

MINERAL PARAGENESES RESULTING FROM WEATHERING ON EARLY MARS AND THE EFFECT OF CO₂ VS SO₂ ATMOSPHERES. V.F. Chevrier¹, E. Dehouck², C.G. Lozano², T.S. Altheide¹ Arkansas Center for Space and Planetary Science, FELD 202, University of Arkansas, Fayetteville, AR 72701, USA, ²Laboratoire de Planétologie et Géodynamique de Nantes, UMR 6112 CNRS/Université de Nantes, BP 92208, 44322 Nantes cedex 3, France, ³Departamento de Geociencias Marinas, Universidad de Vigo, Lagoas Marcosende, Vigo 36200, Spain. vchevrie@uark.edu.

Introduction: The surface of Mars is covered with secondary phases resulting from various alteration processes in different conditions which remain quite unclear today. Early Mars was supposed to be covered by a thick CO₂ atmosphere, which was necessary to maintain warm conditions and 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]. In the second hypothesis, carbonates were prevented from forming by the presence of SO₂ in an early reducing atmosphere which resulted in the formation of sulfite [3,4].

In our previous work on weathering of the early martian surface, we focused on the formation of sulfates in a thick CO₂ atmosphere due to the presence of large amounts of sulfides like pyrrhotite alone [5,6] or mixed with silicates [7,8]. These experiments were performed in moderately (H₂O) or strongly (H₂O + H₂O₂) oxidizing environments. In this abstract we compare the mineralogy resulting from experimental weathering with pyrrhotite or SO₂ to understand the possible source of sulfur and sulfates on Mars.

Without sulfide	Ol1		Ol2		CPx		OPx	
	H ₂ O	H ₂ O ₂	H ₂ O	H ₂ O ₂	H ₂ O	H ₂ O ₂	H ₂ O	H ₂ O ₂
Olivine	+++	+++	+++	+++				
Clinopx					+++	+++		
Orthopx	++	++					+++	+++
Amphibole							+	+
Nesquehonite		+	+	+				
With sulfide	Ol1-HPo		Ol2-HPo		CPx-HPo		OPx-HPo	
	H ₂ O	H ₂ O ₂	H ₂ O	H ₂ O ₂	H ₂ O	H ₂ O ₂	H ₂ O	H ₂ O ₂
Olivine	+++	+++						
Clinopx					+++	+++		
Orthopx	+	+					+++	+++
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 in a CO₂ atmosphere, based on semi-quantitative XRD analyses. A distinction is made between minor (+), intermediate (++) and major phases (+++). H₂O: atmosphere containing water vapor; H₂O₂: atmosphere containing water and hydrogen peroxide vapor.

Protocol: We selected phases identified on Mars: basaltic 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. In the CO₂ experiments, only the primary silicates were used (Ol, CPx, OPx) and were used pure or as 50/50 wt% mixtures with pyrrhotite. 3 to 5 of powdered samples were put in a desiccator filled with 1L either of pure water or of water plus 33% hydrogen peroxide H₂O₂ (the samples were not in contact with the liquid). The desiccators were then equilibrated with gaseous CO₂ or SO₂ at 0.8 bar and the temperature was maintained 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 pressure was controlled every 2-3 months and SO₂ was reinjected if necessary. The desiccators were opened after 4 years (for CO₂) and 2 years (for SO₂). All solid products were analyzed so far using X-ray diffraction (XRD) and FTIR reflectance spectroscopy.

Results:

CO₂ experiments – The silicate/sulfide mixtures showed extensive weathering: all samples produced secondary phases, including elemental sulfur, hydrated sulfates and Fe-(oxy)hydroxides (Table 1). Among these, sulfur S⁰ is a direct product of pyrrhotite oxidation, whereas the formation of Mg- and Ca- sulfates (hexahydrate and gypsum) results from the alteration of both pyrrhotite and Mg- or Ca-bearing silicates. Indeed, the amount of hexahydrate is strongly correlated with the chemistry of the initial silicate: minor in the pyroxene samples, but in larger quantities in the olivine samples, which have the higher Mg content. Jarosite was observed in three samples of pyroxene but not in any sample of olivine. The formation of jarosite shows that pyrrhotite weathering caused severe acidification in the pyroxene samples. Its absence in the olivine/pyrrhotite mixtures is possibly due to the release of basic Mg²⁺ cations by olivine caused a buffering effect in these samples. Finally, goethite was found in all samples and hematite in only one.

FTIR. Infrared spectra of initial silicate/sulfide mixtures show the typical absorption bands of olivine and pyroxenes, although strongly attenuated by the pres-

ence of pyrrhotite, which is featureless in this wavelength range and has a very low reflectance, contrary to the weathered samples. Moreover, the signature of silicates is not detectable anymore, despite the high quantity of remaining silicates at the end of the experiment (>30 vol%). Instead, absorption features of goethite (<1 μm) and hydrated sulfates (at 1.4, 1.9 and 2.4 μm) became dominant.

SO₂ experiments – Our preliminary results focused mostly on carbonates. All the phases in the H₂O atmosphere showed significant transformation after 2 years, some samples having a large liquid fraction while the samples in the H₂O₂ atmosphere remained essentially unchanged and dry.

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

XRD of siderite shows that the sample in the SO₂ + H₂O₂ atmosphere did not suffer much alteration while the sample in the SO₂ and H₂O atmosphere was transformed into iron (oxy)hydroxides (lepidocrocite and goethite). XRD of the sample crystallized from the liquid part also contains some FeSO₃ and some other ferric and ferrous sulfates. The NIR spectrum of the solid samples were strongly resembling siderite in both atmospheres, while the dried liquid in the H₂O atmosphere was very different and showed features typical of hydrated phases with absorption bands at 1.4 and 1.9 microns. The magnesite was completely transformed into Mg-sulfates in the H₂O atmosphere and almost unchanged in the H₂O₂ atmosphere.

Discussion and conclusions: Although we have not yet analyzed all the weathered phases in SO₂, some interesting conclusions emerge already. Mineral parageneses are relatively different between SO₂ and CO₂ plus pyrrhotite as a source of sulfur. The most interesting result we observe so far is the absence of ferric sulfates, especially jarosite in the SO₂ atmosphere, mainly because pyrrhotite is the source of iron, sulfur and acidity at the same time. Transformation in SO₂ + H₂O showed intermediate sulfites like hannebachite in calcite or FeSO₃ in siderite, confirming previous observations [3]. Hannebachite appears quite resistant to further oxidation and could be possibly observed on Mars if protected from water. Alternatively, if the atmosphere was more oxidant, then only sulfate would directly form by weathering. Future analysis of pri-

mary and secondary silicates will help refining the mineralogical differences and the possible source of sulfur during weathering on Mars.

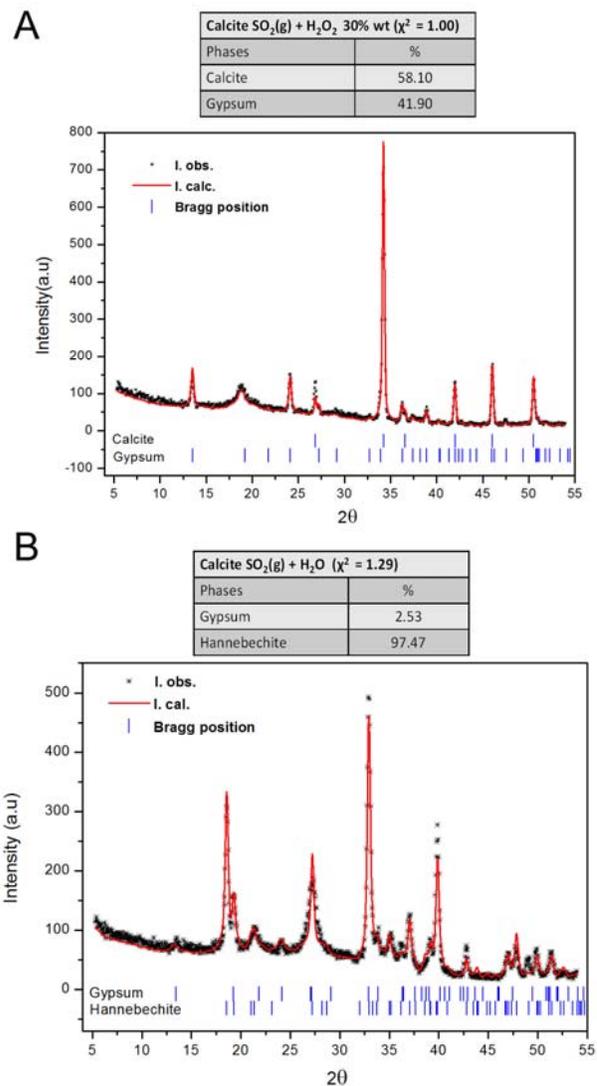


Figure 1. XRD diffraction patterns and Rietveld refinement results for calcite in SO₂ atmosphere and A H₂O + 30% H₂O₂ and B H₂O.

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