.5 L either of deionized water or of a solution containing ~33% of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Thus, there was no direct contact between the solid samples and the liquid phase. The desiccators were then equilibrated with gaseous SO<sub>2</sub> at 0.8 bar and the temperature was maintained in the range 15-20°C. Such conditions were used mainly to increase kinetics of weathering processes, but even if it is highly unlikely that the martian atmosphere ever had 0.8 bar of SO<sub>2</sub>, such high pressure could model local conditions in the vicinity of large volcanoes. The desiccators were opened after 2.5 years (vs 4 years in [13]). Samples were then centrifuged and oven-dried in order to stop the weathering reactions.

We selected as initial materials several silicate minerals typical of basaltic rocks, including forsteritic (i.e., Mg-rich) olivine and several pyroxenes. The ex-

periment also included other types of minerals (phyllosilicates and carbonates) not addressed here [14].

**Preliminary results:** In this paper, we focus on the weathered samples of forsteritic olivine, which have been analyzed – so far – by near-infrared (NIR) reflectance spectroscopy and powder X-ray diffraction (XRD). Analyses of pyroxene samples are in progress.

*NIR spectroscopy.* The NIR reflectance spectra of the two weathered samples of forsteritic olivine are presented in Figure 1. Both clearly show evidence for alteration in the 1.8-2.5 μm range when compared to the spectrum of the initial olivine. However, the broad, Fe<sup>2+</sup>-related absorption band centered at ~1.04 μm remains almost unmodified, indicating that a large part of the initial olivine has been preserved.

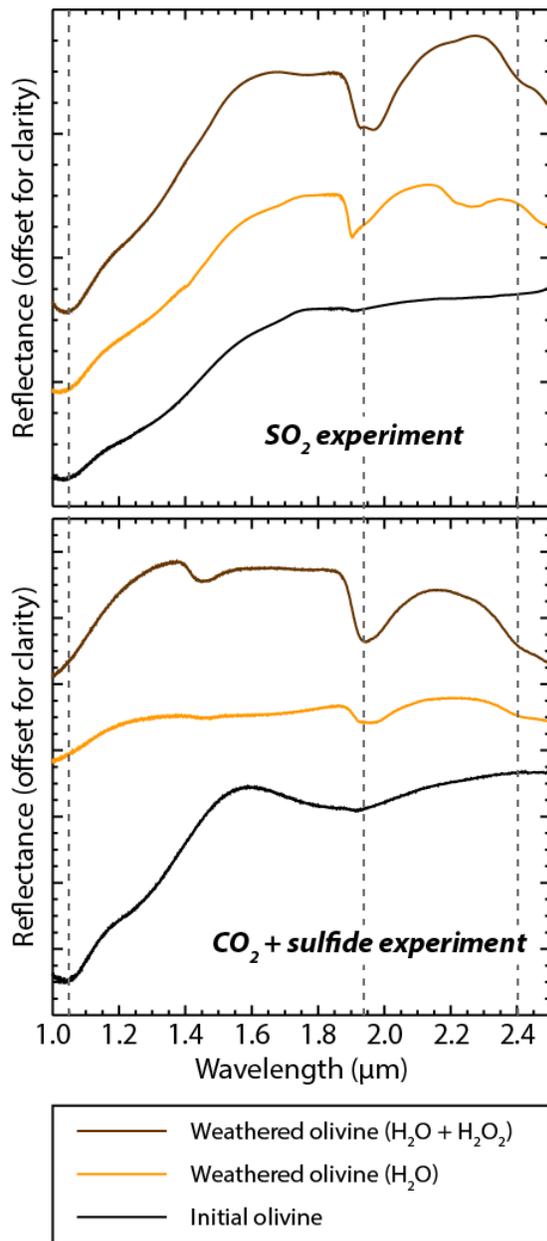
The sample weathered in the SO<sub>2</sub>+H<sub>2</sub>O atmosphere exhibits a sharp water-related band with a reflectance minimum at 1.91 μm, as well as a broader and shallower band at ~2.25 μm. These features are consistent with an hydrated secondary phase, possibly amorphous silica [15]. However, confirmation by other analytical methods is required (see below).

Interestingly, the spectrum of the sample weathered in the SO<sub>2</sub>+H<sub>2</sub>O+H<sub>2</sub>O<sub>2</sub> atmosphere is quite different from the previous one. It also exhibits a water-related absorption band, but with a plateau-shaped minimum located at a slightly longer wavelength (~1.94-1.97 μm). In addition, an absorption band typical of sulfate minerals is observed at ~2.4 μm [16]. Taken together, these features are strongly indicative of the presence of a Mg-bearing sulfate, most likely hexahydrite [16].

*XRD.* A preliminary assessment of the XRD patterns of the two weathered samples of forsteritic olivine show no new diffraction peaks compared to the initial olivine. This suggests that secondary phases responsible for the changes observed in the NIR spectra are in low abundance and/or not well crystallized. Consistently, a broad but shallow “hump” located at ~21° 2θ (Cu) is observed in the pattern of the SO<sub>2</sub>+H<sub>2</sub>O sample (Fig. 2). This feature is likely related to the amorphous silica phase suspected from NIR results.

**Discussion:** Compared to the weathered olivine/pyrrhotite mixtures of [13], the samples of forsteritic olivine weathered under SO<sub>2</sub> atmospheres seem less altered. First, their NIR spectra still show the Fe<sup>2+</sup>-band of the initial olivine, which was not the case in [13] (Fig. 1, bottom panel). Second, and perhaps more importantly, their XRD patterns show no clear diffraction

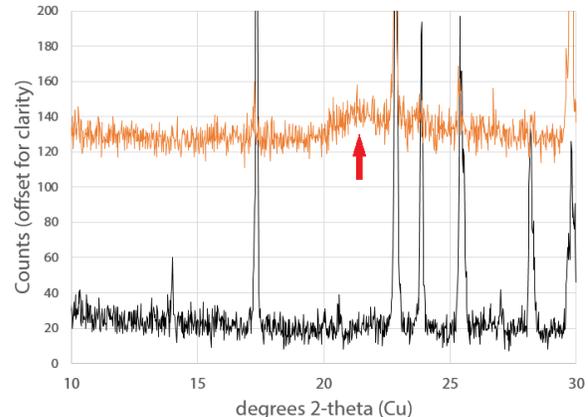
peaks related to newly-formed phases, again in contrast with what was observed by [13]. Although the  $\text{SO}_2$  experiment was shorter than the silicate/sulfide one (2.5 vs 4 years), it is unlikely that the duration alone explains these differences. Instead, the high reactivity of Fe-sulfides – especially pyrrhotite [12] – may be the reason of the more extensive modifications in [13].



**Figure 1** – Near-infrared reflectance spectra (1.0 to 2.5  $\mu\text{m}$ ) of forsteritic olivine weathered under  $\text{SO}_2$  atmospheres (top) and under  $\text{CO}_2$  atmospheres mixed with pyrrhotite [13] (bottom). Spectra of the initial (not weathered) samples are shown in black.

**Conclusions and future work:** Our preliminary results regarding the olivine samples tend to indicate that weathering under  $\text{SO}_2$  atmosphere is less efficient in producing well-crystallized secondary sulfates than a physical mixtures with Fe-sulfides under a  $\text{CO}_2$  atmosphere. In the near future, we plan to pursue the study with the analysis of the pyroxenes samples. In addition, other analytical tools – such as electron microscopy – may be helpful to further characterize our samples.

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**Figure 2** – XRD pattern of the sample of forsteritic olivine weathered under  $\text{SO}_2+\text{H}_2\text{O}$  atmosphere (top, orange) compared to the initial, not-weathered sample (bottom, black). The arrow indicates a “hump” in the weathered sample probably related to a poorly-crystalline secondary phase.