

**THE IMPACT OF IRON PERCHLORATES ON THE PRESERVATION AND DETECTION OF MARTIAN CARBON PHASES.** J. M. T. Lewis<sup>1-3</sup>, J. L. Eigenbrode<sup>2</sup>, G. M. Wong<sup>4</sup>, and A. C. McAdam<sup>2</sup>, <sup>1</sup>Department of Physics and Astronomy, Howard University, Washington, D.C. (james.m.lewis@nasa.gov), <sup>2</sup>NASA Goddard Space Flight Center, Greenbelt, MD, <sup>3</sup>Center for Research and Exploration in Space Science and Technology, Greenbelt, MD, <sup>4</sup>Department of Geosciences, The Pennsylvania State University, University Park, PA.

**Introduction:** The widespread presence of perchlorate salts ( $\text{ClO}_4^-$ ) on the surface of Mars necessitates investigations into their roles in Martian geochemical processes and their impacts on *in-situ* analyses by flight instrumentation [1]. Existing studies have demonstrated how perchlorates can significantly lower the freezing point of brines, enhancing the potential for liquid water on Mars, and how perchlorates release oxygen and chlorine when heated, complicating the search for Martian organic matter via pyrolysis methods [2,3].

In this project, we are examining how Fe perchlorates behave when dissolved in aqueous solution and when heated during flight-like pyrolysis. Fe perchlorates have previously been described as potentially occurring on Mars [e.g., 4,5], but there are relatively few studies of Fe perchlorates within the field of planetary science. Fe perchlorate solutions are known to be acidic and are thus potentially reactive [6,7]. Additionally, Fe perchlorates decompose at significantly lower temperatures than other Mars-relevant perchlorate species, which has implications for the interpretation of pyrolysis data [8].

Our work consists of three key tasks: 1) measure the pH of Fe perchlorate solutions at different concentrations, 2) investigate how Fe perchlorates behave during pyrolysis experiments analogous to those conducted by the Sample Analysis at Mars (SAM) instrument suite on board the Mars Science Laboratory Curiosity rover, and 3) examine whether acidic Fe perchlorate solutions react with Mars-relevant carbon phases, i.e., oxalates ( $\text{C}_2\text{O}_4^{2-}$ ) and carbonates ( $\text{CO}_3^{2-}$ ).

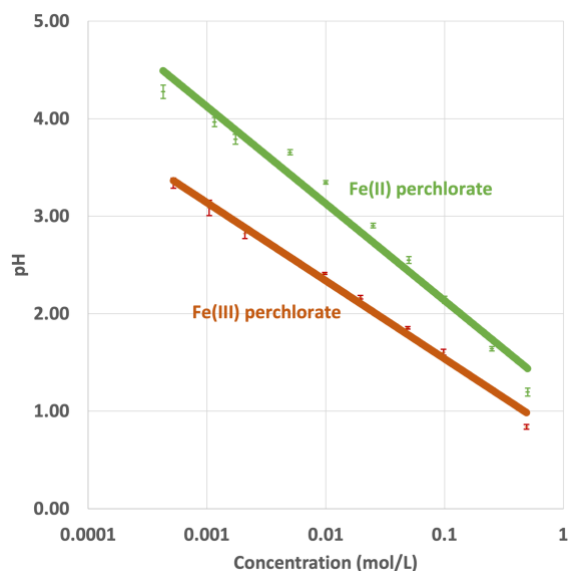
**Materials and Methods:** To achieve Task 1, Fe(III) and Fe(II) perchlorate standards were purchased from Sigma Aldrich and dissolved in ultrapure water at a range of concentrations. The pH of each solution was measured using two Hanna pH meters, with the measurements for each meter repeated in triplicate.

To achieve Tasks 2 and 3, the Fe perchlorates and a range of Sigma Aldrich oxalates (Fe(III), Fe(II), Ca, and Mg) were first dispersed in an inert fused silica matrix. This mixing enabled the use of very small amounts of perchlorates, protecting the liner of the laboratory pyrolysis oven, which can be damaged by excess chlorine. The oxalates were physically mixed with the silica in a solvent-cleaned agate pestle and mortar, while the perchlorates were dissolved in ultrapure water and

added to the mixtures via syringe, followed by drying down in a 60°C oven.

The mixtures were then pyrolyzed in stainless steel cups within a Frontier Laboratories 3030D multi-shot pyrolyzer interfaced with an Agilent 5975T low thermal mass gas chromatograph-mass spectrometer. Pyrolysis was conducted at a SAM-like ramp rate of 35°C/min up to 850°C. A subset of each silica-oxalate mixture was pyrolyzed before the addition of the Fe perchlorate solution to deconvolve the impact of the perchlorate. If the data required further deconvolution, the Fe perchlorate solutions were added to larger masses of the oxalate, enabling XRD analyses of the solid residues.

**Preliminary Results:** The Fe(III) and Fe(II) perchlorate solutions were found to be highly acidic (Fig. 1), with 0.5 to 0.001 mol/L concentrations giving pH values between a range of ~1-4.

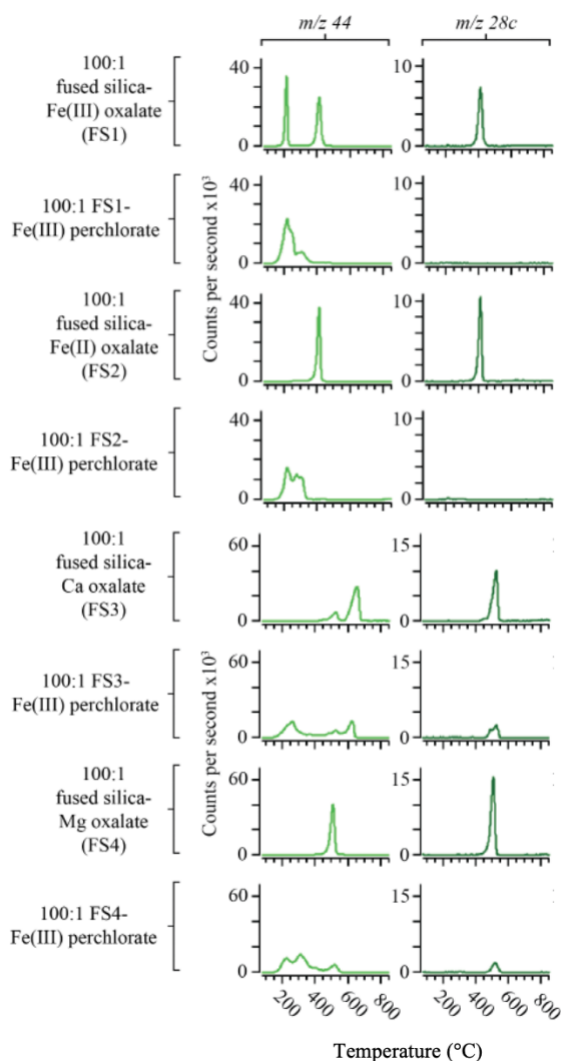


**Figure 1.** The pH of Fe perchlorate solutions at different concentrations.

Fe(III) perchlorate evolved two  $\text{O}_2$  peaks during SAM-like pyrolysis (at 225°C and 345°C), a low-temperature HCl peak at 195°C, and a broad high-temperature HCl release at ~750°C.

The evolutions of  $\text{CO}_2$  (mass to charge ratio ( $m/z$ ) 44) and CO ( $m/z$  28) from the oxalate standards during pyrolysis changed significantly after the addition of a Fe(III) perchlorate solution (Fig. 2). For the Fe oxalates (Mixtures FS1 and FS2), the  $\text{CO}_2$  peaks shifted to lower

temperatures and CO releases were no longer observed. For the Ca and Mg oxalates (Mixtures FS3 and FS4), the CO<sub>2</sub> and CO peaks weakened and additional low-temperature CO<sub>2</sub> releases were observed, at a similar temperature to those seen in the Fe-oxalate-Fe(III)-perchlorate experiments.



**Figure 2.** CO<sub>2</sub> ( $m/z$  44) and CO ( $m/z$  28) evolutions from fused-silica-oxalate mixtures (FS1-FS4) and FS1-FS4 after the addition of Fe(III) perchlorate. Note that CO is plotted as  $m/z$  28c, as the trace is corrected for the  $m/z$  28 fragment from CO<sub>2</sub> formed in the mass spectrometer.

**Discussion:** Previous pyrolysis studies of organic salts have demonstrated the sensitivity of Fe oxalates to the presence of O<sub>2</sub> in pyrolysis ovens [9] and the behavior of the Fe oxalates (FS1 and FS2) in Fig. 2 was consistent with these observations. Our work indicates that Fe perchlorates can be included on the list of O<sub>2</sub>-evolving species that can impact Fe oxalate decomposition.

The low-temperature CO<sub>2</sub> peaks produced by the FS3 and FS4 mixtures in the presence of Fe(III) perchlorate were not observed in studies of Ca and Mg oxalates mixed with Ca and Mg perchlorates [9]. These studies also illustrated that the CO<sub>2</sub> and CO releases from Ca and Mg oxalates resist shifting in the presence of O<sub>2</sub> [9]. We infer that the acidic Fe(III) perchlorate solution reacted with the Ca and Mg oxalates to form some Fe(III) oxalate. Ca and Mg oxalates are usually insoluble, but oxalates are known to be reactive at low pH [10]. Our conclusion is supported by the fact that the O<sub>2</sub> releases produced by the FS3- and FS4-perchlorate mixtures occurred at temperatures higher than expected for Fe(III) perchlorate and were instead consistent with the O<sub>2</sub> release temperatures of Ca/Mg perchlorates [9].

Our preliminary results indicate that Ca and Mg oxalate deposits on Mars would be susceptible to alteration by concentrated Fe perchlorate solutions. We are currently investigating the impact of Fe perchlorate solutions on carbonate species.

**References:** [1] Clark B. C. and Kounaves S. P. (2016) *IJoA*, 15(4), 311-318. [2] Chevrier V. F. et al. (2009) *GRL*, 36(10). [3] Navarro-González R. et al. (2010) *JGR: Planets*, 115(12). [4] Leshin L. A. et al. (2013) *Science*, 341. [5] Hennings E. et al. (2014) *Acta Crystallographica*, 70(12), 477-479. [6] Hemmes P. et al. (1971) *JPC*, 75(7), 929-932. [7] Loeppert R. H. et al. (1984) *SSSoAJ*, 48(3), 677-683. [8] Sutter B. et al. (2017) *JGR: Planets*, 122(12), 2574-2609. [9] Lewis J. M. T. et al. (2021) *JGR: Planets*, 126(4). [10] Sasaki E. (1971) *The Journal of the Society of Chemical Industry, Japan*, 74(12), 2426.