IRON OXIDE WEATHERING IN SULFURIC ACID: IMPLICATIONS FOR MARS. S.M. Arlauckas, J.A. Hurowitz, N.J. Tosca and S.M. McLennan. Department of Geosciences, State University of New York at Stony Brook, Stony Brook, NY 11794-2100 (sarlauck@ic.sunysb.edu).

Introduction: The presence of liquid water at some point in the history of Mars may explain many of its dramatic surficial features [1]. The intense volcanism that took place in the past is the probable source for the abundant sulfur in Martian surface material [2]. Liquid water present on Mars may have therefore been acidic due to the high concentrations of sulfur (as H_2SO_4) in the system. It is likely that acidic fluids would have weathered the basaltic crust to varying degrees.

Both Viking and Pathfinder missions have yielded data in support of magnetic materials present on the surface and in the atmospheric dust of Mars. From Viking magnetic experiments, Hargraves et al. [6] have determined that there is approximately 1-7 wt% of a magnetic phase that is present on the Martian surface. It is widely believed that the magnetic mineral present on the surface of Mars is maghemite (γ Fe_2O_3) [3,6,7,8,], although it is recognized that magnetite ($[Fe^{2+}Fe^{3+}_2]O_4$) may supply either some, or possibly all of the magnetic character of the soil [3,6,8,9].

Primary iron oxides exist as minor constituents in the SNC meteorites and are believed to exist in typical Martian basalt as well. These oxides represent a substantial fraction of the overall Fe budget of a given basalt. Therefore, it is important to understand the geochemical reactions they will undergo in acidic environments. There has been little work performed on the dissolution behavior of iron oxides [3,7,10,12], therefore, reactions are poorly understood. If such reactions can be constrained, it will lead to a better understanding of the processes that operated during the history of Mars.

Experimental Methods: Static batch experiments were performed at room temperature in Teflon® screw top beakers. Magnetite and aqueous sulfuric acid were allowed to react for 365 hours in the capped beakers, which were opened once daily for fluid sampling. Three acid mixtures of increasing pH were prepared using combinations of deionized water and sulfuric acid. The resulting sulfuric acid mixtures had concentrations of roughly 0.1M, 0.01M and 0.001M. Approximately 30 mL of each of the prepared acid solutions were separated into the screw top beakers. The beakers were designated A, B and C, in order of decreasing concentration.

Magnetite grains from Wards Scientific, Inc. were crushed and sieved to determine grain size distribution. After sieving and weighing the separated particles, the grains, ranging in size from approximately 250 μm to 125 μm, were rehomogenized into one mixture, which was then divided between the three beakers. Each beaker was assumed to have approximately the same proportions of particle sizes. About 300 mg of magnetite grains were added to each of the acid solutions, thus making the water/rock ratios equal to 100 at the start of all three experiments.

Fluid samples were taken on average every 24 hours, during which 0.09 mL of fluid was removed and diluted with 1 mL of deionized water. Fluid samples were kept refrigerated until their analyses. Throughout the entire experiment, roughly 4% of the total starting volume of the liquid was extracted from each beaker.

After 15 days of sampling, the remaining fluids were carefully separated from the solids. The residual fluids were carefully poured off into open top Teflon® beakers, and allowed to evaporate. The evaporites that formed were sealed for later analyses. The residual magnetite was rinsed with ethanol and over a vacuum filter apparatus with a 0.45 μm nitrocellulose filter. The solids were allowed to completely air dry, before being transferred into a vial until further analysis.

Analysis and Results: The mineralogy of the starting solid was analyzed by XRD. The diffraction pattern indicated that the starting mineral was pure magnetite. No other mineral phases were detected. Chemical analysis by electron microprobe was performed to determine the elemental composition of the magnetite. Results indicated that it was pure Fe magnetite, with a negligible amount of Al substitution (0.21 wt% Al_2O_3), and much less Ti substitution.

Analyses of the fluid samples was performed on a Direct Current Plasma Atomic Emission Spectrophotometer (DCP-AES), which is capable of determining dissolved concentrations of both Fe and Ti in solution at the level of 0.004 ppm for Fe, and 0.01 ppm for Ti.

Since titanium was scarcely present in the original solid, it was consistently below the detection limit. The concentration of iron in the solution increased through time for all experiments, A, B and C. The Fe was most concentrated in the 0.1M solution (A), and the concentration increased linearly throughout the 15 day experiment. The concentration of the iron in solution decreases with decreasing acidity.

Smaller Fe concentrations, as well as the dilution of fluid samples with DI water upon extraction from the beaker, accounted for more variable concentration data in experiments B and C. Concentrations, especially from experiment C, are either at or approaching the minimum detection limit for Fe. In conditions of higher pH, concentration data show an increase through time, but not in the precise linear fashion as seen for experiment A.

From the Fe concentration of the liquid, the percent of iron removed during the experiment relative to the total solid iron at the start of the experiment can be calculated. Figure 1 shows the percent of solid iron removed through time for each experiment. There is a direct relationship between percent removed and increasing time, indicating that the magnetite has reached a steady state rate of dissolution.
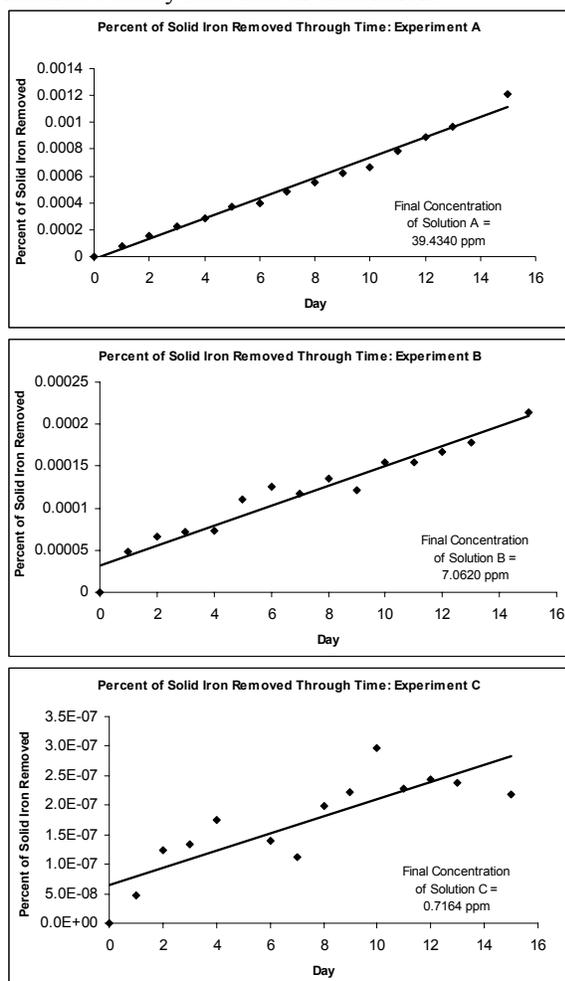

Figure 1 – Percent of solid Fe released into solutions A (0.1M), B (0.01M) and C (0.001M). The final concentration of Fe in each solution is also shown.

Discussion: Iron oxide dissolution and alteration are not widely studied because iron oxides are considered to be some of the most resistant minerals to terrestrial conditions [10]. On Mars, however, there may have been acidic aqueous environments operating, in which iron oxides may not have been as resistant.

The pH of the past aqueous environments is an important factor affecting the rates of dissolution of iron oxides. Under acidic conditions, primary iron oxides, which can account for a significant portion of Fe in a given basalt, contribute substantial amounts of dissolved Fe to solution. Therefore, primary oxides

under certain conditions could be an important source of Fe in the Martian hydrologic system.

Temperature may also be important in determining how these processes operated in the past on Mars. It may be useful to define the dissolution behavior of iron oxides under a range of temperature conditions. Past temperatures on Mars are unconstrained, but similar experiments performed at varying temperatures may be able to further constrain rates of dissolution on Mars.

Aside from determining rates of dissolution, it may be important to determine oxide alteration products at a variety of possible Martian conditions. Swaddle and Oltmann [7] discuss alteration from magnetite to maghemite to hematite. This may be an important reaction pathway in terms of Martian alteration products. A possible pathway in forming maghemite is by the oxidation of magnetite. The presence of water is required for this reaction [7]. The alteration of maghemite to hematite can also occur through hydrothermal alteration [7]. Hydrothermal alteration on Mars was likely, due to the heat from the many volcanoes and impact craters on the surface.

Conclusions: Magnetite dissolution is greatly dependent on pH at room temperature and can be a substantial source of Fe in altering fluids. In an acidic pH, magnetite dissolves readily on short timescales. During the 15 day experiment, solution A dissolved 5x more Fe than solution B, which dissolved 10x more Fe than solution C. Highly acidic conditions allow for faster Fe dissolution rates. Such aqueous Fe may later be precipitated as secondary Fe-bearing minerals.

Geochemical reactions involving iron oxides are poorly constrained. It will be useful to determine constraints on iron oxides (and iron-titanium oxides, such as ilmenite) to decipher the geologic processes that have operated on Mars in the past. More work remains to be done to fully characterize the behavior of magnetite in aqueous environments, including determination of alteration products and absolute dissolution rates. Under specific conditions, iron oxides may be even more reactive than previously thought, and this may provide insight to the processes operating on Mars.

References: [1] Carr, M. (1996) *Water on Mars*, Oxford Univ Press, 229pp. [2] Burns, R. (1987) *JGR, 92*, E570-74. [3] Morris, R. et al.(1998) *Met. Planet. Sci., 33*, 743-51, 1998. [4] Christensen, P. et al.(2000) *JGR, 105*, 9623-42. [5] Christensen, P. et al.(2001) *JGR, 106,* 873-23. [6] Hargraves, R. et al.(1979) *JGR, 84*, 8379-84. [7] Swaddle, T. and Oltmann, P. (1980) *Can. J. Chem., 58*, 1763-72. [8] Hviid, S. et al.(1997) *Science, 278*, 1768-70. [9] Pollack, J. et al.(1977) *JGR, 82,* 4479-96. [10] White, A. et al.(1994) *GCA, 58*, 859-75. [11] Pollack, J. et al.(1987) *Icarus 71,* 203-24. [12] Burns, R. (1993) *GCA,* 4555-74.