

**CRYOGENIC SULFURIC WEATHERING OF IRON-RICH OLIVINE: IMPLICATIONS FOR MARS.**

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**Introduction:** Iron-rich olivine is widely distributed on the surface of Mars (Fe contents  $\geq 20\%$ ) [1]. Previous studies have shown that under the same aqueous conditions, the dissolution rate of fayalite is approximately ten times that of forsterite [2]. Therefore, the widely distributed Fe-rich olivine on the Martian surface may indicate a surface environment that presents either a limited abundance of liquid water or conditions that substantially inhibit dissolution kinetics [1].

In general, decreasing environmental  $T$  is considered to effectively slow the dissolution kinetics and result in a prolonged lifetime of the olivine particles [3]; however, an exception occurs when freezing of acidic solution that would remove solvent as water ice would substantially concentrate the remaining acids, and the resultant strong acids may efficiently suppress the slow dynamics caused by low  $T$  conditions. Some studies proposed that cryogenic weathering of olivine by sulfuric-rich ice under freezing Mars conditions would account for the formation of large-scale sulfate deposits, as observed at the Meridiani Planum [4,5]. These studies argue that the sediments in Terra Meridiani can be best explained to form via dust and sand captured in a massive ice deposit along with large amounts of volcanic aerosols [4,5]. Recently, the discovery of spontaneous jarosite particles (micron to submicron in size) in the Earth's Antarctic ice core. The jarosite is speculated to form by interacting fine-grained volcanic ash particles with brine under high-pressure freezing conditions [6], strengthening this perspective. These studies support a 'cold and icy' climate model of ancient Mars.

Because these cryogenic weathering experiments related to Mars mentioned above use primarily Mg-rich olivine and the experimental duration is relatively short (15 days), we further explore the acidic cryogenic weathering perspective by testing Fe-rich olivine and increasing the experiment duration (100 days). In addition to sulfuric acidic solutions, we also tested acidic ferric sulfate solutions, which are suggested to be present on ancient and modern Mars [7]. Synthetic Fe-rich olivine samples (Fa100, Fa71, Fa50, Fa29; Fa#

= Fe/(Fe+Mg)) were dissolved by the initial sulfuric acid solution and ferric sulfate solution at 233 K. Dissolution rates and characteristics of weathering products were characterized to provide essential constraints on the olivine dissolution processes relevant to 'cold and icy' Mars.

**Methods:** Fe-rich olivine samples were synthesized for use in this study [8]. The grain size of olivine powder used in weathering experiments is  $\sim 53 \mu\text{m}$ .

All four types of Fe-olivine (Fa100, Fa71, Fa50, and Fa29) were examined in sulfuric acid weathering experiments at 233 K (SA-233K). The experimental procedure has followed ref. [5]. Silica beads (400  $\mu\text{m}$  in diameter, 10 g) were first added to an anti-freeze Teflon tube and then covered with a layer of 0.5 M sulfuric acid solution (pH = 0.96 at 25°C). Then, 50 mg olivine powders were added to the tube, and the mixtures were placed in a freezer set to 233 K. Ten aliquots were prepared initially for each type of olivine, and two of the aliquots were sampled every 20 days for a total of 100 days. Of the two aliquots, the one used for solution analysis was treated by adding 10 mL 0.1 M sodium acetate solution and then filtered with a 0.22  $\mu\text{m}$  Nalgene filter. The sample used for solid-phase analysis was directly freeze-dried.

Fa71 and Fa50 were examined in ferric sulfate solution weathering experiments at 233 K (FS-233 K). The ferric sulfate solution (pH = 0.41 at 25°C) was prepared by adding 31 g  $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$  into 80 g deoxygenated ultrapure water (dissolved  $\text{O}_2 < 1\text{ppm}$ ). Then, 200 mg olivine powder and 2 mL  $\text{Fe}^{(\text{III})}$ -sulfate solution (W/R ratio of 10) were added to the anti-freeze Teflon tube. The tube was capped and immediately transferred to the freezer set to 233 K. Five aliquots were prepared initially for each type of olivine, and one aliquot was sampled every 20 days for a total of 100 days. The frozen mixture was thawed at room temperature for 30 minutes, and the supernatant was filtered for solution analysis. The remaining solid sample was washed twice with ultrapure water and then freeze-dried.

The initial Fe-rich olivine samples were characterized using powder X-ray diffraction (XRD) and digested for composition. The final solid products were characterized by transmission electron microscopy with energy dispersive X-ray spectrometry (TEM-EDS). The concentrations of released  $\text{Fe}_T$  and  $\text{Mg}^{2+}$  were measured by atomic absorption spectrometry, and  $\text{Si}^{4+}$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  were measured by plasma emission spectrometry.

**Preliminary results:** XRD confirms that the synthetic Fe-olivine samples are pure, and their characteristic peaks show a clear transition from the Fe-rich endmember to the Mg-rich endmember (Fig. 1).

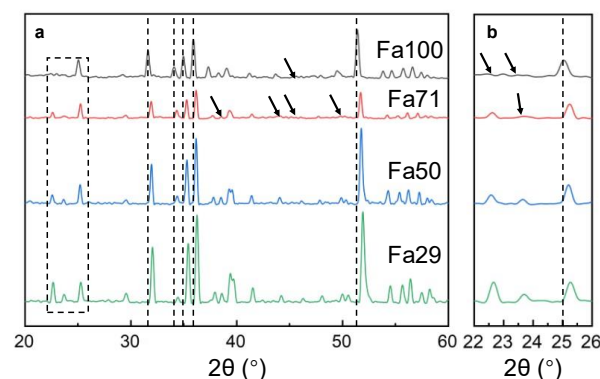


Fig. 1. XRD patterns of initial Fe-rich olivine. (a) Characteristic peaks show a clear transition from Fe-rich to Mg-rich endmembers, including peak offsets (dashed lines) and the appearance of new peaks (arrows). (b) Enlarged view of the dashed box in (a).

In the SA-233K experiments,  $\text{Fe}_T$  and Mg showed congruent release, and the concentrations in the solutions increased throughout the experiments. The released molar  $\text{Fe}/(\text{Fe}+\text{Mg})$  ratios in the weathering solution were slightly lower than those in the initial olivine. The dissolution rates ( $\log r$ ) estimated using  $\text{Mg}^{2+}$  in the solutions range from  $-9.79 \sim -10.20 \text{ mol cm}^{-2} \text{ s}^{-1}$ , which is faster than that obtained by Niles et al. (2017) [5] using natural olivine (Fa10) ( $\log r = -10.58 \text{ mol cm}^{-2} \text{ s}^{-1}$ ). The dissolution rates increase as the Fe content increases in our experiment. Overall, these observations align with the previous conclusions that fayalite dissolves faster than forsterite [3].

In the FS-233K experiments, dissolution rates ( $\log r$ ) estimated using released  $\text{Mg}^{2+}$  are  $11.11 \text{ mol cm}^{-2} \text{ s}^{-1}$  for Fa50 and  $-11.23 \text{ mol cm}^{-2} \text{ s}^{-1}$  for Fa71. The presence of  $\text{Fe}^{\text{III}}$  in the solution may act to inhibit the dissolution of Fe-rich olivine. Overall, the olivine dissolution rates are slower in the Fe-sulfate solution than in pure sulfuric acid.

The dissolution of olivine in sulfuric acid produced two main products, sulfate and amorphous silica. In the SA-233K experiments, Fe sulfate or Fe-Mg sulfate was identified by TEM-EDS. These sulfates, despite showing regular shapes, demonstrate SAED patterns (i.e., selected area electron diffraction) as amorphous diffraction rings, indicating that these sulfates are actually amorphous. The molar  $\text{Fe}/(\text{Fe}+\text{Mg})$  ratios of these sulfates are consistent with the solutions, suggesting that Fe primarily presents as  $\text{Fe}^{2+}$  and behaves associated with  $\text{Mg}^{2+}$ . Although we did not intentionally maintain anaerobic conditions during the experiments, the ice acted well as a shield to prevent oxidation induced from the atmosphere. The final products of the FS-233K experiments were first washed and then frozen-dry, so the soluble components were washed and left only amorphous silica. We will report the completed results at the conference.

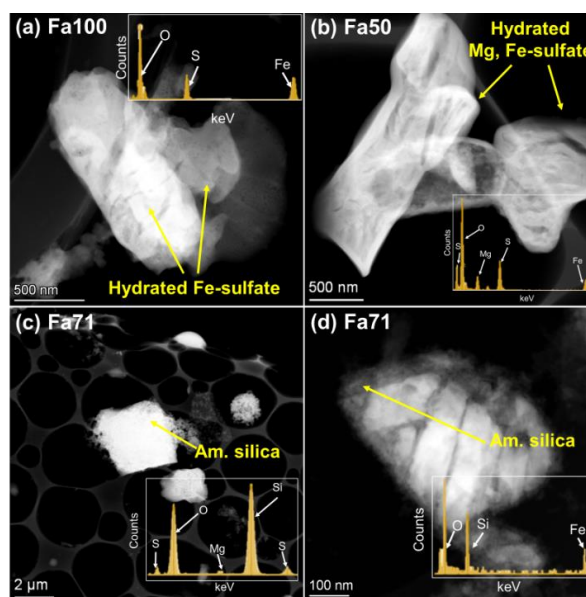


Fig. 2. TEM images and EDS results of the final products of olivine dissolution. (a-c) Hydrated Fe- or Fe-Mg- sulfates and Am. silica (amorphous silica) from the SA-233K experiments. (b) Am. silica from the FS-233K experiments.

**References:** [1] Koeppen, W. C., & Hamilton, V. E. (2008) JRG-Planets, 113(E5). [2] Stopar, J. D. et al. (2006) GCA, 70(24), 6136-6152. [3] Olsen, A. A., & Rimstidt, J. D. (2007) Am. Mineral., 92(4), 598-602. [4] Niles, P. B., & Michalski, J. (2009) Nature Geosci., 2(3), 215-220. [5] Niles, P. B. et al. (2017) Nature Commun., 8. [6] Baccolo, G. et al. (2021) Nature Commun., 12(1), 436. [7] Chevrier, V. F., & Altheide, T. S. (2008) GRL, 35(22). [8] Qi, C., et al., (2021) JGR-Soild Earth, 126, 3.