

**Fe(II) OXIDATION AND Fe(III) MINERAL PRODUCTION BY CHLORATE AT MARS-RELEVANT TEMPERATURES: REACTION RATES & MINERAL PRODUCTS.** K. Mitra, E. L. Moreland, and J. G. Catalano, Department of Earth & Planetary Sciences, Washington University, Saint Louis, MO 63130 USA (k.mitra@wustl.edu)

**Introduction:** Mars today is cold with an average surface temperature of  $\sim 63^{\circ}\text{C}$ . Transient temperatures range from  $>20^{\circ}\text{C}$  in equatorial regions to  $<-150^{\circ}\text{C}$  near the poles [1]. Despite the predominantly sub-freezing temperatures, the presence of salts (e.g., perchlorate, chlorate) on Mars can stabilize liquid water on the surface and in the subsurface through freezing point depression [2, 3]. Liquid water on Mars is hypothesized to have been active during the Amazonian in the form of transient nighttime brines, downward migrating brine fluids, and thin-films around sediment grains in the shallow subsurface [4-7].

Aqueous geochemical processes on Mars are believed to have occurred between brine eutectic points and  $\sim 80^{\circ}\text{C}$ , maximum estimated diagenetic temperatures in Gale crater [8]. Although higher temperature conditions may be possible in a few locations on Mars due to hydrothermal activity associated with impacts or volcanism [9], liquid water on the surface was likely temporally restricted to time periods experiencing transient warming [10]. Therefore, understanding geochemical processes, such as oxidation, as a function of temperature is imperative. Our recent study [11] demonstrated the efficiency of chlorate ( $\text{ClO}_3^-$ ), a prominent oxychlorine species on Mars, to oxidize dissolved Fe(II) at  $22^{\circ}\text{C}$ . The rate of Fe(II) oxidation by  $\text{ClO}_3^-$  was found to be faster than by  $\text{O}_2$  or by UV photooxidation. However, reactions rates for such systems are unexplored at low temperatures [11,12]. This rate is expected to show a strong temperature dependence owing to the reported large activation energy ( $80 \pm 5$  kJ/mol [12]). In this study, the rate of Fe(II) oxidation by  $\text{ClO}_3^-$  in Mars-relevant fluids is explored between 0 and  $15^{\circ}\text{C}$ . The effects of temperature on the products are also investigated and compared, as mechanistic controls of mineral formation are expected to vary with temperature.

**Methods:** Kinetic experiments were conducted to explore the rate of Fe(II) oxidation by  $\text{ClO}_3^-$  in Mars-relevant fluids at 0, 4, 10, and  $15^{\circ}\text{C}$  at ambient pressure (1 atm). In order to isolate the effects of  $\text{ClO}_3^-$  on dissolved Fe(II), all samples were prepared inside an anaerobic chamber [ $\text{N}_2 = 97\%$ ,  $\text{H}_2 = 3\%$ ,  $\text{O}_2 < 1$  ppmv] to inhibit oxidation by  $\text{O}_2$  and wrapped in Al foil to inhibit photooxidation. Solutions were prepared in bottles inside of the anaerobic chamber that were chilled to  $0^{\circ}\text{C}$  in water-ice baths. 40 ml solutions containing  $\sim 10$  mM Fe(II) with equimolar amounts of  $\text{ClO}_3^-$  ( $\text{Fe(II)}/\text{ClO}_3^- = 1$ ) in background salt mixtures of 0.1 M Mg-chloride and Mg-sulfate were prepared to simulate Mars-relevant fluids with initial pH set to 7 or 5. The

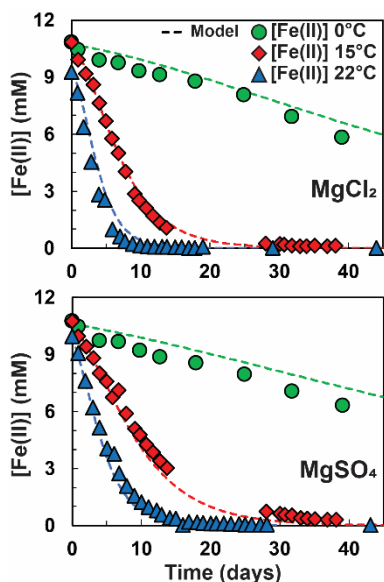
background salts serve as ionic strength buffers and provide anions with different ability to complex dissolved iron. The rate of Fe(II) oxidation by equimolar  $\text{ClO}_3^-$  in perchlorate fluids previously showed similar rates to chloride systems [11] and hence are not investigated in the present study. The pH values of the solutions were set by addition of 1 M HCl or NaOH and then allowed to drift with the progress of the reaction. Fe(II)-oxidation has been suggested as a major source of acidity on Mars [13] and pH changes serve as a secondary indicator of Fe(II) oxidation.

All sealed reactors were transferred to a  $4^{\circ}\text{C}$  cold room equipped with a digital temperature controller and real-time monitor. The 10 and  $15^{\circ}\text{C}$  reactors were placed in digital heating water baths operating in the cold room. The  $4^{\circ}\text{C}$  reactors were placed in unheated water baths in the cold room to buffer the minor temperature fluctuations that may occur due to periodic opening of the cold room. The  $0^{\circ}\text{C}$  reactors were kept inside an insulated icebox filled with water-ice inside the  $4^{\circ}\text{C}$  cold room. Temperature inside the ice-box was maintained at  $0^{\circ}\text{C}$  by replacing the ice every 4-5 days. Chlorate-free control experiments were set up at pH 7 at  $24^{\circ}\text{C}$  to ensure the efficacy of the experimental set-up. The reactors were kept static during the entire course of the reaction. The above static approach is valid as relevant diffusion rates are faster than the expected maximum reaction rates. The reactors were periodically transferred to iceboxes and brought inside the anaerobic chamber for extracting small aliquots to measure Fe(II) concentration and pH. The total time the reactors were kept at near-freezing temperatures during sampling was not more than 15 minutes. The brief temperature depression likely has little effect on the reaction kinetics as complete oxidation is expected to occur on timescale of several weeks to months.

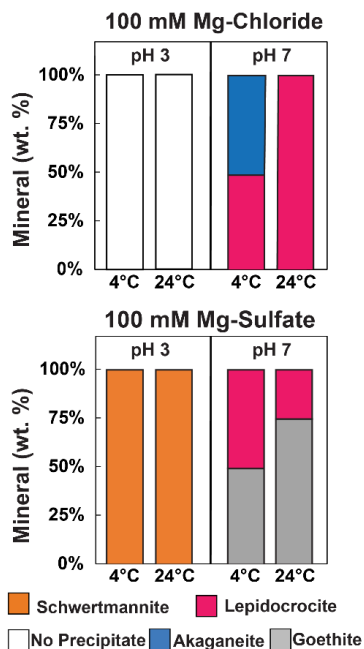
Experimental replicates with higher volumes (150 mL) were prepared to investigate the mineral products at 4 and  $24^{\circ}\text{C}$ . Samples were prepared at pH 3 and 7 containing  $\sim 10$  and 100 mM Fe(II) in equimolar  $\text{ClO}_3^-$  in 100 mM  $\text{MgCl}_2$  and  $\text{MgSO}_4$ . The reactors were initiated inside the anaerobic chamber and sealed in serum bottles. The reactors for the  $4^{\circ}\text{C}$  experiments were then transferred to the cold room, while the  $24^{\circ}\text{C}$  reactors were kept in secondary containers on the laboratory benchtop. The  $24^{\circ}\text{C}$  studies were designed to explore whether the stagnant experimental systems led to distinct nucleation processes compared to well-mixed systems studied previously [11]. After  $\sim 100$  days, the samples were returned to the anaerobic chamber and filtered using a  $0.22$   $\mu\text{m}$  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 and Discussion:** All reactors displayed a substantial decrease in Fe(II) concentration and pH with time (Fig. 1). The SO<sub>4</sub>-rich samples displayed slower



**Figure 1:** Oxidation of  $10^{-2}$  M Fe(II) by  $10^{-2}$  M NaClO<sub>3</sub> in  $10^{-1}$  M MgCl<sub>2</sub> at initial pH 3 at 0, 15, and 22°C (from [5]) compared to kinetic model developed by [5].



**Figure 2:** Mineral proportions of precipitates determined via Rietveld refinement. Oxidation of  $10^{-1}$  M Fe(II) by  $10^{-1}$  M NaClO<sub>3</sub> in  $10^{-1}$  M MgCl<sub>2</sub> and MgSO<sub>4</sub> at initial pH 3 and 7 at 4 and 24°C.

oxidation rates compared to Cl-rich systems, consistent with prior study [11]. Temperature exerted a dominant control on the rate of reaction as demonstrated by the drastic decrease in reaction rate at lower temperatures (Fig. 1). The results of the current study were compared to reaction kinetics predicted by the model developed in [11]. This model agreed well with the experimental results despite having been parameterized at higher temperatures [11,12]. Longer timescales are being explored to fully evaluate the nature of low temperature Fe(II) oxidation by chlorate.

The mineral products showed primary dependence on fluid type, pH, and Fe(II) concentration (Fig. 2). Cl-rich solutions at initial pH 3 did not yield substantial mineral for characterization using XRD. The reactors at pH 7 with 10 mM Fe(II) in Cl-rich solutions produced lepidocrocite and goethite in equal amounts in both 4 and 24°C reactors, with a minor increase in goethite proportion at 24°C (not shown). Experiments with 100 mM Fe(II) primarily produced a lepidocrocite-akaganeite mixture at 4°C. Only lepidocrocite formed at 24°C under the sample conditions, apparently promoted by faster Fe(II) oxidation at the higher temperature [14]. SO<sub>4</sub>-rich solutions containing 10 and 100 mM Fe(II) at pH 3 produced schwertmannite at both 4 and 24°C. Our previous studies conducted at 22°C in similar fluids produced jarosite [11]. This demonstrates the importance of physical effects on mineral formation, with nucleation processes in physically stagnant systems (e.g., lake or pore water) at least temporarily stabilizing precursor minerals. SO<sub>4</sub>-rich solutions at pH 7 produced goethite and lepidocrocite, with the amount of goethite increasing with temperature.

**Conclusions:** Chlorate readily oxidized Fe(II) at low temperatures (~0°C) to produce Fe(III) minerals in Mars-relevant fluids on relatively short timescales. The results demonstrate the broad range of conditions under which chlorate is an effective Fe(II) oxidant on Mars. This potentially extends to cold conditions in the Amazonian that persist to the present day.

**References:** [1] Carr M. H. (2006) *The Surface of Mars*. [2] Chevrier V. F. et al. (2009) *GRL*, 36, L10202. [3] Hanley J. et al. (2012) *GRL*, 39, L08201. [4] Martin-Torres F.J. et al. (2015) *Nat. Geo.*, 8, 357–361. [5] Boxe C. S. et al. (2012) *Int. J. Astrobio.*, 11, 169–175. [6] Martinez G. M. and Renno N.O. (2013) *Space Sci. Rev.*, 175, 29–51. [7] Möhlmann D. T. F. (2008) *Icarus*, 195, 131–139. [8] Vaniman D. T. et al. (2014) *Science*, 343, 1243480. [9] Rathbun J. A. and Squyres, S. W. (2002) *Icarus*, 157, 362–372. [10] Wordsworth R. (2017) *GRL*, 44, 665–671. [11] Mitra K. and Catalano J.G. (2019) *JGRP*, 10.1029/2019JE006133. [12] Madlo K. (1979) *Coll. Czech. Chem. Comm.*, 44, 2760–2768. [13] Hurowitz et al., 2010, *Nat. Geo.*, 3, 323–326 [14] Schwertmann U. et al. (2004) *Clays Clay Min.*, 52, 221–226.