

# AQUEOUS DISSOLUTION OF OLIVINE ENHANCED BY ION IRRADIATION

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## Abstract

Recent laboratory experiments investigating the effect of ion irradiation on planetary minerals, show that changes in the surface composition differ depending on whether the analysis is done *in situ*, without removing the sample from vacuum, or *ex situ*. We find that olivine samples, irradiated with keV ions, show preferential loss of magnesium when exposed to water or the atmosphere. Irradiations were performed with 4 keV Ar ions to fluences between  $10^{14}$  and  $10^{18}$  ions/cm<sup>2</sup>. Soak times in high purity water (pH = 7) ranged from minutes to days, and exhibit the same degree of Mg depletion independent of soak time. The concentration of magnesium on the surface of irradiated natural olivine decreases by as much as 60% upon contact with water, as measured with x-ray photoelectron spectroscopy. This finding is important for laboratory simulations of regolith processes and for establishing procedures for the handling of irradiated samples, especially those returned to Earth from space.

## Introduction

Olivine-group minerals are ubiquitous throughout the universe. They have been detected on Earth, meteorites (Nehru et al. 1983), the surface of Mars (Hoefen et al. 2003), asteroids (Robinson et al. 2001), Trans Neptunian Objects (Wooden et al. 1999), comets (Zolensky et al. 2006), and interstellar dust (Tielens 2005). On airless bodies, the surfaces are exposed to energetic ion irradiation from the sun, planetary magnetospheres and cosmic rays, which may change their surface chemical composition and optical properties. Thus it is important to study those changes; this is normally done through measurements on returned samples or laboratory simulations. In these two cases the

question arises as to the effect of the environment and material handling on surface composition.

The study of space weathering and its effects on the structure and composition of minerals has been the focus of multiple papers. Bradley et al. measured the compositions of interstellar dust particles (IDPs) and chondritic meteorites using energy dispersive x-ray analyses on a TEM (Bradley 1994). A cross section of the IDP revealed a depletion of magnesium and calcium from the weathered surface with respect its the core (Bradley 1994). Furthermore, 20 keV proton irradiation of the Allende (CV3) chondritic meteorite to a fluence of  $1.3 \times 10^{18}$  ions/cm<sup>2</sup> reproduced the depletion of magnesium from the amorphous surface (Bradley 1994). Bradley attributed non-stoichiometric sputtering to be the mechanism by which magnesium was depleted from the mineral surfaces.

Demyk et al. 2001 also measured the compositional changes in olivine resulting from 4 keV and 10 keV He<sup>+</sup> irradiation. After the samples were irradiated, their composition was determined by TEM, presumably *ex situ*. They observe a 30% decrease in the magnesium to silicon ratio when crystalline olivine was irradiated with 4 keV He<sup>+</sup> ions to a fluence of  $10^{18}$  ions/cm<sup>2</sup>. Toppani et al. 2006 report a reduced magnesium to silicon ratio in the amorphous rim of an olivine interstellar dust particle compared to the unirradiated substrate. Conversely, studies by Dukes et al. (1999), showed that *in situ* keV ion bombardment of olivine to a fluence of  $5 \times 10^{17}$  ions/cm<sup>2</sup> does not significantly change the relative concentrations of Mg, Fe, O and Si as measured by XPS. In a similar study, Jager et al. found no change in chemical composition of enstatite (MgSiO<sub>3</sub>) due to 50 keV He<sup>+</sup> bombardment as observed *in situ* by SEM, TEM and EDX (Jager et al. 2003).

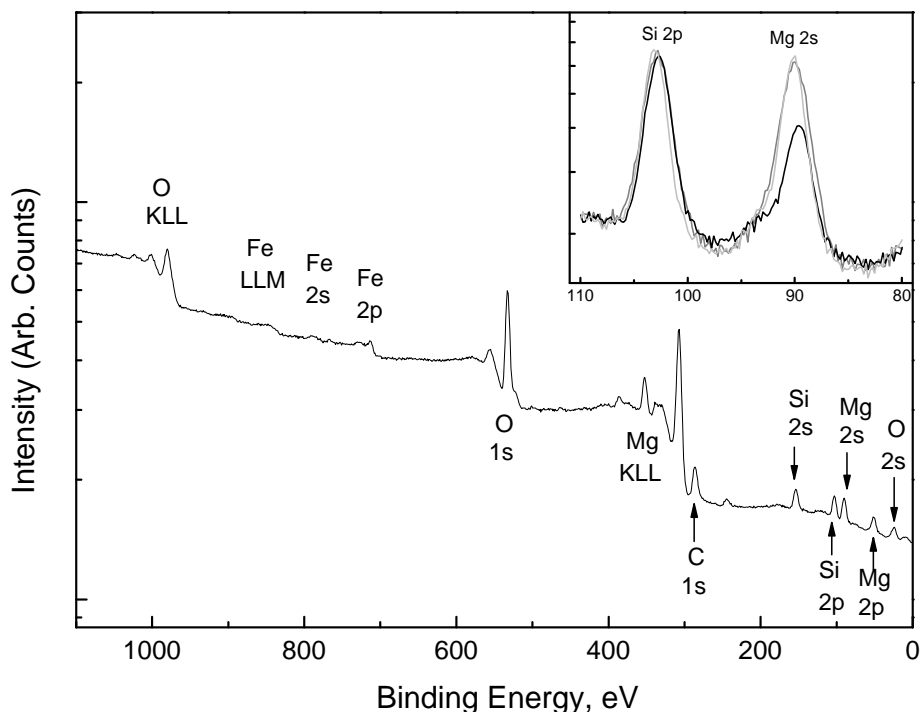


Figure 1: X-ray photoelectron spectra of Olivine upon admission to vacuum is shown above. The inset shows the XPS spectra of olivine upon admission to vacuum (light grey), after irradiation (dark grey), and after three minute exposure to water (black). The sample was irradiated to a fluence of  $1e17 \text{ Ar}^+/\text{cm}^2$ .

In three of the above studies, investigators found using TEM that keV ion irradiation significantly reduced the magnesium to silicon ratio of olivine (Bradley 1994, Demyk et al. 2001, Toppani et al. 2006). However, studies by Dukes et al. (1999) and Jager et al. (2003), showed that keV ion bombardment of magnesian silicates does not significantly change the relative concentrations of Mg, O, and Si. We speculate that environmental changes on irradiated surfaces are the cause of conflicting results between experiments where surfaces irradiated in vacuum have been analyzed *in situ* or analyzed after handling outside vacuum, such as is typical for specimen preparation for electron microscopy. Below we present experimental results that suggest the discrepancy may be due to the preferential

dissolution of magnesium by exposing an ion-irradiated olivine surface to water.

### Experimental Methods

Olivine,  $(\text{Mg,Fe})_2\text{SiO}_4$  consists of isolated silicate tetrahedra separated by metal cations. The ratio of Mg to Fe in the olivine mineral group varies between the end member compositions:  $\text{Mg}_2\text{SiO}_4$  (Forsterite) to  $\text{Fe}_2\text{SiO}_4$  (Fayalite). These experiments used natural forsterite samples from the Twin Sisters Range in Washington (Ward's Scientific). Samples, 2mm thick, were cut with a diamond blade and rinsed in successive ultrasonic baths of acetone, methanol, and HPLC water. Samples larger than the acceptance area of our analyzer (6mm-dia.) were mounted to copper platens, and analyzed by X-ray photoelectron

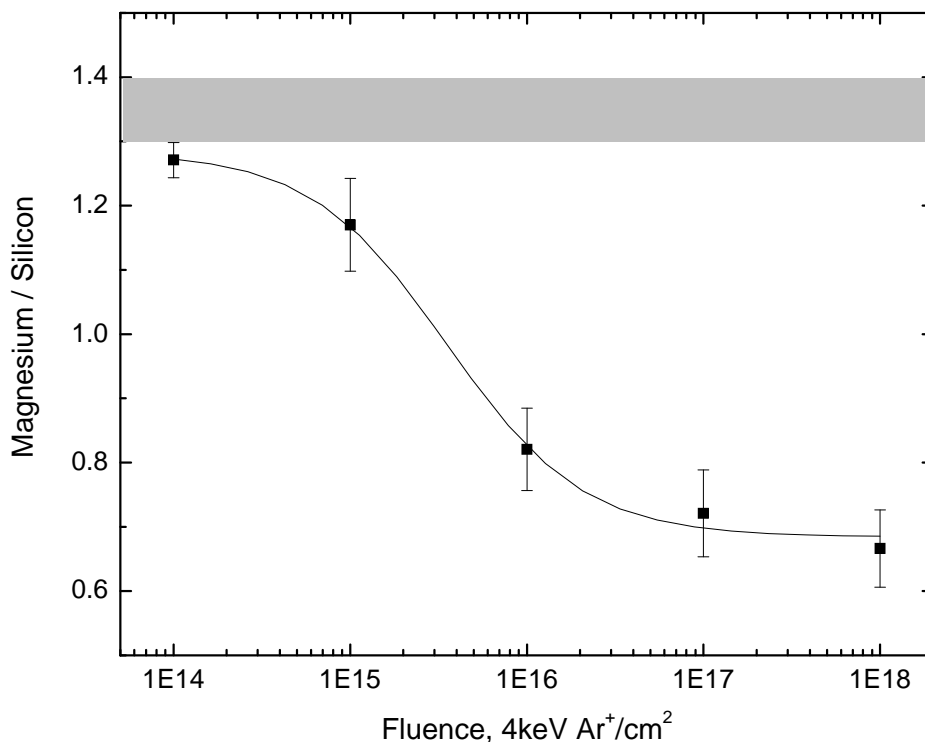


Figure 2: The magnesium to silicon ratio of olivine after irradiation with 4 keV Ar<sup>+</sup> and subsequent soaking in water for three minutes. The horizontal band indicates the range of Mg/Si ratio observed for unirradiated olivine.

spectroscopy (XPS) in a clean ultrahigh-vacuum system with a base pressure of 10<sup>-9</sup> Torr. The mean escape depth for photoelectrons from solids is between 5 and 15Å, which establishes the information depth for XPS. Additional experimental details can be found in Dukes et al.(1999).

Figure 1 shows a representative XPS spectra of olivine before and after irradiation with 4 keV Ar<sup>+</sup> to a fluence of 10<sup>17</sup> ions/cm<sup>2</sup>. No changes in stoichiometry were observed *in situ* as a result of the irradiation, except for the removal of adventitious carbon. All ion irradiations were performed at normal incidence and beam current densities never exceeded 10<sup>14</sup> ions/cm<sup>2</sup>/s. After irradiation and subsequent XPS analysis, the samples were removed from the vacuum chamber and immersed in neutral HPLC water for a period of time, after which they were returned to the vacuum chamber without further treatment. A

final XPS measurement shows the depletion of magnesium with respect to silicon (Figure 1, inset).

Control experiments were performed to test whether magnesium would dissolve preferentially from an unirradiated olivine sample. After an initial XPS spectra was collected, the olivine sample was removed from vacuum and immersed in water for two hours. After immersion, the sample was returned to the experimental chamber, and a final XPS spectra revealed a 5% reduction in surface magnesium and an increase in carbon. The dependence of irradiated olivine surface stoichiometry on water immersion time and ion fluence was investigated. In addition, data were also collected on irradiated samples that were exposed only to the moisture in the air and not directly immersed in water. A sputter depth profile was performed to quantify the depth of the magnesium depleted layer.

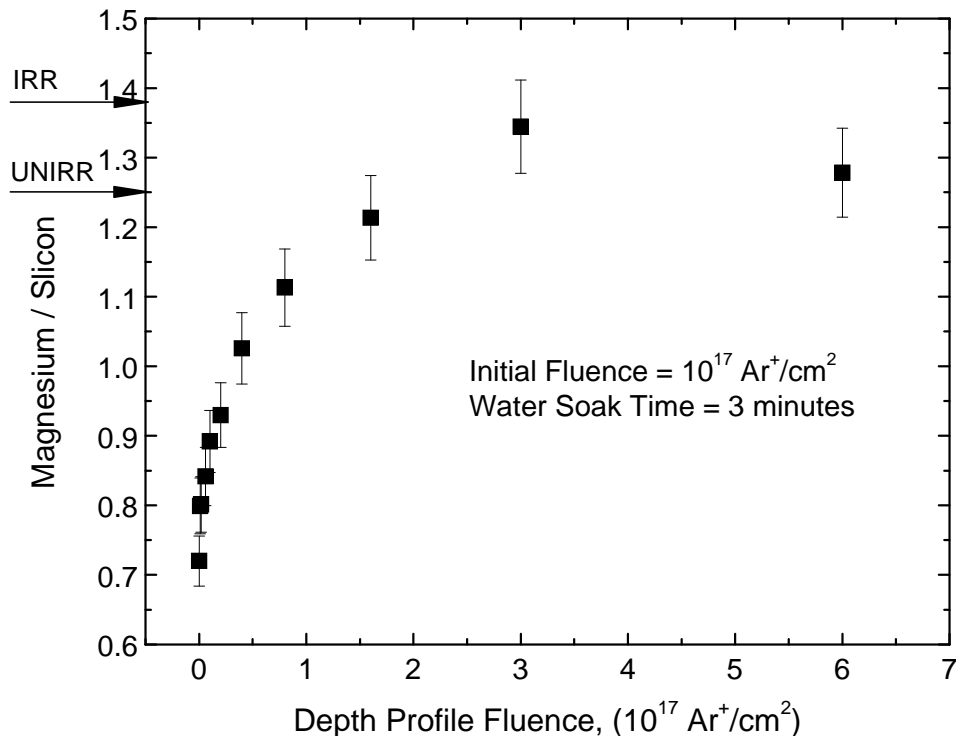


Figure 3: The marks on the y-axis indicate the magnesium to silicon ratio upon admission to vacuum (UNIRR) and after irradiation with  $10^{17}$ , 4 keV  $\text{Ar}^+/\text{cm}^2$  (IRR). After 3 minutes in water the sample was depth profiled (squares), again with 4 keV  $\text{Ar}^+$ .

### Results

The magnesium to silicon ratio used to describe the Mg depletion from forsterite is calculated from the area ratios of the Si 2p and the Mg 2s photoelectron peaks, shown in Figure 1. This data was corrected for atomic cross section using published PHI sensitivity factors. The photoelectron peak areas have been corrected for non-monochromatic excitation, by subtracting the major satellite peaks  $a_3$  ( $\Delta E=9.8\text{eV}$ , 6.4%) and  $a_4$  ( $\Delta E=11.8\text{eV}$ , 3.2%) from their known positions. XPS performed on irradiated forsterite revealed preferential dissolution of magnesium from the surface layer. We find that surface Mg depletion occurs in all forsterite samples that are immersed in water, but this depletion is strongly enhanced by prior ion irradiation of the samples.

When forsterite samples are exposed to water, the magnesium dissolves preferentially with respect to iron, silicon, and oxygen (Pokrovsky and Schott 2000). We find the magnesium to silicon ratio in unirradiated forsterite reduces by 5% after soaking in water for two hours. For comparison, the Mg/Si ratio in a sample irradiated with  $10^{17} \text{ Ar}^+/\text{cm}^2$  and soaked for only three minutes, reduces by 55%. We measured the pH of the water before and after the olivine samples were immersed within. The pH was found to be neutral and did not change appreciably upon the addition of the sample.

We measured the Mg depletion as a function of 4 keV  $\text{Ar}^+$  fluence from  $10^{14}$  to  $10^{18} \text{ Ar}^+/\text{cm}^2$  (Figure 2). These results show a strong dependence on fluence. After  $10^{16} \text{ Ar}^+/\text{cm}^2$  and three minutes in water, more than

40% of the Mg is removed from the surface. The surface depletion of Mg was also measured as a function of water immersion time. We find that preferential dissolution of magnesium from irradiated forsterite occurs quickly, in less than 3 minutes. Prolonged exposure to water does not decrease the Mg/Si ratio any further. After several days in water, the magnesium depleted layer flakes off due to a crystallographic misfit with the bulk mineral (Casey and Bunker 1990).

From the results above, it seems clear that the surface of ion irradiated forsterite, will preferentially lose Mg upon exposure to water. However, it is important to determine the effect of atmospheric conditions on irradiated minerals, as storing and transporting samples in air is standard practice. We find that forsterite, bombarded by  $10^{17}$  Ar<sup>+</sup>/cm<sup>2</sup> and exposed to air for two days, will lose up to 15% of its surface magnesium. This depletion of Mg upon contact with air did not always occur, and we attribute the inconsistency to a variation in relative humidity.

Sputter depth profiles were performed to estimate the depth of the magnesium depleted layer (Figure 3). The forsterite was irradiated with 4 keV Ar<sup>+</sup> to a fluence of  $10^{17}$  ions/cm<sup>2</sup> and then immersed in water for three minutes. After reintroducing the sample to vacuum, 4 keV Ar<sup>+</sup> ions were again used to sputter away the surface layer. We found that the magnesium to silicon ratio returns its initial value after a fluence of  $3 \times 10^{17}$  Ar<sup>+</sup>/cm<sup>2</sup>. Using the sputtering yield of 1 atom ejected per incident ion reported by Betz and Wehner (1983), we estimate the thickness of the magnesium depleted layer to be between 10 and 30 nanometers. We note that the range of 4 keV Ar<sup>+</sup> in forsterite is 5 nanometers, as calculated with SRIM 2003.

## Discussion

Olivine is an orthosilicate consisting of SiO<sub>4</sub> tetrahedra and two cations (magnesium, iron, or manganese). Forsterite is considered a loosely connected molecular solid because no cross-linking exists between the silicate molecules. In orthosilicates, cations generally dissolve first in neutral

solutions, followed by the slower removal of intact silicate tetrahedra. The incongruent dissolution of silicate minerals has been explored by many workers (Casey and Bunker, 1990, Banfield et al. 1995, Chen and Brantley, 2000, Pokrovsky and Schott 2000). Their work will illuminate a mechanism by which magnesium is depleted from irradiated olivine surfaces.

Pokrovsky and Schott interpret the initial release of Mg from forsterite to be a magnesium for proton exchange at the solid solution interface (Pokrovsky and Schott 2000). The preferential dissolution of cations and the subsequent formation of leached surface layers rich in silica, are not typically observed in loosely connected molecular solids such as olivine. In contrast to orthosilicates, inosilicates exhibit interlocking chains of silicate tetrahedra that will permit the formation of an thick leached layers. Wollastonite and diopside have been observed to form thick leached layers up to several thousands of angstroms in thickness, depleted of magnesium and calcium and rich in silica (Casey et al. 1993). The leaching of crystalline olivine is confined to the first few atomic layers because no cross linking exists among the silicate groups to hold the mineral together in the absence of cations (Casey and Bunker, 1990). The work of Seyama et al. and Fujimoto et al. confirm the formation of a leached layer, depleted of magnesium on the surface of forsteritic olivine following acidic dissolution (pH < 7). The magnesium ions are reported to have been replaced by protons leaving behind the silicate anion structure (Seyama et al. 1996, Fujimoto et al. 1993).

In analogy to heavy ion bombardment, the mechanical activation of olivine can also increase the mineral's surface reactivity (Kleiv and Thornhill, 2006). The structural disordering of the olivine surface exposes the cations at depth and facilitates the penetration of water molecules into the bulk. We propose that heavy ion bombardment results in a low density amorphous network of olivine. When irradiated olivine is exposed to water, the magnesium sites are readily protonated, and the silica network remains. This accounts for the magnesium depleted layer observed in

irradiated samples that were exposed to water and the humid atmosphere.

### Conclusion

In conclusion, we find that magnesium is easily and substantially depleted from the surface of irradiated forsterite subject to water immersion and even ambient atmospheric conditions. Conflicting reports that magnesium is preferentially sputtered from the surface of olivine can be attributed to *ex situ* measurement techniques. The amorphous surface of an ion-irradiated crystalline material is susceptible to alteration by the atmosphere. Chemically active elements in an amorphous layer can be preferentially weathered by the Earth's atmosphere. Therefore, spectroscopy of irradiated materials should always be conducted *in situ* to prevent alteration of the surface by the atmosphere. When *in situ* examination is impossible, as in sample return missions from space, care should be taken to avoid alteration by the atmosphere. This will provide the best possible analyses of the surface stoichiometry, as well as preserving the true physical and optical effects of ion bombardment on planetary minerals.

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