Sub-surface alteration and related change in reflectance spectra of space-weathered materials

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ABSTRACT

Context. Airless planetary bodies are studied mainly by remote sensing methods. Reflectance spectroscopy is often used to derive their compositions. One of the main complications for the interpretation of reflectance spectra is surface alteration by space weathering caused by irradiation by solar wind and micrometeoroid particles.

Aims. We aim to evaluate the damage to the samples from H\(^+\) and laser irradiation and relate it to the observed alteration in the spectra.

Methods. We used olivine (OL) and pyroxene (OPX) pellets irradiated by 5 keV H\(^+\) ions and individual femtosecond laser pulses and measured their visible (VIS) and near-infrared (NIR) spectra. We observed the pellets with scanning and transmission electron microscopy. We studied structural, mineralogical, and chemical modifications in the samples. Finally, we connected the material observations to changes in the reflectance spectra.

Results. In both minerals, H\(^+\) irradiation induces partially amorphous sub-surface layers containing small vesicles. In OL pellets, these vesicles are more tightly packed than in OPX ones. Any related spectral change is mainly in the VIS spectral slope. Changes due to laser irradiation are more detectable on the material’s melting temperature. Of all the samples, only the laser-irradiated OL contains nanophase Fe particles, which induce detectable spectral slope change throughout the measured spectral range. Our results suggest that spectral changes at VIS–NIR wavelengths are mainly dependent on the thickness of (partially) amorphous sub-surface layers. Furthermore, amorphisation smooths micro-roughness, increasing the contribution of volume scattering and absorption over surface scattering.

Conclusions. Soon after exposure to the space environment, the appearance of partially amorphous sub-surface layers results in rapid changes in the VIS spectral slope. In later stages (onset of micrometeoroid bombardment), we expect an emergence of nanoparticles to also mildly affect the NIR spectral slope. An increase in the dimensions of amorphous layers and vesicles in the more space-weathered material will only cause band-depth variation and darkening.

Key words. methods: laboratory; solid state – methods: data analysis – techniques: spectroscopic – planets and satellites: surfaces – solar wind – meteorites, meteors, meteoroids

1. Introduction

Reflectance spectroscopy of planetary surfaces enables the determination of the mineralogy and physical state of airless planetary surfaces (see, for example, Burns 1989). Planetary spectra contain complex information as they are influenced by multiple additional factors, including temperature, the roughness of the surface, or the space weathering state. In this article, we focus on how space weathering influences planetary materials at the microscale and what consequences it has for the spectra. Such knowledge is crucial for the correct interpretation of spectroscopic observations.

Space weathering is caused by two major processes – solar wind irradiation and micrometeoroid bombardment – which alter the topmost layers of planetary surfaces (Hapke 1965, 2001; Wehner et al. 1963). As a result, the spectra of silicate-rich bodies darken, the spectral contrast decreases, and the visible (VIS) and near-infrared (NIR) slopes increase (reddening of the spectra), as documented, for example, by Hapke (2001), Pieters et al. (2000), and Pieters & Noble (2016). Other processes that influence the space weathering state are, for example, galactic radiation, sublimation, and mixing with the material of impactors, but these were not identified as the main drivers of space weathering change in previous studies of the Moon and of near-Earth asteroids (Pieters & Noble 2016).

Earlier studies reported on the sub-surface changes related to space weathering, especially changes due to solar wind sputtering and impact melting with associated vaporisation and vapour
re-deposition. Already in the lunar samples from the Apollo missions, Keller & McKay (1993, 1997) observed thin, 200 nm, amorphous rims with randomly dispersed inclusions of Fe metal, which they identified as the solar wind irradiation products. Since then, so-called nanophase Fe (npFe\(^+\)) particles have been identified in many laboratory simulations (see, for example, Fazio et al. 2018; Weber et al. 2020; Wu et al. 2017) and also in samples from asteroid (25143) Itokawa (Noguchi et al. 2014a,b) and the Moon (Kling et al. 2021). Other abundant types of structures in the altered sub-surface layers are vesicles and blisters, as documented, for example, by Dobrič̆ & Ogliore (2016) and Matsumoto et al. (2015) for Itokawa particles.

Because of the sparsity of the natural samples and the slow natural evolution of space weathering, a significant part of our understanding comes from laboratory experiments. The effect of the solar wind is usually simulated by irradiation of the samples by various ions (see, for example, the work of Brunetto et al. 2014; Demyk et al. 2001; Hapke et al. 1970, or Loefler et al. 2009 for more details). The effect of micrometeoroid impacts is mainly studied using individual or repeated laser pulses of various durations and energies (see, for example, Sasaki et al. 2001, 2002, and Yamada et al. 1999 for usage of nanosecond laser pulses or Fazio et al. 2018 and Chrbolková et al. 2021 for femtosecond laser pulses). Only rarely do experiments include actual impacts of dust particles, such as in Fiege et al. (2019).

This article is a follow-up of Chrbolková et al. (2021), where we evaluated the difference in the spectra influenced by solar-wind irradiation and micrometeoroid bombardment. This was done through laboratory irradiations of olivine and pyroxene pellets using low-energy 5 keV H\(^+\) ions and individual femtosecond laser pulses as in Fazio et al. (2018). We found that there was a difference in the influence of the two types of irradiation on NIR wavelengths; the laser influenced VIS and the NIR range, while ion irradiation had only a mild effect in the NIR wavelength range. However, in general, the spectral evolution was determined more by the original mineralogy of the samples than by the space weathering agent. This result agreed with earlier observations of Sasaki et al. (2002).

In Chrbolková et al. (2021), we only evaluated the spectral change, but we did not have information on the material changes within the pellets. In this article, we aim to find the connection between the spectral changes and the sub-surface alteration caused by the different space weathering agents.

2. Methods

2.1. Samples, irradiations, and spectroscopy

We used samples identical to those in Chrbolková et al. (2021), that is pellets made of a pressed powder (with particle sizes < 106 µm) of olivine (forsterite number Fo90), further denoted as OL, and pyroxene (enstatite number En67), further denoted as OPX, on top of a KBr base. We refer the reader to Chrbolková et al. (2021) for more details.

For the microscopical observations, we used four different irradiated pellets from Chrbolková et al. (2021). Two of them were produced by H\(^+\) irradiation, and the other two by femtosecond laser irradiation. In each case, one OL and one OPX pellet were selected.

The H\(^+\)-irradiation was done using 2 \times 10^{17} \text{H}^+ \text{cm}^{-2} 5 \text{keV} ions. The ion beam covered the whole 13-mm pellet and was oriented perpendicularly to the surface of the pellet. Samples were placed in a vacuum chamber with a pressure of \approx 10^{-7} \text{mbar} during the irradiations.

A femtosecond laser was set to shoot individual, spatially separated 800-nm pulses perpendicularly to the surface of the pellet. The duration of one pulse was 100 fs, and for the OL sample the energy of one pulse corresponded to 1.5 mJ, while for OPX it was 1.8 mJ. The laser spot on the surface of the pellet was \approx 50 \mu \text{m} in diameter. The pressure in the vacuum chamber was \approx 10^{-4} \text{mbar}. For microscopic observations, we selected pellets in which the spatial separation of the individual laser-induced microcraters was the largest possible so that we were sure that the studied crater is not influenced by the neighbouring craters, that is OL irradiated by 1.7 mJ cm\(^{-2}\) (equivalent crater distance 300 µm) and OPX irradiated by 1.5 mJ cm\(^{-2}\) (200 µm).

To compare the spectral evolution with the observed microstructures, we used spectra measured in Chrbolková et al. (2021). The H\(^+\)-irradiated spectra were measured using an OL-750 automated spectroradiometric measurement system by Gooch & Housego with polytetrafluoroethylene (VIS) and gold (NIR) standards and an incident angle of 10° (Chrbolková et al. 2021; Penttilä et al. 2018). The laser-irradiated spectra were measured using a Vertex 80v from Bruker with an A513/Q variable angle reflection accessory using the Spectralon standard, an incident angle of 0°, and a collection angle of 30°. As we only compared relative trends within one dataset, the differences in the experimental set-up do not inhibit further interpretation.

A straightforward visualisation of the spectral change is the ratio plot of the weathered to fresh material. For H\(^+\) irradiation, we used the ratio plot for the 2 \times 10^{17} \text{H}^+ \text{cm}^{-2} case, which exactly matched the samples studied here with the microscope. For laser irradiation, we studied individual craters. To obtain a representation of the spectrum of one crater, which is too small to be captured by our spectrometer, we selected a spectrum captured over a surface homogeneously covered by craters that lie tightly next to each other but do not overlap. Based on microscopical observations, the craters are approximately 100 µm in diameter; we thus selected spectra of the pellet in which the centres of the craters were 100 µm apart. These spectra were influenced by the unaltered material located in the corners of the squares circumscribed to the craters, but its contribution was smaller than that from the irradiated material.

2.2. New analyses

Using the pellets described in the previous section, we carried out the following analyses to study the surface structures related to space weathering: scanning electron microscopy (SEM) using secondary electrons (SEM-SE) for morphology, backscattered electrons (SEM-BSE), and energy-dispersive X-ray analysis (SEM-EDS) for compositional information. For sub-surface structures, we used transmission electron microscopy (TEM) in conventional (CTEM), high-resolution (HR-TEM), and scanning (STEM) modes combined with EDS for compositional information.

2.2.1. Scanning electron microscopy

A Tescan Lyra 3GMU Dual-Beam Scanning Electron Microscope equipped with a field emission gun (FEG) and focused Ga ion beam was used for SEM and in situ lift-out of the lamellae dedicated to TEM analysis. The pellet samples were coated with carbon prior to the electron microanalysis to prevent charging.

The samples were at first characterised with top-view SEM and EDS imaging. The SEM operational conditions were as
follows: i) surface imaging conditions – accelerating voltage of 10 kV, 5–9 mm working distance, SE or in-beam SE imaging modes; ii) analytical conditions – accelerating voltage of 15 kV, 9 mm working distance, SE, and BSE imaging modes. Chemical analysis was carried out using an EDS system composed of an 80 mm² X-Max² Oxford Instruments Silicon Drift Detector and Oxford Instruments AZtec acquisition and processing software.

After the SEM characterisation, thin lamellae for subsequent TEM were prepared by focused ion beam milling. To avoid charging and drifting during the ion preparation, the non-conductive pellets were coated with a 100 nm layer of gold. Thin, cross-sectional specimens were extracted from the regions of interest of the pellet samples with the use of an OmniProbe OP400 nanomanipulator and attached to a copper grid for further ion thinning and polishing to electron transparency (<100 nm thickness). The protective Pt strip was deposited on the surface at the area of interest before the milling process to prevent Ga⁺ ion beam damage of the laser- and H⁺-irradiated sample surface. The ion beam operational conditions were as follows: accelerating voltage of 30 kV and beam current of 2 nA for the trench milling, 500 pA for cross-section polishing, 160 pA for further thinning, and 10 kV and 40 pA for the final polishing steps to minimise the Ga ion damage of the thin lamellae.

### 2.2.2. Transmission electron microscopy

The CTEM, HR-TEM, and STEM investigations were carried out using a Jeol JEM 2200FS FEG microscope equipped with an Oxford Instruments Ultim Max TEM EDS system, which was used for the acquisition of elemental maps, line scans, point analysis and chemical quantification. The microscope was operated at 200 kV. TEM images were acquired using conventional imaging mode for the bright field (BF) and HR. In STEM, high-annular dark-field, BF, and dark-field detectors were used. Selected area diffraction patterns and HR images were captured on a TVIPS TemCam-XF416 4k × 4k CMOS camera.

Analyses with STEM-EDS were obtained using a spot size of 1 nm and integration time of 120 s. Acquisition of the EDS elemental maps had a typical duration of ≈30 min. Mapping and line scans were acquired using the AutoLock function for drift correction. The data were further processed using the AZtecTEM software, and deconvolution of the elements was solved using the Tru-Q technology. Factory standards (Oxford Instruments) were used for quantification. Quantitative analysis used background subtraction by filtered least-squares fitting.

### 2.3. SRIM irradiation simulations

To support our observations from the H⁺ irradiations, we conducted The stopping and range of ions matter (SRIM; Ziegler & Biersack 1985) simulations using 1000 5 keV H⁺ ions propagating through the OL and OPX materials with compositions matching our samples. We focused on ion penetration depths and also on the distribution of the collision events in the samples to correlate these with the distribution of the disturbances in the samples.

### 3. Results

#### 3.1. Surface changes

All four samples show visible darkening of their irradiated surfaces. The OL and OPX irradiated by H⁺ ions do not show major changes in surface morphology. The only visible alteration in the SEM images is in the form of blisters, which are more frequently found in the OPX than in the OL, where the blisters are observed only rarely (see Fig. 1). We estimated that the size of the blisters is ≈1.7 µm in the OL, while in the OPX it is ≈0.9 µm. The morphology of the two surfaces differs, which could have influenced the blister size.

Considering the laser-irradiated samples, the surface changes are more extensive, as expected. We observe extensive melting in the area of the crater. In the OL, melting is restricted to the area of the crater and the melt is smooth with a minor amount of bubbles and depressions after gas release. In the OPX, the melting is more pronounced, and we also see melt splashes and melt drops (see Fig. 2). The bubble-rich melted layer often encompasses large continuous areas of the sample surface, and it is more difficult to identify individual craters.

Maps of irradiated surfaces from SEM-EDS (Fig. 3) do not show any measurable spatial variation in the composition related to the space weathering experiments. The only visible features are linear structures in one OPX sample related to terrestrial weathering (amphiboles).
3.2. Sub-surface changes

The images of H\textsuperscript{+}-irradiated samples from TEM reveal radiation damage with abundant vesicles in thin altered layers. In the OL, the influenced layer is approximately 200 nm thick, while in the OPX it is approximately 150 nm thick (see Figs. 4a, b). The two samples differ also in the size and abundance of the vesicles. In the OL, the vesicles are in multiple, tightly packed layers. Their shape is elongated, with a size of approximately 10×50 nm (longer side parallel to the surface). In the OPX, the vesicles are more spherical and less abundant, with sizes of approximately 20 nm.

Diffraction patterns of the sub-surface layers show that the crystalline structure is extremely damaged and in both cases contains fully amorphous areas. We refer to such a structure as a partially amorphous layer.

Laser-irradiated OL and OPX samples differ significantly from each other. While the OL sample is the only one in which we identify Fe nanoparticles (npFe\textsuperscript{0}, 7–10 nm in diameter), the OPX sample is characterised by a huge number of vesicles with sizes ranging from several nm to 2 μm and no nanoparticles (see Fig. 4c, d). In the OL, the completely amorphous surface layer is approximately 300 nm thick, and the nanoparticles are directly below it concentrated in a thin irregular zone. The thickness of the fully amorphous layer in the OPX is typically around 400 nm but it significantly varies and can reach up to 2.5 μm in some extreme cases. Tiny black dots in the TEM image of the OPX irradiated by laser represent redeposited particles of Pt and Au that we used for imaging and extraction of the thin section for TEM analyses (see Fig. 4 d).

In Fig. 5, we show the ratio of irradiated to fresh spectra of the samples, as described in Sect. 2.1. Spectral ratios of the OL and OPX irradiated by H\textsuperscript{+} show similar behaviour, that is a strong decrease of the albedo at shorter wavelengths (resulting in an increase of the spectral slope) and nearly no change at longer wavelengths. The spectrum of the laser-irradiated OPX also behaves similarly but shows additional changes in the NIR slope. In contrast, spectra of the laser-irradiated OPX do not show changes in spectral slope, although darkening and enhancement of mineral absorption bands are observed.

In Fig. 6, we show depth profiles of the chemical composition of all four samples. All the samples show a similar change – depletion of Mg and enrichment of Si within the sub-surface amorphous and partially amorphous zones compared to the unaltered part of the sample. This trend is more pronounced in the OL samples. This happens at ≈250 nm for H\textsuperscript{+} irradiation and at ≈800 nm for laser irradiation. The composition is stabilised as we approach underlying unaltered areas. The depths below which the composition does not change significantly are as follows: ≈350 nm and 1000 nm for H\textsuperscript{+}- and laser-irradiated OL, respectively, and ≈180 nm and 900 nm for H\textsuperscript{+}- and laser-irradiated OPX, respectively. In general, the influenced layer in the OL is always slightly thicker than in the OPX irradiated by
the same agent. Laser irradiation results in a thicker layer than ion irradiation.

Figure 7 shows a zoomed-in STEM-BF image of the zone containing nanoparticles in the OL irradiated by laser together with a composition profile. The locations of the nanoparticles correlate positively with the abundance of Fe. Also, based on the TEM-EDS point analysis, there is a significant increase in the amount of Fe in the particles, which points to the fact that these are indeed the npFe\(^0\) particles.

4. Discussion

4.1. Observed changes

Our experiments show that the sample surface (viewed from the top) does not exhibit elemental abundance variations. We thus cannot discern between the two weathering agents by observation of changes in elemental abundances on the surface. The immediate sub-surface layers, on the other hand, experience changes in the abundance of some elements. These changes go even deeper into the sample than the amorphous zone. Sudden drops in elemental abundances are indicative of the presence of even deeper into the sample than the amorphous zone. Sudden changes in the abundance of some elements. These changes go even deeper into the sample than the amorphous zone.

Using the SRIM software (see Sect. 2.3). Based on the SRIM results, we plotted the distributions of the collision events with respect to the depth below the surface for the two samples, as shown in Fig. 8. We can see that both in OL and OPX, the collisions of H\(^+\) ions within the sample happen in a very similar range of depths below the surface. These simulations thus do not explain the different distributions of vesicles we observe in our samples. Nevertheless, the SRIM simulations operate in the so-called zero-dose regime. This means that each ion, when impacting the sample in the simulation, behaves as if the sample was un-irradiated. It thus does not take into account the cumulative damage in the sample caused by the previous ions. Olivine is known to be more compliant to maintaining structural changes than pyroxene (Quadery et al. 2015). We therefore hypothesise that the collision events in the OL sample were distributed differently to the SRIM simulation as the incoming ions experienced a more altered environment than in the case of OPX, where the vesicles could have had a more heterogeneous distribution.

The penetration depths of H\(^+\) ions in OL and OPX, which we obtained from SRIM, agree with the similar thicknesses of the altered layers. In the OL and OPX, we observe that approximately the top 200 nm and 150 nm, respectively, are altered. The penetration depths are not significantly different; they are approximately 60 nm with dispersions of \(\pm 30\) nm.

The changes in the laser-irradiated samples are mainly caused by melting. The OPX sample shows a more global melting pattern spanning across individual laser spots, while in the case of the OL, the melting is rather localised to the area near the laser spot (Fig. 2). This observation agrees with the fact that OPX melts already at lower temperatures than OL. The melting temperature of OL of our composition is approximately 1820\(^\circ\)C (Weizman et al. 1997; Ctibor et al. 2015), while for OPX it is approximately 1500\(^\circ\)C (Huebner & Turnock 1980). The OPX
thus has a more developed molten surface full of melt drops and melt splashes than the OL sample.

For all the space weathering agents, the altered layers in the OL are thicker than those in the OPX irradiated by the same agent. This is potentially connected to the fact that OPX has a greater ability to heal the defects than OL, as was mentioned by Quadery et al. (2015).

4.2. Comparison with previous work

The images of our samples from TEM reveal stratigraphy in the sub-surface layers. Some samples show a purely amorphous layer, such as the laser-irradiated OL; other samples show a partially amorphous layer, such as the H\(^+\)-irradiated OL. Similar to our findings, Noguchi et al. (2014a,b) observed olivine- and pyroxene-rich Itokawa particles and found that their sub-surface structure may be divided into (three) zones. The first zone is composed of sputter and vapour deposits. We observed this only in the laser-irradiated samples. The second zone is composed of partially amorphous material, and the third zone is the underlying unchanged mineral. Weber et al. (2020) also observed nano-stratigraphy of the sub-surface layers in their laser-irradiated pressed pellets. In agreement with us, they found that the nano-stratigraphy differs for olivine and pyroxene samples. The thickness of the altered zone observed in our samples is similar to the work of Fazio et al. (2018) and Weber et al. (2020).

Our samples contain abundant vesicles, which are small in the H\(^+\)-irradiated samples and large in the OPX irradiated by laser. Demyk et al. (2001) observed vesicles in their samples irradiated by He\(^+\) ions as well. The sizes they saw are similar to those in our ion experiment. Even Laczniak et al. (2021) observed vesicles in olivine irradiated by H\(^+\) and He\(^+\) ions. Based on Laczniak et al. (2021), the vesicles are usually smaller than 80 nm for the Moon, which agrees with our H\(^+\) experiments. Kaluna et al. (2018) carried out ion irradiations of pristine lunar soils, predominantly made of pyroxene with accessory olivine, and in agreement with us they found vesicles in glassy rims, with sizes similar to our OL case. Olivine- and pyroxene-rich Itokawa particles contain lenticular vesicles that were, based on Matsumoto et al. (2015), created by He\(^+\)-irradiation. Lenticular vesicles with a longer side parallel to the surface, observed not only by Matsumoto et al. (2015) but also Noguchi et al. (2014b), match our H\(^+\)-irradiated OL observations.

Blisters observed in the H\(^+\)-irradiated samples are significantly larger than those observed on natural samples. For example, the olivine-rich samples from asteroid Itokawa showed abundant blistering with blister sizes around 30 nm (varying by a factor of two; see Dobrică & Ogliore 2016). This may be because Itokawa grains are young and not exposed to the space environment for a long time, as suggested by the presence of completely unblistered regions on the grains (our samples represent approximately 10\(^3\) yr of exposure at 3 au). We only observe blisters in the H\(^+\)-irradiated samples. In agreement, Matsumoto et al. (2018) observed blisters in the surroundings of the micrometeoroid impact craters but never inside them.

There are several possible reasons for the discrepancy in the blister size between our samples and natural samples. One of them may be the five-times-higher energy of individual H\(^+\) ions we used for irradiation compared to the standard solar wind. Demyk et al. (2001) used standard solar wind energy of He\(^+\) ions and a five-times-higher fluence than in our experiment. As a result, the bubbles they observed did not exceed the size of \(\approx 400\) nm. Also, the size of blisters may be influenced by the crystalline orientation to the incident angle of the ion beam of low-Ca pyroxene as was pointed out by Matsumoto et al. (2015). Based on Sznajder et al. (2018), the size of blisters is proportional to the irradiation time, which matches the observations of Demyk et al. (2001). We disregard the too high fluence as a reason for the discrepancy as Demyk et al. (2001) and Keller et al. (2015) used a higher fluence and did not obtain such large blisters. Matsumoto et al. (2013), on the other hand, also used a five-times-higher fluence and obtained blisters as large as \(3\)\(\mu\)m (which is larger than blisters in our experiment). However, in their experiments, H\(^+\) ions were used, not H\(^+\), which results in a significant difference.

We observe chemical changes in sub-surface layers in agreement with Laczniak et al. (2021), who observed Mg-depleted, Si-enriched layers in their samples. Their explanation is that this may be due to preferential sputtering of Mg, which leads to non-stoichiometric concentrations (see also, for example, Cassidy & Hapke 1975; Lantz et al. 2017). Similarly to us, they found that the chemically distinct layer is thicker than the visually observed one, which may be due to radiation-enhanced diffusion that makes sputtered atoms mobile.

The only sample in which we identify npFe\(^0\) particles is the laser-irradiated OL. Weber et al. (2020) observed similar behaviour. While the npFe\(^0\) particles were observed in olivine, they were sparse and smaller or completely absent from pyroxene in their experiment with nanosecond laser pulses. The npFe\(^0\) particles we observe are of similar size or smaller than in other experiments or natural samples. Nanoparticles of a similar size have been identified in the laser experiments of Wu et al. (2017) or in ion-irradiated pristine lunar soils and mature lunar soils from the Apollo 17 mission (Kaluna et al. 2018; Kling et al. 2021). Based on Noguchi et al. (2014a,b), Itokawa grains contain only small npFe\(^0\) particles (5 nm) induced by solar wind ions, while particles from the Moon have greater nanoparticle size variation (Noble et al. 2007). Larger npFe\(^0\) particles were observed, for example, by Fazio et al. (2018) and Weber et al. (2020). The greater size of nanoparticles may be due to a slightly different set-up of the laser compared with our set-up (e.g. smaller spot size resulting in a higher concentration of energy or greater energy and repeating pulses). As Fulvio et al. (2021) noted, the laser spot size significantly influences the resulting craters. Also, the difference in the forsterite content of our samples and samples in Fazio et al. (2018) could have

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig8}
\caption{Histogram of collision events in H\(^+\)-irradiated samples of olivine and pyroxene. \(d\) stands for the depth below the sample surface, and \(N\) is the number of events.}
\end{figure}
played a role. The nature of the sample was different as well; Fazio et al. (2018) used a monocrystalline sample, while we used a porous pressed powder surface, which may influence the laser sputtering. Fazio et al. (2018) found npFe\textsuperscript{0} particles both in the glassy layer and in the polycrystalline layer below it. In our case, the majority of the npFe\textsuperscript{0} particles are situated below the glassy layer.

Notes on laser set-up

The main difference between (previously widely used) ns laser pulses and fs laser pulses is in the interaction between the laser and the material. Nanosecond pulses mainly cause heating and melting of a target. In this regime, a thermal wave propagates through the material, which results in a significant and widespread layer of melt. In the fs regime, on the other hand, the thermal conduction to the target may be, in the first approximation, neglected (Chichkov et al. 1996). Because of the short timescale of the pulse, the interaction proceeds in a different way. The material may undergo fragmentation and immediate transformation from solid to vapour. The brevity of the pulse also disables the interaction of the laser with the vapour plume. At high peak irradiance, the material undergoes melting, which is only confined to the area of the laser spot, which contrasts with the ns regime (Fazio et al. 2018; Perez & Lewis 2003).

The wavelength of the laser pulse we used (800 nm) is different to the usually applied Nd-YAG or ultraviolet (UV) lasers (1064 nm or 248 nm see, for example, Sasaki et al. 2001; Brunetto et al. 2006; Matsuoka et al. 2015). As Brunetto et al. (2006) noted, the 1064-nm pulses cause the laser to behave as a heat source, resulting in uncontrolled melting. The UV pulses, on the other hand, cause direct breaking of the bonds in the target with little damage to the surrounding material. The wavelength of our laser experiment is closer to the 1064 nm than to the UV experimental set-up. Also, both, the 800 and 1064-nm lasers operate at the wavelengths matching the main absorptions in the olivine (and pyroxene) materials. Nevertheless, the evaluation of the differences in the influence of the two set-ups on the final state of the material is beyond the scope of this article, and we refer the reader to the original publication (Fazio et al. 2018) for a deeper discussion of the experimental set-up.

4.3. Sub-surface structure and reflectance spectra

While the OPX irradiated by laser shows a major layer of amorphous material, for all the other types of irradiation, the sub-surface alteration does not exceed 300 nm. If we compare this information with the spectral evolution (Fig. 5), we see that at shorter wavelengths the thickness of the altered layer is similar to the wavelength of light. With longer wavelengths, this does not hold. The incident light at longer wavelengths probes more deeply into unaltered layers, and the spectral change is thus smaller as the spectrum represents a mixture of the fresh and mature material.

The H\textsuperscript{+} irradiation causes a similar sub-surface change in the OL and OPX sample (Fig. 4), that is partial amorphisation of topmost 200 nm and 150 nm, respectively. The subsequent spectral change is characterised by a strong decrease in reflectance in the VIS and nearly no change in the NIR region. This darkening may be explained by a change in the imaginary part of the refractive index after amorphisation that can be of up to several orders of magnitude (see, for example, olivine refractive indices in Dorschner et al. 1995 and Zeidler et al. 2011). The absorption

| Table 1. Sub-surface structure for different materials and irradiation sources. |
|-----------------|--------------|---------------|------|
|                | npFe\textsuperscript{0} | Vesicles | Amorphization | t (nm) |
| OL – H\textsuperscript{+} | No | Yes | Partial | 200 |
| OL – laser | Yes | No | Full | 300 |
| OPX – H\textsuperscript{+} | No | Yes | Partial | 150 |
| OPX – laser | No | Yes | Full | 400–2500 |

Notes. OL stands for olivine, OPX for pyroxene, npFe\textsuperscript{0} for nanophase Fe particles, and t for thickness of the altered layer. The individual columns state whether we identified the object in our samples or not.

in the volume is a function of the thickness of the volume compared to the wavelength. As the thickness of the amorphous layer is small (a few hundred nanometres), the VIS wavelengths are absorbed much more than the longer wavelengths. The partially amorphous layer is thicker in the OL sample, which causes the greater change in the spectrum (see Fig. 5). The small vesicles in the samples probably cause scattering, which may mildly increase the brightness. Nevertheless, this effect seems to be minor compared to the darkening.

The OL irradiated by laser shows a similar spectral change to the one irradiated by H\textsuperscript{+}, but the absolute value of the change differs. The reason for this may be that the amorphous layer is thicker and the amorphisation in the laser-irradiated sample is complete compared to the partial amorphisation in the ion irradiation case. Also, the laser-irradiated samples show a molten surface, which is smoother than the original surface. As a result, the spectra darken because of the smaller contribution of the reflection from the rough surface. Laser irradiation of OL causes the additional creation of npFe\textsuperscript{0} particles. Their presence also causes a slight change in the NIR spectral slope, as observed in previous work (see, for example, Pieters & Noble 2016).

The OPX irradiated by laser shows a different sub-surface structure to the OL, the main features being a thick glassy layer and plenty of large (tens to hundreds of nm) vesicles. The light scatters on the vesicles, which decreases the effect of darkening compared to the other cases. On the other hand, we hypothesise that the significant amorphous layer makes the material in the top layers compact, causing that the scattering on the micro-roughness is disabled. Due to the presence of large vesicles, the light penetrates deep into the material, where the volume scattering and absorption are enhanced, which may hypothetically increase the absorption bands’ depths compared to the pristine sample, where surface scattering on the individual grains diminishes the contribution of the volume absorption. All these observations are summarised in Table 1.

4.4. Application to Solar System research

Based on our findings we can make the following prediction of the sub-surface and spectral evolution due to space weathering. In the first 10\textsuperscript{3}–10\textsuperscript{4} yr after exposure of the material to the space environment, the solar wind dominates (e.g. Blewett et al. 2011) and the airless planetary surfaces will mainly suffer from partial amorphisation, which will induce rapid changes in the VIS spectral slope. Only later will small (<5 nm) npFe\textsuperscript{0} particles appear, as we now see in Itokawa particles brought by the Hayabusa mission, which will also mildly influence the NIR slope. On timescales longer than 10\textsuperscript{5} yr, we expect micrometeoroid bombardment to become significant (Blewett et al. 2011;
Noguchi et al. (2011), which may create larger npFe\textsuperscript{0} particles (as seen in the OL sample) and/or large vesicles in thick amorphous layers (as seen in the OPX sample). The OPX changes will not influence spectral slope any more but will have an effect on absorption bands, as we observe in asteroids (433) Eros and (4) Vesta.

5. Conclusions

Our analyses revealed a significant difference in the morphology of laser- and ion-irradiated surfaces. While ions (simulating the influence of solar wind) induced the creation of blisters, laser shots (representing micrometeoroid impacts) caused melting with the associated creation of bubbles and melt splashes. We did not identify any spatial variation in chemical abundances of the surfaces irradiated by laser and by H\textsuperscript{0}, which means that the two space weathering agents are not distinguishable by this analysis.

Samples irradiated by H\textsuperscript{0} showed a very similar sub-surface structure rich in small vesicles in thin (up to 200 nm), partially amorphous layers. The laser-irradiated OL showed a fully amorphous layer below which we identified npFe\textsuperscript{0} particles. The laser-irradiated OPX contained, unlike the previous cases, a thick amorphous layer full of large vesicles.

Based on a comparison of the irradiation-induced structures and their reflectance spectra, we found that the thickness and the structure of the amorphous layer have a major influence on the spectra. In both materials, H\textsuperscript{+} irradiation resulted mainly in VIS spectral slope changes due to the thickness of partially amorphous layers being comparable to VIS wavelengths. Spectral slope changes throughout the VIS-NIR wavelengths observed in the olivine sample irradiated by laser resulted from the presence of thicker, completely amorphous layers together with the presence of the npFe\textsuperscript{0} particles. The pyroxene sample irradiated by laser showed the thickest, entirely amorphous layer that, in combination with large vesicles, probably caused changes of the absorption bands’ depths and no continuum changes.

We may thus predict the sub-surface and spectral evolution of material exposed to the space environment with time: initially thin, partially amorphous layers with a thickness comparable to the wavelength of observation will cause significant changes to the VIS spectral slope. The later appearance of npFe\textsuperscript{0} particles will also influence the NIR slope, and a subsequent increase in the thickness of the amorphous layer and vesicle size will induce only mild darkening and modification of depths of the absorption bands.

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