

**IRON OXIDATION BY CHLORATE: IMPLICATIONS FOR AKAGANÉITE AND JAROSITE FORMATION ON MARS.** K. Mitra and J. G. Catalano, Department of Earth & Planetary Sciences, Washington University, Saint Louis, MO 63130 USA (k.mitra@wustl.edu)

**Introduction:** Perchlorate and chlorate are the most common oxychlorine species on Mars [1]. These oxidants are produced continuously on the Martian surface and often have concentrations as high as 0.5 to 1.0 wt.% in soil [2]. Oxychlorine species have wide implications for both past and present Martian environments, affecting preservation of organic compounds, forming metastable brines and possibly flowing water in recurring slope linea, contributing to the oxidizing nature of the regolith, and serving as a potential electron donor, as occurs in microbial metabolisms on Earth [3, 4]. One role of oxychlorine species on Mars that has been largely overlooked to date is their potential to serve as oxidants of reduced iron. While perchlorate is chemically unreactive with  $\text{Fe}^{2+}$  despite the favorable thermodynamics of such reactions, chlorate is kinetically more reactive [5] and thus may be a major oxidant on the surface of Mars. However, the rates and mineral products of  $\text{Fe}(\text{II})$  oxidation by these oxychlorine species is currently unclear. The kinetics of oxidation of dissolved  $\text{Fe}(\text{II})$  by perchlorate and chlorate at pH 3, 5 and 7 have been studied in Mars-relevant fluids. The mineralogy of the solids generated during oxidation was then determined for different initial fluid compositions.

**Methods:**

**Kinetic Experiments:** 40 ml solutions were prepared that contained 10 mM  $\text{FeCl}_2$  along with equimolar  $\text{NaClO}_3$  or  $\text{NaClO}_4$ . All studies were conducted in a 0.1M  $\text{MgCl}_2$  or  $\text{MgSO}_4$  electrolyte to buffer the ionic strength and to provide anions with different ability to complex dissolved iron. An oxychlorine-free control experiment was set up with 1 mM  $\text{FeCl}_2$  in 0.1 M  $\text{MgCl}_2$  with no chlorate or perchlorate. 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. Experiments were conducted with initial pH values of 3, 5 and 7 in both chloride- and sulfate-rich fluids. 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].

**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  $\text{Fe}(\text{II})$  and chlorate (100 mM each) to explore the effect of concentration on the type(s) of mineral precipitated; lower initial pH was also investigated. 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 membrane. The resulting solid samples were dried in the anaerobic chamber in a vacuum desiccator for 3-4 days. The mineralogy of the dried solids were then characterized using powder X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS) spectroscopy, and visible and near infrared (VNIR) spectroscopy.

**Results:**

**Kinetics of  $\text{Fe}^{2+}$  Oxidation:** Perchlorate was found to induce negligible oxidation of  $\text{Fe}^{2+}$  in  $\text{MgSO}_4$  solution (Fig. 1). In contrast, chlorate caused near-complete  $\text{Fe}^{2+}$  oxidation within 30 days for all fluid compositions examined. The rate of oxidation differed for the two fluid types: for sulfate, pH 5 > pH 3 > pH 7, for sulfate, pH 7 > pH 3 > pH 5. No oxidation was detected in the oxychlorine-free control experiment.  $\text{Fe}^{2+}$  oxidation was coupled with a drop in pH for all chlorate experiments, while little pH changes were observed for the oxychlorine-free control and perchlorate studies.

**Mineral Products:** The mineralogy of the solids produced during  $\text{Fe}^{2+}$  oxidation by chlorate varied with

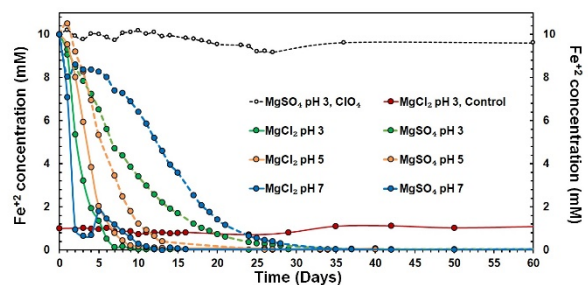


Figure 1:  $\text{Fe}(\text{II})$  concentrations as function of reaction time for different initial fluid compositions. Solid lines represent chloride fluids and dashed lines sulfate fluids.

fluid composition. At pH 7, lepidocrocite [ $\gamma\text{-FeOOH}$ ] formed at low (10 mM)  $\text{Fe}^{+2}$  concentration in both chloride and sulfate fluids along with minor magnetite and goethite, respectively. At higher  $\text{Fe}^{+2}$  concentration

(i.e., 100 mM) at all pH values akaganéite [ $\beta$ -FeO(OH,Cl)] formed in chloride fluids and mixed natro- and hydronium-jarosite [ $XFe_3(OH)_6(SO_4)_2$ , X=Na<sup>+</sup> or H<sub>3</sub>O<sup>+</sup>] formed in sulfate fluids. EXAFS and VNIR spectroscopy confirm the XRD results.

#### Discussion:

**Lack of Fe<sup>2+</sup> Oxidation by Perchlorate:** These studies show that perchlorate does not cause detectable Fe<sup>2+</sup> oxidation in both chloride and sulfate fluids, in agreement with prior work [5]. The results support the consensus that perchlorate is a kinetically inert oxidant at temperatures relevant to the surfaces of Earth and Mars despite such reactions being thermodynamically favorable. Perchlorate thus likely induces little to no oxidation of iron on the surface of Mars.

**Extensive Fe<sup>2+</sup> Oxidation by Chlorate:** In contrast, all experiments that contained chlorate displayed a substantial decline in dissolved Fe<sup>2+</sup> with time and the formation of ferric iron-bearing solids. The rate of reaction depended on the initial pH and the dominant anion in the solution, i.e., chloride or sulfate. The rate of Fe<sup>2+</sup> oxidation by chlorate is faster in chloride fluids than in those containing sulfate because of substantially

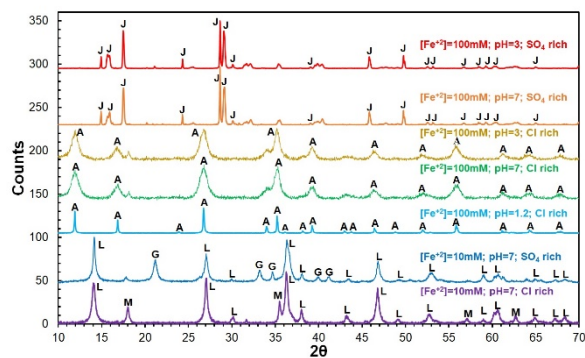


Figure 2: XRD patterns of solids produced during Fe<sup>2+</sup> oxidation by chlorate. Diagnostic peaks are marked as follows: J=Jarosite, A=Akaganéite, L=Lepidocrocite, G=Goethite, M=Magnetite

stronger complexation of Fe<sup>2+</sup> by SO<sub>4</sub><sup>2-</sup>. The complex pH-dependence of the observed oxidation rates likely reflect the oxidation mechanisms, which are known to vary with pH [7], the differing aqueous complexation of Fe<sup>3+</sup> by chloride and sulfate, and the mineral products that form. The increase in oxidation rate in many systems after an initial period of slow oxidation appears to be an autocatalytic phenomenon. The increase in acidity associated with hydrolysis and precipitation of Fe<sup>3+</sup> produced during oxidation acts to increase the kinetics. This suggests that oxidation of Fe<sup>2+</sup> by chlorate on Mars may drive local microenvironments into the stability fields of minerals associated with highly acidic condition even when the initial systems began at, and the broader mineral assemblages, indicate circumneutral pH.

**Mineral Products of Iron Oxidation by Chlorate:** An array of Fe(III) minerals form when chlorate oxidizes dissolved Fe(II). Dilute Fe(II) solutions lack the concentration needed to produce highly acidic fluids and produce lepidocrocite with minor additional goethite or magnetite, depending on the anion present. The mineralogy of the systems differs when more concentrated solutions are used, even when the initial pH is 7. In chloride fluids, akaganéite forms for initial pH values ranging from 7 to 1.2. The most acidic initial solution (pH 1.2) produced highly crystalline akaganéite but in low overall abundance because of the high solubility of Fe<sup>3+</sup> at very low pH. At higher initial pH values (3 to 7), the XRD patterns show that the akaganéite produced is nanocrystalline in nature. Jarosite formed in concentrated solutions containing sulfate. This occurred as a mixture of natro- and hydronium-jarosite, with the sodium contributed by the initial NaClO<sub>3</sub> salt; Mg(ClO<sub>3</sub>)<sub>2</sub> is not commercially available. Hydronium jarosite likely would be the sole phase formed if sodium was absent. Similar amounts of jarosite and akaganéite formed at pH 7 and 3, but in the presence of sulfate no solids were produced at pH 1.2, with Fe<sup>3+</sup> staying in solution due to the acidity and complexation by sulfate. The formation of akaganéite and jarosite 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 have been reported at various locations on Mars [8, 9]. Despite being a minor component in the Martian regolith, these minerals are key indicators phases. Both require acidic and highly saline conditions to form [10]. Oxidation of dissolved Fe(II) by concentrated chlorate fluids, such as brines, may represent key formation mechanisms for both akaganéite and jarosite on Mars, including in Gale Crater. 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] Sutter et al. (2016) *Int. J. Astrobiol.*, 16, 203-217. [2] Hecht et al. (2009) *Science*, 325, 64-67. [3] Ojha et al. (2015) *Nat. Geosci.*, 8, 829-832. [4] Kounaves et al. (2010) *Env. Sci. Tech.*, 44, 2360-2364. [5] Urbansky et al. (1998). *Bioremediation J.*, 2, 81-95. [6] Viollier et al. (2000). *Appl. Geochem.*, 15, 785-790. [7] Madlo et al. (1982) *Collect. Czech. Chem. Comm.*, 46, 1069-1077. [8] Bhattacharya et al. (2016) *JGR*, 121, 402-411. [9] Carter et al. (2015) *Icarus*, 253, 296-310. [10] Papike et al. (2006) *Geochim. Cosmochim. Acta*, 70, 1309-1321.