

**OLIVINE WEATHERING ON MARS: GETTING BACK TO BASICS.** N.J. Tosca, J.A. Hurowitz, L. Meltzer, S.M. McLennan and M.A.A. Schoonen. Department of Geosciences, State University of New York at Stony Brook, Stony Brook, NY 11794-2100 (ntosca@ic.sunysb.edu)

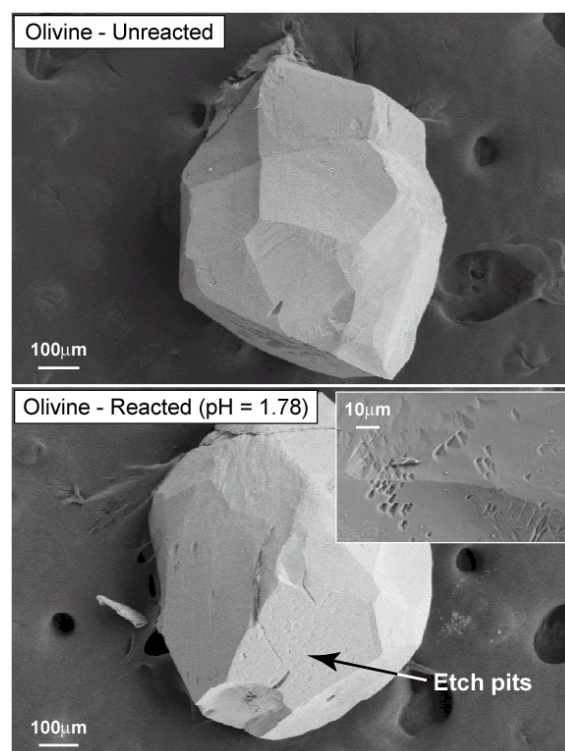
**Introduction:** With recent advances in remote sensing (e.g. MGS-TES, -MOC, Odyssey THEMIS and GRS), it has become possible to obtain detailed physical and chemical information from the Martian surface. Therefore, mineralogical markers existing on the surface may provide clues to the history of water on Mars. Recently, it has been suggested that olivine may be one mineralogical marker providing such information [1]. The detection of specific olivine-rich areas on the Martian surface has led to several interpretations on the history of water in these areas as well as the nature of olivine weathering on the surface of Mars. In order to apply what is currently known about the behavior of olivine weathering in terrestrial systems to Mars, it is important to highlight some of the fundamentals of olivine weathering. Here, based on experimental investigations of olivine weathering, we report that distinction between weathered and unweathered olivine on Mars may be more difficult than previously thought. With this complication introduced, the use of olivine as a mineralogical marker on Mars relies heavily on the kinetics of dissolution under Martian conditions, which, as discussed below, can be exceedingly complicated.

**Experimental Investigations of Olivine Weathering: Methods:** The alteration experiments discussed here used olivine having a composition of  $(\text{Mg}_{1.81}\text{Fe}_{0.18})\text{Si}_{1.00}\text{O}_4$ . Two types of alteration experiments were conducted: flow-through experiments and batch experiments, simulating dynamic and static fluid flow regimes, respectively. Each type of experiment was conducted using two different sulfuric and hydrochloric acid mixtures, corresponding to pH values of 1.8 and 3.6. Flow-through experiments were conducted using a single pass packed bed reactor, composed of PEEK<sup>®</sup> and Teflon<sup>®</sup> tubing, where fluid is passed over a packed column of olivine (containing 100 to 200 mg) at a constant rate (0.01 mL/min.) by a syringe pump. These experiments were run for approximately 100 hours, corresponding to a total of 60 mL of fluid pumped. Also, flow-through experiments were duplicated using deoxygenated fluids and sealed under a  $\text{N}_2$  atmosphere to isolate the effect of Fe oxidation on the dissolution behavior of olivine. Batch experiments were conducted in sealed 30 mL Teflon<sup>®</sup> beakers using the same solutions described above. The fluid-to-rock ratio was maintained at 100 throughout the experiments, which were conducted for approximately 350 hours.

Fluid was sampled from all experiments at varying intervals and analyzed for major element composition

by direct current plasma atomic emission spectroscopy (DCP-AES). The total amount of fluid removed from the batch experiments did not exceed 4% of the total. At the conclusion of the experiments, the residual solids were analyzed by SEM and XRD.

**Experimental Investigations of Olivine Weathering: Results and Discussion:** The crystallographic structure of olivine is primarily responsible for its behavior and relatively rapid dissolution in natural environments in that breaking the  $\text{M}^{2+}\text{-O}$  bond leads to al-



**Figure 1** – Unreacted and reacted olivine grains. Etch pits are observed on the surface of the reacted grains.

most complete dissolution [e.g., 2,3]. As a result of this mechanism, olivine dissolves stoichiometrically under a range of fluid compositions. Our experiments confirm this and show that olivine dissolution becomes stoichiometric within the first few hours of dissolution. This behavior is exhibited in all experiments, including those using static and dynamic fluids.

One important consequence of this dissolution behavior is that the surface of reacted olivine appears unaltered on a physical and chemical level, especially in flow-through environments where precipitation of new alteration phases is more difficult. This is confirmed in our experiments by SEM analysis of reacted

olivine (Figure 1). Furthermore, X-ray spectroscopic analysis of the reacted olivines shows that the original chemical composition is maintained at the surface of the olivine. This is important from a remote sensing standpoint in that distinction of altered olivine on Mars may be difficult, if the chemical and physical characteristics are not changed appreciably at the surface during weathering, especially in dynamic fluid regimes.

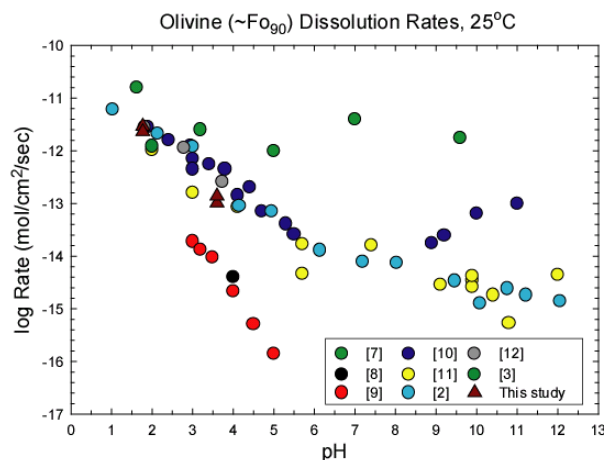
Fe oxidation of these olivines occurred in experiments exposed to the atmosphere at pH 3.6 as well as under “deoxygenated” ( $O_2(aq) = 0.2$  ppm) conditions. This oxidation prevents Fe from entering the fluids, but the dissolution is still stoichiometric with respect to Mg and Si. Fe-oxide coatings are likely to form on an olivine surface, but only if molecular  $O_2$  is the oxidant. If this is the case, these coatings may not be preserved for any appreciable length of time given the extreme aeolian conditions, which currently prevail on Mars.

**Kinetic Evaluations of Olivine Dissolution on Mars:** With the added complication of the similarity between reacted and unreacted olivine and the likelihood that physical weathering may further obscure chemical weathering products, the use of olivine as a marker for the presence of water now becomes an issue of dissolution kinetics under Martian conditions. There is currently a large body of literature on the dissolution kinetics of olivine in laboratory and natural settings. The rates derived from laboratory studies of dissolution typically have uncertainties in the range of 20% and are difficult to reproduce [4]. Rates typically are reproducible to within 0.25 log units within one laboratory and vary as much as 3 or more orders of magnitude between different laboratories [5,6] (see Figure 2).

Also, there exists a large, well-established discrepancy between laboratory derived rates of dissolution and field rates of dissolution. This discrepancy is approximately 1 to 3 orders of magnitude slower for observed field rates of dissolution and has been attributed to several factors [5,6]. For this reason, it has been suggested by several workers [e.g., 5,6,13] that it is unreasonable to quantitatively compare laboratory and terrestrial weathering rates, however, reactivity trends and mechanisms prove to be the same in both settings.

For olivine in particular, other complications arise such as significant dissolution rate inhibition (0.5 to 1.5 orders of magnitude) by  $CO_3^{2-}$  and  $SiO_2(aq)$  [2,11]. Also, it has been noted in several studies that precipitation of alteration phases such as iddingsite and smectite during olivine weathering proceeds in channels as small as 25 Å wide, only detectable by TEM [e.g., 13]. This may also complicate the distinction of weathered olivine by remote sensing methods. These effects are

of great relevance to olivine dissolution on Mars and much work remains to be done to fully evaluate their importance for the surface of Mars.



**Figure 2** – Reported laboratory dissolution rates for  $Fo_{90}$  compositions as a function of pH.

**Conclusions:** In summary, our experiments agree well with other weathering studies of olivine in that stoichiometric dissolution occurs over a wide range of fluid compositions and results in a surface indistinguishable from unweathered olivine on a  $\mu m$  scale. With this observation, the use of olivine as a mineralogical marker for water on Mars depends largely on the kinetics of weathering. Stopar et al. [14] have taken an important first step in addressing this problem through mean mineral lifetime calculations. However, the non-trivial uncertainties mentioned above lead to many orders of magnitude variations in weathering rates and consequently, residence times, using what little experimental data relevant to Martian conditions are available. The mean lifetime of olivine in some cases has been reported to be up to 10 times larger than that of anorthite and other high-Ca plagioclase compositions and only as little as 5 times less than some pyroxene compositions [4,5].

**References:** [1] Christensen, P. (2003) *6th Mars Conf.*, Abst. #3126. [2] Pokrovsky, O. & Schott, J. (2000) *GCA*, 64, 3313. [3] Oelkers, E. (2001) *Chem. Geo.*, 175, 485. [4] Lasaga, A. (1998) *Kinetic Theory in the Earth Sciences*, Princeton, 811 pp. [5] Kump, L. et al. (2000) *Annu. Rev. Earth Planet. Sci.*, 28, 611. [6] Velbel, M. (1993) *Chem. Geo.*, 105, 89. [7] Luce, R. et al. (1972) *GCA*, 36, 35. [8] Siegel, D. & Pfannkuch, H. (1984) *GCA*, 48, 197. [9] Grandstaff, D. (1986) In *Chemical Weathering Rates of Silicate Minerals*, p. 87, Min. Soc. of Am. [10] Blum, A. & Lasaga, A. (1988) *Nature*, 331, 431. [11] Wogelius, R. & Walther, J. (1991) *GCA*, 55, 943. [12] Rosso, J. & Rimstidt, J. (2000) *GCA*, 64, 797. [13] Casey, W. et al. (1993) *Chem. Geo.*, 105, 1. [14] Stopar, J. et al. (2003) *6th Mars Conf.*, Abst. #3151.