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A STEM-EELS Study of the Effect of Solar-wind Irradiation on the Ilmenite from Lunar Soil

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Introduction: The surfaces of fine ilmenite grains from lunar soil are exposed to solar-wind irradiation that results in a damaged layer (~50 nm) showing Fe-Ti segregation [1]. The mechanism responsible for the Fe/Ti distribution in these layers is still unclear. The depth dependent profile of Fe/Ti valence variation as well as oxygen distribution within the ilmenite rims would provide critical data to answer this question. In this study, we employed coupled STEM/EELS methods to investigate the correlation between Fe and Ti valence change with depth in the ilmenite rims. In addition, the effect of solar-wind irradiation on the oxygen variation in these rims was determined.

Materials and experimental procedures: Aliquots of the <20mm fraction of soil 10084, which was returned by Apollo 11, were embedded in low viscosity epoxy and thin sections (~60 nm thick) were prepared using ultramicrotomy. The STEM-EELS analysis was obtained using the JEOL 2500SE 200 kV field-emission STEM equipped with a Tridiem GIF operated with a 4 nm probe, 4 s dwell time, 0.2 eV /channel dispersion, 0.8 eV energy resolution, and 4×4 nm pixel size.

Results and discussion: In the solar wind irradiated layer of ilmenite, nanophase (<10 nm) iron metal ($npFe^0$) grains occur adjacent to the Ti-rich phase (Fig.1b). Qualitative comparison of Fe/Ti valence with depth across the ilmenite rims can be obtained by calculation of integrated intensity ratio of L_3/L_2 for Fe and Ti, respectively. STEM-EELS mapping of the rim shows the amount of Ti^{3+} increases towards the surface, and more Fe^{2+} in ilmenite was reduced to $npFe^0$ [Fig.2]. This observation is consistent with the preferential loss of oxygen, compared with the Fe/Ti cations in ilmenite, due to solar wind irradiation, as also demonstrated by the depth dependent profile of O/Ti ratio (Fig.2). Thus, the Fe-Ti segregation in the rims of lunar ilmenite likely results from *in situ* reduction induced by the solar wind irradiation. In this process, with the loss of oxygen, part of Ti^{4+} and Fe^{2+} is reduced to Ti^{3+} and Fe metal, respectively.

The stoichiometry of the Ti-enriched phase, i.e. Ti^{3+}-bearing ilmenite or pure Ti oxide, in the ilmenite rims is intriguing. With negligible over- or undersampling effect as described in the experimental method section, STEM-EELS analysis of the $npFe^0$ commonly shows considerable presence of Fe^{2+}, and a mixture of Ti^{3+} and Ti^{4+}, which is likely from the Ti-bearing phase buried underneath the Fe metal. Similarly, the Ti-enriched region was observed to have mixed valence of Fe^{2+} and Fe^0, though occasionally it is simply pure reduced Ti oxide. High resolution TEM examination of the Ti-rich zone typically shows defect microstructures, such as stacking faults, which likely arise from the reconstruction of Ti/Fe layer in ilmenite. The seemingly pure Ti oxide regions are amorphous or nanocrystalline. Therefore, given the fluence of the solar-wind irradiation the lunar ilmenite had experienced, the majority of the *in situ* reduction products are confined to the Ti^{3+}-bearing intermediate ilmenite and $npFe^0$. Continued bombardment of the rims by the solar-wind ions could eventually lead to reduced Ti oxide in replace of intermediate ilmenite. The mineralogical and chemical analysis of the ilmenite rims in lunar soil, therefore, could provide quantitative constraints on their formation conditions.

Reference: [1] Christoffersen, R. *et al.* (1996) *Meteoritics & Planet. Sci. 31,* 835-848.

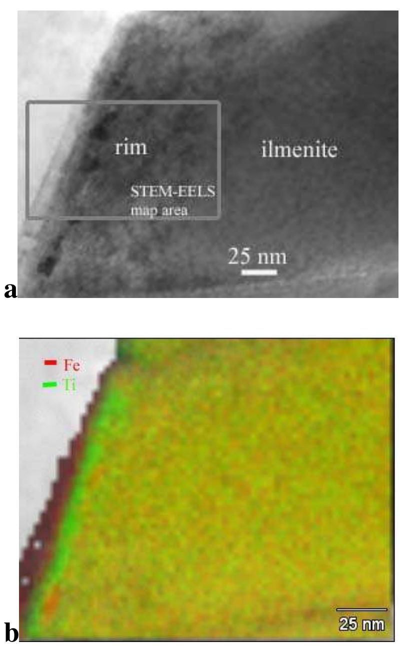

Figure 1. STEM-EDS mapping of the ilmenite rim.

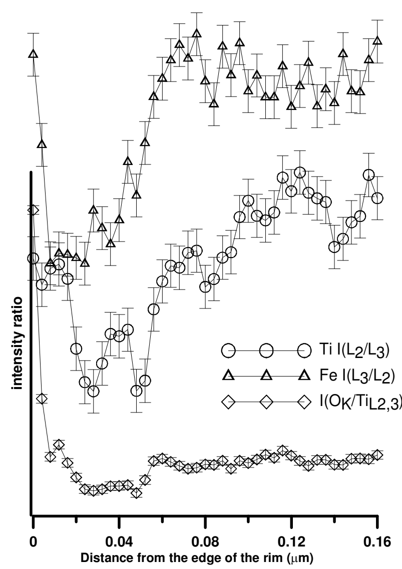

Figure 2. A depth dependent profile showing correlations among Fe/Ti valence variation and oxygen distribution in the rim. The rim in the first 20 nm is formed through vapor deposition, not discussed here.

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