

EXPERIMENTAL CONSTRAINTS ON LOW-TEMPERATURE ACID-WEATHERING OF OLIVINE: IMPLICATIONS FOR MARS E. W. Worsham¹, P. B. Niles², and M. D. Kraft³ ¹University of Tennessee (Department of Earth and Planetary Sciences 1412 Circle Drive Knoxville, TN 37996-1410 eps@utk.edu), ²Astromaterials Research and Exploration Science, NASA/Johnson Space Center (Houston, TX 77058) ³School of Earth and Space Exploration, Arizona State University (Tempe, AZ).

Introduction: The Opportunity rover at Meridiani Planum Mars has discovered a large-scale sulfate-rich deposit with fine layering, cross bedding, and hematite spherules [1]. Recently, it has been suggested that the sediments of Meridiani Planum underwent acid-weathering in a massive dust-ice deposit and were later reworked by aeolian processes [2].

The rate of acid weathering at sub-zero temperatures, typical of Mars, is poorly understood. Olivine weathering has been the subject of many studies which have examined the effects of pH and temperature on weathering at temperatures above 0 °C [3, 4, 5]. In particular, the effect of temperature on pH dependence is not well constrained [5]. Understanding the rate of olivine weathering at sub-zero temperatures is complicated by the fact that as ice forms, the remaining acidic solution becomes more concentrated with the potential to form highly concentrated eutectic brines [6].

The goal of this study is to investigate the rate of acid-weathering at very low temperatures (<0 °C) in order to test the ice-weathering hypothesis [2]. At temperatures below 0 °C the reaction kinetics would necessarily be slower, but the concentration of H₂SO₄ would be higher, possibly mitigating the affect of the cold [2,6]. This study will expand our knowledge of olivine weathering to lower temperatures and provide insights into what may have been an important weathering environment on Mars.

Experimental Methods: Fine-grained olivine (< 10 µm) from Jackson co., N.C. and coarser grained olivine (53-124 µm) from San Carlos were exposed to sulfuric acid in batch reactors under different temperature conditions for varying amounts of time. The San Carlos olivine was cleaned through sonication in ethanol to remove ultra-fine particles adhering to grain surfaces [3]. The molalities of the H₂SO₄ used were 5 *m* at -52 °C and 3 *m* at -20 °C and 4 °C in order to obtain solutions just above the aqueous H₂SO₄ liquidus [6]. For the room temperature experiments, 3 *m* H₂SO₄ was used for fine-grained olivine and 0.1 *m* was used for coarse. Separate test tubes containing 2 ml of acid and 10 mg of olivine were put into four different temperature conditions (-52°, -20°, 4°, and 20 °C). After cooling sufficiently, the olivine and acid were quickly combined and returned to their proper temperature. Samples were run for 1 hr, 5 hrs, 24 hrs, 48 hrs, 5 days, 10 days, or 20 days. At the end of each run 1 ml

of the liquid was drawn off the top, put into a new test tube, and diluted with 10 ml of DI H₂O. The solid residue was obtained by filtering the remaining liquid with a vacuum filter and letting it dry in an oven for at least 24 hours. The liquid was analyzed using atomic absorption spectroscopy (AAS) to obtain the amount of dissolved Mg²⁺ and Fe²⁺. The solid residue was examined for evidence of weathering with an SEM using backscatter electron (BSE) imaging and energy-dispersive spectroscopy (EDS).

Results: The AAS results for fine and coarse-grained olivine dissolution show that the Mg²⁺ and Fe²⁺ concentrations generally increase with temperature and duration, with the coarse concentrations lower than the fine. The concentrations of Fe²⁺ roughly mirror those of Mg²⁺, but at lower levels. However, the Fe:Mg ratio is slightly lower than that of the 9:1 ratio in Jackson co. and San Carlos olivine, suggesting some fractionation. The 4 °C coarse-grained samples overtake the 20 °C in highest concentrations. Mg²⁺ concentrations were converted into dissolution rates using the equation $R_{Mg} = (n / (800 * m * s))$, where R_{Mg} is the rate of dissolution of Mg, *n* is the number of moles of Mg²⁺ in the solution after the reaction, 800 is the approximate surface area in cm²/g (from Pokrovsky and Shott [4], whose grain sizes are comparable to this study's coarse grain sizes), *m* is the original mass of olivine in grams, and *s* is the duration of the reaction in seconds. The Mg²⁺ dissolution rate decreases swiftly at first and then approaches a steady state between 5 and 48 hrs for each temperature (Fig. 1). Additionally, the rate of dissolution in 4 °C goes above that of room temperature.

The SEM results reveal the formation of secondary material that is fine-grained and more silica rich than olivine, as illustrated by BSE and EDS analyses from the longest duration test performed at -20 °C (Fig. 2)

Discussion: The results of the experiments are comparable to previous work, which reported dissolution rates for San Carlos olivine in a pH 2.13 solution to be -11.65 [Log (R_{Mg})] after 8 hours [4] (R_{Mg} is the weathering rate in mol/cm²/s). Our results for the room temperature experiment at pH = 1.97 showed an average rate of -11.16 after 24 hours [Log (R_{Mg})].

Initial rates for the low-temperature experiments were also comparable to higher temperature experiments indicating that for the initial 24 hours the higher

acid concentrations compensate for the lower temperatures (Fig. 1). It is possible that the higher initial rates are due to small adhering particles not removed by sonication, or due to surface modification by crushing. However, the constant rates exhibited by the above freezing experiments suggests that this is not a large affect.

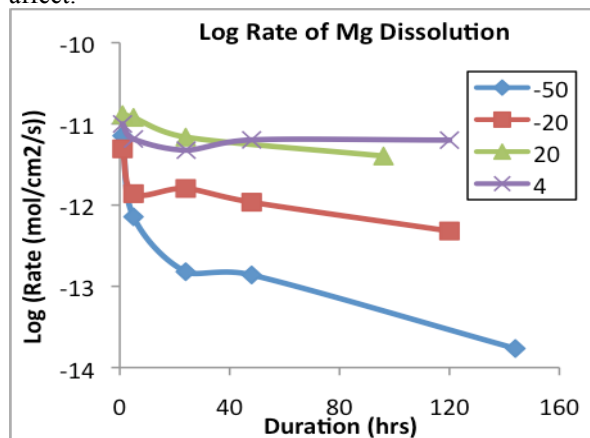


Fig. 1. The log rates of Mg and Fe dissolution in mol/cm²/s in each different temperature condition for coarse-grained olivine versus duration of the reaction. These are not steady-state rates, rather they are cumulative dissolution rates for a particular time, i.e. the initial dissolution rates are included in the final cumulative rate because the experiments were done in a closed system.

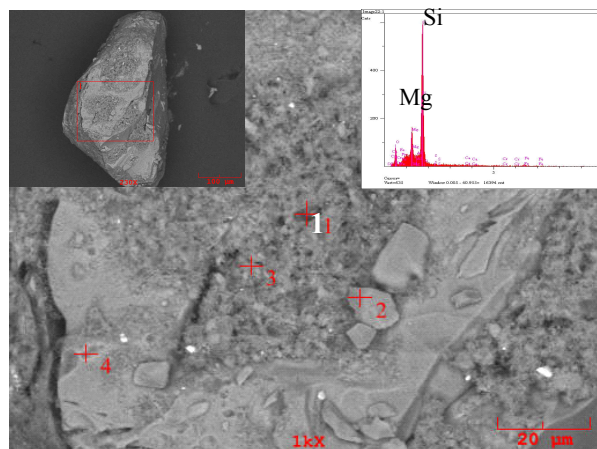


Fig. 2. Backscatter image of the -20° C, 20 days, fine-grained sample. Note different colors of smooth and rough areas. Rough areas of adhering particles are more weathered than the smooth areas. Top right inset: EDS of point 1. The Si is much higher than the Mg, presumably because of the dissolution of some Mg as a result of weathering.

The AAS results for the coldest temperature experiments show the lowest concentrations in both Mg²⁺ and Fe²⁺. The average rate of dissolution rapidly decreases with time suggesting that temperature plays an

important role in the dissolution process. All the -52 °C samples show a much more rapid decrease in dissolution rate than the higher temperature runs (Fig 1). At very cold temperatures we might expect a much smaller portion of the acid solution to come in contact with the olivine grain surfaces due to much slower diffusion rates. Dissolved ions will not travel as far in cold temperatures creating a micro-environment around the outside of the grains, potentially slowing the reaction rate considerably.

SEM analysis: The results of the SEM data show some weathering of the solid in the coldest temperatures. The EDS data for the least weathered sample (-52 °C freezer, 1 hr) shows a typical forsterite composition with no compositional differences or weathering textures. Figure 4 shows a grain of the 20 day fine-grained sample in the -20 °C freezer and a close up of an area of adhering particles. The backscatter image of the whole grain shows that the areas of adhering particles are darker, indicating compositional differences. The EDS of the rougher area shows that the Mg to Si ratio is much lower than that of forsteritic olivine, possibly indicating that the olivine-acid solution has produced a magnesian phyllosilicate mineral that is stable at low pH, like sepiolite, or simply an amorphous weathering residue.

Conclusions and Future Work: Weathering rates of forsteritic olivine in sulfuric acid solutions at temperatures as low as -52 °C are comparable to weathering rates observed for acidic solutions (pH ~3) at room temperature. However, there does seem to be a strong limiting factor, possibly caused by slow diffusion, that slows down the weathering reaction after the initial 8 to 24 hours. Thus stronger acid concentrations in colder subzero temperatures do not overcome the effects of lower temperatures, but do make weathering rates comparable to those at room temperatures. Clearly understanding the cause of the low-temperature limitations will greatly aid in understanding the importance of this process on Mars.

Future work includes weathering experiments using different materials such as anorthite, enstatite, and basaltic glass with compositions similar to the martian meteorite Shergotty.

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