

EXPERIMENTAL EVIDENCE FOR WEATHERING AND MARTIAN SULFATE FORMATION UNDER EXTREMELY COLD WATER-LIMITED ENVIRONMENTS.

P. B. Niles¹, D. C. Golden², and J. Michalski^{3,4};

¹Astromaterials Research and Exploration Science, NASA Johnson Space Center, Houston, TX (paul.b.niles@nasa.gov); ²ESCG, Houston, Texas; ³Planetary Science Institute, Tucson, Arizona. ⁴Dept. of Mineralogy, Natural History Museum, London, United Kingdom.

Introduction: High resolution photography and spectroscopy of the martian surface (MOC, HiRISE) from orbit has revolutionized our view of Mars with one of the most important discoveries being widespread layered sedimentary deposits associated with sulfate minerals across the low to mid latitude regions of Mars [1, 2]. The mechanism for sulfate formation on Mars has been frequently attributed to playa-like evaporative environments under prolonged warm conditions [3]. However, there are several problems with the presence of prolonged surface temperatures on Mars above 273°K during the Noachian including the faint young Sun [4] and the presence of suitable greenhouse gases [5]. The geomorphic evidence for early warm conditions may instead be explained by periodic episodes of warming rather than long term prolonged warm temperatures [6].

An alternate view of the ancient martian climate contends that prolonged warm temperatures were never present and that the atmosphere and climate has been similar to modern conditions throughout most of its history [6]. This view is more consistent with the climate models, but has had a difficult time explaining the sedimentary history of Mars and in particular the presence of sulfate minerals.

We suggest here that mixtures of atmospheric aerosols, ice, and dust have the potential for creating small films of cryo-concentrated acidic solutions that may represent an important unexamined environment for understanding weathering processes on Mars [7, 8]. This study seeks to test whether sulfate formation may be possible at temperatures well below 0°C in water limited environments removing the need for prolonged warm periods to form sulfates on early Mars.

Methods: To test this idea we performed laboratory

experiments to simulate weathering of mafic minerals under Mars-like conditions. 0.5 mL of 0.5 M H₂SO₄ was pipetted into 40-mL freezer-proof polycarbonate tubes containing 10g of acid-washed 400-μm silica beads, providing enough to coat the silica beads to a ~10 μm thickness, and frozen at a predetermined temperature in a precisely temperature-controlled freezer. Fifty milligrams of San Carlos olivine ground under acetone (5-53 μm) were then added on top of the acid-treated silica beads and the tube was removed from the freezer and shaken vigorously using a vortex mixer for 1 minute to mix the reactants and immediately transferred back to the freezer. Care was taken to be sure that the mixtures did not melt while being shaken in the vortex mixer. The reaction products were then sampled at predetermined times by adding 10 mL of 0.1M sodium acetate buffer (pH = 7) to neutralize remaining acidity and to melt all the ice. The quenched mixture was shaken for 30 seconds and filtered immediately using 0.2 μm Nalgene filter unit under vacuum to separate the supernatant. The elements Mg and Fe in buffered extracts were determined by using a Perkin Elmer AAnalyst 800 atomic absorption spectrometer using matrix matched reference standards.

The longest duration experiments (9 days) yielded sulfate minerals (Fig. 1) with very little of the original igneous minerals. While these experiments intentionally and artificially induce contact between the mineral grains and acidic fluids, it is likely that this will occur naturally on Mars where dust grains in the atmosphere will serve as nucleation points for ice and acidic aerosols [8].

The results of these experiments were converted into dissolution rates by using a disappearing sphere model [9]. Calculated rates of dissolution from the Mg measurements in our preliminary work were 1.7x10⁻¹³ mol/cm²/s for -40°C experiments, and 1.1x10⁻¹⁴ mol/cm²/s for the -60°C experiments (Fig. 2).

Discussion: The dissolution rates measured in this study at -40° C are comparable to forsterite dissolution rates in a pH 4 solution at 25°C [10], suggesting that acid weathering under subzero conditions may be more efficient than the temperature alone would predict. In this system, the strength of the acidic solution is maximized through eutectic freezing in an environment where the silicate minerals are extremely fine grained and have high surface areas. This provides an ideal environment despite the very low temperatures.

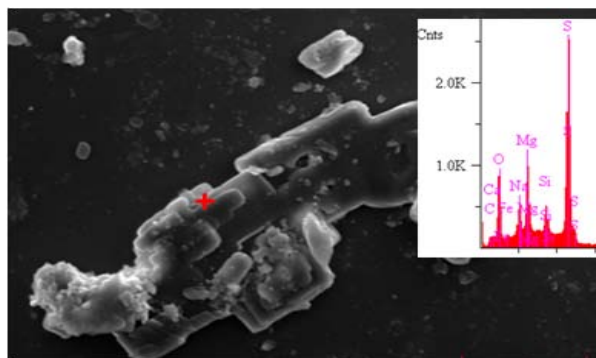


Figure 1. SEM image of experimental products recovered after freeze-drying rather than quenching with NaOH solution. EDS indicates primarily Mg-SO₄ minerals. Crystal is ~50 μm long.

Significantly lower dissolution rates are observed at -60°C for both olivine and pyroxene which indicate that as the system moves below the eutectic, weathering drops off very quickly. This result validates our experiments, essentially providing a blank analysis where it is clear that the weathering we do observe at -40°C is not occurring at some other time in the experimental procedure.

Implications: These results demonstrate that low-T weathering is a viable process for producing sulfate minerals from a silicate protolith in the presence of sulfuric acid on Mars. The presence of large deposits of mixed ice and dust on Mars is undisputed. The presence of substantial sulfur-rich volcanism, and sulfur-rich surface deposits also makes it very likely that sulfate aerosols have also been an important component of the martian atmosphere [8]. Thus mixtures of ice, dust, and sulfate aerosols are likely to have been common on the martian surface.

The variation in orbital obliquity on Mars through history requires that at certain periods of high orbital obliquity the polar regions received greater solar insolation than the equatorial regions [11]. This high orbital obliquity would almost certainly result in the movement of ice away from the modern poles to lower latitude regions [12]. It seems likely, given the frequency and magnitude of the obliquity variations, that a substantial sedimentary record could be produced by this process if the ice deposits contained substantial amounts of dust, and provided a means for altering and cementing that dust.

Analogues on Earth and Mars: The current polar regions of Mars provide an interesting analog that can be used for a comparison. Large regions of sulfate-rich material have been detected on and around the modern north polar region of Mars [13]. The prevalence of ice-dust mixtures in this region and the existence of sulfates within the ice cap itself are strong evidence for the origin of the sulfates from inside the ice deposits [13].

There is also evidence for the ice weathering process on Earth. Sulfates have been found in ice deposits in Greenland and Mount Fuji on Earth that have been attributed to forming within the ice deposit [14-16]. These sulfates can form either through interaction with dust particles in the atmosphere or through weathering inside the ice itself [14-16].

Gale Crater and MSL: Gale crater provides an opportunity to test this hypothesis in a new way using the Mars Science Laboratory (MSL) rover. The crater contains a large sedimentary deposit that has many characteristics in common with other large low latitude deposits on Mars including ILD's in Valles Marineris,

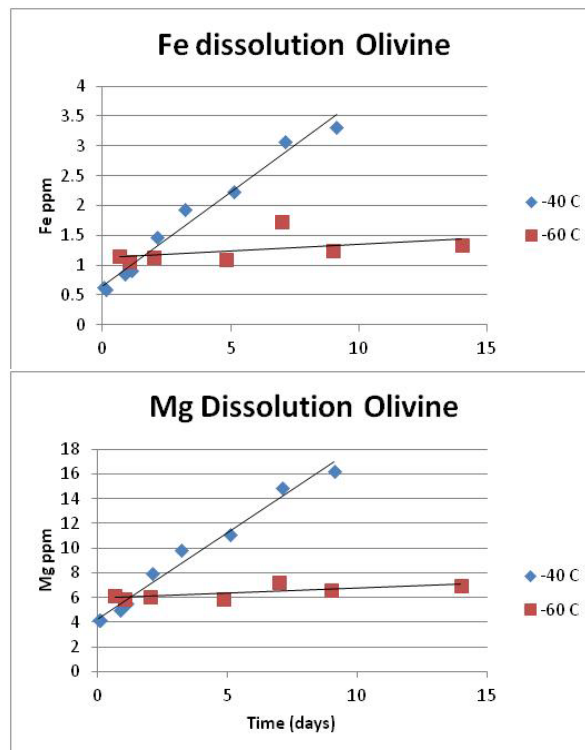


Figure 2. Plots of Mg and Fe measured in NaOH buffering solution used to quench the experiments. Calculated rates from these data are similar to dissolution rates of olivine in pH 4 solution at 25°C . Analyses performed in triplicate with uncertainties $\sim 1\%$.

crater mounds in Arabia, and the layered sediments at Meridiani Planum [7, 17].

Conclusions: The weathering rates measured in this study suggest that fine grained olivine and pyroxene on Mars would weather into sulfate minerals in short time periods if they are exposed to H_2SO_4 aerosols at temperatures at or above -40°C . Given the abundance of ice and dust on the surface and the fact that it is not difficult to achieve surface temperatures above -40°C on Mars throughout its history, it seems likely that sulfate formation is controlled by the availability of sulfate aerosols and not by the martian climate.

References: 1. Malin M.C. and Edgett K.S. (2000) *Science*, 290, 1927-1937. 2. Bibring J.P., et al. (2005) *Science*, 307, 1576-1581. 3. Squyres S.W., et al. (2004) *Science*, 306, 1709-1714. 4. Gough D.O. (1981) *Solar Physics*, 74, 21-34. 5. Tian F., et al. (2010) *Earth and Planetary Science Letters*, 295, 412-418. 6. Gaidos E. and Marion G. (2003) *Journal of Geophysical Research-Planets*, 108, 7. Niles P.B. and Michalski J. (2009) *Nature Geoscience*, 2, 215-220. 8. Settle M. (1979) *Journal of Geophysical Research*, 84, 8343-8354. 9. Lasaga A.C. (1984) *J. Geophys. Res.*, 89, 4009-4025. 10. Pokrovsky O.S. and Schott J. (2000) *Geochimica Et Cosmochimica Acta*, 64, 3313-3325. 11. Laskar J., et al. (2004) *Icarus*, 170, 343-364. 12. Jakosky B.M. and Carr M.H. (1985) *Nature*, 315, 559-561. 13. Masse M., et al. (2010) *Icarus*, doi: 10.1016/j.icarus.2010.04.017. 14. Iizuka Y., et al. (2008) *J. Geophys. Res.*, 113, D07303. 15. Iizuka Y., et al. (2009) *Journal of Glaciology*, 55, 552-562. 16. Ohno H., et al. (2006) *Geophysical Research Letters*, 33, 08501. 17. Michalski J. and Niles P.B. (2012) *Geology*.