**STOICHIOMETRIC EFFICIENCY OF IRON OXIDATION BY CHLORATE ON MARS.** E. L. Moreland, K. Mitra, and J. G. Catalano, Department of Earth & Planetary Sciences, Washington University, Saint Louis, MO 63130 USA (morelandellie@wustl.edu)

Introduction: Diverse processes generate oxychlorine species on Mars [1-2], possibly dating back to 4 Ga [3]. These species occur in quantities as high as ~1 wt.% in soil, sediment, and rock samples [4-6]. Perchlorate (ClO_4^-) and chlorate (ClO_3^-) are the two most common oxychlorine species found on Mars [1]. Despite its large redox potential, ClO_4^- is kinetically inert as an oxidant except at high temperature [7, 8]. In contrast, ClO_3^- readily oxidizes dissolved Fe(II) [9] at rates under many conditions that are orders of magnitude faster than UV-photooxidation or oxidation by O_2 [7]. This produces an array of Fe(III)-bearing minerals found on Mars. These observations suggest that ClO_3^- is a potentially important Fe(II) oxidant on the martian surface [7].

Each ClO_3^- theoretically oxidizes six Fe(II) atoms:

$$6Fe^{2+} + ClO_3^- + 6H^+ = 6Fe^{3+} + Cl^- + 3H_2O \ (1)$$
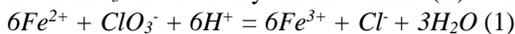
This process likely proceeds stepwise through six individual reactions that produce intermediate chlorine species [10]. It is uncertain if these intermediates react with Fe(II) before decomposing, and the effective capacity for Fe(II) oxidation by ClO_3^- is thus unknown. Since ClO_3^- is present in small quantities on Mars, it is essential to assess the capacity of ClO_3^- to oxidize Fe(II) under Mars-relevant conditions. The rates and products of dissolved Fe(II) oxidation by ClO_3^- were measured at different Fe(II)/ClO_3^- ratios, fluid types, and pH values to investigate the effective oxidative capacity of ClO_3^-.

Methods: *Kinetic Experiments:* All experiments were prepared inside of an anaerobic chamber (N_2 = 97%, H_2 = 3%) with <1 ppmv O_2 concentration. 40 ml solutions with [Fe(II)]:[ClO_3^-] approximately 6:1 or 10:1 were prepared with ~10 mM of Fe(II) and 1.67 and 1 mM ClO_3^-, respectively. Background salts of ~100 mM $MgCl_2$ or $MgSO_4$ were used to explore Mars-relevant solutions [11-13] and buffer the ionic strength. The pH was initially set to 3, 5, or 7 and allowed to drift with the reaction as Fe(II) oxidation is a primary source of acidity on Mars [14]. All samples were prepared in 50 mL polypropylene centrifuge tubes wrapped in Al foil to prevent photochemistry and were continuously mixed on end-over-end rotators. Chlorate-free control experiments were also prepared. pH and Fe(II) concentration were monitored twice per week over the course of ~100 days, the latter using UV-Vis spectrophotometry [15].

Mineral Precipitate Studies: The conditions explored in the kinetic studies were replicated at 150 ml volumes and aged without semiweekly sampling to precipitate enough volume of minerals to enable characterization. Solutions were prepared in foil-wrapped serum bottles inside of the anaerobic chamber before being sealed and transferred outside of the chamber for continuous mixing on a shaker table at ~170 RPM. A chlorate-free control experiment was also established to verify that Fe(II) oxidation was not from O_2 leakage into the serum bottles. After ~100 days, the samples were returned to the anaerobic chamber and filtered using a 0.22 μm pore size MCE membrane. Precipitates were then dried in a vacuum desiccator. These solids were characterized using X-ray diffraction (XRD), with mineral abundances quantified via Rietveld refinement.

Results: *Kinetics of Fe(II) Oxidation by Chlorate:* All experiments displayed a decrease in Fe(II) concentration and pH over time. Final pH values were between 2.0 to 2.6 regardless of the initial pH. Fe(II) oxidation in chloride-rich solutions was slightly faster than sulfate-rich solutions, as previously reported by [7], caused by complexation by sulfate. The rate of Fe(II) oxidation was proportional to ClO_3^- concentration (Fig. 1), consistent with the prediction of our recent kinetic model [7]. Notably, the ability of the rate law to describe the present experiments (Fig. 1), where ClO_3^- is not in excess, demonstrates the full oxidizing capacity of ClO_3^- is utilized in these systems, as this is an explicit assumption of the model. Had ClO_3^- displayed incomplete stoichiometric efficiency, the observed extents of Fe(II) oxidation would have been substantially less than the model predictions. The close agreement of the kinetic data to the predictive kinetic model in all different experimental conditions further demonstrates the accuracy and applicability of the kinetic model to investigate Fe(II) oxidation in Mars-relevant fluids. Transient precipitation of a fraction of the Fe(II) as green rust is hypothesized to have caused the initial abrupt decline in the 6:1 experiment in $MgCl_2$ fluid.

Mineral Precipitates: The mineral precipitates varied with [Fe(II)]:[ClO_3^-], pH, and fluid type. Goethite formed as a major product in sulfate-rich, 6:1 and 10:1 solutions. Some sulfate solutions at initial pH 3 witnessed schwertmannite formation, while magnetite dominated in sulfate solutions at pH 7 with lower Fe(II) (Fig. 2). Magnetite formed only in pH 7 solutions and coprecipitated with goethite in both chloride- and sulfate-rich systems of near-neutral pH. Lepidocrocite was formed only in chloride-rich solutions with ratio 6:1 and pH 7. Minor amounts of fougerite (i.e., green rust) were preserved in chloride-rich solution at pH 7, which is posited to have caused the abrupt decline in Fe(II) concentration. However, 6:1 reactions at pH 7 witnessed complete removal while 10:1 experiments facilitated fougerite preservation owing to the excess Fe(II) in the

solution. Cl-rich solutions at final pH < 2.5 did not yield adequate solids for mineral identification.

Discussion: The close agreement of the data to our kinetic model [7] shows the ability of ClO_3^- to oxidize dissolved Fe(II) at its maximum theoretical capacity
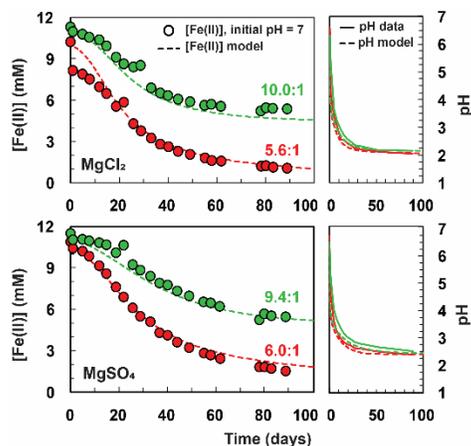

Figure 1: Dissolved [Fe(II)] and pH vs. time compared to the kinetic model containing ~10 mM Fe(II) with 1.67 mM (6:1) or 1 mM (10:1) ClO_3^- in (top) 10^{-1} M $MgCl_2$ and (bottom) 10^{-1} M $MgSO_4$ at initial pH = 7 at 24°C.
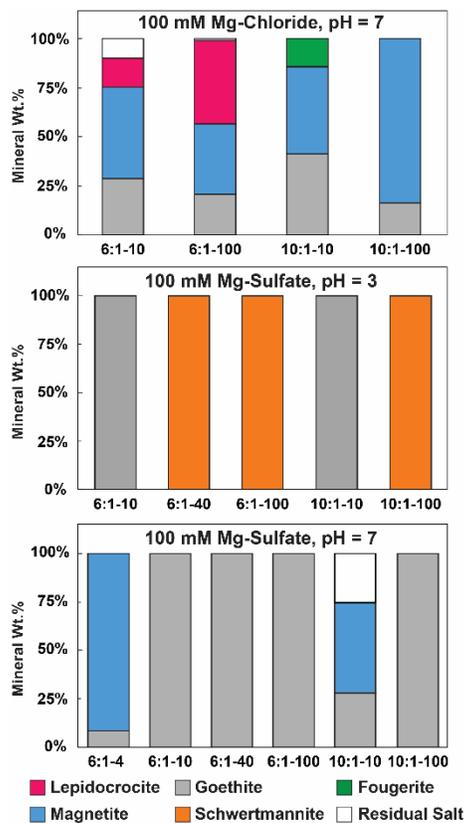

Figure 2: Mineral proportions of precipitates determined via Rietveld refinement. The abbreviated names of each experiment represent the initial ratio of Fe(II) to ClO_3^- (6:1 or 10:1) and concentration of Fe(II) in mM.

(each ClO_3^- ion can oxidize 6 Fe(II) ions). The Fe(II) oxidation rate was confirmed to depend on the amount of ClO_3^- present in the system and fluid type, as noted by [7]. The types of minerals formed from these reactions depend on fluid composition, pH, and Fe(II) oxidation rate. Fe(III) bearing minerals produced are similar to other oxidants (e.g., O_2, UV) [14]. The solution pH and fluid composition determine the mineral products by controlling the homogeneous nucleation of Fe(III), a process determined by reaction kinetics rather than energetics. This combined effect is verified by the formation of schwertmannite in pH 3 solutions with relatively faster Fe(II) oxidation only. Lepidocrocite and magnetite formed in pH 7 solutions with slower oxidation. Magnetite formation in both 6:1 and 10:1 solutions suggests that the relative amount of oxidant alone may not be a critical factor in determining the mineral products as proposed by [16]. The oxidation rate is shown to exhibit a predominant effect on the mineral products as chemically analogous solutions in our previous study [7] produced minerals like akaganeite or jarosite.

Although ClO_3^- occurs in relatively low abundance on the Martian surface (<1 wt.%) [1-3], the oxidizing capacity demonstrated here suggests that even small amounts of ClO_3^- can produce large amounts of Fe(III)-bearing minerals. Stoichiometric calculations show that 1 gram of ClO_3^- can ultimately produce 5.7 grams of hematite (following diagenesis). Furthermore, the Cl^- product from this reaction (Eq. 1) can be re-oxidized to ClO_3^- as part of the chlorine cycle on Mars. The possible continuous regeneration of ClO_3^- further compensates for the small amount on the Martian surface.

Conclusion: ClO_3^- displays its maximum capability to oxidize 6 Fe(II) ions per ClO_3^- molecule in Mars-relevant fluids. ClO_3^- can produce Fe(III)-bearing minerals even when present in small quantities and may be regenerated through an active oxychlorine cycle on Mars. The minerals produced are dependent on the fluid composition, pH, and the rate of the reaction, corroborating their importance to be used as paleo-environmental and paleo-geochemical indicators on Mars.

References: [1] Carrier & Kounaves et al., 2015, *GRL.*, *42*, 3739-3745. [2] Catling et al., 2010, *JGRP*, *115*, E00E11. [3] Georgiou et al., 2017, *Astrobio.*, *17*, 319-336. [4] Sutter et al., 2017, *Int. J. Astrobiol.*, *16*, 203-217. [5] Hecht et al., 2009, *Sci.*, *325*, 64-67. [6] Ming et al., 2014, *Science, 343,* 1245267. [7] Mitra & Catalano, 2019, *JGRP.* [8] Urbansky, 2002, *Env. Sci Poll. Res.*, *9*, 187-192. [9] Madlo., 1979, *Collect. Czech. Chem. Comm., 44,* 2760-2768. [10] Shakhashiri & Gordon, 1969, *JACS, 91*, 1103-1107. [11] Rapin et al., 2019*, Nat. Geosci.*, *12,* 889–895. [12] Léveille et al., 2014, *JGRP, 119*, 2398-2415. [13] Nuding et al., 2014, *Icarus, 243,* 420-428. [14] Hurowitz et al., 2010, *Nat. Geo.*, *3*, 323-326. [15] Viollier et al., 2000, *Appl. Geochem.*, *15*, 785-790. [16] Hurowitz et al., 2017, *Science, 356*, eaah6849.