EXPERIMENTAL CONSTRAINTS ON IRON-RICH OLIVINE WEATHERING UNDER MARS ATMOSPHERE.

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Introduction: Over the past decades of Mars exploration, lines of evidence have suggested that liquid water has once persisted on ancient Mars, producing records of various secondary minerals via water-rock reactions [1]. However, the climate and geological conditions under which secondary minerals, such as phyllosilicates and carbonates, are produced are still controversial [2-3].

In all the rock-forming minerals of the Martian basalts, olivine is the first mineral phase susceptible to aqueous alteration [4]. The secondary minerals detected on Mars (i.e., phyllosilicates, carbonates, Fe-oxides) may derive from weathering of olivine under the Mars atmosphere. In turn, by understanding the formation pathways and characteristics of secondary mineral assemblages, one can further constrain the physicochemical conditions of liquid water and the climate and geological history on Mars.

Previous experimental studies relevant to Mars mainly use natural Mg-rich olivine (forsterite) as the analog. One study found that nesquehonite, an Mg-carbonate precursor of hydro-magnesite and magnesite, would form by weathering Fo90 under low water/rock conditions [5]. After increasing the water/rock ratio to 10, weathering Fo90 would form a combination of a silica-rich phase, Mg-rich smectite and traces of carbonates during a three-month experiment [6]. If the reaction time is prolonged and stirred continuously, the yields of secondary minerals are higher in abundance and are mainly composed of amorphous silica and Mg carbonates [7]. However, in contrast to the Earth, Fe-rich olivine (Fa# >20; Fe/(Fe+Mg)) is widely distributed on the Martian surface [8]. Fayalite is found to dissolve faster than forsterite [9], so the ubiquitous preservation of Fe-rich olivine across the Martian surface may further limit the duration of the water-rock reaction on Mars. One additional relevant study demonstrated that magnetite could form in solutions containing Fe^{2+}, Mg^{2+}, and SiO_2 (aq) in an anoxic environment (25°C) [10].

In this study, we investigated the weathering of synthetic Fe-rich olivine (Fa100, Fa71, Fa50, Fa29; grain size < 50 μm) under a 1 bar CO_2 atmosphere and 45°C by batch experiments. Purchased forsterite (Fa0; grain size ~250 nm) was also examined for comparison, although the Fa0 sample is smaller in size than the Fe-rich samples. The dissolution process and weathering products were characterized to provide new insights into the water-rock interactions and olivine stability on the Martian surface.

Experimental methods: Fe-rich olivine samples (Fa100, Fa71, Fa50, and Fa29) were synthesized with details in ref. [11]. The Fa0 sample (purity 99%) was purchased from Alfa Aesar. The purity and composition of olivine samples were obtained by X-ray diffraction (XRD) and Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectrometry (SEM-EDX), digestion and Inductively coupled Plasma Optical Emission Spectroscopy (ICP–OES) (Table 1). The specific surface area was obtained by Brunauer-Emmett-Teller (BET) analysis

Table 1. Composition of the initial synthetic olivine.

	Fa100	Fa71	Fa50	Fa29	LOD
FeO wt%	70.9	54.8	41.6	26.3	0.10
MgO wt%	0.01	12.5	23.3	35.8	0.01
SiO_2 wt%	27.8	31	33.2	35.9	0.20
Al_2O_3 wt%	0.06	0.07	0.19	0.26	0.01
CaO wt%	0.25	0.22	0.24	0.32	0.05
MnO wt%	0.03	0.05	0.16	0.11	0.01
Ni wt%	0.03	0.06	0.08	0.23	0.01

Note. LOD represents limit of detection.

The batch experiments were run for 180 days in a glovebox filled with a CO_2 atmosphere (99.9%; ~1 bar; O_2 concentration <1 ppm). The water/rock ratio was set to 10. Deoxygenated carbonated water (dissolved O_2 < 1 ppm; pH 4.0) used for the experiments was prepared by placing deoxygenated ultrapure water (~1 L) in a glovebox filled with CO_2 for 48 h. The temperature was set at 45°C.

Two groups of experiments were set up to track changes in the solution and solids. One group was set to examine solution compositions. Eight parallel aliquots were prepared for each olivine type. Approximately 0.2 g olivine powder was added to 2 g deoxygenated carbonated water. One aliquot was sampled at 3, 15, 30, 60, 90, 120, 150, and 180 days. The extracted solutions were analyzed for pH, Eh and compositions of Fe, Mg, and Si (by ICP-OES). The other group was set to examine solid-phase changes, and approximately 5 g olivine powder was added to 50 g deoxygenated carbonated water. On day 180, the solid samples were sampled and frozen to dry. The solid analyses included TEM-EDX, SEM-EDS, micro-X-ray diffraction, Mössbauer spectroscopy, magnetic characteristics, and infrared spectroscopy.

The olivine-water suspensions were continuously stirred on a multi-position magnetic stirrer during the experiments. The suspension containers were capped but opened weekly to exchange with the CO_2 atm.

Preliminary results: Dissolution of olivine effectively buffers the acidity in the initial solution. The pH of the solution for all types of olivine increased from 4.0 to 7.0 ~ 8.2 at 180 days. Olivine samples with higher initial Fe contents produce slightly lower pH, which may be related to the release of H^+ due to Fe hydrolysis. Notably, the solution pH of all experiments increased to ~6.0 at the first sampling point (3 days), and circumneutral aqueous conditions lasted throughout the experiments. All Fe-bearing olivine samples show a similar trend of the incongruent release of Fe versus Mg and Si (Fig. 1). Fe was released to the solution initially and rapidly decreased, likely due to the formation and precipitation of Fe(hydr)oxide phases. Si was first released but soon reached a plateau lasting toward the end of the experiments. Only Mg kept releasing into the solution. We calculated the dissolved portion of olivine of the 180-day experiment using released Mg^{2+} and found that the altered portions of Fe-rich olivine were substantially low (Table 2). In general, Fa71 dissolves faster than Fa50 and Fa29, while the latter two show no substantial difference. We infer that Fa100 should dissolve even faster than Fa71.

Due to the limited alteration in our experiments, secondary mineral assemblages can only be characterized using TEM and μXRD. Fa100 produces hematite, magnetite, SiO_2, and amorphous silicate phases bearing both Fe-poor (molar Fe/Si ~1.4) and Fe-rich (Fe/Si ~3) signatures identified on the rim of the fayalite (initial molar Fe/Si of 2). These amorphous silicate phases are likely the precursors of Fe-phyllosilicates. Forsterite (Fa0) produces Mg-carbonate and amorphous silicate phases, both Mg-rich and Mg-poor, on the rim of

olivine. In Fa71, secondary products include SiO_2 and amorphous silicate phases that are low in Fe and Mg compared to initial olivine, which indicates leaching of Fe and Mg. The Fa50 and Fa29 samples show similar final products of amorphous silicate phases low in Mg, and no SiO_2 is identified in these two samples, which might be due to limited alteration (~1 wt%). Nevertheless, the Fa50 and Fa29 samples show a preferential release of Mg compared to Fe. We will report completed results at the conference.
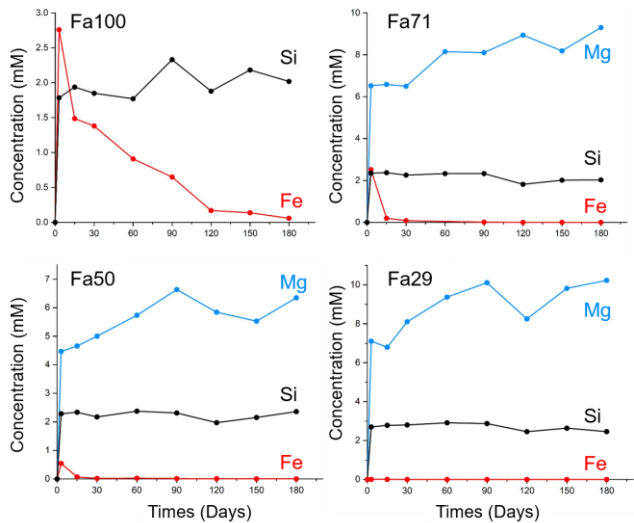

Fig. 1. Fe_T, Mg, Si concentrations versus time. All Fe-bearing olivine samples show a similar trend of the incongruent release of Fe versus Mg and Si.

Table 2. Final products of batch experiments.

	Dissolved portion [a]	Phases identified
Fa100	--	Hematite, magnetite, SiO_2; (am.) Fe-poor silicate and Fe-rich silicate
Fo71	2.9%	SiO_2, am. silicate phases poor in Fe-Mg
Fa50	1.0%	Am. silicate phases poor in Mg
Fa29	1.1%	Am. silicate phases poor in Mg
Fa0	6.9% [b]	Am. Mg-carbonate, SiO_2, hydro-magnesite; (am.) Mg-poor silicate and Mg-rich silicate

Note. [a]Calculated using released Mg^{2+} except for Fa. [b]Fa0 (forsterite) has a much smaller grain size than synthetic Fe-rich samples and thus shows higher reaction rates. "Am" represents amorphous phases

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