

# Iron Oxidation State Distributions in Space-Weathered Pyroxene and Olivine

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## Introduction

NASA recently opened samples from the Apollo missions that, for the past ~50 years, have been specially curated in controlled conditions. These samples are being examined as part of the Apollo Next Generation Sample Analysis (ANGSA) initiative to assess lunar regolith using modern instrumentation and methodologies. Our team will use synchrotron X-ray and aberration-corrected transmission electron microscopy (TEM) methods to examine the oxidation states of metals and oxygen in normally and specially curated regolith to determine whether terrestrial oxidation has occurred and whether reactive oxygen species are present in typically curated lunar samples. In preparation for subsequent analyses on ANGSA samples in our laboratories, we analyzed mineral standards [1] as well as pyroxene and olivine that was laser-irradiated to simulate space-weathering effects on the Moon. Here we report iron oxidation state mapping on the laser-irradiated silicates with and without synchrotron X-ray exposure.

## Methods

Pyroxene and olivine standard powders were irradiated with a Nd:YAG laser (1064 nm, 20 Hz pulse, 5-7 ns pulses). Laser spot size on the sample was 0.25 mm with 30 mJ per shot, to reproduce impact energies of micrometeorites (1x10<sup>-12</sup> kg). The samples were irradiated in ~10e-6 torr vacuum in one minute increments using a rastered beam with total accumulated duration of laser weathering of 50 minutes for pyroxene and 40 minutes for olivine. Some of the laser-irradiated powder was analyzed with synchrotron X-rays. Laser-irradiated powder grains were processed into TEM specimens using focused ion beam at the Advanced Electron Microscopy Center at the University of Hawaii at Mānoa. X-ray-exposed, laser-irradiated powders were also prepared to investigate the effect of X-ray exposure on the oxidation state of Fe. Electron energy loss spectroscopy (EELS) data were collected from the TEM specimens in scanning mode using 300 kV and 200 pA on the TEAM I (Thermo Fisher) TEM at Lawrence Berkeley National Laboratory. Spectral data collected with a Continuum energy-loss spectrometer (Gatan) were extracted from each data point and intensity maps were generated for Fe<sup>0</sup>, Fe<sup>2+</sup> and Fe<sup>3+</sup> using MLLS fitting.

## Results and discussion

As expected from prior work [2], we observe formation of nano-phase iron particles (npFe<sup>0</sup>) in the amorphous layer on the irradiated surfaces of laser irradiated pyroxene and olivine. In the amorphous layer in pyroxene, we observe that the Fe content is lower than in the crystal substrate, attributable to the formation of npFe<sup>0</sup> particles. Olivine also shows a similar trend, but we find Fe is more locally depleted around npFe<sup>0</sup> particles. In pyroxene and olivine crystal substrates, Fe has an oxidation state of predominantly 2+, but in the irradiated layer (amorphous phase), it is 3+. Comparison with laser-weathered samples that were also exposed to X-rays showed no differences, indicating that synchrotron X-ray analyses carried out after laser-weathering does not alter the Fe oxidation state of the as-weathered samples.

Space weathering is reported to form npFe<sup>0</sup> by reduction of higher valence iron [e.g., 2]. We observe that where npFe<sup>0</sup> formed, the surrounding amorphous phase oxidized. Hence the laser photon energy is inducing a redox reaction resulting in two different oxidation states originated from one phase. Thompson et al. discussed reduction and oxidation of npFe<sup>0</sup> particles in lunar soil [3], and Hicks et al. discussed a redox reaction in Itokawa space-weathered rims, which was induced by H<sup>+</sup> ion irradiation [4]. In the case of Itokawa sample, an iron charge disproportionation reaction was considered that included presence of minor Fe<sup>3+</sup> in the matrix mineral (pyroxene and olivine); however, in both cases, the weathered materials were irradiated with H<sup>+</sup> ions requiring production of water vapor to be considered. In the present study, the samples were exposed only to photons, so the redox reaction in the amorphous oxide should be simpler; the photon energy introduced into the silicate system causes vaporization and melting. The npFe<sup>0</sup> causes a charge disproportionation reaction with mobile iron in the melt. Charge disproportionation of iron in molten silicate has been discussed by Bindi et al. and references therein [5].

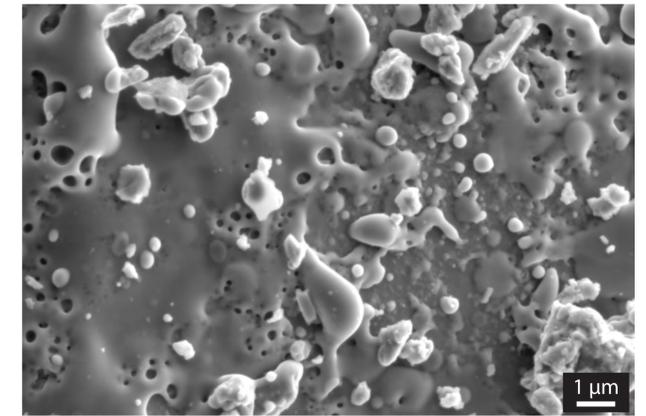
We plan to look for evidence of higher oxidation state Fe in local regions around npFe<sup>0</sup> in the ANGSA samples for direct comparison with these laboratory simulants.

## References

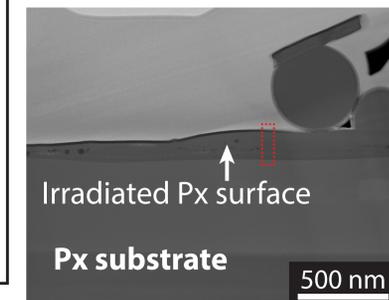
[1] Colina-Ruiz et al. (2021) LPSC LII, Abstract #1713. [2] Pieters et al. (2000) Meteoritics & Planetary Science 35: 1101-1107. [3] Thompson et al. (2016) Meteoritic & Planetary Science 51: 1082-1095. [4] Hicks et al. (2020) Meteoritics & Planetary Science 55: 2599-2618. [5] Bindi et al. (2020) Science Advances 6:eaay7893.

## Acknowledgements

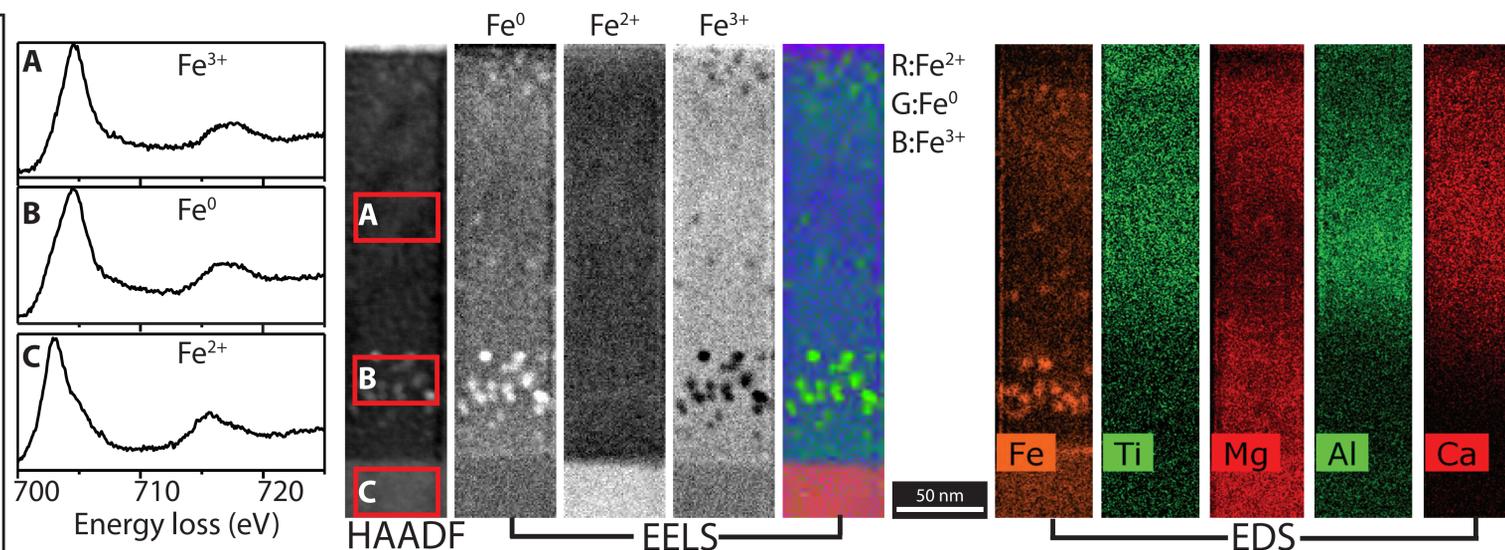
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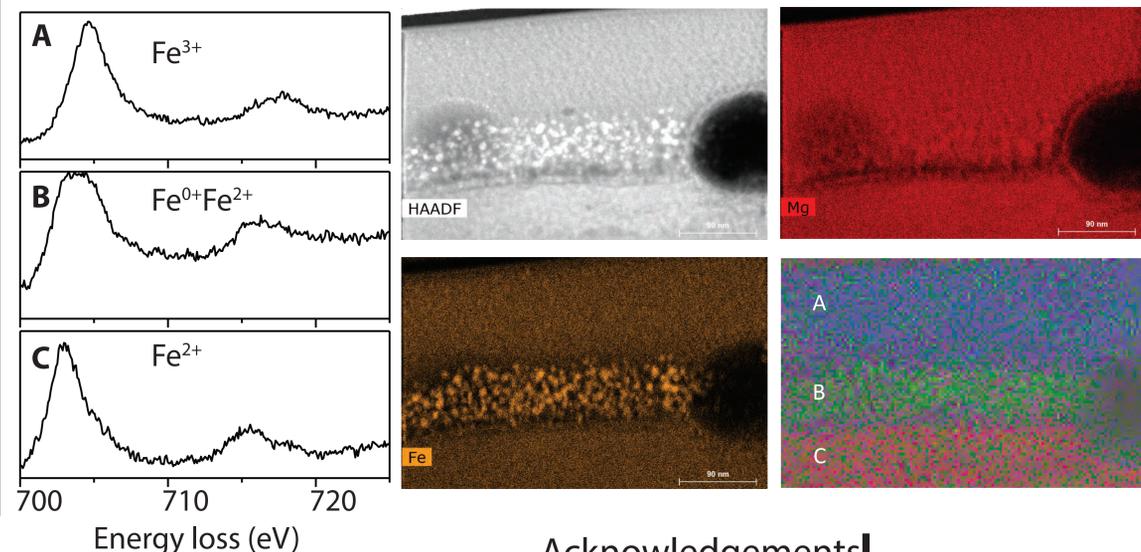
SEM image of irradiated pyroxene crystal surface



HAADF image of irradiated pyroxene crystal. Red box indicates the site where EELS data were collected.



EELS spectra of Fe-L<sub>2,3</sub> edge corresponding to area where spectra were collected (red boxes A-C) in the irradiated pyroxene. Overlaid EELS map illustrates that npFe<sup>0</sup> in the irradiated surface and Fe in amorphous pyroxene oxidized by irradiation. (d) EDS maps show inhomogeneous distribution of Ti, Mg, Al and Ca in am-pyroxene and less Fe in the amorphous pyroxene due to the formation of npFe<sup>0</sup>.



EDS and EELS maps of irradiated olivine crystal. Fe is depleted around the npFe<sup>0</sup> particles in the irradiated layer. The poor signal to noise ratio results from short data integration required by specimen drift during data acquisition.