

EXPLORING THE MINERAL SEQUENCES THAT CAN BE FORMED FROM A DISULFIDE-RICH SOIL ON EARLY MARS. Gil-Lozano C.¹, Mateo-Martí, E.¹, Gago-Duport, L.³, Losa-Adams, E.³, Chevrier, V.⁴ and A. G. Fairén^{1,2}. (¹ Centro de Astrobiología (CSIC-INTA), Madrid, Spain. cgil@cab.inta-csic.es ² Department of Astronomy, Cornell University, New York, USA. ³ Departamento de Geociencias Marinas, Universidad de Vigo, Spain. ⁴ Arkansas Center for Space and Planetary Science, Fayetteville, USA).

Introduction: Mg-Fe-phyllsilicate, sulfate and carbonate bearing rocks have been identified on the Mars surface in the last decades. This wide range of weathering products point to different environmental conditions of formation in the past of Mars, usually explained by separated geochemical events occurring in different periods of time [1].

In this work, we explore the effect of varying the host-rock composition on the resulting mineral sequences under a CO₂ atmosphere. In particular, we investigate the effect of increasing pyrite (FeS₂) content in olivine (Mg₂SiO₄) powder samples. The effect of sulfide alteration has been previously investigated [2, 3], but only in oxidizing conditions. We chose pyrite, an iron disulfide, because is able to act as a natural "Fenton reagent" (i.e., as oxidizer without the addition of any oxidizing agent as H₂O₂ or O₂), inducing the formation of iron oxyhydroxides and iron sulfates by its own dissolution process [4]. We also performed geochemical models in order to analyze the mineral sequence arising from a long-term weathering process (>100 years) by using a kinetic approach. Our objective is to obtain a representative sample of the secondary mineralogy observed on Mars, starting from equal geochemical conditions and varying only the initial pyrite content. In order to do that, we combine short-time laboratory experiments with long-term geochemical models.

Methods: Olivine and pyrite mixtures prepared by weight were grinded to increase their reactive surface, and allowed to react with pure water under an early Mars analog atmosphere (PCO₂ = 0.5 atm), and at a low fluid-to-rock ratio (~10) during 42 days. After that time, the water was removed by using silica gel as desiccant during 5 days, keeping the same atmosphere. On the other hand, to analyze pyrite stability under current Mars surface conditions, the sample with the highest pyrite content (60% wt) was exposed to UV irradiation (200-400 nm) inside the simulation Planetary Atmosphere and Surface Chamber (PASC) at CAB (atmospheric composition was 99% CO₂ and 0.6% H₂O, P = 7 mbar). The oxidation capacity of pyrite may be incremented under UV irradiation because its electronic band structure can promote the formation of vacancies in the valence band, which in turn can catalyze the electron transfer to adsorbed water, thereby increasing the formation of free radicals. Weathering products

were analyzed by FTIR using DRIFT accessory, XRD, SEM and XPS.

Geochemical models were performed with the PHREEQCI 3.06 speciation-reaction code [5], allowing us to simulate the kinetic rates of the minerals, as well as the evolution of a multicomponent solution associated with the formation of altered minerals in the long-term. The models cover a wide range of situations, based on a geological scenario represented by the aqueous alteration of olivine-pyrite-rich deposits in a hypothetical early Mars cold ocean, under a CO₂ atmosphere.

Results: Experimental results showed changes in the altered samples despite the short time of aqueous reaction under a reducing atmosphere. DRIFT spectra revealed an increase in contribution in both carbonate and sulfoxy species. In particular, the irradiated (UV) sample showed the highest increment of the sulfate and iron oxide contribution in detriment of the disulfide component (Fig. 1). Earlier studies have reported that the capacity of pyrite to produce free radicals resides in its iron surface species [6, 7]. Since pyrite is a semiconductor and iron is an efficient UV absorber, it is reasonable to assume that the photoactivation of this mineral can efficiently catalyze the formation of oxidizing species (e.g., H₂O₂ and OH[•]) by splitting adsorbed H₂O. Therefore, pyrite oxidation would be able to form iron oxyhydroxides-oxides and sulfate compounds under current Mars surface conditions.

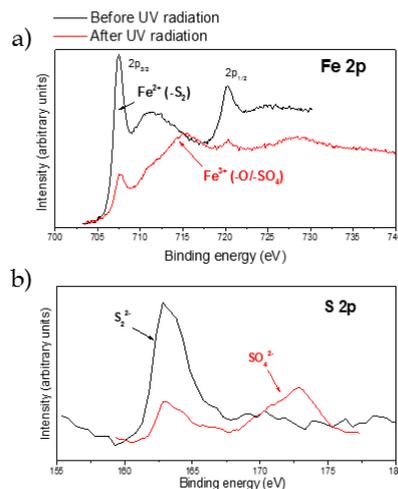


Fig. 1. XPS spectra of the sample before and after UV irradiation inside PASC: a) Fe2p and b) S2p orbital.

This hypothesis is consistent with the lack of pyrite detection on the surface of Mars to date, which is limited to just minor concentrations reported by MSL in Yellowknife mudstone deposits [8], compared to the pervasive detection of oxidized sulfur in the Martian regolith.

Our model results show the evolution of different scenarios, arising from varying the assumed initial composition of the Martian soil. As the pyrite content increased, the most acidic and oxidizing conditions of the leaching solution modified the formation pathways of the secondary products (Fig. 2). At low pH and more oxidized conditions, the mineral sequence was dominated by iron sulfates compounds. When the leaching solution evolves to neutral-alkaline conditions (i.e., by decreasing the initial content of pyrite), the system is dominated by Fe-Mg-phyllsilicates. In an intermediate situation, with mildly-acidic to mildly-alkaline conditions, the precipitation of oxihydroxides, carbonates, SiO₂ and some phyllsilicates can overlap along the simulation.

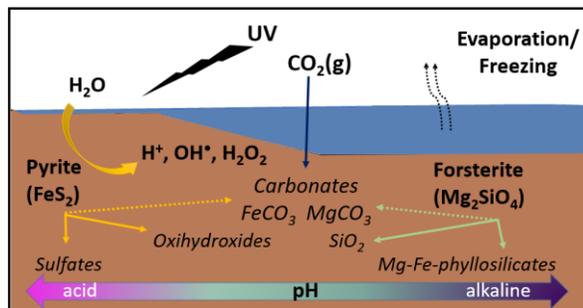


Fig. 2. Mineral sequences obtained with the geochemical models.

Conclusions: Our results suggest that the formation of free radicals by the mechanically grinded pyrite, together with the photocatalytic effect of UV irradiation, can help explain the oxidizing potential of Martian soils. In addition, geochemical models allowed us to analyze the evolution of a Martian substrate composed by different mixtures of pyrite and basalt deposits. Our model results show that a great diversity of altered products identified on Mars, such as the mixtures of carbonates, phyllsilicates and olivine-rich units located in Nili Fossae [9], or the mineral assemblage characterized by sulfate-rich phases observed in the rock outcrops at Meridiani Planum [10], can be explained without the necessity to evoke different geochemical events on early Mars.

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References: [1] Bibring, J. P. et al. (2006). *Science*, 312(5772), 400-404. [2] Chevrier, V. et al. (2004). *Geology* 32(12), 1033-1036. [3] Dehouck, E. et al. (2012). *GCA* 90, 47-63. [4] Gil-Lozano, C. et al. (2014) *8thMars*, Abstract # 1355. [5] Parkhurst, D. L. and C. A. J. Appelo (2013). *Techniques and Methods*. Reston, VA: 519. [6] Borda, M. J., et al. (2003). *GCA* 67(5), 935-939. [7] Nesbitt, H. W. et al. (1998). *Am Min* 83 (9-10), 1067-1076. [8] Vaniman, D. T. et al. (2014). *Science* 343(6169). [9] Ehlmann, B. L. et al. (2008). *Science* 322(5909), 1828-1832. [10] Squyres, S. W. et al. (2004). *Science* 306(5702), 1709-1714.