

EXPERIMENTAL WEATHERING OF SILICATES AND CARBONATES IN A SO₂ ATMOSPHERE: IMPLICATIONS FOR THE MARTIAN SURFACE MINERALOGY. V.F. Chevrier¹, C.G. Lozano², T.S. Altheide¹ Arkansas Center for Space and Planetary Science, FELD 202, University of Arkansas, Fayetteville, AR 72701, USA. ²Departamento de Geociencias Marinas, Universidad de Vigo, Lagoas Marcosende, Vigo 36200, Spain. vchevrie@uark.edu.

Introduction: The surface of Mars appears covered with secondary phases resulting from various processes of alteration in different conditions which remain quite unclear today. For a long time, it has been supposed that Mars was covered by a thick CO₂ atmosphere, which appeared necessary to maintain warm conditions through greenhouse effect to allow liquid water for long periods of time. However, carbonate deposits are limited to only a few small spots on the surface of Mars [1,2]. Thus several hypotheses tried to explain this apparent discrepancy. In the first hypothesis, Mars never had a thick atmosphere of CO₂ and possibly remained cold or warmed by other greenhouse gases [3,4]. In the second hypothesis, carbonates were prevented from forming by other geochemical processes, like the formation of sulfite due to the presence of SO₂ in an early reducing atmosphere [5,6].

In our previous work on the weathering of the early martian surface, we focused on a thick CO₂ atmosphere in contact with iron phases like magnetite and pyrrhotite [7,8], and on the mixtures of sulfides and silicates [9,10]. These experiments were performed in moderately (H₂O) or strongly (H₂O + H₂O₂) oxidizing environments. Previous experiments on SO₂ have only focused on the relative abundance compared to CO₂ and in reducing conditions [5]. Here we test the effect of weathering of various phases relevant to early Mars in an SO₂ atmosphere.

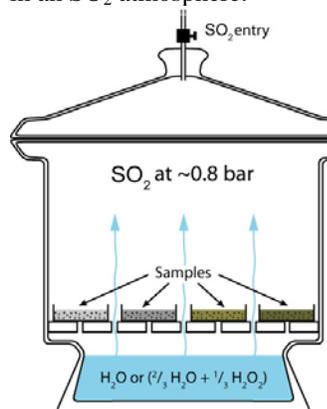


Figure 1. Apparatus used in the SO₂ weathering experiments

Protocol: We selected several phases previously identified on Mars, and including primary silicates (olivine, orthopyroxene and clinopyroxene), phyllosilicates (nontronite and montmorillonite) and carbonates (Fe²⁺ siderite, Mg magnesite and Ca calcite). Fe^{II} and Mg poles were selected for the basaltic silicates. 3 g of finely powdered phases were put in a desiccator filled

with 1L either of pure water or of water containing 33% of hydrogen peroxide H₂O₂ (the samples were not in contact with the liquid, e.g. Fig. 1). The desiccators were then equilibrated with gaseous SO₂ at the initial pressure of 0.8 bar and the temperature was controlled to remain in the range 15-20°C. Such conditions were used to increase kinetics of weathering processes, and even if it is highly unlikely that Mars ever had 0.8 bars of SO₂, such high pressure can model local conditions in the vicinity of large volcanoes. The very high solubility of SO₂ in liquid water probably prevented it from diffusing very far from the source. Pressure was controlled every 2-3 months and SO₂ was reinjected if necessary. The desiccators were opened after two years of weathering and the cups were weighted.

Powders in the H₂O + H₂O₂ desiccator remained dry during the entire experiment while powders in the H₂O desiccator became progressively wetter and were almost entirely liquid by the end of the 2 years. In this case the solid residue was separated from the liquid by centrifugation, while a fraction of the liquid phase was dried at 50°C. All solid products were analyzed so far using X-ray diffraction (XRD) and FTIR reflectance spectroscopy.

Results: Our preliminary results focused mostly on carbonates. All the phases in the H₂O atmosphere showed significant transformation after 2 years, while the samples in the H₂O₂ atmosphere remained essentially unchanged and dry. The original sample of magnesite appeared completely liquefied in the H₂O atmosphere, while the sample siderite showed some residual solid and the calcite sample was mostly dry. XRD confirms that samples in H₂O₂ are relatively unaltered while samples in H₂O show significant changes with sometime no residue of the original sample.

Mineralogically, the initial calcite sample transformed into gypsum in the H₂O₂ environment. Gypsum represented about 40% of the final sample (Fig. 2A). Alternatively, in the H₂O alone environment, nearly all the initial calcite sample transformed into hannebachite, the Ca-sulfite CaSO₃·1/2H₂O (Fig. 2B).

The NIR spectrum of calcite in H₂O₂ is practically the same that the gypsum spectrum while the NIR spectrum of the sample in H₂O shows a displacement in their peaks with respect of gypsum spectrum and some peaks seem to be CaSO₃·1/2H₂O.

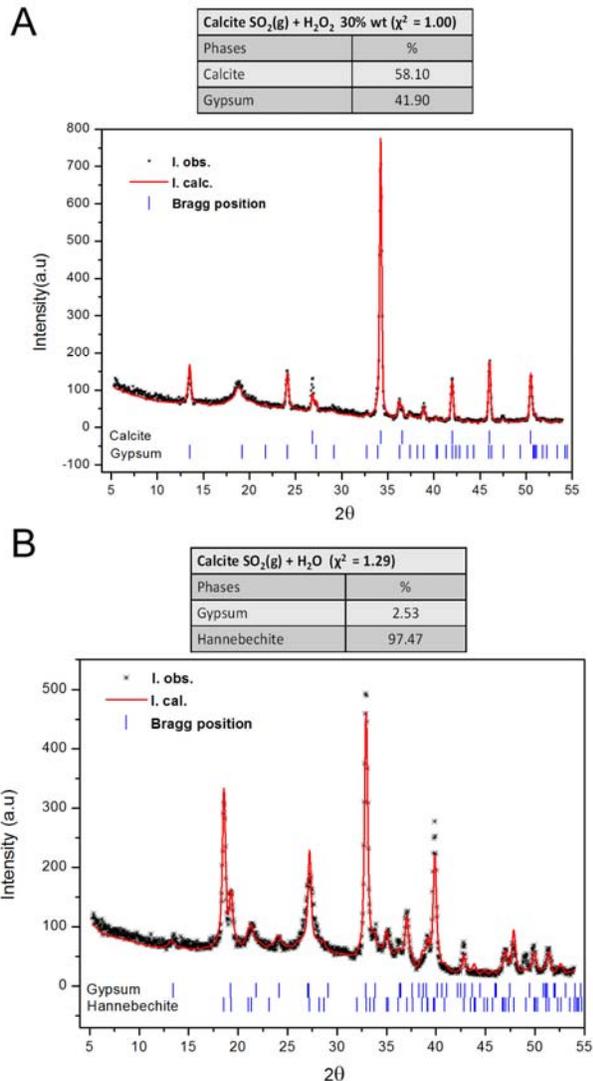


Figure 2. XRD diffraction patterns and Rietveld refinement results for calcite in SO₂ atmosphere and A H₂O + 30% H₂O₂ and B H₂O.

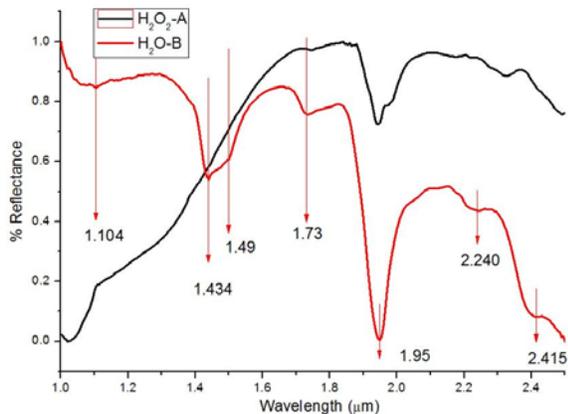


Figure 3. Reflectance spectra of siderite in SO₂ atmosphere, black: H₂O + 30% H₂O₂, red: H₂O.

In the case of siderite, XRD shows that the sample that was in the SO₂ + H₂O₂ atmosphere did not suffer much alteration (it is virtually only siderite) but the sample that was under the SO₂ and H₂O atmosphere was partially transformed into (oxy)hydroxides minerals (lepidocrocite and goethite). The analysis of the XRD of the sample crystallized from the liquid part seem to contain some FeSO₃ and some other iron phases (possibly ferric and ferrous) but its complexity makes the identification of the phases complicated. The NIR spectrum of the samples were practically identical between both solids in both atmospheres, strongly resembling siderite, while the liquid crystallized in the H₂O atmosphere was strongly different and exhibits features typical of hydrated phases with absorption bands at 1.4 and 1.9 microns (Fig. 3). This suggests the presence of one or several hydrated salts (sulfates or sulfites).

Finally, the magnesite was completely transformed into Mg-sulfates in the H₂O atmosphere and almost unchanged in the H₂O₂ atmosphere.

Discussion and conclusions: The most interesting result we observed so far is the transformation of calcite into sulfite in the H₂O atmosphere while in the more oxidizing atmosphere, gypsum forms directly. Thus our results confirm the previous observations by [5] but also demonstrate that calcite could be replaced by hannebachite after precipitation (pseudomorphosis). The resulting hannebachite appears quite resistant to further oxidation since no gypsum formed even after two years. The alteration of siderite in the H₂O atmosphere shows also the possibility of ferric or ferrous sulfites is important for early Mars and possibly further formation of ferric/ferrous sulfates.

We are only in the very early steps of the work and are only starting to analyze the silicate, although it seems that iron-bearing silicates have undergone the most significant transformations. We will also investigate the chemical composition of the remaining liquids for the possible presence of the sulfite ion.

References: [1] Ehlmann B. L. et al. (2009) *Science* 322, 1828-1832. [2] Michalski J. R., P. B. Niles (2010) *Nature Geosci.* 3, 751-755. [3] Chevrier V. et al. (2007) *Nature* 448, 60-63. [4] Fairen A. G. et al. (2009) *Nature* 459, 401-404. [5] Halevy I., D. P. Schrag (2009) *Geophys. Res. Lett.* 36 (L23201). [6] Halevy I. et al. (2008) *Science* 318, 1903-1907. [7] Chevrier V. et al. (2006) *Geochim. Cosmochim. Acta* 70, 4295-4317. [8] Chevrier V. et al. (2004) *Geology* 32 (12), 1033-1036. [9] Dehouck E. et al. (2012) *Geochim. Cosmochim. Acta* In prep. [10] Dehouck E. et al. (2012) *LPSC* 43, This conf.