

**WEATHERING OF OLIVINE UNDER CO<sub>2</sub> ATMOSPHERE: A MARTIAN PERSPECTIVE.** E. Dehouck<sup>1</sup>, A. Gaudin<sup>1</sup>, N. Mangold<sup>1</sup>, L. Lajaunie<sup>2</sup>, A. Dauzeres<sup>3</sup> and E. Le Menn<sup>1</sup>. <sup>1</sup>Laboratoire de Planétologie et Géodynamique de Nantes, UMR 6112 CNRS/Université de Nantes, Nantes, France ([erwin.dehouck@univ-nantes.fr](mailto:erwin.dehouck@univ-nantes.fr)); <sup>2</sup>Institut des Matériaux Jean Rouxel, UMR 6502 CNRS/Université de Nantes, Nantes, France; <sup>3</sup>Institut de Radioprotection et de Sécurité Nucléaire, Fontenay-aux-Roses, France.

**Introduction:** Olivine has been detected in several regions of Mars using orbital data [1-3] and is locally associated with secondary minerals such as Fe-Mg smectites, serpentine or Mg-carbonates [4-5]. Since it is one of the most fragile primary silicate in near-surface conditions, it could be used as a mineralogical marker of alteration processes on early Mars [6].

Previous experimental studies of weathering of olivine under CO<sub>2</sub> mainly focused on kinetics and dissolution rates [*e.g.*,7]. Here, we focused on secondary phases by applying various analytical techniques, including near-infrared spectroscopy, transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (TEM-EDX), thermogravimetry (DTG) and X-ray diffraction (XRD). We also tested the possible effect of oxidizing molecules such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), which are known to be present in the Martian regolith and atmosphere. The results can help to understand the origin of the secondary mineralogy observed on Mars and to interpret it in terms of paleo-environment [6].

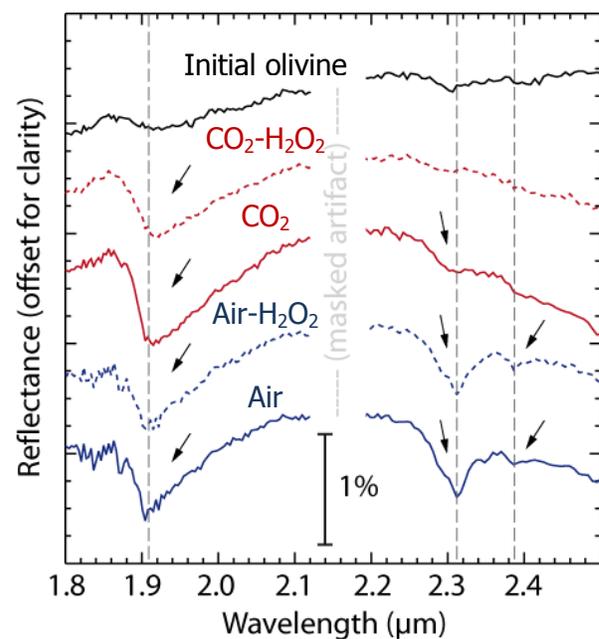
**Experiment:** Mg-rich olivine (Fo<sub>90</sub> from San Carlos) was weathered as a fine powder in four batch experiments, giving four types of conditions abbreviated as follows: “Air”, “Air-H<sub>2</sub>O<sub>2</sub>”, “CO<sub>2</sub>” and “CO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub>”. For the last two reactors, the initial CO<sub>2</sub> pressure was set at 1.5 bar (this value was chosen to ensure that any tiny leak would cause the escape of CO<sub>2</sub> and not the entrance of ambient air). For the two reactors containing H<sub>2</sub>O<sub>2</sub>, it was added to the bath of ultrapure water at a concentration of 2 vol%. The initial liquid-to-rock ratio was 10 (30 g of olivine in 300 mL of water). The solutions were heated at ~45°C, a value chosen as a compromise between two opposite requirements: (1) increasing reaction kinetics and (2) keeping realistic conditions for surficial aqueous processes. The experiment lasted three months, during which the flasks were manually shaken up daily. At the end of this period, the “CO<sub>2</sub>” and “CO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub>” flasks were dried using a vacuum pump to avoid contact with ambient air, while the “Air” and “Air-H<sub>2</sub>O<sub>2</sub>” flasks were dried in an oven.

**Results:** “Air” and “Air-H<sub>2</sub>O<sub>2</sub>” samples. These two samples show very similar characteristics. Their near-infrared spectra, although still dominated by the signature of olivine, exhibit clear 1.91- and 2.31- $\mu$ m absorption bands indicative of Mg-rich clay minerals

like saponite (Fig. 1). The formation of such phase is confirmed by the observation of its typical “filamentous” morphology by TEM (Fig. 2) [8] and by the chemical analyses performed by EDX. However, XRD patterns obtained from bulk samples as well as oriented <2- $\mu$ m fractions show no signal of clays, suggesting either a low abundance (due to the limited time of the experiment) and/or a low crystallinity. Therefore, this phase can reasonably be referred as a smectite precursor. No other secondary phase was found in these two samples by any of the analytical techniques employed.

“CO<sub>2</sub>” and “CO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub>” samples. These samples differ from the previous ones in most data sets, highlighting the effects of a CO<sub>2</sub> atmosphere on the weathering processes, compared to terrestrial conditions. They also show some slight differences between each other.

The near-infrared spectrum of the “CO<sub>2</sub>” sample shows a clear 1.91- $\mu$ m absorption band, and a more subtle one at 2.31  $\mu$ m (Fig. 1). Compared to the



**Figure 1** – Near-infrared spectra of our weathered olivine powders (red and blue) compared to the initial olivine (black). The arrows highlight new or deeper absorption bands in the weathered samples.

“Air” and “Air-H<sub>2</sub>O<sub>2</sub>” samples, this suggests that a smectite precursor is also present, but in lower abundance. In addition, another secondary phase is needed to explain the depth of the 1.91- $\mu$ m band. Observations and chemical analyses performed by TEM-EDX indeed confirm the presence of both a smectite precursor and a second neoformed phase, characterized by a “cotton-like” texture (Fig. 2) and a composition tending toward pure silica. Although traces of gaseous CO<sub>2</sub> were released from this sample during the thermogravimetric analysis, no carbonate mineral has been definitively identified.

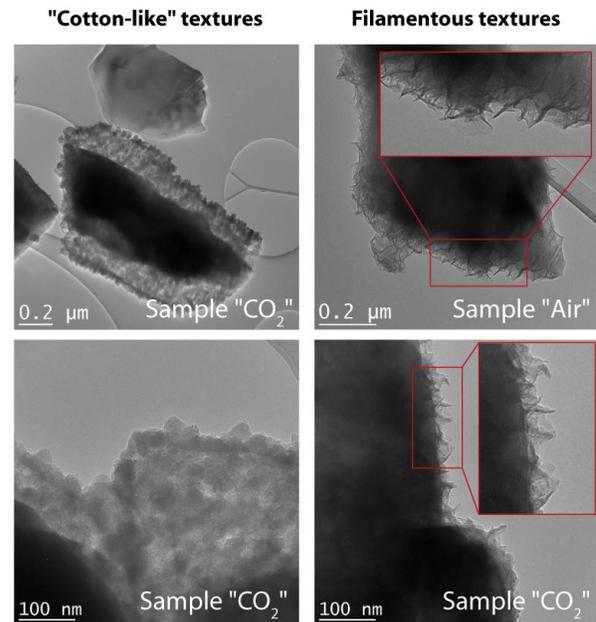
For the “CO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub>” sample, the near-infrared spectrum again shows a clear 1.91- $\mu$ m band, but no 2.31- $\mu$ m one. Consistently, TEM observations reveal only the cotton-like, Si-rich phase and no smectite precursor. No carbonate is detected.

**Discussion:** Although direct quantification of the secondary phases is not possible given the low abundances involved, rough estimates can be established by combining data from the various analytical techniques employed. These estimates are synthesized in Fig. 3.

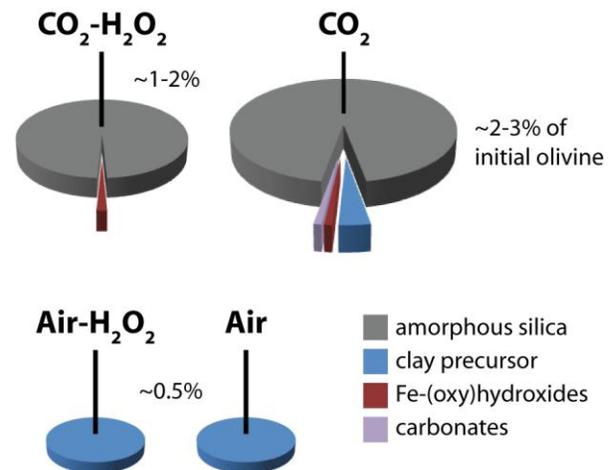
**Going back to Mars:** Our experimental results provide new data about the weathering of primary silicates under CO<sub>2</sub> and can therefore be useful to interpret the secondary mineralogy observed on Mars. One of the most important observations is that, even under a dense CO<sub>2</sub> atmosphere (>1 bar), the weathering of olivine produces more clays than carbonates, which is broadly consistent with the secondary mineralogy found in olivine-rich regions of Mars [4,5,9]. On the other hand, the most abundant phase formed under CO<sub>2</sub> is amorphous silica. This suggests that Si would have been highly mobile during surficial aqueous processes on early Mars. This could explain numerous detections of silica in alluvial and delta fans by [10], as well as the high Si content measured in the northern plains by Mars Pathfinder and by the Thermal Emission Spectrometer instrument [11].

In the near-future, similar experiments currently in progress using a basalt and other silicates will complete the results obtained here for olivine.

**References:** [1] Mustard J.F. et al. (2005) *Science*, 307, 1594-1597. [2] Mustard J.F. et al. (2007) *JGR*, 112, E08S03. [3] Ody A. et al. (in press) *JGR*. [4] Ehlmann B.L. et al. (2009) *JGR*, 114, E00D08. [5] Gaudin A. et al. (2011) *Icarus*, 216, 257-268. [6] Christensen P. R. (2003) *6<sup>th</sup> Int. Conf. Mars*, abstract #3126. [7] Olsen A. A. and Rimstidt J. D. (2007) *Am. Min.*, 92, 598-602. [8] Jones C.L. and Brearley A.J. (2006) *GCA*, 70, 1040-1058. [9] Mangold N. et al. (2007) *JGR*, 112. [10] Carter J. et al. (2012) *LPSC XLIII*, abstract #1978. [11] McLennan S.M. (2003) *Geology*, 31, 315-318.



**Figure 2** – TEM micrographs of weathered olivine grains (which appear as dark areas) with secondary phases developed on their surface. Left: “cotton-like”, Si-rich phase. Right : filamentous smectite precursor.



**Figure 3** – Estimated abundances of secondary phases in our weathered olivine powders.