

EXPERIMENTAL OXIDATION OF PYRITE, PYRRHOTITE, MAGNETITE, & SMECTITE BY CHLORATE & BROMATE: OXYHALOGEN SPECIES AS ACTIVE OXIDANT ON MARS. K. Mitra¹, Y. Bahl¹, V. B. R. Banuchi¹, J. G. Catalano^{2,3}, and J. A. Hurowitz¹, ¹Department of Geosciences, Stony Brook University, Stony Brook, NY 11727 USA, ²Department of Earth & Planetary Sciences, Washington University, Saint Louis, MO 63130 USA, ³McDonnell Center for the Space Sciences, Washington University, St. Louis, MO, 63130, United States (kaushik.mitra@stonybrook.edu)

Introduction: Ferrous (Fe(II)-containing) minerals, including olivine, pyroxenes, pyrite, pyrrhotite, magnetite, and smectites, have been detected on the surface of Mars and in Martian meteorites [1,2,3,4,5,6]. Interaction of primary silicate minerals with aqueous fluids is hypothesized to be the primary source of dissolved Fe(II) in Martian groundwater and surface water. Previous studies have reported extensive oxidation of dissolved Fe(II) by oxyhalogen species (chlorate and bromate) [7,8,9] with rates orders of magnitude faster than oxidation by O₂ or via photooxidation. Oxidation by oxyhalogens produces ferric iron minerals, such as jarosite, goethite, and akaganeite, with variations in mineralogy determined primarily by the solution composition and temperature. While the oxidation of dissolved Fe(II) by oxyhalogen species has been thoroughly investigated [6,7,8], the direct oxidation of ferrous minerals by oxyhalogen brines have not been studied under Mars-relevant conditions.

Ferric iron minerals have been reported to coexist with mineral hosts of Fe(II) at several locations on Mars (e.g., [6,9]). Contact with oxyhalogen brines could result in direct heterogeneous oxidation resulting in the (i) dissolution of the minerals and the formation of Fe(III)-bearing coatings on the substrate, (ii) extensive oxidative weathering to form a variety of Fe(III)-bearing minerals including iron oxides, oxyhydroxides, or sulfates, or (iii) oxidation of Fe(II) with resulting Fe(III) remaining in the structure of the host mineral. The presence of oxic brines have been suggested by previous studies [9,10]. Oxyhalogen brine percolation on early Mars may have oxidatively weathered sulfide minerals and led to the formation of iron sulfates and oxides. Such brines were likely active on Mars during the Amazonian (~2.4 Ga) [11] and may still be present on the (sub)surface of Mars today.

However, the role of oxyhalogen brines in ferrous mineral oxidation and the subsequent formation of alteration minerals in Mars-like conditions has not been investigated and therefore needs experimental study. Here, we investigate the susceptibility of pyrite (FeS₂), pyrrhotite (FeS), magnetite (Fe₃O₄), and smectite to oxidation and subsequent alteration mineral formation by chlorate and bromate via laboratory experiments under anoxic conditions in Mars-relevant fluids.

Methods: Laboratory experiments were conducted to investigate the mineral products of oxidative weathering of pyrite, pyrrhotite, magnetite, and smectite with

chlorate (ClO₃⁻) and bromate (BrO₃⁻) at ambient conditions (24°C, 1 atm). ACS-grade pyrite and pyrrhotite reagents were purchased from Fisher Scientific. Magnetite and smectite were synthesized in the lab following established procedures [12,13]. All synthesis and experimental procedures were conducted inside an anaerobic chamber [N₂ = 97%, H₂ = 3%, O₂ < 1ppmv] in Al-foil wrapped, glass serum bottle reactors to inhibit inadvertent oxidation by oxygen or via UV photooxidation. The experiments were conducted without stirring in order to replicate a stagnant surface/pore water environment. Experiment duration was ~100 days except pyrrhotite (~50 days), owing to its high reactivity.

The experiments were designed to evaluate the alteration of ferrous minerals as a function of oxidant type (ClO₃⁻ and BrO₃⁻), initial pH (7, 5, and 3), and background fluid (MgCl₂ and MgSO₄). The background salt solutions of MgCl₂ or MgSO₄, represent the most relevant fluid compositions on Mars [14]. The background salts also serve as ionic strength buffers and provide anions with different ability to complex any dissolved Fe(II/III) in the solution, thereby having the capacity to affect reaction rates and the mineral products of sulfide alteration. Solutions containing 2 g L⁻¹ of either pyrite, pyrrhotite, magnetite, or smectite were allowed to react with ~100 mmol L⁻¹ NaClO₃ or NaBrO₃ in background salt mixtures of 100 mmol L⁻¹ Mg-chloride or Mg-sulfate at initial pH 7, 5, or 3, which was set using 1 mol L⁻¹ solutions of HCl and NaOH. The experimental pH was allowed to drift freely as a response to mineral dissolution and oxidation to determine the effect of mineral oxidation and precipitation on fluid pH, which was measured at the end of each experiment. Analogous oxidant-free control experiments were also prepared at pH 7 and 3.

After the completion of experiments, the reactors were filtered using a 0.22 μm pore size MCE membrane and dried in the anaerobic chamber in a vacuum desiccator at 24°C. The filtered samples were analyzed and characterized using XRD and SEM and the supernatant was analyzed using ICP-OES and IC.

Results: Pyrite and pyrrhotite show evidence of extensive oxidative alteration by chlorate and bromate in all fluid conditions (Figs. 1 and 2). Smectite reactions are currently ongoing and show visual evidence of Fe(III) formation in both chlorate and bromate containing solutions within ~30 days of reaction (Fig. 3). Interestingly, magnetite has resisted dissolution, exten-

sive Fe(III) formation, and any variation in XRD patterns after ~100 days of reaction. Currently, Fe(II)/Fe(III) ratios are being determined.

Extensive Sulfide Oxidation: Chlorate and bromate can oxidatively weather pyrrhotite and pyrrhotite to form Fe(III) sulfates and (oxyhydr)oxides in both chloride- and sulfate-rich solutions across near-neutral to acidic pH conditions (Fig. 1 and 2). Bromate demonstrated faster and more extensive sulfide alteration than chlorate in all experimental conditions. The products of

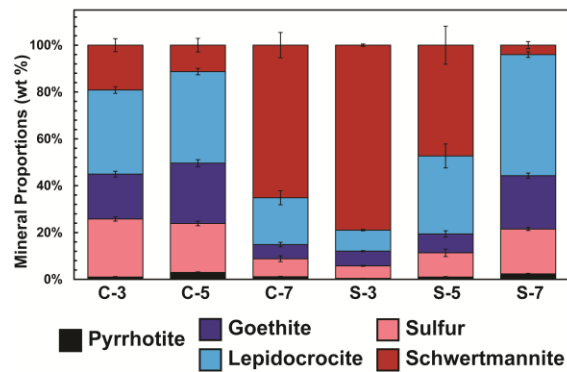


Figure 1: Mineral proportions from pyrrhotite alteration by 100 mmol L^{-1} chlorate generated using Rietveld refinement of X-ray diffraction scans. The sample labels at the bottom of each column depict the fluid type (C = Mg-chloride fluid, S = Mg-sulfate fluid) and the initial pH.

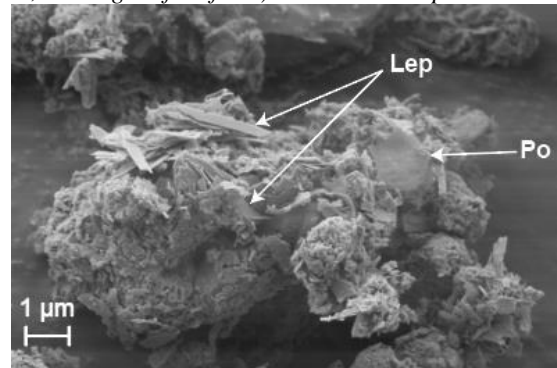


Figure 2: Scanning electron microscopy (SEM) images of the mineral products of the precipitates formed by the oxidation of pyrrhotite by 100 mmol L^{-1} chlorate (ClO_3^-) in MgSO_4 fluid at pH 3. Po = Pyrrhotite; Lep = Lepidocrocite.



Figure 3: The photographic image of the reactors (Al foil removed) containing smectite and 100 mmol L^{-1} chlorate in different MgCl_2 and MgSO_4 fluids at pH 3, 5, and 7 (see sample labels) after 30 days of reaction. The last two reactors are control experiments with no chlorate at pH 3 and pH 7.

sulfide weathering are dependent on the sulfide composition, oxidant type, the background fluid, and initial pH. Sulfur and Fe(III) oxyhydr(oxides) minerals including goethite, lepidocrocite, and magnetite precipitated in solutions that underwent lower levels of sulfide alteration. Sulfate minerals like jarosite and schwertmannite formed during more extensive alteration of sulfide thereby suggesting a sequence of sulfide alteration products primarily controlled by the rate and extent of sulfide weathering. Jarosite and schwertmannite formed in both chloride- and sulfate-rich fluids demonstrating the oxidation of S^- to SO_4^{2-} .

Smectite Alteration: Early results show evidence of oxidative alteration in both chlorate and bromate. While smectite alteration by chlorate at the end of a month remain mostly confined to acidic fluids (Fig 3), reactors containing bromate show visual evidence of alteration (similar to low pH chlorate reactors) in all fluids (not shown). Analysis will be performed on the end products at the end of the reaction period.

Magnetite Alteration. Secondary minerals did not form but the stoichiometry of post-reaction magnetite has not been determined yet. Ongoing analysis of Fe(II)/Fe(III) ratios will provide further information on whether the magnetite is non-reactive, or if it is undergoing ~isostructural oxidation to form, e.g., non-stoichiometric magnetite or maghemite.

Conclusion: Oxyhalogen species can oxidatively weather iron sulfide to form a range of secondary minerals that have been detected on the surface of Mars. Fe/Mg smectite oxidation also occurs in the presence of such fluids, and might form secondary mineral products such as jarosite, goethite, and/or nontronite. Magnetite reactivity appears to be more limited, but ongoing work will confirm if Fe(II) oxidation to Fe(III) in the mineral structure results in structural modification. Ultimately, our results provide a guide for interpreting the mineralogy of samples returned from Mars.

Acknowledgments: Funding from Simons Foundation, NASA Astrobiology Program and FINESST supported the research. L Wehrmann, D Black, T Glotch, and J Quinn are thanked for help with analysis.

References: [1] Ehlmann B. & Edwards, C. (2014) *AREPS*, 42, 291-315 [2] Tomkins A. et al. (2020) *GCA*, 290, 59-75 [3] Greenwood et al. (2000) *GCA* [4] Niles P. et al. (2013) *SSR*, 174, 301-328 [5] Koeppen W. & Hamilton V. (2008) *JGRP* 113 [6] Vaniman D.T. et al. (2014) *Sci*, 343, 1243480 [7] Mitra K. & Catalano J. (2019), *JGRP*, 124, 2893-2916 [8] Mitra K. et al. (2020) *Min.*, 10, 729 [8] Mitra K. et al. (2022) *Ear. Spa. Chem.* 6, 250-260 [9] Rampe E. et al. (2017), *EPSL*, 471, 172-185 [10] Stamenkovic V. et al. (2018), *Nat. Geo.* 11, 905-909 [11] Martin P. et al. (2017), *JGRP*, 122, 2803-2818 [12] Schwertmann U. & Cornell R. (2008) *Iron Oxides in the Lab* [13] Chemtob S. et al., (2013) *JGRP-P*, 120, 1119-1140 [14] Rapin W. et al. (2019) *Nat. Geo.*, 12, 889-895.