

NANOSCALE COMPOSITIONAL RELATIONS IN LUNAR ROCK PATINA: DECIPHERING SOURCES FOR PATINA COMPONENTS ON AN APOLLO 17 STATION 6 BOULDER. R. Christoffersen¹, S. K. Noble² and L. P. Keller³, ¹Jacobs, NASA Johnson Space Center, MC JE23, 2101 NASA Pkwy, Houston, TX 77058, USA, roy.christoffersen-1@nasa.gov, ²NASA GSFC Mail Code 691, Greenbelt, MD 20771, USA, sa-rah.k.noble@nasa.gov, ³NASA Johnson Space Center, Mail Code KR, 2101 NASA Pkwy, Houston, TX 77058, USA, lindsay.p.keller@nasa.gov.

Introduction: Space weathering on the Moon and other airless bodies modifies the surfaces of regolith grains as well as the space-exposed surfaces of larger rocks and boulders [1-6]. As space weathering witness plates, rocks and boulders are distinguished from regolith grains based on their ability to persist as physically intact substrates over longer time scales before being disaggregated by impact processes. Because lunar surfaces, including exposed rocks, quickly develop an optically thick layer of patina [6], it is important to understand the compositional relationship between patinas and their underlying rock substrates, particularly to support remote-sensing of rocky lunar terrains. Based on analytical TEM techniques, supported by focused ion beam (FIB) cross-sectioning, we have begun to systematize the multi-layer microstructural complexity of patinas on rock samples with a range of space exposure histories [4-6]. Our on-going work has particularly focused on lunar rock 76015, both because it has a long (~22 my) exposure history [4-6], and because its surface was exposed to patina development approximately 1 m off the regolith surface on a boulder in the Apollo 17 Station 6 boulder field [7]. Potential sources for the 76015 patina therefore include impact-melted and vaporized material derived from the local rock substrate, as well as from the mix of large boulders and regolith in the Station 6 area. While similar, there are differences in the mineralogy and chemistry of the rocks and regolith at Station 6 [7,8]. We were interested to see if these, or other sources, could be distinguished in the average composition, as well as the compositional nanostratigraphy of the 76015 patina. To date we have acquired a total of 9 TEM FIB cross-sections from the 76015 patina, giving us reasonable confidence of being able to arrive at an integrated average for the patina major element composition based on analytical TEM methods.

Methods: The 76015 patina FIB sections were characterized using a JEOL 2500SE analytical field-emission scanning transmission electron microscope (FE-STEM) at JSC. The ability of the 2500SE to acquire quantitative compositional spectrum images, along with associated element maps and area-specific energy-dispersive X-ray (EDX) spectra were of particular use in the current study. Both element maps and EDX spectra were quantified by applying empirically-

determined Cliff-Lorimer k-factors [9]. Post-acquisition data analysis included spectral principal component analysis (PCA) by the Thermo COMPASS routine [10].

Results: The 76015 patina is dominantly comprised of patina of the previously-described “classic” type [3-6], with a microstructure made up of compositionally contrasting glassy layers intermixed on the sub-micron scale in a “schlieren”-like manner, or as more geometrically flat stratified layers [4-6]. The layers are characteristically defined by variable amounts of nanophase Fe metal (npFe⁰), although, thicker glass units lacking npFe⁰ are also intermixed [4-6]. In addition to classic patina, the surface of 76015 also contains local regions of “fragmental” patina consisting of chemically homogeneous glassy clasts adhering to the surface of the rock in various stages of welded compaction [3-6]. We assessed the average major element oxide composition of the classic and fragmental patinas on 76015 from quantified EDX spectra extracted from contiguous compositional spectrum images collected along the entire length of classic patina on three FIB sections, and fragmental patina on two FIB sections. The results are shown on ratio plots in Fig. 1 designed to compare enrichment/depletion of the major oxides relative to an average 76015 whole-rock composition [7], an average of selected Station 6 soils [8], and an average value for Apollo 17 soil agglutinates [11].

Discussion. Relative to Station 6 soil (as well as Apollo 17 soil agglutinates) the fragmental patina shows a relatively flat major oxide enrichment/depletion trend with significant depletions only for FeO and TiO₂ (Fig. 1a). By contrast, the enrichment/depletion pattern relative to the 76015 rock would require a relatively complex fractionation pattern if the fragmental patina were derived primarily from a local, rock-dominated source. There is, however, a complementary relationship between the rock and soil enrichment/depletion patterns for MgO, FeO and TiO₂. This may suggest the fragmental patina is a mixture of rock-derived and soil-derived material. Based on the Fig. 1a relations, and other factors such as the overall homogeneity of the fragmental patina in elemental maps, we currently hypothesize that the fragmental patina may represent an airfall of well-

homogenized ejecta from a larger scale (non-micrometeorite) cratering event into the regolith.

Compared to the fragmental patina, the major oxide enrichment/depletions patterns for the classic patina are more complex relative to all three potential source materials (Fig. 1b). MgO is consistently depleted relative to all sources, with less consistent trends for the other oxides. Most notably there is less complementarity between the trends, i.e. they are mostly all greater than or less than 1. This makes it more difficult to explain the classic patina as a simple linear mixture of rock and soil material without fractionating source processes such as preferential impact melting or vaporization. The classic patina microstructural relations clearly indicate a complex accumulation of variously sized packets of impact-derived melt. However, attempts to explain the MgO depletion (and less prominent CaO depletion) based on preferential non-melting of pyroxene in impacts into either a rock or soil source [12], are generally thwarted by the need to account for the high FeO content of the patina, both locally and on average. The Fe source problem is made worse if ilmenite, similar to pyroxene, is likewise considered to be resistant to impact melting as discussed by [12]. Replacing the average soil source with a more agglutinate-like one does little to improve the fit, because the compositions are very similar, suggesting the classic patina coatings cannot be simply thought of as ballistically-transported packets of soil-derived agglutinitic melt.

Variation diagrams and spatially-analyzed trends and PCA analysis of compositional maps all show that FeO is highly un-correlated, mathematically or spatially, with any of the major oxides, including MgO and TiO₂. Instead, a significant amount of the overall Fe in the patina, whether oxidized in glass or as npFe⁰, appears to be held in Fe-rich (18-20% FeO) continuous “river-like” layers, or in thinner layers of similar composition within fine-scale glass laminae. The overall relations speak to a spatial and compositional decoupling of Fe from other elements, reflecting a process or processes that cause Fe to concentrate in spatially-resolvable domains in the patina glass. A mixing model using these Fe-rich domains as a unique component (possibly with its own unique source) added to a pyroxene-depleted impact melt shows a potential fit, but works without discriminating between a rock or soil source.

Conclusions. The very Fe-rich layers and domains in the classic patina are intriguing because they don't appear to have an analog source material in either the rock or soil, including agglutinates. The vapor-deposited rims on regolith grains in mature mare soils are one subcomponent of the regolith known to be both Fe-enriched and relatively MgO depleted [2]. Invoking

this material as a source presents problems, but is intriguing. We are currently considering whether processes might exist to concentrate Fe-rich, rim-derived material into patina deposits during multiple cycles of impact melting and vaporization, possibly along with Fe-rich vapor deposits directly condensed on the host rock surface, and/or Fe from meteoritic sources.

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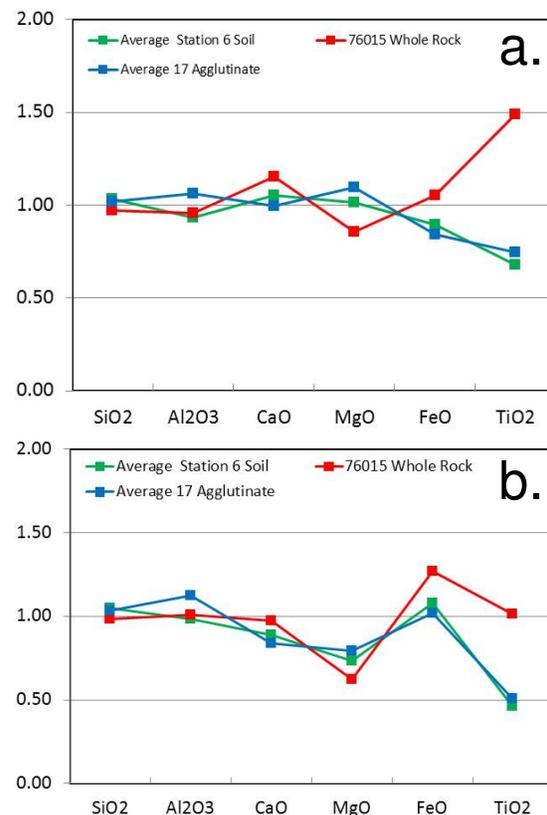


Fig. 1. Wgt. % major element oxide concentrations in average compositions of 76015 fragmental patina (a) and classic patina (b) ratioed to 76015 whole rock [7], average Apollo 17 Station 6 soil [8], and average Apollo 17 agglutinate compositions. [11].