

MEASURING MINERAL DISSOLUTION RATES IN PERCHLORATE BRINES: METHOD DEVELOPMENT AND APPLICATIONS. C. Legett IV¹, B. N. Pritchett², A. S. Elwood Madden¹ and M. E. Elwood Madden¹, ¹School of Geology and Geophysics, University of Oklahoma, 100 E. Boyd St., Ste. 710, Norman, OK 73019, clegett@ou.edu, ²Oklahoma Geological Survey.

Introduction: The Viking [1], Phoenix [2], and MSL [3] missions have reported detections of perchlorate compounds on the surface of Mars, and perchlorate brines are one of the possible sources of the recurring slope streaks observed by MRO [4]. Rates of mineral dissolution and alteration products generated in perchlorate brines have not been well established. We set out to determine the dissolution rates of jarosite in sodium perchlorate brine by measuring the concentration of iron and sulfate in solution after varying lengths of exposure for comparison with previous jarosite dissolution results in solutions of varying pH, T, and salinity [5, 6, 7, 8]. In particular, we are interested in comparing iron release rates in brines of different anion composition (NaCl, NaClO₃, NaClO₄) due to previous works, which suggest anion complexation with structural iron may affect dissolution rates [5, 9].

However, traditional methods of aqueous iron analysis are not feasible due to the highly oxidizing nature of perchlorate salts. We ruled out the use of flame atomic absorption spectroscopy to determine iron concentrations due to concerns about reported spray chamber explosions associated with perchlorate analysis [10]. Inductively coupled plasma mass spectrometry was ruled out due to instrument sensitivity concerns with analyzing high concentration brines. We chose to investigate ultraviolet-visible spectrophotometry (UV-vis) as a safe alternative to analyze the brines. However, the standard 1,10-phenanthroline methods for the determination of iron listed strong oxidizers as interfering with the method. Given the limitations of existing methods, we have worked to develop a simple protocol requiring a minimum of reagents for measuring Fe concentrations within perchlorate brines.

Method Development: Two sets of mineral dissolution experiments were carried out in 20wt% sodium perchlorate (NaClO₄) brine. The first set reacted powdered clinopyroxene and olivine for 79 days while being continuously stirred on magnetic stir plates with standard PTFE-coated magnetic stir bars. The second set reacted powdered jarosite (KFe₃(OH)₆(SO₄)₂) for twenty days in Erlenmeyer flasks placed on an orbital shaker plate. Samples were taken at predetermined intervals between 30 minutes and two days. Each sample was filtered through a 0.2 μm filter and stored in a plastic sample container in a refrigerator at approximately 4°C.

We prepared iron standards by diluting 1000ppm Fe (ferric sulfate hydrate in 20wt% perchlorate brine) stock with the perchlorate brine to iron concentrations between 0.1 and 60ppm. A small number of these samples were placed in cuvettes providing a 1cm light path and scanned from 190-1100nm in a Thermo Scientific GENESYS 6 scanning spectrophotometer. Only the portion between 250 and 400nm showed any absorbance not present in a blank containing only the sodium perchlorate solution. All standards were then scanned between 250 and 400nm and the absorbance recorded every 0.1nm. After analyzing the data, wavelengths of 251.9, 254.0, 270.4, and 273.3nm were selected for calculating the Beer-Lambert Law relationships. 251.9nm is near the peak for the lower concentration standards, which shifts to approximately 254.0nm in the higher concentrations (Figure 1A). 270.4 and 273.3nm were selected due to having a very high (>0.99) calculated R² value over subsets of the standards.

Results and Discussion: Iron concentrations from the first set of experiments involving clinopyroxene and olivine were never analyzed using this method due to the unexpected destruction of the PTFE-coated magnetic stir bars. The bars began deteriorating less than two weeks into the experiment, exposing the internal metal magnet, thus potentially adding additional iron to the system. The stir bar disintegration resulted in a 0.1-1 mm- thick hydrophobic film forming on the top of the liquid in the experiment. Later, piles and balls of small PTFE particles formed on top of the film (Figure 2A). This material collected around the stir bar (Figure 2B) before coming loose and floating to the surface. However, this deterioration only occurred in beakers containing both a mineral powder and the perchlorate. As a control, we placed an identical, clean stir bar in a beaker with perchlorate without mineral powder; as of this writing it has been in the perchlorate solution for over 300 days without deterioration. The observed PTFE breakdown may be due to free radicals produced in solution as the silicate minerals react with the perchlorate [11].

Jarosite dissolution experiments were conducted on an orbital shaker plate to avoid using stir-bars in the reactors. While Fe concentrations in solution were easily measured at the end of the experiment using the UV-vis method developed here (Figure 1B), we believe that these iron concentrations under-

represent of the iron release from jarosite dissolution due to adsorption and iron oxide precipitation in the sample containers during storage. Absorbance readings on the same standards taken a few days apart differed more than 50% in some cases. After orange precipitate was observed to be forming at the bottom of the 5 and 10ppm Fe standards, it became clear that the iron wasn't stable in the lower concentration standards. While the 1000 ppm stock appears stable based on visual observations and UV-vis measurements, any dilution at or below 10ppm resulting in removal of iron from solution. Furthermore, acidification of all standards failed to prevent large variations in absorbance readings likely due to precipitation of iron oxides and and/or adsorption of iron onto the plastic sample containers over time. However, new standards prepared on different days were observed to have nearly identical readings if measured immediately after preparation.

These results suggest that aqueous iron is not stable in perchlorate brines at low concentrations, leading to rapid precipitation, while higher concentrations (1000 ppm) of iron appear to be more stable. The pH of the standards may be affecting iron stability within the perchlorate brines. As iron oxides precipitate, H^+ ions are produced, lowering the pH of the solution: $2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+$ Iron oxide solubility increases as pH decreases, thus buffering the solution at lower pH and stabilizing iron concentrations. Since the 1000 ppm standard contains abundant iron, some precipitation and acid generation to may occur without significant changes in the concentration, whereas the lower concentration standards do not have sufficient iron to allow precipitation to buffer the system.

Figure 4 shows a representative analysis of the concentration of iron in solution over time using the four different wavelengths. The general trends in concentration are in good agreement regardless of the wavelength chosen, however the actual value for the concentration may vary by 50%.

Conclusions and Future Work: We plan to replicate the conditions that led to the deterioration of the PTFE stir bars and attempt to describe the process and conditions under which it occurs, including tests for free radicals within the solution. These results this may have implications for the future use of PTFE parts on missions in environments which may encounter perchlorate brines.

Jarosite dissolution experiments, as well as silicate dissolution experiments will be repeated using the orbital shaker plate and resulting samples analyzed immediately after collection rather than after days or weeks of storage. In line with that goal, further studies

will be required to determine which wavelength results in the most accurate measurement of iron present.

References:[1] Navarro-González, R. et al. (2010) *JGR*, 90, E12010. [2] Hecht, M. H. et al. (2009) *Science*, 325, 64-67. [3] Glavin, D. P. et al. (2013) *JGR*, 118, 1955-1973. [4] Chevrier, V. F. and Rivera-Valentin, E. G. (2012) *Geophys. Res. Lett.*, 39. [5] Pritchett, B. N. et al. (2012) *EPSL*, 357, 327-336. [6] Elwood Madden, M. E. et al. (2012) *Geochim. Cosmochim. Ac.*, 91, 306-321. [7] Zahrai, S. K. et al. (2013) *Icarus*, 223, 438-443 [8] Kendall, M. R. et al. (2013) *Geochim. Cosmochim. Ac.*, 112, 192-207 [9] Sidhu, P. S. et al. (1981) *Clay. Clay Miner.*, 29, 269-276 [10] Andrew, B. E. (1988) *J. Anal. At. Spectrom.*, 3, 401-405. [11] Schoonen, M. A. A. et al. (2006) *Rev. Mineral. Geochem.*, 64, 179-221.

Figures:

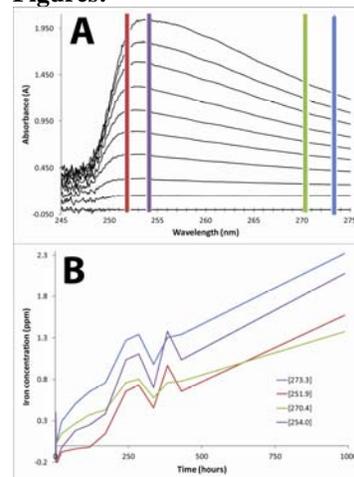


Figure 1. (A) 245-275nm absorbance of 0-45ppm Fe standards. Bold vertical lines at 251.9, 254.0, 270.4, and 273.3nm represent spectra used for analyses in B. (B) Concentration vs. time for one jarosite experiment showing concentrations determined using four different wavelengths.

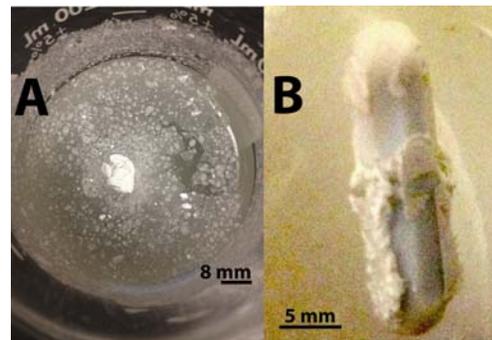


Figure 2. (A) PTFE film and powder on top of solution. (B) Color and contrast enhanced photograph of powder collecting on a deteriorating PTFE stir bar.