

MINERAL-INDUCED FORMATION OF FREE RADICALS: A PLAUSIBLE MECHANISM FOR ANOXIC OXIDATION IN MARTIAN SOILS. C. Gil-Lozano¹, E. Losa-Adams¹, A. F. Davila², A.G. Fairen³ and L.Gago-Duport¹. ¹Universidad de Vigo, 36310 Vigo, Spain (karolina_gil@uvigo.es). ² SETI Institute, Mountain View, CA 94043, USA ³ Cornell University, Ithaca 14853 New York, USA-

Introduction: Since the discovery of oxidizing soils on Mars potential mechanisms for the formation of Reactive Oxygen Species (ROS) on the planet have been invoked. Past studies suggested that ROS may form via photochemical reactions or by electrostatic fields during dust storms [4, 5]. Alternatively, reactive mineral particles could also promote the formation of ROS through water-rock interaction processes. Pyrite, which has been invoked to explain the S sources for the SO₂ and H₂S releases during sediment combustion by the SAM instrument on MSL [6], is known to generate ROS (e.g. H₂O₂) in the presence of water [7, 8, 9]. However, very little is known about the kinetic aspects of this process.

We investigated the kinetic of free radical generation by aqueous pyrite slurries under anoxic conditions as a possible explanation for the oxidative reactivity of Martian soils today and in the past.

Methods: Experiments were performed with acid-washed pyrite aqueous slurries under dark conditions and starting with neutral pH. We used an *ad hoc* batch reactor designed to measure at real-time and under anoxic conditions the concentration of H₂O₂ and O₂ dissolved in solution with sensors (figure 1). Physico-chemical parameters such as pH and temperature were determined simultaneously.

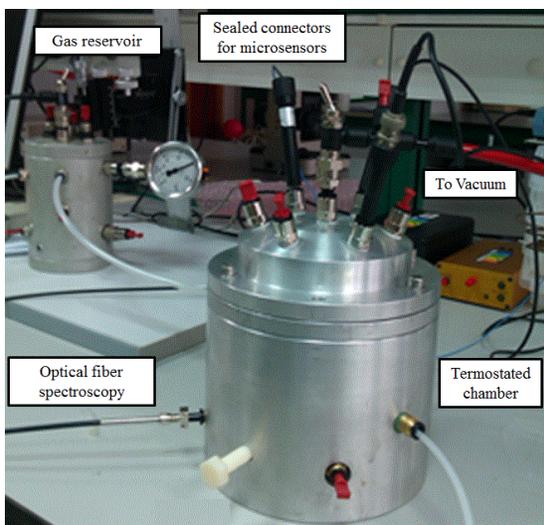
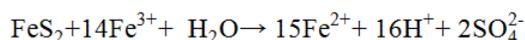
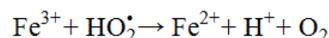
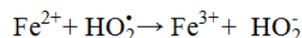
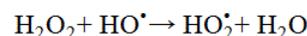
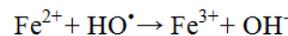
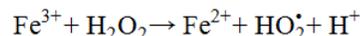
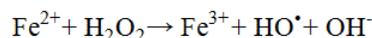
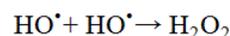
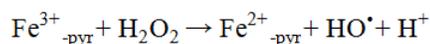


Figure 1: Batch reactor used for experiments with pyrite slurries under anoxic conditions.

In addition, iron species were evaluated by a fiber optic spectrometer connected to the device. Finally, structural modifications induced by dissolution of pyrite single-crystals at mineral-water interface were analyzed by HREM and XPS.

Results: Our experiments show that the amount of H₂O₂ in solution follows a common general trend characterized by the coupled balance between (1) the rate of H₂O₂ formation at iron surface defect sites and (2) the rate of H₂O₂ degradation by Fenton reactions. The kinetic competition between both processes controls the shape of the H₂O₂ curves and seems to be depending on the relative amounts of H₂O₂ and Fe²⁺ in solution during pyrite dissolution.

Although we conducted the experiments under anoxic conditions an appreciable amount of O₂ dissolved was detected in solution. Moreover, in spite of the fact that the measurable amount of H₂O₂ progressively decreased in the course of the experimental time, after water renovation, pyrite slurries were able to form H₂O₂ again (figure 2). This result suggests that the H₂O₂ generation at the mineral surfaces continues but H₂O₂ is rapidly transformed into other ROS species (HO[•], HO₂[•], O₂^{•-}) by the Fenton process (figure 3) due the increase of dissolved iron and the progressive acidification of the solution, according with the following reaction path:



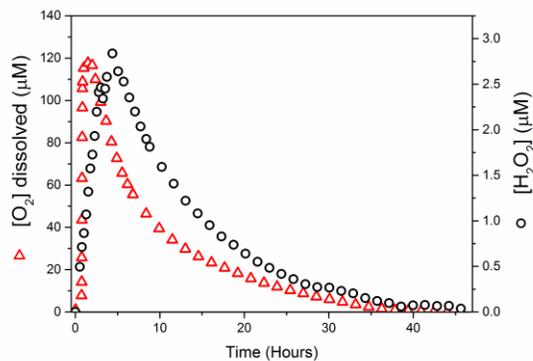


Figure 2. Time course of (a) H₂O₂ and (b) O₂(aq) generated by pyrite surfaces under anoxic conditions.

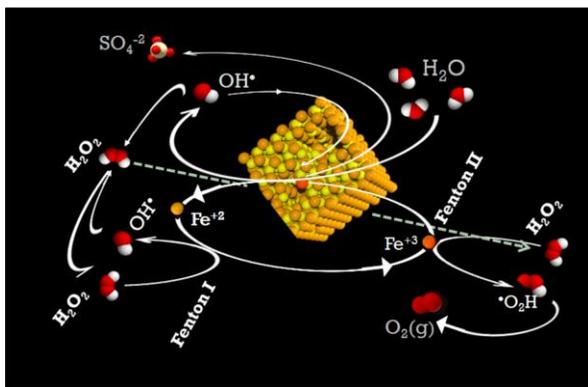


Figure 3. Proposed pathway for pyrite oxidation under anoxic conditions leading to the final formation of O₂(g).

Conclusions: Mineral-water reactions that involve free radicals generation under anoxic conditions may be a plausible mechanism to promote oxidation on Mars up to recent times. Our results show that pyrite slurries are able to form H₂O₂ and O₂ at μM concentrations. The capacity of this mineral to form ROS together with their capacity to act as a Fenton-like reagent [10] suggest that this process could be a way to induce long-term oxidation by a free radical mechanism in geological systems.

References: [1] Klein, H.P. et al. (1976). *Science* 194, 99–105. [2] Clancy, R.T. et al. (2004). *Icarus* 168, 116–121. [3] Encrenaz, T. et al. (2004). *Icarus* 170, 424–429. [4] Atreya, S.K. et al. (2006). *Astrobiology* 6/3, 439–450 [5] Encrenaz, T. et al. (2011). *Planet.Space.Sci.* [6] Ming et al. (2014). *Science*, 343 6169 [7] Borda et al (2003) *GCA*, 67 (5), 935-939 [8] Schoonen et al (2010) *GCA*, 74 (17) [9] Davila et al. (2008). *EPSL*, 272,456–463. [10] Wang et al. (2012) *Chemosphere* 86 (4), 376-382.