

Using a mineral lifetime diagram to evaluate the persistence of olivine on Mars

AMANDA ALBRIGHT OLSEN AND J. DONALD RIMSTIDT*

Virginia Polytechnic Institute and State University, Department of Geosciences, Blacksburg, Virginia 24061, U.S.A.

ABSTRACT

We present a diagram that shows the effect of pH, temperature, grain size, composition, hydrodynamics, and the laboratory/field discrepancy on the lifetime of olivine grains in weathering environments. Because the persistence of olivine grains on Mars can be used to constrain the duration of liquid water, we can use this diagram to predict a range of possible maximum contact times for olivine grains with liquid water before they dissolve away completely. Depending upon the physicochemical conditions, this contact time could range between a few thousand and several million years.

Keywords: Mineral lifetime, olivine, Mars, kinetics, water, dissolution rate, origin of life

INTRODUCTION

We have available a large database of laboratory-determined mineral dissolution rates that were collected with the intention of applying this information to understand chemical weathering in the field. However, application of these experimental results to predict weathering patterns has proved somewhat elusive. In this paper we show how to present these laboratory rate measurements in a way that allows visualization of the effect of pertinent rate-controlling variables on the lifetime of mineral grains in the weathering environment. Because of the current interest in olivine weathering and its implication for the duration of liquid water on Mars, we use this as an example of how this mineral lifetime diagram can be applied.

One of the most compelling scientific questions of space exploration is whether we can find evidence of living organisms elsewhere in the solar system. Because its surface composition and climate overlap with terrestrial conditions, Mars provides an excellent prospect for finding evidence for the independent development of life (Knoll and Grotzinger 2006). However, a key ingredient needed for the development of life is liquid water so the likelihood of finding traces of life depends upon the sustained occurrence of liquid water in Martian history. Numerous observations, including aqueous alteration phases, cross lamination, hematite-rich concretions, thick weathering rinds on basalts, resistant siliciclastic fracture fills, and polygonal crack systems (Christensen et al. 2000, 2004; Clark et al. 2005; Klingelhöfer et al. 2004; Squyres et al. 2004, 2006; Squyres and Knoll 2005; Yen et al. 2005) show that liquid water did exist on the Martian surface. However, most studies suggest that the amounts and duration of liquid water were limited (Christensen et al. 2004; Madden et al. 2004; Squyres et al. 2006). An important constraint on the duration of liquid water is the observed presence of olivine crystals on the Martian surface. Because olivine dissolves relatively quickly in the presence of liquid water, its continued presence on the Martian surface suggests that the

amount and duration of liquid water were limited. Stopar et al. (2006) produced a similar analysis of olivine lifetimes. However, our mineral lifetime diagram shows how olivine grain lifetimes relate to rate-controlling variables so that new estimates of grain lifetimes can be made as our knowledge of Martian surface conditions evolves.

Olivine is present on Mars in two distinct environments: within Surface Type 1 basalts consisting of primarily plagioclase and clinopyroxene with small amounts of olivine (Bandfield et al. 2000; McSween et al. 2003) and in olivine-rich basalts (Bibring et al. 2005; Mustard et al. 2005; Rogers et al. 2005), which are generally present as small outcrops, often inside impact craters, but are exposed over 30 000 km² at Nili Fossae (Hamilton and Christensen 2005). Although an understanding of Martian mineralogy is incomplete, no terrain containing significant quantities of both olivine and aqueous alteration products has been observed. Because olivine is not reported in contact with any alteration products, it is difficult to constrain the pH of an aqueous fluid that might have reacted with olivine on Mars. However, based on the work of Madden et al. (2004) we expect the pH of a solution in contact with jarosite to range approximately from 2.5 to 4.5. Additionally, groundwater in high-olivine basalts in Iceland, a possible Earth analog for Martian basalts, has an average pH of 7.5 at an average temperature of 277 K (Stefánsson and Gíslason 2001). We believe that these two end-members reasonably bracket the pH range of solutions that might have reacted with olivine on Mars.

METHODS

We have used the large body of published information about olivine dissolution rates along with a shrinking particle model for grain lifetimes to predict the maximum time that olivine grains could persist in an aqueous environment. Our goal is to systematically examine the effects of known or suspected rate-controlling variables. We have compiled laboratory dissolution rates and used them to construct a baseline model for the lifetime of a 1 mm grain in dilute solutions with pH between 0 and 12 at 298 K. Then we evaluate how changing other important rate controlling parameters affects this lifetime.

Data from eight olivine dissolution studies (Blum and Lasaga 1988; Grandstaff 1986; Luce et al. 1972; Oelkers 2001; Pokrovsky and Schott 2000b; Rosso and Rimstidt 2000; Siegel and Pfannkuch 1984; Wogelius and Walther 1991) were

* E-mail: jdr02@vt.edu

used to develop empirical dissolution rate expressions for forsteritic olivine over the pH range of 0 to 12 (Fig. 1). All experiments were conducted at 298 K, at low ionic strength, and at low P_{CO_2} . In total, 175 Si release rates and 167 Mg release rates were compiled. Both Si and Mg release rates were used to compute rates of olivine destruction in mol/m²s. Mg rate data were adjusted for olivine compositions ranging from fo91 to fo100 to account for the fayalite component (Rosso and Rimstidt 2000). Experiments showing strong incongruent dissolution with Si/Mg release ratios greater than 5 or less than 0.2 were discarded. All data from Siegel and Pfannkuch (1984) were discarded due to anomalously high Si/Mg ratios and do not appear on the figure. Results from Grandstaff (1986) were excluded from the figure and regression because the rates are anomalously slower than the other studies by 1.5 to 2.5 orders of magnitude. Outliers in the regression models were identified and discarded using Chauvenet's criterion, a procedure which identifies outliers by calculating the number of points that would be expected to fall outside of a given number of standard deviations; if a higher than expected number of data points fall outside of this range, they can then be rejected (Taylor 1982).

RESULTS AND DISCUSSION

Because the olivine dissolution rates show a clear break in slope near pH 6, we chose to fit them with two separate equations, one for pH < 6 and the other for pH > 6:

$$\log r_{\text{pH}<6} = -0.48(0.01)\text{pH} - 6.90(0.03) \quad R^2 = 0.88 \quad (1)$$

$$\log r_{\text{pH}>6} = -0.18(0.02)\text{pH} - 8.8(0.2) \quad R^2 = 0.49 \quad (2)$$

where the numbers in parentheses represent one standard error of the regression coefficients.

We then used these equations to construct the line in Figure 2, which predicts olivine lifetimes in dilute solutions at 298 K as a function of pH. The lifetime (t) of a dissolving spherical olivine grain is related to its rate of dissolution (r) by the expression

$$t = \frac{d}{2V_m r} \quad (3)$$

where d is the grain diameter and V_m is the molar volume of olivine (Lasaga 1998). This olivine lifetime model constrains the maximum time that an olivine grain could have been in contact with liquid water before dissolving away completely.

Several factors could change olivine lifetimes from the reference case shown in Figure 2. These factors include dissolved carbonate (Golubev et al. 2005; Pokrovsky and Schott 2000b; Wogelius and Walther 1991), SiO₂ (aq) (Oelkers 2001; Pokrovsky and Schott 2000b), Mg²⁺ (aq) (Oelkers 2001; Pokrovsky and Schott 2000b), grain coatings (Weissbart and Rimstidt 2000), ionic strength, fayalite/forsterite ratio (Westrich et al. 1993), temperature (Jonckbloedt 1998; Oelkers 2001; Rosso and Rimstidt 2000; Van Herk et al. 1989), grain size, hydrodynamics (Rimstidt et al. 1996), and an unexplained discrepancy between field and laboratory dissolution rates (Velbel 1986, 1993; White and Brantley 2003). The effect of each of these factors on olivine lifetime has been evaluated and the magnitude of each effect is shown by the vertical scales on Figure 2. Those scale bars that lie above the lifetime versus pH reference line represent factors that increase grain lifetime and those that lie below this line represent factors that shorten grain lifetime.

Although there have been some reports that P_{CO_2} or dissolved carbonate species affect olivine dissolution rates, the most recent results (Golubev et al. 2005) indicate that carbonate ions do not have a significant effect. One early study (Wogelius and Walther 1991) reported that the presence of dissolved CO₂ at atmospheric partial pressures decreased the dissolution rate of forsterite by

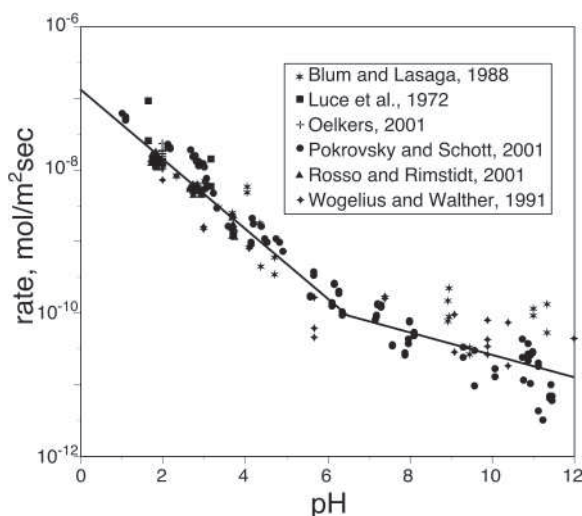


FIGURE 1. Reported rates of forsterite dissolution in mol/m²s.

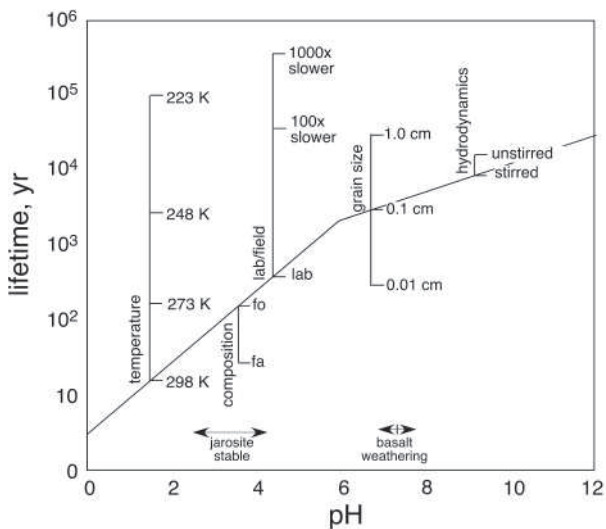


FIGURE 2. Forsterite grain lifetime diagram. Forsterite grain lifetimes are given as a function of pH for laboratory conditions at 298 K. Vertical scales show how changing temperature, olivine composition, field conditions, grain size, and hydrodynamics increase (scales above graph) or decrease (scales below graph) olivine grain lifetimes. Scales have been placed at arbitrary pH values and can describe conditions at any pH.

approximately ten times. However, these dissolution experiments were not stoichiometric, suggesting that the measured rates were influenced by another factor. A similar study (Pokrovsky and Schott 2000b) showed that as $\log a_{\text{CO}_3^{2-}}$ increases from -5 to -2, dissolution rates decreased by 1.5 orders of magnitude at pH > 8. However, dissolution rates in that study were calculated using rates of Mg release, which may have been reduced by incongruent dissolution and the development of a brucite-like leached layer or by the formation of magnesite in the experiments. More recent experiments (Golubev et al. 2005) show no effect on the rate of HCO₃⁻ up to 0.01 M or of CO₃²⁻ up to 0.005

M. Based on these more recent, carefully executed experiments we conclude that carbonate ions do not significantly affect olivine dissolution rates.

The olivine dissolution reaction is far from equilibrium so we do not expect that Mg^{2+} (aq) and SiO_2 (aq) will reprecipitate as olivine. Oelkers (2001) and Pokrovsky and Schott (2000b) showed that olivine dissolution rates are not affected by Mg^{2+} (aq) concentrations up to 0.05 *M*. Olivine dissolution does not seem to be affected by SiO_2 (aq) concentrations up to 0.0005 *M* at low pH (Oelkers 2001). However, Pokrovsky and Schott (2000b) report that SiO_2 (aq) concentrations of 0.001 *M* decreased the dissolution rate by approximately five times at pH above 8.8. We have not shown this effect in Figure 2 because it is relatively small and because this pH falls outside of the target pH range that we discussed in the Introduction. However, the effect of SiO_2 (aq) may be significant at pH above 8.8.

Various coatings could form on weathering olivine. For example, silica-rich leached layers can form on silicate minerals that have Si-O-Si bonds (e.g., Weissbart and Rimstidt 2000). Although olivine has been reported to develop a Si-enriched surface at low pH and a Mg-enriched surface at high pH (Pokrovsky and Schott 2000a), this layer is only 10–20 Å in thickness and there is no evidence that it affects dissolution rates. Secondary mineral precipitates such as sepiolite or chrysotile could grow as coatings on olivine surfaces in high pH silica- and magnesium-rich solutions. Iddingsite, a poorly defined mixture of hydrous silicates of iron and magnesium, has been observed as an alteration product on iron-rich olivine grains both terrestrially (Kuebler et al. 2003; Wilson 2004) and on meteorites (Leshin and Vicenzi 2006). However, because olivine has been detected using remote sensing, we can conclude such coatings must be thin to absent on some Martian olivine or they would obscure the olivine signal. Our analysis applies only to those observable uncoated olivine grains so that the effect of coatings can be neglected.

Increasing the amount of the fayalite component in olivine can increase dissolution rates by up to six times (Wogelius and Walther 1992). Signatures for fo_{91} , fo_{60} , and fo_{68} , and fo_{53} have all been detected on Mars using the Mars Global Surveyor Thermal Emission Spectrometer (Koeppen and Hamilton 2006). Although most olivine dissolution studies have been performed at near-end-member forsterite and fayalite compositions, Westrich et al. (1993) showed an exponential relationship between dissolution rate and composition. Because dissolution rates of both forsterite and fayalite have been determined (Wogelius and Walther 1992), we can use this relationship (Westrich et al. 1993) to postulate that all Martian olivine dissolution would be bracketed between these two end-member dissolution rates (Fig. 2).

Lowering the temperature would significantly slow olivine dissolution rates and extend grain lifetimes. Martian soil temperatures range from approximately 210 to 290 K depending on time of day (Smith et al. 2004). It is possible that Mars was much warmer early in its history (Carr 1996), although recent studies suggest that Mars has likely been at its current temperature for the past 4 billion years (Shuster and Weiss 2005). Numerous studies have examined the effect of temperature on forsterite dissolution rates and determined activation energy values for forsterite dissolution (Jonckbloedt 1998; Oelkers 2001; Rosso and Rimstidt 2000; Van Herk et al. 1989; Wogelius and Walther

1992). Although no experiments have been done at temperatures less than 298 K, we can use the Arrhenius equation

$$\ln k_T = \ln k_{T,R} - \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_R} \right) \quad (4)$$

where k_T is the rate constant at temperature (T , K), $k_{T,R}$ is the rate constant at the reference temperature ($T_R = 298$ K), E_a is the activation energy, and R is the universal gas constant (Langmuir 1997), to predict how rates will slow with decreasing temperatures. Activation energies from five studies (Jonckbloedt 1998; Oelkers 2001; Rosso and Rimstidt 2000; Van Herk et al. 1989; Wogelius and Walther 1992) were averaged to obtain an activation energy of 63 kJ/mol. Figure 2 shows that olivine grain lifetimes increase by about ten times if the temperature is reduced from 298 K to the freezing point of pure water (273 K). The freezing point of acidic sulfate solutions, which have been postulated for Mars, could be as much as 70 °C lower (Knoll et al. 2005; Knoll and Grotzinger 2006). If we chose either the smallest activation energy of 42 kJ/mol (Rosso and Rimstidt 2000) or the largest activation energy of 79.5 kJ/mol (Wogelius and Walther 1992), it would either decrease the lifetime by 16 times or increase the lifetime by 10 times, respectively.

The shrinking particle model (Lasaga 1998) shows that each order of magnitude increase in grain size increases grain lifetime by one order of magnitude. Typical olivine crystals on Earth are a few millimeters in diameter. Some Martian meteorites have olivine grains ranging in size from 50 μm to 2 mm (Barrat et al. 2002; Wang et al. 2004). We chose 1 mm as our reference grain size; however, larger grains would have proportionally longer lifetimes (Fig. 2).

If the liquid water on Mars were stagnant, lack of mixing could slow down the transport of H^+ to the olivine surface and thus slow the dissolution rate. Preliminary studies show that transport limitation could slow olivine dissolution in unstirred settings by as much as 2.5 times (Fig. 2) (Rimstidt et al. 1996).

Numerous studies have shown that laboratory dissolution rates are two to three orders of magnitude faster than field rates (Velbel 1986, 1993; White and Brantley 2003). Similarly, sedimentary grain lifetimes are up to three orders of magnitude longer than lifetimes predicted from laboratory rate measurements (Kowalewski and Rimstidt 2003). Some possible reasons for this discrepancy include uncontrolled or unaccounted effects on reactive surface area, energetically reactive sites, chemical affinity, temperature, dislocation densities, coatings, hydrodynamics, and grain aging (Velbel 1986, 1993; White and Brantley 2003). Many of these effects have already been considered in this paper. None of these factors alone seem to account for the entire observed difference between laboratory and field rates. Although there is no widely accepted explanation for this lab/field difference, we postulate that similar processes acting on the Martian surface will create a similar discrepancy, which would increase grain lifetimes by 100 to 1000 times (Fig. 2). Because we have already considered some of these effects in Figure 2, we propose that a lab/field discrepancy correction of about two orders of magnitude would be appropriate.

How can we use Figure 2 to constrain the lifetime of olivine, and therefore, the duration of liquid water on Mars? The rate effects in Figure 2 are multiplicative; therefore, because the y-

axis is a log scale, the scale bars shown in Figure 2 can simply be added onto each other to estimate a total lifetime. We cannot completely constrain the pH of a solution in contact with olivine on the Martian surface. However, our model allows a lifetime prediction for any pH value. For example, if we consider the fate of olivine in locations that now contain jarosite, the pH is constrained to 2.5 to 4.5. If we consider a 1 mm forsterite grain at 298 K and pH 3.5, its reference lifetime would be approximately 140 years. Assuming that the discrepancy between laboratory and field rates under these conditions is approximately two orders of magnitude, the lifetime could increase to 14 000 years. If the temperature were 273 K rather than 298 K, the lifetime could be about ten times longer, making it 140 000 years. Unstirred conditions would increase the lifetime by no more than 2.5 times (0.5 log units) to 350 000 years. Similarly, if we assume that the olivine-rich basalts have been in contact with water in a setting similar to Iceland (Stefánsson and Gíslason 2001), a 1 mm forsterite grain at 273 K at pH 7.5 and unstirred conditions would have a lifetime of up to 30 million years, assuming a two order of magnitude discrepancy between laboratory and field rates.

Validating this mineral lifetime diagram by comparing its predictions with olivine lifetimes on Earth is difficult because of the lack of quantitative lifetime information for field conditions. However, Kowalewski and Rimstidt (2003) used an entirely different approach to estimate that the lifetime of 1 mm diameter olivine grains in soils with a pH near 5.5 is around 3.9 million years. For comparison, our olivine lifetime diagram predicts a lifetime for 1 mm olivine grains at pH 5.5 and at 10 °C of 1.5 million years. This suggests that our diagram gives estimates that are in the correct order of magnitude.

Many other scenarios are possible, and reasonable estimates of olivine lifetimes must be constrained by a more complete knowledge of the surface conditions over Martian history. For example, if we assume relatively dilute solutions then the minimum temperature for the existence of liquid water will be slightly below 0 °C. If we assume briny conditions, which allow aqueous solutions to exist at much lower temperatures (which would result in a much longer lifetime), the activity of water would be lower, perhaps too low to be tolerated by organisms (Knoll and Grotzinger 2006). Regardless of what physiochemical conditions that we postulate for early Martian history, we can now propose a scenario and ask, "Is it reasonable to expect that life could have originated in this time frame?"

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