FORMATION OF ILMENITE RIMS IN LUNAR SOILS: VAPOR DEPOSITION, IRRADIATION AND THERMAL EFFECTS. Shouliang Zhang[1] and Lindsay P. Keller[2], [1]Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston, TX 77058 and [2]ARES, Mail Code KR, NASA Johnson Space Center, Houston, TX 77058, (zhang@lpi.usra.edu).

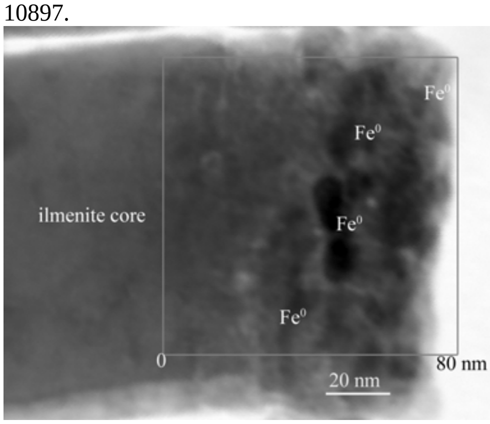
Introduction: Space weathered rims on ilmenite grains from mature lunar soils are commonly attributed to micrometeorite impact-generated vapor deposition and solar wind irradiation [1, 2]. The portion of the rims that result from vapor deposition is confined to the outermost ~10 nm. The space weathering effects extend deeper (~50-100 nm) into the ilmenite grains and are believed to be a product of solar wind irradiation. Several mechanisms have been proposed to explain these complex rims [e.g. 2], but progress is hampered by a lack of sufficient analytical resolution to resolve the nanometer-scale reactions recorded in the ilmenite rims. Here, highly improved resolution of scanning transmission electron microscopy (STEM) combined with energy dispersive x-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) were employed to analyze the Fe/Ti/O chemical variations across the rims to gain new insights into the formation of the rims and lunar regolith processes. Parallel studies are underway with synthetic ilmenites in order to provide quantitative constraints on their formation conditions [3]. We propose that the complex ilmenite rims, in addition to vapor deposition and irradiation, require an impact-related thermal event in order to explain their mineralogy and microstructure.

Materials and experimental methods: Aliquots of the <20 μm fraction of soil 10084 were embedded in low viscosity epoxy and thin sections were prepared using ultramicrotomy. Numerous ilmenite grains in the thin sections were analyzed using the JSC JEOL 2500SE 200 kV field-emission STEM equipped with a Noran ultra-thin window EDX spectrometer and a Tridiem Gatan Image Filter (GIF). EELS data were acquired using a 4 nm probe with a dispersion of 0.1 eV /channel. EELS maps were obtained using a dwell time of 2 s and 4 s per pixel (4 nm) for Ti and Fe, respectively. The energy resolution at the zero-loss peak under these conditions was 0.8 eV.

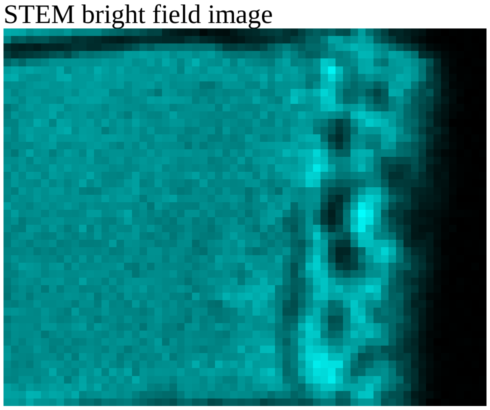
Results and discussion: Most ilmenite grains in the sections of 10084 are surrounded by complex rims where most of the nanophase Fe metal particles ($npFe^0$) are concentrated within 50 nm of the grain surface (Figure 1). The origin of these $npFe^0$ particles at the uppermost surface is generally attributed to vapor deposition, since the $npFe^0$ particles are embedded in a Si-rich matrix (Figure 2). Contributions from solar wind irradiation and sputter deposition, however, cannot be ruled out. Irradiation experiments [3] on synthetic ilmenite using 4 KeV He^+ with fluence of $3x10^{17}$ He^+/cm^2 show an ~50 nm thick surface layer of $npFe^0$ has developed due to preferential sputtering of O leading to production of metallic state of Fe. Beneath the $npFe^0$ layer is an ~10 nm thick Ti-enriched layer with He bubbles. A similar compositional pattern is observed in the lunar ilmenites which corresponds to the the first Ti-enriched layer overlain by concentrated $npFe^0$ particles in element zoning profiles (Figure 2). Further into the rim interior, the Fe^0 particles tend to be coarser-grained (~20 nm) and elongated parallel to the surface of ilmenite grains. High resolution STEM-EDX mapping reveals the regions surrounding the $npFe^0$ particles are highly Ti-enriched (Figure 2). The EELS data from the same regions show a mixture of Ti^{3+} and Ti^{4+} in these areas with little detectable Fe^{2+} remaining. Most of Fe^{2+} has been reduced to Fe^0, along with the production of the reduced Ti oxides. The features we observe in the lunar ilmenites have some similarities and some differences compared to experimentally irradiated ilmenite samples. Both types of ilmenite show a surface depletion of O from preferential sputtering that results in the formation of nanophase Fe^0 underlain by a deeper Ti-enriched layer [3]. There is continued Fe-Ti chemical zoning (Fe^0 + reduced Ti oxides) with depth in lunar ilmenite (Figure 2), which is not present in the irradiated sample [3]. We also have not observed He bubble formation in any of the lunar ilmenites thus far. The irradiation experiments were performed at room temperature and we hypothesize that the differences are related to the thermal history of the lunar grains. The discrepancies could be bridged by taking into account heating from impacts, which would enhance the reaction of ilmenite with implanted hydrogen to produce additional $npFe^0$ and Ti oxides. In fact, SRIM simulation of solar-wind H bombardment of ilmenite shows the penetration depths of H (~60 nm for 2 KeV H) fits well with that of $npFe^0$ distribution (~50 nm) in the lunar ilmenite.

Heating of ilmenite in a hydrogen-rich gas produces abundant Fe^0 and reduced Ti oxides and the resulting textures at the μm-scale [4] show similarities to our observations at the nm-scale. There is a pronounced difference in the reaction scale, where the size of iron blebs (μm-sized) in the experiment is much larger than those in the lunar ilmenite. Additionally, the reduced Ti oxides are very well crystallized at high temperature compared to the poorly crystallized or even amorphous Ti-bearing phase(s) in the ilmenite rims from lunar soil. Such difference could result from very short annealing time given by impact-generated thermal pulse, compared to much longer heating in the experiment. In summary, the formation of ilmenite rims in the lunar soil is likely a mixed process of vapor deposition, solar wind irradiation and impact-generated heat reduction. The formation of $npFe^0$ would be only limited to the top surface of ilmenite without thermal contribution, as demonstrated by irradiation experiment. The impact-generated heat could expand the reduction to where hydrogen was implanted in the ilmenite, i.e. ~50 nm depth. Additional laser-pulse heating experiments simulating micrometeorite impact on the H implanted ilmenite is underway to test this hypothesis.

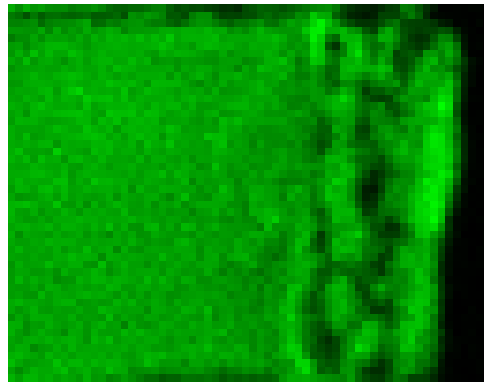
References: [1] Bernatowicz, T.J. *et al.* (1994) *LPS XXV*, 105-106. [2] Christoffersen, R. *et al.* (1996) *Meteoritics & Planet. Sci. 31,* 835-848. [3] Christoffersen, R. *et al.*, this volume. [4] Gibson, M. *et al.* (1994) *JGR*, 99, 10887-10897.



STEM bright field image



Ti map



Fe map

Figure 1. STEM-EDX analysis of a lunar ilmenite rim. Bright areas in Ti and Fe elemental maps represent Ti oxides and Fe metal, respectively. Boxed area is plot in Figure 2.

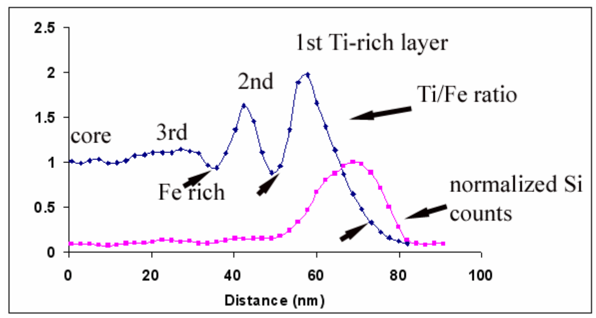


Figure 2. Elemental profile of Fe, Ti, and Si, generated from STEM-EDX mapping in the ilmenite rim (boxed area in Fig. 1). Intensity ratio of Ti/Fe, and normalized Si intensity *vs.* distance, are plotted respectively.