HIGH TEMPERATURE, NANOSCALE CHANGES IN FILMS PRODUCED BY IRRADIATION OF IRON BEARING SILICATES: LABORATORY SIMULATIONS OF SPACE WEATHERING IN HERMEAN ENVIRONMENT. S. S. Rout[1] , T. Stockhoff[2], L. Moroz[1,3], H. Hofsäss[4], R. Dohmen[5], K. Zhang[4], D. Baither[2], U. Schade[6], A. Bischoff[1], and H. Hiesinger[1]. [1]Institut für Planetologie, Wilhelm-Klemm-Str. 10, 48149-Münster, Germany (suryarout@uni-muenster.de), [2]Institut für Materialphysik, Wilhelm-Klemm-Str. 10, 48149-Münster, Germany, [3]Institut für Planetenforschung, DLR, Berlin, Germany, [4]II. Institut of Physics, University of Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany, [5]Institute of Geology, Mineralogy and Geophysics, Ruhr- Universität Bochum, Universitätstr. 150, 44780 Bochum, Germany, [6]Helmholtz-Zentrum Berlin für Materialen und Energie, Berlin, Germany.

Introduction: Space Weathering (SW) of regoliths of airless solar system bodies produces nanometer thick patinas on the regolith grains. These patinas/films are generally believed to be formed by redeposition of a vapor produced during micrometeorite impact or by deposition of elements that are sputtered by impacting energetic ions. Such films with nanophase iron ($npFe^0$) inclusions have been well documented in lunar soil grains [1]. The mean size of $npFe^0$ have been experimentally shown to affect VNIR spectra [2]. Another important product of SW are micron-sized melt layers and melt spherules (e.g., lunar agglutinates). These melt products contain relatively larger $npFe^0$ inclusions as compared to the amorphous rims formed by sputtering or vapor deposition [2].

For solar system bodies with high surface temperatures, for example Mercury, the $npFe^0$ inclusions can grow within an amorphous matrix to larger sizes due to a process called Ostwald ripening [3]. However, it is difficult to calculate the absolute or mean size of the $npFe^0$ inclusions at particular temperatures as there has been no experimental work on the growth of nano inclusions of iron within an amorphous matrix.

In our present experiment, we plan to prepare thin films on sapphire substrates by pulsed laser deposition and ion irradiation of San Carlos olivine samples. Supposing that these films contain $npFe^0$, the substrates will be heated to ~ 450° C. The changes in the film and size of $npFe^0$ inclusions will then be studied using electron microscopy and IR spectroscopy. Here only the preliminary results from the study of a film produced by ion irradiation of San Carlos olivine are presented.

Samples and Experimental procedures: San Carlos olivine samples were cleaned by 1 mol HCl and ethanol in an ultrasonic bath. The sample was then dried in an oven and then crushed to fine powder. The olivine powder was finally pressed into a pellet of 80 mm in diameter.

Thin films on a silicon substrate were deposited by Ar^+ ion irradiation of the pressed olivine pellet (target). Ar^+ ions were produced from a RF source (HF field) and accelerated towards the target with an acceleration voltage of 600V. The ions impacted the target with an angle of 45 degrees and were neutralized before striking the target using electron pulse. The ion beam had a diameter of ~40 mm and carried a current of 25 mA. Sputtering was carried out at room temperature and the pressure inside the UHV chamber was maintained at 2-3x10^{-4} mbar. For TEM characterization electron transparent cross-sections were prepared by grinding and ion-milling using a Gatan PIPS.

TEM studies were carried out by a Zeiss Libra 200 FE TEM operating at 200 kV. A part of the sputter deposited silicon wafer was placed in an evacuated glass tube (with Ar gas) and heated to 450°C for 24 hours. Biconical reflectance spectra were acquired from 0.9 to 25 µm at *i*=*e*=20° using a BRUKER Vertex 80v FTIR spectrometer equipped with a "Seagull™" variable-angle reflectance accessory. The spectral reflectance measurements were performed in vacuum relative to a gold-plated sand paper standard.

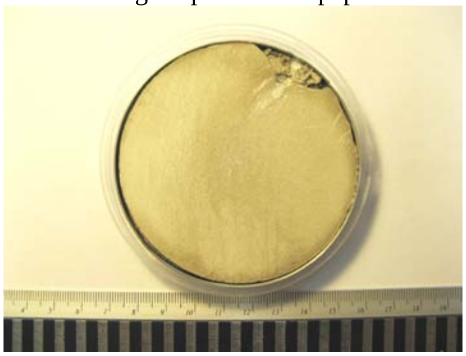

Figure 1: San Carlos olivine pellet after Ar^+ ion irradiation. The top right part was broken during the preparation of the pellet but it did not affect the experiment. The scratches on the pellet show the original colour of the unirradiated pellet.

Preliminary results and Planned experiments: The target was darkened after the Ar^+ ion irradiation (Fig.1). The infrared (IR) spectra of the target did not show any significant change after irradiation. Moderate decrease in overall IR reflectance was evident at wavelengths shorter than 9 µm, but dark color of the irradiated target suggests more significant drop in reflectance in the visible range.

TEM studies of a cross-section of the unheated silicon substrate showed the presence of an 80 nm-thick amorphous film with numerous nanoclusters (Fig. 2). These nanoclusters are mostly < 1-2 nm in size. The 80-nm thick layer contains an underlying 30 nm-thick amorphous layer of similar composition but without any nano inclusions. It is most probably an artifact from the experiment.

The TEM and STEM analysis of the cross-section of the heated silicon substrate revealed the presence of many nanoinclusions of different metallic species on the surface of the amorphous film (Fig. 3). These nanoinclusions of different species were also found within the amorphous film and their size (2-4 nm) is larger than the nanoclusters in the unheated substrate. Nanoinclusions on the amorphous film are surprisingly much larger (10-15 nm) compared to the inclusions within the amorphous film. STEM-EDX point analysis shows that these inclusions are composed of metallic Fe, Cu and Ni and the matrix is rich in Mg, Si, and O. Sometimes, the inclusions of Ni, Cu and Fe have grown vertically out of the matrix as nanorods (Fig. 4) due to diffusion processes. Ni and Cu are certainly contaminants produced during the irradiation experiment and derived from the sputtering chamber.

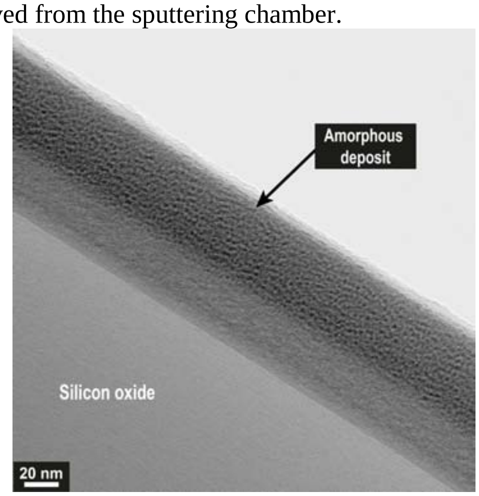

Figure 2. Bright field TEM image of cross section from the unheated silicon wafer.

To prevent the problem due to contamination, we plan to repeat the experiment using a cleaner chamber and Ar^+ ions of higher energy. We will also use a sapphire (0001) substrate instead of the silicon substrate, so that the transmission VNIR spectra of the heated and the unheated substrate can also be acquired before TEM analyses.

Using another setup, we plan to irradiate San Carlos olivine pellets with a nano-second pulse laser. Similar to the above ion irradiation experiments, the vapor plasma produced during the laser irradiation will be captured on a sapphire substrate. Assuming that such a deposit contains $npFe^0$ inclusions the effects of heating

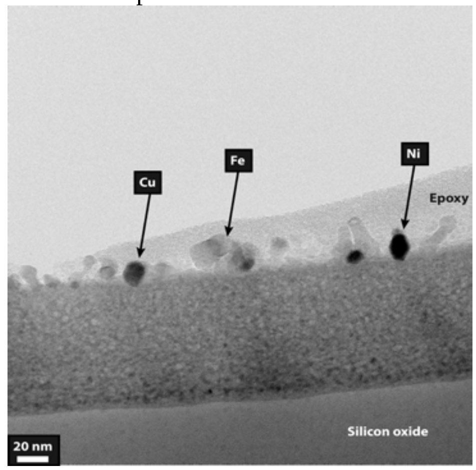

Figure 3: TEM bright field image of the cross section from the heated silicon substrate.

the substrate will then be studied. Such a study might also help us to differentiate between the films produced by ion and laser irradiation processes and subsequently the products of solar wind ions sputtering and micrometeoritic impacts, respectively.

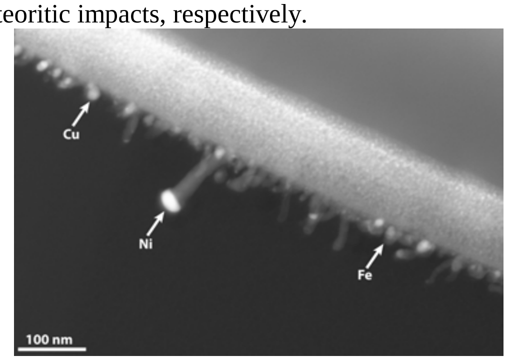

Figure 4: STEM image of the cross section from the heated silicon substrate.

Conclusions: Films produced by Ar^+ ion irradiation of San Carlos olivine samples contain nanoclusters, which are difficult to identify. However, after heating the substrate to 450° C for 24 hours, the nano-clusters grew in size both within the film and also on the surface. The nanoinclusions were identified as metallic Fe, Ni and Cu within a matrix rich in Mg, Si and O. Some nanoinclusions grew vertically out of the film as nanorods. Due to contamination issues, the experiments will be repeated in a cleaner environment.

References: [1] Keller L. P. and McKay D. S. (1997) *Geochim. et Cosmochim., 61*, 2331–2341. [2] Noble S. K. et al. (2007) *Icarus, 192*, 629-642. [3] Noble S. K. and Pieters C. (2003) *Solar Sys. Res.,37*, 31-35.