Irradiation of olivine by 4 keV He\(^+\): Simulation of space weathering by the solar wind

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\[1\] We have studied the effects of 4 keV He\(^+\) ion irradiation on olivine while measuring, in situ, changes in the near-infrared (NIR) reflectance and in the chemical composition of the surface. The observed changes in reflectance are reddening and the attenuation of the Fe-3d absorption bands in the NIR. Spectral reddening of irradiated olivine powder (<45 \(\mu\)m) correlates with the amount of metallic iron formed by ion impact, consistent with the idea that space-weathering effects in the reflectance of olivine-bearing S type asteroids are due to the formation of metallic iron. The metallization rate of the powder is about half that of a sectioned rock of olivine, which we propose is a consequence of redeposition of sputtered material. The NIR spectral changes observed in ion irradiation experiments are similar to those observed in our previous experiments on vapor redeposition, indicating that different space weathering mechanisms can lead to similar final effects on reflectance. Finally, we estimate that at 1 AU the spectral reddening caused by the solar wind saturates approximately 2 orders of magnitude faster than comparable reddening caused by micrometeorite impacts.


1. Introduction

[2] Space weathering is the physical and chemical alteration of surfaces of airless bodies exposed to the space environment [Hapke, 2001; Clark et al., 2002; Chapman, 2004]. There they are subject to bombardment by ions from the solar wind, magnetosphere ions, energetic electrons, cosmic rays, ultraviolet photons and fast interplanetary dust (micrometeorites), with the relative flux of each of those projectiles depending on the location of the surface in the solar system. Any of these impacts can produce chemical alterations by breaking molecular bonds, synthesizing new molecules or by changing the elemental composition via ion implantation and preferential sputtering. Micrometeorites may, in addition, physically alter the particle size distribution through impacts that melt and reform surface particles, sinter them, break them into smaller pieces, or bring larger subsurface particles to the surface, mixing the soil. Changes in grain size alter the path of the light in the solid leading to changes in extinction and, therefore, reflectance. Many of these alterations caused by space weathering can be inferred from the spectral reflectance of the planetary body and, in some cases, seen directly on returned samples, such as lunar soil [Pillinger, 1979; Keller and McKay, 1993; Christoffersen et al., 1996] and interplanetary dust [Bradley, 1994].

[3] Most laboratory simulations of space weathering phenomena on the Moon, Mercury and asteroids have focused on what are believed to be the two most important types of weathering agents: solar wind ions and micrometeorites. The solar wind, consisting of mostly hydrogen and helium ions (>99%), has a broad velocity distribution with a mean value of 468 km/sec (~1 keV/amu) [Gosling, 2007]. For this reason, most laboratory studies have been done with 1 keV H and 4 keV He.

[4] Several keV ion irradiation experiments on minerals have been published on the simulation of solar wind impact on mineral surfaces [Nash, 1967; Hapke, 1973; Dukes et al., 1999; Davoisne et al., 2008]. Hapke [1973] showed that H\(^+\) irradiation of loose mineral powders, analogous to the Moon regolith, visibly darkens the irradiated surface, which he attributed to the formation of metallic iron in the sputtered vapor and their redeposition on nearby grains. Dukes et al. [1999] showed, by in situ surface analysis, that ion irradiation of olivine can reduce its Fe\(^{2+}\) into metallic iron, Fe\(^0\), near the surface and that the reduction is more efficient for He\(^+\) than for H\(^+\). These experiments were done on cleaved rock surfaces, showing that metallization did not require redeposition of Fe atoms on nearby grain surfaces. Other experiments with higher-energy ions (60–400 keV H, He, Ar), more characteristic of high-velocity shocks found in the interstellar media [Bringa et al., 2007], were shown to darken and redden the reflectance spectra of mineral rocks and powders between 0.25 and 2.5 \(\mu\)m [Brunetto and Strazzulla, 2005; Strazzulla et al., 2005; Brunetto et al., 2006b].
[5] The correlation between optical effects and metallic iron content that was observed on lunar soil has been simulated in the laboratory. Adding metallic iron to silicate gels having featureless spectra causes the reddening of spectral slopes and darkening in the visible-NIR [Noble et al., 2007], consistent with the effects seen on lunar rocks.

[6] The second source of space weathering, micrometeorite impact, has been simulated in the laboratory using pulsed laser beams with instantaneous power densities similar to those of typical impact by micron-sized meteorites [Moroz et al., 1996; Sasaki et al., 2001; Brunetto et al., 2006a; Loeffler et al., 2008a, 2008b]. Those studies show changes in the reflectance spectra of silicates that can be larger than those seen in ion irradiation experiments. However, to compare these two effects, one needs to consider relative fluxes of the impactors. The relative role of solar wind versus micrometeorites has been a subject of controversy for several decades. Recently, it has been argued that the inverse dependence of the degree of reddening of asteroids with their distance from the Sun implies that the solar wind is likely the primary mechanism for space weathering [Marchi et al., 2006]. However, this inverse dependence is tenuous because of the large scatter of the data, and may be affected by the differences in composition with distance to the Sun. Thus, even if this dependence is related to space weathering, it does not preclude the importance of micrometeorite impacts, as closeness to the Sun not only implies larger ion fluxes but also micrometeorites at higher fluxes and velocities [Cintala, 1992].

[7] To further the understanding of the role of ion irradiation on space weathering, we performed experiments on olivine, a common mineral found on many asteroids [Gaffey et al., 1993; Clark et al., 2002] that has been shown to be susceptible to space weathering [Moroz et al., 1996; Sasaki et al., 2001; Brunetto et al., 2006a; Loeffler et al., 2008a, 2008b]. Specifically, in these experiments, we irradiated sectioned (“flat”) rock fragments and powders of San Carlos olivine with 4 keV He⁺ ions. A unique aspect of experiments is that during irradiation, we monitor the NIR spectra and the surface chemical composition of olivine in situ, e.g., without exposing the samples to the atmosphere. This ability will enable us to directly determine whether there is a correlation between irradiation-induced changes in the reflectance spectra and chemical composition of olivine.

2. Experimental Methods

2.1. Sample Preparation and Analysis

[8] Olivine samples used in these experiments were natural San Carlos olivine (Mg1.8Fe0.2SiO4) from Penn Minerals (Scranton, PA, USA) and from Arizona Gems and Crystals (Tucson, AZ, USA). We also used synthetic forsterite (99.4% Mg2SiO4) from Reade Advanced Materials (Riverside, RI, USA) with the percent concentration of impurities listed as: Al2O3 (0.03), Fe2O3 (0.02), TiO2 (0.09), Na2O (0.11), CaO (0.22), and K2O (0.12). To prepare olivine powder samples for use, we separated the large grains from rock inclusions, crushed them with agate mortar and pestle and used a sieve to obtain a grain size <45 μm. Chemical analysis, using X-ray photoelectron spectroscopy (XPS), showed no discernable difference between the uncrushed grains and the powder. To obtain the sample size needed for XPS measurements (∼6–8 mm), we pressed the powder to ∼3000 psi inside an aluminum ring (inner diameter ∼10 mm), placed between two stainless steel disks. In addition, we also performed experiments on a solid piece of olivine, since we were interested in learning whether changes induced by irradiation depend on physical properties of the sample, such as grain size, as has been noted previously [Hapke, 2001, and references therein]. To obtain flat specimen, we cut sections of olivine using a diamond blade, and removed the cutting fluid from the surface with successive acetone, isopropanol, and HPLC water baths.

[9] The samples were mounted on a copper holder and transferred into an oil free ion-pumped ultra-high vacuum (UHV) chamber with a base pressure between 5 and 10 × 10⁻¹⁰ Torr (Figure 1). Surface analyses of the samples were performed before, during and after irradiation using XPS and near infrared reflectance (NIR) spectroscopy.

[10] XPS is a widely used surface analysis method, which gives both elemental abundance and chemical information. In this technique, X-rays eject photoelectrons from a sample surface with a kinetic energy (Ek) given by Ek = Ee,corr − Eb − ϕ, where the X-ray energy, Ee,corr, is 1486.6 eV (Al-K), Eb is the electron binding energy with respect to the Fermi level, and ϕ is the work function of the spectrometer. The energy distribution (spectra) of photoelectrons is given as number of counts versus binding energy. The spectra show a continuous background on which photoelectron and Auger peaks are superimposed. The escape depth of the electrons analyzed by XPS depends on their kinetic energy; it is ∼5 nm for the Fe-2p and O-1s, and ∼8 nm for Si-2p, and Mg-2p electrons in olivine [Seah and Dench, 1979]. The relative area of the photoelectron peaks is used together with sensitivity factors to obtain elemental composition, whereas the precise value of the electron binding energy gives information on the chemical state of the element [Moulder et al., 1992].

[11] XPS analysis was performed in a Physical Electronics 5600 system, equipped with a double-pass, cylindrical mirror electron energy analyzer (CMA) [Dukes et al., 1999; Loeffler et al., 2008b]. The spectrometer was operated in fixed transmission mode at 200 eV pass energy for survey spectra and 40 eV for high-resolution spectra, providing energy resolutions of 3.2 eV and 0.6 eV, respectively. The ultimate energy resolution of the XPS spectra is limited by the width of the Al-K X-ray line, 0.85 eV FWHM. Survey spectra were measured in ∼5 min, while the more detailed spectra took ∼60 min.

[12] After taking an XPS spectrum, we moved the sample within the vacuum chamber to the focus of our Thermo-Nicolet Nexus 670 Fourier Transform Infrared Spectrometer (FTIR). The NIR spectrum was measured in the 5000–4000 cm⁻¹ region (0.66–2.5 μm) at a spectral resolution set to 16 cm⁻¹, each spectrum was an average of 800 scans, taking ∼10 min. Light from a halogen lamp was incident normal to the sample and the reflected light was collected at 17 degrees with mirrors and focused onto an InGaAs detector. To obtain the absolute bidirectional reflectance of the samples, the raw spectrum of the olivine was divided by that of a PTFE (Teflon) powder (Avocado Research Chemicals), which has been calibrated against an absolute reflect-
2.2. Ion Irradiation

[13] Irradiations were performed with a differentially pumped, low-energy ion gun. During irradiation the chamber pressure remained in the mid 10^{-8} Torr range, where the mean free path of residual gas in the chamber is low enough that it does not affect the trajectory of the projectiles or of the sputtered particles. We used He gas of purity better than 99.99%; the lack of significant amounts of implanted contaminants was verified in the XPS analyses. Four keV He ions, which simulate the solar wind, were rastered uniformly over the sample surface analyzed by XPS at normal incidence. The ion current density was measured before and after each experiment with a Faraday cup to be \(1.4 \times 10^{13}\) ions/cm/sec; precise to within \(\sim 5\%\). During irradiation, we used an electron flood gun, which emits low-energy (<1 eV) electrons, to prevent electrostatic charging of the sample, which could ultimately deflect the ion beam away from the sample.

3. Results
3.1. Fluence Dependence of Near-Infrared Reflectance

[14] Figure 2 (top) shows the in situ NIR spectra of a <45 \(\mu\)m powder of synthetic forsterite and olivine after different fluences of ion irradiation. The spectrum of forsterite, which contains \(\sim 10\) times less iron than San Carlos olivine, is featureless in this region and changes only slightly during irradiation. The olivine spectrum has the absorption features characteristic of polycrystalline olivine, because of electronic excitation of the outer shell (3d) electrons of Fe^{2+} [Burns, 1993]. The spectrum of the unirradiated sample is similar to spectra reported in previous studies on San Carlos olivine [Yamada et al., 1999; Sasaki et al., 2001; Brunetto et al., 2006a].

[15] During irradiation, there are clear changes in the spectral slope, termed “reddening,” generally consistent with previous experiments that use comparable ion fluences [Hapke, 2001]. We define reddening, \(r\), from reflectance values \(R\) outside the main absorptions as: \(r = (R_{1.07\mu m} - R_{1.3\mu m})/1.3\mu m\), where 1.3 \(\mu\)m is the difference in wavelength. We note that after subtracting a fitted continuum (see below in Figure 8), we find that there is no shift in the band center. Even after smoothing each spectrum and taking the derivative, we find that the shift in the \(\sim 1\) \(\mu\)m absorption band is at most 0.001 \(\mu\)m as a result of irradiation. These spectral alterations can be seen more clearly in Figure 2 (bottom), where we have divided the spectrum of the irradiated sample by the spectrum of the unirradiated sample. Interestingly, this change in spectral shape is similar to that reported previously for an olivine powder sample coated by pulsed-laser deposition of olivine [Loeffler et al., 2008a], laser ablation of olivine [Brunetto et al., 2007], olivine impacted by higher-energy ions [Strazzulla et al., 2005; Brunetto et al., 2006b]. Furthermore, the reddening is also similar to many asteroid spectra, including, but not limited to that of Eros [Clark et al., 2002].

[16] The similarity of the weathered and unweathered San Carlos olivine reflectance curves in Figure 2 show the difficulty that would be encountered when estimating the degree of space weathering in an actual asteroid spectrum. The small differences can be emphasized by differentiating the spectrum. This is shown in Figure 3, where it is quite clear that reddening occurs essentially below 1.07 \(\mu\)m, and that the degree of weathering can be ascertained by taking the ratios of the dips at 0.77 and 0.90 \(\mu\)m to the peaks at 1.11 and 1.4 \(\mu\)m. For this reason we propose to use derivative spectra to analyze weathering from asteroids.

3.2. Chemical Analysis of the Surface Using X-Ray Photoelectron Spectroscopy

[17] In addition to measuring the NIR spectrum of olivine during irradiation we also monitored chemical changes in
the surface with X-ray photoelectron spectroscopy. We monitored O, C, Fe, Mg, and Si and list the measured electron binding energies in Table 1. Electrostatic charging of the surface by photoelectron emission and changes in the work function of the spectrometer may cause the peak position to shift between irradiations, and thus the spectra were compared after the following procedure. First, the spectra were all energy shifted so that the peak position of Si-2p oxide coincided at a particular binding energy; this small shift was always <0.5 eV. Next, the absolute binding energy scale was obtained by using the standard energy of 284.8 eV [Powell et al., 1979; Dukes et al., 1999] for the 1s peak of the adventitious carbon (present in the unirradiated spectra because of exposure to atmospheric contaminants).

The photoelectron peak due to adventitious carbon quickly disappears to the noise level after a fluence of \(10^{17}\) ions/cm\(^2\). However, there is a weak low-energy shoulder at 283.8 eV, which remained throughout the experiment indicating that it is intrinsic to the olivine sample, as expected from terrestrial olivine.

Besides the removal of atmospheric contaminants at low fluences, the other major change observed with XPS is in the Fe-2p photoelectron region. The spectra are shown as a function of fluence in Figure 4. The initial Fe-2p\(_{3/2}\) peak position at 711 eV indicates the presence of Fe\(^{3+}\) in addition to the intrinsic Fe\(^{2+}\) in olivine (at 709.1 eV). These results are in agreement with previous experiments [Schott and Berner, 1983; Dukes et al., 1999] and are attributed to oxidation of surface iron. During bombardment, the surface ferric iron (Fe\(^{3+}\)) was removed and reduced to Fe\(^{2+}\) and Fe\(^0\) (at 706.7 eV), because of the preferential loss of oxygen from the surface, detected by XPS, via the breaking of Fe-O bonds.

No significant change in the binding energy of Si or Mg core electrons was observed under ion bombardment (Figure 5). The different behavior of Si and Mg compared to Fe is expected on the basis of the higher strength of the Si-O and Mg-O bonds. Finally, through the irradiation series, the peak position of the O-1s transition remained at 531.2 ± 0.2 eV, indicative of the intact SiO\(_4\) silicate tetrahedra.

Previous in situ XPS studies of irradiation of olivine are in general agreement with our results: ion irradiation of olivine forms metallic iron in the sample. The notable exception is the result by Davoisine et al. [2008], which shows the iron in olivine oxidized toward Fe\(^{3+}\) rather than reduced to Fe\(^0\) when the flux of He ions was below \(6 \times 10^{14}\) ions/cm\(^2\)/sec, but reduced to Fe\(^0\) at higher fluxes. We speculate that this effect was caused by some minor contamination, e.g., an oxygen containing species in the background gas. In our experiments, where irradiations were done at much lower pressures and with He\(^+\) flux 40 times lower than their threshold flux of Davoisine et al.
[2008], we found that the iron reduced toward Fe\(^0\) and did not form additional Fe\(^{3+}\). Furthermore, increasing the ion flux by a factor of six yielded the same results.

### 3.3. Comparison of Reddening and Metallization

[22] To compare our XPS data with spectral reddening data, we quantified the fraction of surface Fe that is metallic by taking peak areas after deconvolving the Fe 2p\(^{3/2}\) photoelectron region (Figure 4) into oxide (Fe\(^{3+}\) and Fe\(^{2+}\)) and metallic (Fe\(^0\)) components using the known positions of each component and a Shirley baseline fit [Shirley, 1972]. In Figure 6, we show the fluence dependence of metallization of iron (based on the XPS data) and the fluence dependence of spectral reddening. From this plot, it is clear that the reddening is correlated with the increase of metallic iron in the sample. This result agrees with previous observations that lunar soils containing metallic iron nanoparticles had strong red slopes in the visible (380–850 nm) reflectance [Keller et al., 1998b].

[23] We note that the rate of metallization of the <45 \(\mu\)m powder olivine sample is \(\sim\)2 times slower than for a flat olivine section (Figure 7). That the reduction of iron occurs in the flat surface, where redeposition is unimportant, will be discussed below.

### 3.4. Attenuation of the Fe\(^{2+}\) Absorption Band and Darkening

[24] In addition to the reddening, we also quantified the area of the 1 \(\mu\)m absorption band by converting the spectrum to optical depth units, taking the natural logarithm of the reflectance, and subtracting a polynomial baseline (Figure 8). This method is similar to the one used in our previous works on ices [Loeffler et al., 2006]. Figure 8 shows that, as the sample is irradiated, the area of the 1 \(\mu\)m absorption band decreases by \(\sim\)11% after \(3 \times 10^{18}\) He\(^+\)/cm\(^2\). One can see from Figure 2 that darkening by ion irradiation is at most 2% at 2.0 \(\mu\)m.

### 3.5. Reoxidation Upon Exposure to Atmosphere

[25] These studies are the first in which ion-induced chemical and reflectance changes in olivine have been measured simultaneously in situ. We also addressed whether in situ measurements were necessary, by studying the effect of exposing samples to air before analysis. After He\(^+\) irradiation, we removed a sample from vacuum, exposed it to atmosphere and remeasured its reflectance and XPS spectra. The NIR reflectance did not change, within 3%, after exposure to atmosphere for \(\sim\)10 min. However, the amount of metallic iron on the surface decreased signifi-

### Table 1. Electron Binding Energies in San Carlos Olivine\(^a\)

<table>
<thead>
<tr>
<th>Olivine Constituents</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(^{3+}) (2p(^{3/2}))</td>
<td>711.4</td>
</tr>
<tr>
<td>Fe(^{2+}) (2p(^{3/2}))</td>
<td>709.1</td>
</tr>
<tr>
<td>Fe(^0) (2p(^{3/2}))</td>
<td>706.7</td>
</tr>
<tr>
<td>O (1s)</td>
<td>531.4</td>
</tr>
<tr>
<td>C (1s)</td>
<td>283.8</td>
</tr>
<tr>
<td>Si (2p)</td>
<td>101.8</td>
</tr>
<tr>
<td>Mg (2p)</td>
<td>50.1</td>
</tr>
</tbody>
</table>

\(^a\)The binding energies reported here are the experimental values shifted as described in the text. The value listed for C (1s) is for the intrinsic carbon left at high fluences. Adventitious carbon (E\(_b\) = 284.8 eV) is used to fix the absolute binding energy scale.
cantly because of reoxidation, as first pointed out by Dukes et al. [1999]. Figure 9 (top) shows the Fe-2p region after we exposed it to atmosphere by placing it beside our vacuum system in our air-conditioned laboratory for different time periods for the powder and rock previously irradiated with 4 keV He+. Our shortest exposure time (10 min) causes the percentage of surface Fe metal to drop by a factor of two. After long exposures, up to a month, this effect saturates, leaving 15% metallic iron on the surface from an as-irradiated level of 75%. This effect suggests that the lunar soils which had been exposed to the air and had a weak metallic peak in XPS, [e.g., Baron et al., 1977] may have been completely metallic before handling in the laboratory.

Interestingly, there are stronger effects of exposing olivine to atmosphere when irradiation was done with 4 keV Ar+ ions, as shown in Figure 9 (bottom). After 10 min, only a weak shoulder of metallic iron remained in the Fe-2p XPS spectrum, indicating nearly full reoxidation over the depth of XPS; measurements a few days later show that the entire surface had reoxidized. This difference in the reoxidation times for different ions is attributed to easier oxidation of the shallower and more damaged region created by Ar, as compared to He.

4. Discussion
4.1. Overview of Sample Reflectance
[27] Electromagnetic radiation incident on the surface of a grain can be absorbed, reflected, or transmitted. The degree to which each occurs depends on the optical constants of the material. For samples that contain grains much larger than the wavelength of light, the reflected wave will leave in a specular direction from each point on the surface. Because of roughness, the surface normal varies locally causing light to reflect in a variety of directions. The reflected and transmitted light may enter another grain, where it can be reflected or transmitted with some loss of intensity because of absorption by the sample. In the range of 0.6–2.5 μm, absorption is typically due to electronic transitions between levels split by the crystal field, color centers, or overtones of fundamental molecular vibrations that occur at longer wavelengths [Hapke, 1993; Clark, 1999]. As mentioned earlier, the olivine absorption in this wavelength range is due to electronic excitation of the outer shell 3d electrons in the Fe2+ ions.

[28] If the sample also contains particles of size d, smaller than the wavelength of light, e.g., iron nanoparticles, then the reflectance spectra will be altered by the wavelength dependence of scattering and absorption. The efficiencies for scattering and absorption decrease as \((d/\lambda)^4\) and \(d/\lambda\), respectively and, for \(d/\lambda < 0.3\) for iron [Hapke, 1993], the spectral reddening is dominated by absorption. We note that

Figure 6. Comparison of reddening (circles) in the NIR and formation of metallic iron (crosses) measured with XPS on <45 μm olivine powder as a function of 4 keV He+ fluence. See text for definition of reddening.

Figure 7. Metallization of iron, as described by XPS, as a function of fluence for the flat olivine rock and <45 μm powder samples.
only a small amount of metallic iron is needed to significantly alter the reflectance. As can be seen in Figure 10, Fe has an extremely low absorption length, compared to olivine (e.g., at a wavelength of 1 \( \mu \)m, 20 nm for Fe [Johnson and Christy, 1974] and 500 microns for olivine [Brunetto et al., 2007]).

4.2. Overview of Irradiation of Silicates

KeV ions entering a solid sample lose energy mainly as a result of binary collisions with target atoms. Some of the collisions displace target atoms from their equilibrium lattice positions and ultimately lead to damage. A small fraction of the projectile are reflected, the majority come to rest in the solid. The cascade of displaced target atoms produces atomic mixing in multicomponent samples. While the cascade cools (times of the order of picoseconds) diffusion allows the lattice to heal, but some point defects (vacancies and interstitials) remain, which accumulate to form line defects and voids. A large accumulation of damage leads to amorphization. Voids assist in the formation of projectile aggregates, and He atoms are known to aggregate into bubbles of gas. Futagami et al. [1990] found that irradiation of olivine and other minerals with 3.6 keV He ions produced an accumulation of implanted He with a maximum concentration of \( 0.5 \times 10^{17} \text{cm}^{-2} \) that saturated above a fluence of \( \sim 10^{18} \text{cm}^{-2} \), as expected from the competition with sputtering. The overlap of damage regions with increasing fluence in olivine irradiated by 4 keV He leads to amorphization above a fluence of \( 10^{16} \text{ ions/cm}^2 \) [Bradley et al., 1996; Demyk et al., 2001; Carrez et al., 2002], to swelling [Wilson et al., 1996] and surface roughness [Wilson et al., 1996; Davoisine et al., 2008].

A direct manifestation of the atomic displacements is sputtering, the ejection of atoms and molecules via collisions with the solid, a process known to be an important surface alteration mechanism for both rocky and icy bodies in space that are subject to radiation [Johnson, 1990; Hapke, 2001; Baragiola, 2003]. Sputtering results in erosion of the surface, but because the probability of ejection depends on the local binding energy of the atoms and on their mass, it is often (though not always) the case that the chemical composition is altered significantly by differential sputtering.

Figure 8. (top) Decrease in the 1 \( \mu \)m band area (circles) as a function of He ion fluence for a <45 \( \mu \)m olivine powder. (bottom) Polynomial fit of the baseline in the olivine optical depth spectra (in \(-\ln (R)\) units) used to measure the band area, before (a) and after (b) irradiation with 4 keV He\(^+\) to a fluence of 3.1 \( \times 10^{18} \) ions/cm\(^2\).

Figure 9. XPS spectra of olivine rock and <45 \( \mu \)m powder samples after different times of exposure to the atmosphere. (top) Effects after He\(^+\) irradiation. From top to bottom, samples after exposure to atmosphere for 0 min (rock), 0 min (powder), 10 min (rock), 10 min (powder), 100 min (powder), 3 days (powder), and 8 days (powder). (bottom) Effects after Ar\(^+\) irradiation. From top to bottom, samples after exposure to atmosphere for 0 min (rock), 0 min (powder), 10 min (rock), 10 min (powder), and 2 days (rock).
ing, i.e., the sputtering yield depends on the type of atom, in addition to its surface concentration. The depth of the altered layer is of the order of the penetration range of the ions [Kelly, 1989]. In our in situ experiments, we only detect slight oxygen loss correlated with reduction of iron. Previous reports of Mg loss [Bradley et al., 1996; Demyk et al., 2001; Toppani et al., 2006] were likely affected by exposure of the irradiated samples to the air, water or solvents prior to analysis, as mentioned in our previous reports [Cantando et al., 2009].

[31] On very rough surfaces, such as powders, the sputtering yield decreases because of the redeposition of some of the sputtered flux. The amount of redeposition depends on the shape of the surface. An experimental report indicated that a powder sample lost \( \approx 10 \) times less mass than a bulk sample [Hapke and Cassidy, 1978], but this was done with a unidirectional ion beam at extremely high fluences \( (8 \times 10^{20} \text{ H/cm}^2) \). Even at fluences one tenth as large, needle structures in the direction of the ion source develop from the irregular grain surfaces [McDonnell and Flavill, 1974]. These extreme structures allow redeposition of a large fraction of the sputtered ejecta, which strongly darken the surface [Wu et al., 2001]. Thus, the darkening of surfaces by ions reported by Hapke [2001] is likely complicated by trapping of light by structures generated via large, unidirectional irradiation. These structures would not exist on a surface in space, which is irradiated at different angles of incidence as it rotates with respect to the solar wind.

4.3. Test for the Effect of Redeposition

[32] Hapke and collaborators [Hapke, 2001, and references therein] have clearly shown the importance of high-fluence ion irradiation (hence the solar wind) in the darkening of Fe-bearing minerals. Whereas they conclude that metallic Fe only forms in redeposited coatings, we found that it is created also in flat rocks, where redeposition is negligible. [33] Thus, we need to examine in more detail the relative role of direct alteration of the surface versus redeposition. We find that, although the changes in chemical composition of the olivine rock and the powder samples are very similar, the formation rate of metallic iron is a factor of two slower for the powder, which we postulate to be related to redeposition.

[34] To test the magnitude of redeposition that occurred in our experiments, we analyzed the relative rate of surface depletion of adventitious carbon on the flat rock versus the powder. After sputter-cleaning each surface we exposed it to the atmosphere for 10 min to allow the deposition of atmospheric hydrocarbons. Then, we reinserted the samples into vacuum and measured with XPS the amount of adventitious carbon on the surface and its decrease as a result of He\(^+\) irradiation. Since the hydrocarbon content in the air can change from day to day and with time, we repeated each experiment on different days but found variations of less than 10%. Our results for the carbon depletion versus fluence are shown in Figure 11 for flat rock and powder samples. We found that the carbon removal rate for the powder is about a third lower than that for the flat surface. Thus, we can conclude that about two thirds of the ejecta is redeposited. This rough estimate is similar to the to 0.70 predicted by modeling of redeposition [Cassidy and Johnson, 2005]. The difference with the value of 0.9 measured by Hapke and Cassidy [1978] is most likely due to the needle topography that is expected in the experiments by these authors, as discussed above.

[35] To understand the different conclusions proposed by us and Hapke [2001, and references therein] on the role of direct metallization of a surface, we note that those authors’
conclusions that only sputtered deposits will contain metal-
lic iron were based mainly on experiments where irradiation
was done on a ball situated in an alumina crucible, both
made of impure alumina (clean alumina did not darken)
[Hapke, 2001]. In such geometry, only the top of the ball
and the crucible were irradiated and only the lower half of
the ball would have sputtered material deposited onto it.
The results showed that the lower half darkened much more
than the top half of the ball, and were not affected by ion-
induced topography mentioned above. However, they were
interpreted to mean that redeposition of the aluminum (on
the bottom of the ball) was more important than direct
irradiation (of the top of the ball) in altering the optical
reflectance. We argue that this difference is caused simply
by the fact that the thickness of the altered region of the
top of the ball is on the order of the ion range and is
limited by sputtering, whereas the thickness of the deposit
in the bottom of the ball can increase indefinitely with
fluence, since it is being sputtered from another surface
(the crucible).

[36] The fact that metallization does not require redepo-
position, as evidenced in this and previous work on sectioned
surfaces [Dukes et al., 1999; Davoise et al., 2008], does not
imply that irradiation of sectioned surfaces will cause
significant optical effects. The effect on the spectral reflect-
tance will be larger on powders, only because scattering of
the grains causes light to pass through the altered regions
multiple times, irrespective of whether the main mechanism
for formation of metallic iron is vapor redeposition or direct
ion bombardment.

[37] In closing this discussion, we propose that the reason
why the powders metallize at a slower rate than a flat
surface is that there is more more redeposition in the powder
and the redeposited material is partially oxidized, as com-
monly happens in the sputter deposition of oxides in vacuum [Mauvernay et al., 2007].

4.4. Mechanism for Alteration of Reflectance Spectra
of Silicates

[38] As mentioned above, Hapke [2001] has shown that
darkening of visible reflectance spectra in several types of
mineral oxides was correlated with the sputter redeposition
of coatings containing metallic iron.

[39] Recent experiments in Catania [Brunetto and
Strazzulla, 2005; Strazzulla et al., 2005; Brunetto et al.,
2006b] have shown that higher-energy (60–400 keV) heavy
ions can also cause significant alteration of spectral reflect-
tance but at much lower ion fluences than used by Hapke
[2001]. Although heavy ions are unimportant in the solar
wind, these experiments can help in understanding weath-
ering mechanisms. The Catania group proposed that the
alteration they observed at lower fluences was caused by
amorphization, which would be an additional mechanism
independent of the metallic iron in the sample. However, we
suggest that the lower fluences needed to change the
spectral reflectance in these higher-energy heavy ion experi-
ments are due to the difference in density of energy
deposition and projectile range, not to a separate mecha-
nism. The 60–400 keV Ar ions used by the Catania group
have ~100 times higher stopping power and penetrate 2.5–
14 times more than the 1 keV H ions used by Hapke’s group
(J. F. Ziegler and J. P. Biersack, Stopping and Range of Ions
and will cause more damage, create more metallic iron, and
cause more spectral alteration for the same ion fluence. As
an additional test, we irradiated a sectioned olivine rock
with 4 keV Ar, which has a stopping power ~11 times
higher than 4 keV He used in our experiments and found
that the metallization rate is ~26 times faster than it was for
He. Regarding the role of amorphization, we note the subtle
change of optical properties due to amorphization would
have a negligible effect in optical reflectance at near infrared
wavelengths. In fact, we detected no reflectance changes at
fluence of $10^{17}$ ions/cm² where olivine has already
been amorphized by 4 keV He [Carrez et al., 2002], and no
rereddening after irradiating iron-free forsterite with 2\times$10^{19}$ He
ions/cm² (Figure 2 (top)). It is only at the high fluences
of irradiation of olivine, where formation of metallic iron
is significant (Figure 4), that we observe spectral reflectance
changes. Therefore, we conclude that metallization, rather
than amorphization, is responsible for the changes in the
spectral reflectance.

4.5. Formation of Metallic Iron in Silicates by the Solar
Wind

[40] During irradiation of olivine, metallic iron is formed
in the sample, because oxygen is preferentially removed by
sputtering, and radiation enhanced diffusion assists in the
nucleation of the reduced iron. Metallic iron can also form
in a sputtered deposit because Fe atoms deposit preferen-
tially compared to the lighter O atoms, as shown by Hapke
[2001].

[41] The effect of metallic iron particles on the reflectance
spectra will depend on their size. Lunar soil analysis has
shown spectrally darker soils contain large iron nanoparticles
(>10 nm), while smaller nanoparticles (<5 nm) are
more prominent in soils that are spectrally reddened [Keller
et al., 1998a]. These results are consistent with more recent
laboratory measurements [Noble et al., 2007] on silicate
so the average flux is actually 1/4 of $F_0$ or $4.8 \times 10^6$ ions/cm$^2$/sec. Using this value, we find that it takes $\sim$13,000 years for an exposed grain to reach a fluence where alteration induced by the solar wind saturates ($2 \times 10^{18}$ He ions/cm$^2$). The additional effects of solar wind protons can be assumed to scale roughly as the product of their flux times the sputtering yield [Johnson and Baragiola, 1991], since sputtering is governed by the same type of collisions that cause surface damage. Thus, we obtain a characteristic time for weathering of $\sim$5000 years. This does not mean that the appearance of all surface material older than $\sim$5000 years will be the same, because there is a complex interaction between the effects caused by the solar wind and micrometeorites.

[43] Calculating the timescales for effects caused by micrometeorite impacts is non trivial. The impacts are not uniform [Gault et al., 1974; Horz et al., 1974] and can modify grains by vaporization and changing their composition. In addition, impacts mix the regolith, break large grains, form craters and eject other grains indirectly by the shock wave induced in the impact. The effect of chemical alterations on reflectance was studied by Sasaki et al. [2001] using ns pulsed laser irradiation as an analog for micrometeorite impacts. In comparison with our experiments, they reported somewhat more spectral reddening and darkening after one laser pulse (24 J/cm$^2$), which they estimated to be equivalent to $\sim$10$^8$ years exposure at 1 A.U. In addition, they assumed that this exposure time might be a lower limit, since laser irradiation may be more efficient than dust impacts in altering the sample. This assertion is supported by experiments comparing thermionic plasma emitted from samples irradiated with pulsed lasers and dust impacts show that similar secondary ion mass spectra and absolute yields could be obtained if the power density of the laser was $\sim$100 times lower than that of the dust [Kissel and Krueger, 1987].

[44] On the other hand, Sasaki et al. [2001] obtained the timescale of 10$^8$ years by estimating that the energy flux could be obtained by applying the cumulative flux of micrometeorites to 10$^{-12}$ g particles. However, we note that it has previously been estimated that >75–80% of the material vaporized by impacts at 1 A.U. comes from heavier projectiles between $10^{-8}$ and $10^{-4}$ g (10–230 $\mu$m particles assuming a density of 2 g/cm$^3$) [Gault et al., 1972; Cintala, 1992], even though their flux is much lower. Thus to obtain a more accurate estimate of timescales for vaporization caused by micrometeorite impacts, we need to integrate the differential energy flux over the range of micrometeorites responsible for vaporization. The differential flux (f(m)) of a micrometeorite is given by $f(m) = \frac{dF}{dm}$ [Grun et al., 2001], where $F$ is the cumulative flux of particles of mass larger than m. An approximation for $F$ has been given by Gault et al. [1972] for $10^{-13}$ g $< m < 10^{-5}$ g at 1 A.U. By integrating the product of the impact energy and $-dF/dm$ over masses between $10^{-13}$ g and $10^{-5}$ g, assuming an average impact velocity of 13 km/sec [Cintala, 1992], we obtain an energy flux of $\sim$1000 J/cm$^2$/10$^8$ a.

[45] In Figure 12, we replot the ratio of the reflectance spectra of irradiated samples to that of the virgin samples, shown in Figure 2 together with previous laser ablation studies [Sasaki et al., 2001; Brunetto et al., 2006a]. We have normalized all spectra at 2 microns before taking the ratios, gels, which show that addition of Fe nanoparticles smaller than 15 nm produce reddening while addition of Fe particles larger than 40 nm induce darkening of the silicate. Therefore we conclude that since the He bombardment reddens our olivine samples but barely darkens their spectral reflectance, the metallic iron formed in our experiments exists in very small precipitates.

4.6. Astronomical Implications

[42] We can scale our results to an effective exposure time in space. The estimates are approximate because fluxes of solar wind ions and micrometeorites have changed through history. We consider the case of the Moon; similar estimates can be done for Mercury and asteroids. For the Moon, we use the mean number density (n/cm$^3$) and mean velocity (468 km/sec) given by Gosling [2007] at 1 AU and obtain a proton flux of $4.1 \times 10^8$ protons/cm$^2$/sec. The incident flux ($F_0$) of He is estimated to be $\sim 1.9 \times 10^7$ He/cm$^2$/sec, obtained from the product of the proton flux by the average relative abundance of helium ions in the solar wind (0.047). However, we note that the cross section being struck by the solar wind is $\pi R^2$, while the surface area of a sphere is $4\pi R^2$, so the average flux is actually 1/4 of $F_0$ or $4.8 \times 10^6$ ions/cm$^2$/sec. Using this value, we find that it takes $\sim$13,000 years for an exposed grain to reach a fluence where alteration induced by the solar wind saturates ($2 \times 10^{18}$ He ions/cm$^2$). The additional effects of solar wind protons can be assumed to scale roughly as the product of their flux times the sputtering yield [Johnson and Baragiola, 1991], since sputtering is governed by the same type of collisions that cause surface damage. Thus, we obtain a characteristic time for weathering of $\sim$5000 years. This does not mean that the appearance of all surface material older than $\sim$5000 years will be the same, because there is a complex interaction between the effects caused by the solar wind and micrometeorites.

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[45] In Figure 12, we replot the ratio of the reflectance spectra of irradiated samples to that of the virgin samples, shown in Figure 2 together with previous laser ablation studies [Sasaki et al., 2001; Brunetto et al., 2006a]. We have normalized all spectra at 2 microns before taking the ratios,
to compare reddening and not darkening, which can depend on microstructure caused by laser ablation. The NIR spectrum measured by Sasaki et al. [2001] after one laser pulse (12 J/cm²) is quite similar to our ion irradiation experiment. The energy fluence of 12 J/cm² is equivalent to ~10⁷ years of exposure to micrometeorite impacts, taking into account the increased efficiency of the laser mentioned above. Thus, we estimate that spectral reddening caused by the solar wind saturates about 2 orders of magnitude faster than estimated to occur by micrometeorite impacts. However, we note that if the grain survives for more than a million years, as is likely the case on the surface of the Moon, micrometeorite impacts may become more important as the spectral reddening effect is not saturated after one impact (see Figure 12).

[46] The importance of the solar wind is substantiated also by the fact that amorphous rims in regolith grains have a thickness of the order of the range of solar wind ions (considering slow and fast components) [Christoffersen et al., 1996; Keller and McKay, 1997]. Furthermore, we note that our experimental results also lead to the conclusion that reduction of iron in the lunar regolith in the irradiated region can explain the formation of submicron Fe particles and their effect on optical reflectance, in contrast to the assertion of Hapke [2001] that direct ion impact produces only negligible effects. Our conclusion, of course, does not preclude the contribution of redeposition of micrometeorite impact ejecta and, perhaps, redeposition of sputtered particles.

[47] With respect to space weathering effects on asteroids, our experiments strengthen the idea that, solar wind irradiation and the consequent formation of metallic iron after the reflectance spectra of olivine-bearing S type asteroids. More specifically we can apply our results, which show ion irradiation of olivine causes reddening and attenuation of the 1 μm absorption band but little darkening of its overall spectrum, to the main belt asteroids 243 Ida (pyroxene rich) and 951 Gaspra (olivine rich). Like in our experiments, the spectra of each of these asteroids show variations in slope and absorption band depth but minor albedo variations across their respective surfaces [Chapman, 1996; Clark et al., 2002]. We speculate that this is a consequence of their location, because although both the solar wind and micrometeorite fluxes decline as one goes from the Sun to the asteroid belt, the impact speed of the micrometeorites also decreases. This will in turn decrease significantly the impact energy and hence, the amount of material vaporized [Bloch et al., 1971; Mandeville and Vedder, 1971; Cintala, 1992]. Thus, micrometeorite impacts in the main asteroid belt will mainly act to bring fresh material to the surface, while the solar wind will be the primary space weathering agent.

[48] Closer to the Sun, micrometeorites have higher fluxes and velocities and thus weathering becomes more complicated. As an example, Itokawa and Eros, near-Earth S type asteroids located at similar heliocentric distances, have spectra that exhibit different space weathering trends and variations across their surfaces [Clark et al., 2002; Murchie et al., 2002; Hiroi et al., 2006; Ishiguro et al., 2007]. These differences likely indicate that other properties, besides ion and micrometeorite impact determine the appearance of those objects. Still, the discovery of weathered large boulders on Itokawa [Ishiguro et al., 2007] can be explained by our results that show metallic iron can be formed by direct ion irradiation of a flat rock of olivine, where redeposition does not occur.

5. Conclusions

[49] Four keV He ions, typical of the solar wind, alter the reflectance spectrum of olivine powders by reddening the spectral slope and attenuating the 1 μm absorption feature, a manner consistent with observations of space weathering. Furthermore, as judged by in situ chemical analysis, spectral reddening corresponds directly to the formation of metallic iron in the outer 50–80 Å of the mineral surface. In addition, we find that exposing the irradiated surfaces to the atmosphere causes the metallic Fe to reoxidize, showing that in situ measurements are necessary to study chemical changes occurring during ion bombardment of minerals and that previous XPS measurements of lunar soils may have underestimated the metallic content of the surface.

[50] Our results show that metallic iron forms more slowly on a powder than on a flat rock of olivine, which we suggest is due to partial oxidation of redeposited sputtered material. Interestingly, the spectral changes observed in our ion irradiation experiments are similar to previous weathering experiments using laser impact, indicating that both processes affect similarly the spectral reflectance of olivine. In addition, we estimate that at 1 A.U. the spectral reddening of olivine induced by He bombardment will saturate 2 orders of magnitude faster than the time it takes for similar reddening effects to occur as a result of micrometeorite impacts.

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References


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