

MAXIMUM RATES OF OLIVINE DISSOLUTION ON MARS. J. D. Stopar¹, G. J. Taylor¹, V. E. Hamilton¹, L. Browning², and D. Pickett², ¹Hawaii Institute of Geophysics and Planetology, University of Hawaii (1680 East-West Rd., Honolulu, HI, 96822, jstopar@higp.hawaii.edu), ²Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute (6220 Culebra Rd., San Antonio, TX, 78228).

Introduction: In order to understand the evolutionary history of Mars, the mineralogy and distribution of elements on the surface must be characterized and quantified. Areas of olivine were identified using the MGS Thermal Emission Spectrometer (TES) by [1-4] in Nili Fossae, craters near Ganges Chasma, and near the rims of Argyre and Hellas basins. Hamilton and coworkers [4-5] identified olivine compositions similar to the martian meteorites Chassigny and ALH A77005 (Fo₆₈) in Aurorae Planum, Nili Fossae, and other locations from deconvolutions of TES spectra. More recently, Hamilton and Christensen [6] have combined TES spectra with images and thermal inertia measurements from the Mars Odyssey Thermal Emission Imaging System (THEMIS) to characterize these olivine deposits. Impact craters in Aurorae Planum olivine-bearing materials may indicate thicknesses ~20-40 m, and their thermal inertia is consistent with bedrock.

Based on the presence of numerous apparently fluvial features on the Martian surface, there is much speculation that liquid water or vapor may have persisted for weeks to millions of years on and beneath the surface of Mars [7]. If so, then much of Mars may have experienced water-rock-gas interactions leading to weathering of surface and near-surface materials. Among those materials most readily dissolved is olivine, whose preservation suggests limited interaction with water. To constrain the residence time of olivine in contact with water, we calculate dissolution rates for olivine at various temperatures, pH, Fe-composition, and particle size. We then determine the minimum time needed to dissolve olivine in each dissolution reaction. From this, we can place limits on the longevity and extent of olivine alteration on Mars.

Maximum Rate of Dissolution: Terrestrial olivine alteration has been investigated by [8-11], among others. Olivine dissolves readily in water, releasing its components (Fe²⁺, Mg²⁺, and silica). These components may precipitate in secondary minerals. The rate of dissolution depends on temperature, pH, olivine composition, and particle size. Experimental data [10-11] yield rate equations for calculation of olivine dissolution using a standard approach to kinetic studies of mineral dissolution. Browning et al. [12-13] used a similar approach to constrain silicate glass alteration on Earth and Mars.

The experiments of Wogelius and Walther [10-11] determined four rate equations (below) for olivine dis-

solution as a function of pH. For forsterite (Mg₂SiO₄) dissolution with pH in the range of 2-12, the rate equation at standard temperature (25°C) becomes:

$$R_{Fo} \text{ (mol / cm}^2 \text{ / sec)} = 9.07 * 10^{-12} * a_{H^+}^{0.54} + 5.25 * 10^{-15} + 2.33 * 10^{-17} * a_{H^+}^{-0.31}$$

where $a_{H^+} = -\log \text{ pH}$. For fayalite (Fe₂SiO₄) dissolution with pH 2-7, the rate equation at 25°C is:

$$R_{Fa} \text{ (mol / cm}^2 \text{ / sec)} = 1.1 * 10^{-10} * a_{H^+}^{0.69} + 3.22 * 10^{-14}$$

For fayalite dissolution with pH 8-12, the rate at 25°C is defined by:

$$R_{Fa} \text{ (mol / cm}^2 \text{ / sec)} = 1.1 * 10^{-10} * a_{H^+}^{0.69} + 3.22 * 10^{-14} + 1.2 * 10^{-16} * a_{H^+}^{-0.3}$$

For intermediate compositions along the fayalite-forsterite solid solution, the rate of dissolution at 25°C can be obtained from:

$$R_{Ol} \text{ (mol / cm}^2 \text{ / sec)} = X_{Fa} R_{Fa} + X_{Fo} R_{Fo}$$

where X is the mole fraction. For non-standard temperatures ($\neq 25^\circ\text{C}$), we can calculate the rate of dissolution by rearranging the Arrhenius relationship [11]:

$$\log R_2 \text{ (kcal / mol)} = \log R_1 + \frac{E_a (T_1^{-1} - T_2^{-1})}{2.303R}$$

where R is the gas constant (1.987216 cal/K/mol), T_i is the standard temperature (273.15K), and R_i is the rate of olivine dissolution at the standard temperature. Differing values for activation energy (E_a in kcal/mol) have been reported by [8, 11]. Wogelius and Walther [11] reported an activation energy of 19 ± 2.5 kcal/mol, which is based on experiments with 0.15-0.42mm diameter grains, and Grandstaff [8] calculated an activation energy of 9.1 ± 0.4 kcal/mol for Hawaiian olivine sand. By substituting activation energy into the Arrhenius relationship above, we can calculate dissolution rates (R_2) for non-standard temperatures (T_2). While we calculated rates for both reported activation energy values (discussed below), we report our primary olivine dissolution rates using 19 kcal/mol in Table 1.

Minimum Dissolution Time: From the rates of dissolution, we calculate the minimum time needed to dissolve one spherical particle of olivine not in contact with any others. We made two additional simplifying assumptions that lead to uncertainties: 1.) We assume the surface area of the particle remains constant over

the course of the reaction. The actual times of dissolution will be a bit longer than calculated because as particle size decreases there is less mass to remove. Nonetheless, reported dissolution times still represent *minimum* values. 2.) We also ignored the effect of surface coatings, which can slow a dissolution reaction. Oxidized iron can coat mineral grains during the

	Table 1		log Rate of Dis-
	pH	T°C	solution
			(mol/cm²/sec)
Fayalite (Fe ₂ SiO ₄)	2	25	-11.34
	5	25	-13.15
	8	25	-13.20
	12	25	-12.29
	2	5	-12.34
	5	5	-14.15
	8	5	-14.20
	12	5	-13.29
	2	100	-8.54
	5	100	-10.35
	8	100	-10.40
	12	100	-9.49
Forsterite (Mg ₂ SiO ₄)	2	25	-12.12
	5	25	-13.62
	8	25	-13.90
	12	25	-12.89
	2	5	-13.12
	5	5	-14.62
	8	5	-14.90
	12	5	-13.90
	2	100	-9.32
	5	100	-10.82
	8	100	-11.10
	12	100	-10.10
Fo50 (FeMgSiO ₄)	2	25	-11.57
	5	25	-13.32
	8	25	-13.42
	12	25	-12.50
	2	5	-12.57
	5	5	-14.32
	8	5	-14.42
	12	5	-13.50
	2	100	-8.77
	5	100	-10.52
	8	100	-10.62
	12	100	-9.70

Table 1: Maximum olivine dissolution rates. For non-standard T, activation energy = 19 kcal/mol.

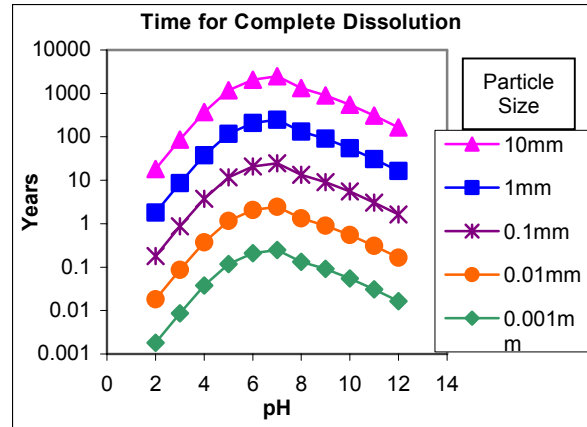


Figure 1: Minimum time for complete dissolution of one fayalite particle at 25°C. Time required depends on particle size. Calculated times do not account for changes in particle size over time.

release of Fe-ions from the fayalitic olivine component. The rate of oxidation depends on the atmospheric partial pressure of oxygen. However, we will pursue the calculation of iron oxidation and its effects on olivine dissolution rates in subsequent analyses.

Dissolution rates are converted to times by:

$$t(\text{sec}) = \frac{M_{Ol}}{R_{Ol} * SA * wt_{mol}}$$

where M_{Ol} is the mass of one particle of olivine calculated from the density and the volume of the particle (g), R_{Ol} is the rate of olivine dissolution in (mol/cm²/sec), SA is surface area (cm²), and wt_{mol} is molecular weight of olivine (g/mol).

Results. Our computations show a decrease in the time necessary for particle dissolution with decreasing particle size (Fig. 1), which relates to surface area by $4\pi(\frac{1}{2}d)^2$, and with increasing temperature (Fig. 2). The difference in dissolution time of a particle at 5°C is ~100 times longer than for a particle at 100°C for the same pH. We use 100°C as a bounding temperature, recognizing that the water boiling point could be lower on Mars. Even relatively large particles 10 mm in diameter can dissolve in fewer than 10,000 years at low temperatures. And at high temperatures, such as those found in hydrothermal systems, a particle can dissolve in less than a year. A note of caution: these are minimum times and the actual time for complete olivine alteration might be longer due to grain coatings or other processes.

Figure 3 shows the variation in dissolution time with composition. Fe-rich particles require less time to completely dissolve than Mg-rich olivines of the same particle size and at the same pH and temperature. Fe-rich olivine deposits can, therefore, dissolve up to a

factor of ~ 10 times faster than forsterite compositions under the same conditions. Hoefen and Clark [1] estimate iron abundances in Martian olivines from TES spectra. Comparisons with terrestrial spectra indicate that the olivine in Nili Fossae generally contains 20-30% FeO (Fo_{66} - Fo_{73}). Martian meteorites Chassigny and ALH A77005 have olivine composition of $\sim \text{Fo}_{68}$, which suggests a similar composition for observed olivines on the surface of Mars because their spectral features match [4]. Thus, on our Figure 3, these compositions would plot between the forsterite and Fo_{50} curves.

pH has a strong affect on alteration rate, as much as a factor of ~ 100 difference in dissolution time. Relatively longer times are needed to dissolve a particle of any size or composition at neutral pH than at highly acidic or basic pHs (Figs. 1-3).

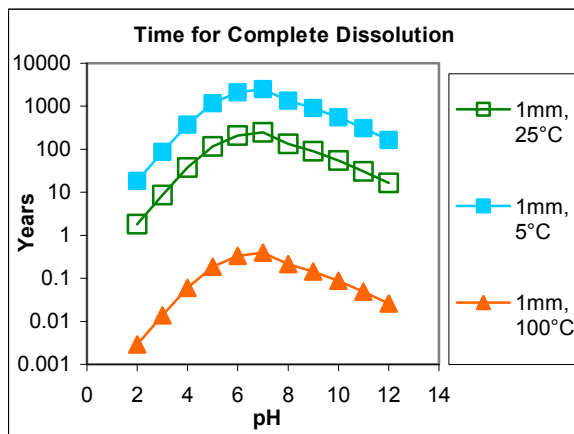


Figure 2: Minimum time for complete dissolution of one fayalite particle at 25°C, 5°C, and 100°C. Time required depends on particle size, but is only shown for 1 mm diameter particles.

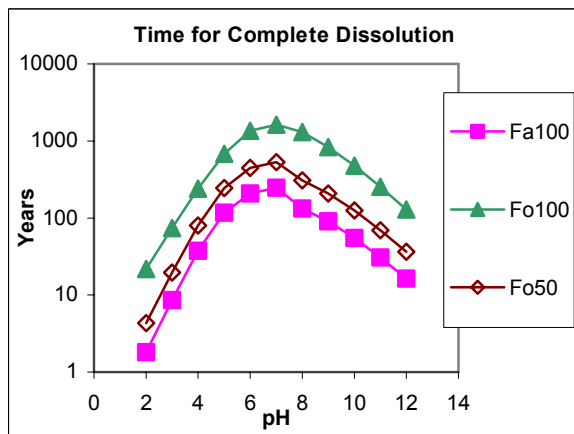


Figure 3: Minimum time for complete dissolution of one olivine particle of different compositions (fayalite, forsterite, and an intermediate Fo_{50}) with diameter of 1 mm at 25°C. Time required depends on particle size. Calculated times do not account for any oxidized iron coatings that may form from dissolution of fayalite components.

While all of our figures show the time required for *complete* dissolution of a *single* olivine particle, these can be adjusted to account for incomplete dissolution by multiplying our values by the fraction of dissolved/undissolved solid, or they can be extended to account for a specific number of particles or moles of olivine. For example, if we hypothetically calculate the surface abundance of olivine on Mars to be 5%, then 95% of a deposit of 100% olivine has dissolved. To calculate a dissolution time for 95% dissolution, we would multiply our reported dissolution times by 0.95.

Finally, we examined the effect of different activation energy values as reported by [8, 11]. The lower E_a of 9.1 kcal/mol produced a narrower range of dissolution times (Fig 4).

Interpretation: This work is a first step in constraining olivine alteration rates on Mars. By bounding dissolution rates of olivine, we can make inferences about the temporal extent of aqueous alteration on the surface. Several hypothesized low-temperature surface aqueous alteration processes include valley network formation from release of groundwater during impact [15] or gully formation from snow melt [16], both of which may occur over a period of several thousand years. Outflow channels may have formed during brief floods lasting less than a year [7]. If large bodies of water were present during a “warm, wet” period, large standing bodies of water may have been present for 10^4 to 10^9 years [7, 17-18]. High-temperature alteration processes include hydrothermal activity associated with impacts and magmatic features [19-20]. These features may remain active for 10^4 to 10^6 years. Table 2 summarizes speculated duration times of these aqueous processes. For comparison, we have determined minimum olivine residence times (time until complete dissolution) for 1 mm diameter particles to range from much less than one year to $\sim 5,000$ years.

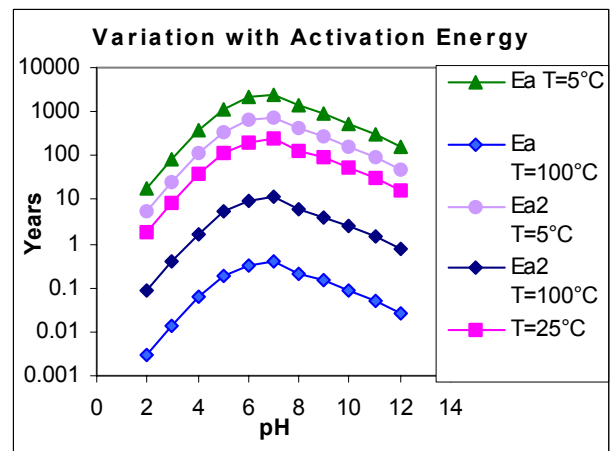


Figure 4: Minimum time for complete dissolution of one fayalite particle with diameter of 1 mm at various temperatures. $E_a = 19$ kcal/mol, and $E_{a2} = 9.1$ kcal/mol.

Aqueous solutions associated with proposed methods of valley network and gully formation could occur on time scales similar to those required for olivine dissolution. Furthermore, if we assume that the maximum times of olivine dissolution are within an order of magnitude of the minimum times we have calculated, then the presence of olivine on the surface of Mars would imply that contact with aqueous solutions is limited to a few 10^4 years at low temperatures. However, if erosion continually exposes new olivine or deposition replenishes olivine deposits at a rate greater than or equal to dissolution, then olivine deposits could endure during long-term aqueous processing. This logic does not work in reverse: the absence of olivine does not prove the existence of an aqueous system.

Because olivine-rich materials in Nili Fossae and Aurorae Planum have survived in abundances large enough to be detected with TES, our data imply that aqueous alteration lasting more than a few hundred to a few thousand years did not occur in the olivine-rich areas. Or if it can be shown that these deposits are in an area affected by aqueous alteration, then we must look for processes that might have slowed the dissolution reaction (e.g., grain coatings). Further study is needed to constrain maximum dissolution times as well as the nature of the observed olivine-rich material in Nili Fossae and other sites. Hamilton and Christensen [6] have begun the latter part of this task.

Lastly, numerous investigators have hypothesized the past presence of a large northern ocean [e.g., 22-23]. If we were to assume that the maximum times of olivine dissolution are within an order of magnitude of the minima we have calculated, then our longest olivine residence times overlap with the shortest estimates for the ocean's lifetime [17]. Thus, olivine might survive in a short-lived ocean. However, our calculations cannot be used in a straight-forward way to assume the duration of a large body of water, as the absence of olivine does not necessarily imply that aqueous processes have occurred.

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Table 2

Aqueous Process	Duration
Low T:	
Outflow Channels formed by periodic flooding through catastrophic release of water	Short-lived, <1 yr [7] over a period of several 100,000 years [21]
Valley Networks formed by release of groundwater during impact	Few 1,000 years [15]
Gullies formed by melting snow	Few 1,000 years [16]
Lake Deposits	10,000 - 1 billion years [7]
Ocean Deposits	10,000 - 100 million years [17-18]
High T:	
Hydrothermal Activity from impact	10,000 - 1 million years [19]
Hydrothermal Activity from magmatic interactions	Few 100,000 years or more [20]

Table 2: Time scale of proposed aqueous processes on Mars. For comparison, we calculated olivine residence times of less than 1 year to ~5,000 years for a 1 mm diameter olivine particle.