

**OXYCHLORINE SPECIES AS AN OXIDANT ON PAST AND PRESENT MARS: NEW OXIDATION PATHWAYS FOR DISSOLVED Fe(II) ON THE MARTIAN SURFACE.** K. Mitra and J. G. Catalano, Department of Earth & Planetary Sciences, Washington University, Saint Louis, MO 63130 USA (k.mitra@wustl.edu)

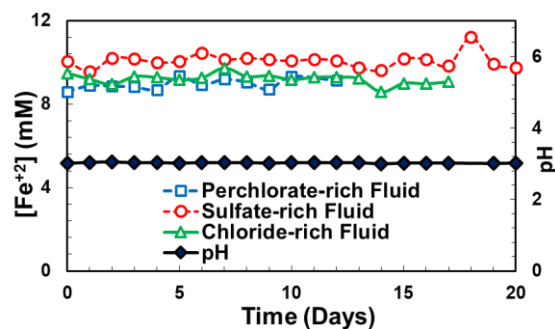
**Introduction:** Oxychlorine (perchlorate, chlorate) salts are common chlorine species on the surface of Mars, having an extensive spatial and temporal distribution [1] with concentrations in soil as high as 0.5 to 1.0 wt.% [2]. Their formation processes are thought to have been active during the entire geological history of Mars [3]. Perchlorate ( $\text{ClO}_4^-$ ) and chlorate ( $\text{ClO}_3^-$ ) are major products in all known oxychlorine formation pathways, and the amount of chlorate produced is either equal to or greater than perchlorate production [4], with minor amounts of chlorite ( $\text{ClO}_2^-$ ) and hypochlorite ( $\text{ClO}^-$ ). The role of oxychlorine species on Mars as oxidants of reduced iron has been largely overlooked to date. While perchlorate is chemically inert towards  $\text{Fe}^{2+}$  despite the favorable thermodynamics of such reactions, chlorate, chlorite, and hypochlorite are likely kinetically more reactive [5]. The rates and mineral products of Fe(II) oxidation by oxychlorine species is currently unclear. In this study, we investigate the kinetics of oxidation of dissolved Fe(II) by perchlorate and chlorate at pH 3, 5 and 7 in Mars-relevant fluids. The influence of fluid composition on the mineralogy of the resulting Fe(III) solids was also determined.

**Methods:** (A) *Kinetic Experiments:* 40 ml solutions were prepared containing 10 mM Fe(II) with 10 mM  $\text{NaClO}_3$  or  $\text{NaClO}_4$ . All studies were conducted at initial pH values of 3, 5, or 7 in a 0.1 M  $\text{MgCl}_2$ ,  $\text{MgSO}_4$ , or  $\text{Mg}(\text{ClO}_4)_2$  electrolyte to buffer the ionic strength and to provide anions with different ability to complex dissolved iron. Oxychlorine-free control experiments were set up with 10 mM Fe(II) in 0.1 M  $\text{MgCl}_2$  and  $\text{MgSO}_4$ . All reactions were carried out in an anaerobic chamber ( $\text{N}_2 = 97\%$ ,  $\text{H}_2 = 3\%$ ) with  $<1$  ppmv  $\text{O}_2$  concentration. The experimental solutions were prepared in 50 mL centrifuge tubes wrapped in aluminum foil to prevent photochemical  $\text{Fe}^{2+}$  oxidation. These were continuously mixed on an end-over-end rotator. The pH was allowed to drift with reaction. The pH and  $\text{Fe}^{2+}$  concentration were measured at regular time intervals, the latter via spectrophotometry following complexation by ferrozine [6].

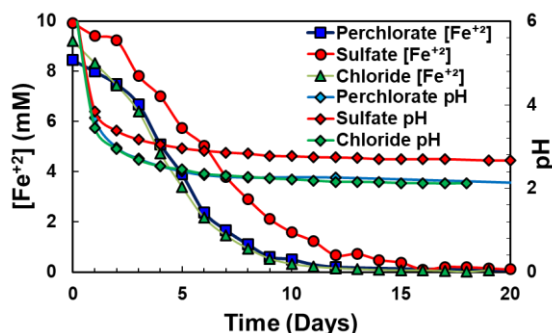
(B) *Mineral Precipitation Studies:* Select kinetic experiments were repeated with a solution volume of 150 mL to generate larger amounts of mineral solids needed for characterization. Additional experiments were also conducted using higher concentrations of dissolved  $\text{Fe}^{2+}$  and chlorate (100 mM each) to explore the effect of concentration on the type(s) of mineral precipitated; lower initial pH (~1) was also investigated for chloride fluids. The solutions were stored in

polypropylene bottles wrapped with aluminum foil and continuously stirred for approximately 4 weeks. The resultant solution was allowed to settle and the fluid separated from the solids via either centrifugation or filtration using 0.22  $\mu\text{m}$  pore size MCE membranes. The resulting solid samples were dried in the anaerobic chamber in a vacuum desiccator for 3-4 days. The mineralogy of the dried solids was characterized using powder X-ray diffraction (XRD).

**Results:** (A) *Kinetics of  $\text{Fe}^{2+}$  Oxidation:* Perchlorate was found to induce negligible oxidation of  $\text{Fe}^{2+}$  in  $\text{MgCl}_2$ ,  $\text{MgSO}_4$ , or  $\text{Mg}(\text{ClO}_4)_2$  solutions (Fig. 1). The pH, which was initially set to 3, did not deviate during the entire course of the experiment. In contrast, chlorate caused near-complete  $\text{Fe}^{2+}$  oxidation within 30 days for all fluid compositions examined (Fig 2). The rate of oxidation almost followed similar trends for various pH conditions: pH 3 > pH 7 > pH 5. The oxidation rate in perchlorate fluid was fastest at pH 3, while those at pH 5 and 7 were comparable.  $\text{Fe}^{2+}$  oxidation was coupled with a decrease in pH for all chlorate experiments. No



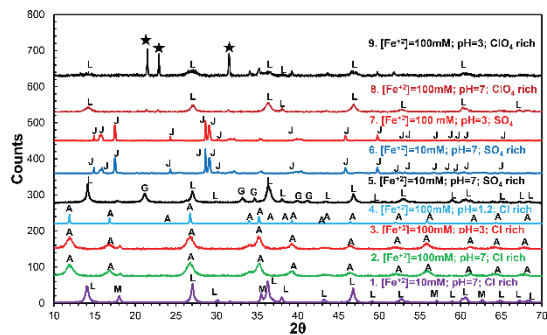
**Figure 1:** Oxidation of  $10^{-2}$  M  $\text{Fe}^{2+}$  by  $10^{-2}$  M  $\text{NaClO}_4$  in  $10^{-1}$  M Mg chloride, sulfate, or perchlorate fluids. Only one pH curve is plotted for clarity as all were indistinguishable.



**Figure 2:** Oxidation of  $10^{-2}$  M  $\text{Fe}^{2+}$  by  $10^{-2}$  M  $\text{NaClO}_3$  in  $10^{-1}$  M Mg chloride, sulfate, or perchlorate fluids.

$\text{Fe}^{2+}$  oxidation or changes in pH were observed in oxychlorine-free control experiments.

(B) *Mineral Products:* The mineralogy of the solids produced during  $\text{Fe}^{2+}$  oxidation (Fig. 3) by chlorate varied with fluid composition. At pH 7, lepidocrocite [ $\gamma\text{-FeOOH}$ ] formed at low (10 mM)  $\text{Fe}^{2+}$  concentration in chloride and sulfate fluids along with minor magnetite and goethite, respectively. At higher  $\text{Fe}^{2+}$  concentration (100 mM) at all pH values akaganéite [ $\beta\text{-FeO}(\text{OH},\text{Cl})$ ] formed in chloride fluids, mixed Na- and  $\text{H}_3\text{O}$ -jarosite [ $\text{XFe}_3(\text{OH})_6(\text{SO}_4)_2$ ,  $\text{X} = \text{Na}^+$  or  $\text{H}_3\text{O}^+$ ] formed in sulfate fluids, and lepidocrocite formed in perchlorate fluids.



**Figure 3:** XRD patterns of solids produced during  $\text{Fe}^{2+}$  oxidation by chlorate. Diagnostic peaks are: J = Jarosite, A = Akaganéite, L = Lepidocrocite, G = Goethite, M = Magnetite, \* = Mg perchlorate.

**Discussion: Lack of  $\text{Fe}^{2+}$  Oxidation by Perchlorate:** Our results show no detectable  $\text{Fe}^{2+}$  oxidation by perchlorate in all three fluids. This corroborates the general understanding that perchlorate is a kinetically inert oxidant [5] at terrestrial and Martian surface temperatures despite the thermodynamic favorability of such reactions [8]. Perchlorate thus likely induces little to no  $\text{Fe}^{2+}$  oxidation on the Martian surface.

**Extensive  $\text{Fe}^{2+}$  Oxidation by Chlorate:** In contrast, chlorate-containing solutions exhibited a substantial decline in dissolved  $\text{Fe}^{2+}$  concentration with time accompanied by the formation of ferric iron-bearing solids. The rate of reaction varied with the initial acidity and fluid composition, i.e., Mg chloride, sulfate or perchlorate solutions. Substantial complexation of  $\text{Fe}^{2+}$  by  $\text{SO}_4^{2-}$  slowed the reaction in sulfate fluids as compared to that in chloride and perchlorate rich fluids. The dependence of the observed oxidation rates on the acidity of the system [7] is more complicated, and are likely affected by the dominant ion present in the solution, their complexation potential, and the solid phases precipitated. The increase in acidity associated with hydrolysis and precipitation of  $\text{Fe}^{3+}$  produced during oxidation acts to increase the initial slow oxidation rate by autocatalysis. Our results suggest that  $\text{Fe}^{2+}$  oxidation by chlorate can precipitate minerals that require acidic formation and stability conditions by

driving local microenvironments into their respective stability fields, even in solutions starting at neutral pH.

**Mineral Products of Iron Oxidation by Chlorate:**  $\text{Fe}^{2+}$  oxidation by chlorate produces an array of Fe(III) minerals. Dilute  $\text{Fe}^{2+}$  solutions lack the concentration needed to produce highly acidic fluids and precipitate lepidocrocite with minor additional goethite or magnetite, depending on the anion present. The mineral products change when more concentrated solutions are used. In chloride fluids, nanocrystalline akaganéite forms for initial pH values ranging from 3 to 7, while small amounts of highly crystalline akaganéite formed from a pH 1.2 fluid. A mixture of Na- and  $\text{H}_3\text{O}$ -jarosite formed in concentrated solutions containing sulfate, with the sodium contributed by the initial  $\text{NaClO}_3$  salt, used because  $\text{Mg}(\text{ClO}_3)_2$  is not commercially available.  $\text{H}_3\text{O}$ -jarosite likely would be the sole phase formed if sodium (and potassium) was absent. Similar amounts of jarosite and akaganéite formed at pH 7 and 3, but no solids were produced at pH 1.2 in the presence of sulfate, with  $\text{Fe}^{3+}$  mostly in solution due to the acidity and complexation by sulfate. Lepidocrocite is formed in perchlorate fluids at all pH conditions by  $\text{Fe}^{2+}$  oxidation by chlorate. The formation of akaganéite, jarosite, and lepidocrocite by chlorate indicates the potential importance of this oxychlorine species as an active oxidant on Mars.

**Conclusion:** Both akaganéite and jarosite are rare in natural terrestrial settings but are present in various locations on Mars [8,9]. Despite being a minor component in Martian sediments, these minerals are key indicators phases of acidic and highly saline formation conditions [10]. Oxidation of dissolved  $\text{Fe}^{2+}$  by concentrated chlorate fluids, such as brines, may represent fundamental formation mechanisms for both akaganéite and jarosite on Mars, including in Gale Crater. Lepidocrocite and/or goethite have been located on Mars [11] and can be an important precursor mineral for hematite. The potential formation of oxychlorine species on early Mars needs to be further evaluated as these species may have provided substantial additional oxidizing capacity as the planet evolved.

**References:** [1] Leshin et al. (2013) *Science*, 341, p. 1238937 [2] Hecht et al. (2009) *Science*, 325, 64-67. [3] Bellucci et al. (2017) *EPSL*, 458, 192-202. [4] Carrier and Kounaves et al. (2015) *GRL*, 42, 3739-3745. [5] Urbansky et al. (1998). *Bioremediation J.*, 2, 81-95. [6] Viollier et al. (2000). *Appl. Geochem.*, 15, 785-790. [7] Madlo et al. (1979) *Collect. Czech. Chem. Comm.*, 44, 2760-2768. [8] Ehlmann and Edwards. (2014) *Annu. Rev. Earth Planet. Sci.*, 42, 291-315 [9] Carter et al. (2015) *Icarus*, 253, 296-310. [10] Papike et al. (2006) *Geochim. Cosmochim. Acta*, 70, 1309-1321. [11] Farrand et al. (2009) *Icarus*, 204, 478-488