



Formation of clay minerals on Mars: Insights from long-term experimental weathering of olivine

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ABSTRACT

Laboratory experiments are useful to constrain the environmental parameters that have allowed the formation of the ancient hydrous mineralogical assemblages observed at the surface of Mars, which are dominated by ferric smectites. Weathering under a dense CO₂ atmosphere on early Mars is a process frequently invoked to explain their formation, but has proven difficult to test in the laboratory due to low reaction rates. Here, we present a long-term weathering experiment (470 days, at 45 °C) of forsteritic olivine specially designed to increase as much as possible the amount of reaction products and thus allow their detailed mineralogical, petrological and chemical characterization by FTIR, SEM and TEM. Our results show the formation of crystalline smectites both under 1 bar of CO₂ and under ambient air. However, important differences are observed between the two types of conditions. The smectite formed under CO₂ has an average chemical formula per half unit-cell of Si_{3.92}Al_{0.16}Fe³⁺_{0.78}Mg_{1.66}Cr_{0.01}Ni_{0.06}K_{0.04}Ca_{0.04}O₁₀(OH)₂. It is thus intermediate between a trioctahedral Mg-rich saponite and a dioctahedral ferric smectite. It is also clearly enriched in Fe compared its counterpart formed under ambient air, which has an average chemical formula per half unit-cell of Si_{3.68}Al_{0.12}Fe³⁺_{0.37}Mg_{2.61}Cr_{0.01}Ni_{0.02}K_{0.04}Ca_{0.25}O₁₀(OH)₂. This result demonstrates that the enrichment in Fe observed for Martian smectites is to be expected if they were formed by low-temperature weathering under a dense CO₂ atmosphere. Another difference is the nature of the accompanying phases, which includes amorphous silica (in the form of opal spheres 10 to 100 nm in diameter) and Mg-carbonates under CO₂, but is limited to rare kaolinite under ambient air. The observation of kaolinite particles under air and the significant amount of Al measured in smectites under both atmospheres, despite the Al-poor nature of the initial material, shows that this element is easily concentrated by low-temperature weathering processes. At a larger scale, this concentration mechanism could be responsible for the formation of Al-rich upper horizons, as frequently observed on Mars.

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1. Introduction

Several lines of evidence point toward the presence of an active hydrosphere on early Mars. These lines of evidence include the extensive networks of fluvial valleys (e.g., Craddock and Howard, 2002; Hynke et al., 2010), the highly degraded impact craters (e.g., Craddock et al., 1997; Mangold et al., 2012) and the widespread secondary minerals, dominated by Fe/Mg-smectites (e.g., Poulet et al., 2005; Carter et al., 2013). However, the implications of all

these observations for the nature of the early Martian climate have been – and continue to be – the subject of intense debate. For example, it has been proposed that a large fraction of the Martian clay minerals were formed in the subsurface by hydrothermal groundwater circulation and thus that the conditions at the surface were not necessarily very different from today (e.g., Ehlmann et al., 2011). In turn, numerous vertical sections of Al-rich clays overlying Fe/Mg-smectites, a setting typical of terrestrial weathering profiles (e.g., Gaudin et al., 2011), have been observed in various regions of the planet and interpreted as a strong evidence for low-temperature, near-surface aqueous alteration of the crust, and thus for a warmer and wetter climate (e.g., Carter et al., 2015).

More recently, the detailed monitoring of the Martian upper atmosphere by the MAVEN (Mars Atmosphere and Volatile Evolu-

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Table 1
Summary of experimental conditions in our previous alteration studies of Fe/Mg-rich silicates.

	Dehouck et al. (2012, 2016)	Dehouck et al. (2014a)	This study
Initial material	Olivine (Fo90), pyroxene Fe/Mg silicates+FeS	Olivine (Fo90)	Olivine (Fo90)
Atmosphere	CO ₂	CO ₂ , Air	CO ₂ , Air
Liquid/Rock	low (evaporite)	10	10
H ₂ O ₂	H ₂ O ₂ , no H ₂ O ₂	H ₂ O ₂ , no H ₂ O ₂	no H ₂ O ₂
Temperature	ambient (15°–20°C)	45°C	45°C
Stirring	no	no continuous	continuous
Duration	4 years	3 months	15.3 months

tion) mission has provided the first reliable estimates of cumulative atmospheric escape over the history of the planet (Jakosky et al., 2017). These results indicate that Mars has lost several tenths of bars to a few bars of CO₂ over the last 4 billion years, as well as several meters to several tens of meters GEL (global equivalent layer) of H₂O (Jakosky et al., 2017). Therefore, independently from the difficulties to generate a warm and wet climate using GCMs (global circulation models; e.g., Forget et al., 2013), the observational evidence—from both the surface and now the upper atmosphere—point toward extensive interactions between the early Martian crust, an active hydrosphere and a relatively thick CO₂ atmosphere. Nevertheless, many long-standing questions related to the duration, amplitude and exact geochemical conditions (e.g., pH, redox) of early Mars surface alteration remain largely unresolved. Yet, low-temperature weathering is not a process that has been thoroughly explored by laboratory experiments using relevant conditions (i.e., CO₂ atmosphere) and starting materials (i.e., basaltic silicates). Here, we present new experimental results obtained under such conditions in order to better understand the weathering processes that occurred at the surface of Mars.

2. Background: experimental alteration under Mars conditions

Laboratory experiments are useful to constrain the environmental parameters that would (or would not) have allowed the formation of the ancient hydrous mineralogical assemblages observed at the Martian surface by orbital and in situ missions. However, most experimental studies aiming at recreating Mars' secondary mineralogy have focused so far on conditions producing fast reaction rates, such as low pH (e.g., Chevrier et al., 2004; Tosca et al., 2004; Dehouck et al., 2012; Marcucci and Hynek, 2014) and/or high temperature (>100 °C; e.g. Schröder et al., 2004; Peretyazhko et al., 2016). These studies thus provide information about acid-sulfate and/or hydrothermal processes, but not about aqueous alteration in milder conditions, here referred to as weathering. Similarly, in the context of Earth's climate change mitigation, there are numerous experimental studies of the “carbonation” of primary silicates such as olivine (e.g., Giammar et al., 2005; Bearat et al., 2006; Gerdemann et al., 2007; Daval et al., 2011), but again these studies are generally carried out in conditions favoring fast reaction rates ($T > 100\text{ °C}$ and/or $p\text{CO}_2 > 100\text{ bars}$) and are thus not applicable to planetary surficial processes. Overall, the search for fast reaction rates, more easy to develop, has biased the experimental literature toward high-T and/or acidic alteration processes occurring on Mars, even though long-term processes such as weathering are fundamental for the understanding of surface conditions.

In the past years, our group has developed a series of laboratory experiments to fill this gap in the experimental knowledge of alteration (Table 1). Low-temperature weathering experiments using olivine and pyroxenes as starting materials were described by Dehouck et al. (2012, 2014a, 2016) and showed that a reaction predicted by geochemical modeling to produce predominantly carbonates could instead produce smectite clays and amorphous silica.

The first series of experiments were carried out over 4 years at room temperature in rock-dominated conditions (i.e., at low liquid/rock ratio) and showed interesting differences in chemical pathways (Dehouck et al., 2016). In particular, it was observed that the addition of an oxidizing compound (H₂O₂) under CO₂ could inhibit the formation of smectites and favor the formation of carbonates – and conversely when the environment is anoxic. These results thus strongly suggest that anoxic conditions were required to form the widespread Fe/Mg-smectites through weathering of the Martian basaltic crust under a CO₂ atmosphere (Dehouck et al., 2016). Moreover, Dehouck et al. (2014a) studied the alteration of forsteritic olivine under CO₂ in water-dominated conditions (i.e., at a liquid/rock ratio of 10). After three months of reaction, the samples exposed to anoxic conditions showed the development of significant amounts of a silica-rich phase as well as Mg-rich smectites on the olivine grains, and only traces of carbonates, whereas the samples exposed to CO₂ and H₂O₂ produced only the silica-rich phase.

Unfortunately, in the two studies described above, the low abundance of the secondary products (especially smectites) hindered their detailed SEM/TEM chemical and petrographic characterization. This may have been due, in part, to the absence of continuous stirring (the reactors were only stirred manually a few times per week in the work of Dehouck et al., 2014a). Therefore, building from our experience, we conducted a new experiment similar in principle to the one presented by Dehouck et al. (2014a), but specially designed to increase as much as possible the amount of reaction products, with the hope of being able to investigate in more details their nature and properties. Specifically, our new experimental setup allowed us to weather forsteritic olivine in a CO₂ glovebox (1) with continuous stirring of the reactors and (2) during 470 days, which is more than five times longer than the study of Dehouck et al. (2014a). The chemistry, mineralogy and petrography of the altered samples were characterized by means of near-infrared spectroscopy (IR), X-Ray diffraction (XRD), thermogravimetric analyses (TGA) and scanning and transmission electron microscopy (SEM and TEM), as detailed in Appendix A.

3. Starting material and experimental setup

Our experiments were conducted from a natural sample of forsteritic (Fo₉₀) olivine (San Carlos), similar to the material used in our previous experiments (Dehouck et al., 2014a). Forsteritic olivine is weakly resistant to alteration and therefore allows us to maintain the experiment in a reasonable time frame, while still providing a relatively complex geochemical system (Table 2). On Mars, olivine has been detected in various regions based on orbital data (Hoefen et al., 2003; Mustard et al., 2005; Poulet et al., 2007; Ody et al., 2013). The large olivine-rich deposits of the Nili Fossae region display a composition estimated to Fo_{68–75} based on TES (Thermal Emission Spectrometer) observations (Hamilton et al., 2003). Olivine analyzed by the CheMin X-ray diffractometer aboard the Curiosity rover shows compositions ranging from Fo₄₀ to Fo₇₅ (Morrison et al., 2018). Thus, although our starting material is

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