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GRAIN RIMS ON ILMENITE IN THE LUNAR REGOLITH: COMPARISON TO VAPOR DEPOSITS ON REGOLITH SILICATES; R. Christoffersen, D.S.

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Introduction. In efforts to understand regolith evolution on airless bodies increasing attention is now being paid to those processes and events that alter or "weather" the surfaces of regolith grains [1]. This attention has developed partly out of the ongoing need to optimize models of planetary reflectance spectra and the growing recognition that diverse types of grain coatings and surface alterations occur which can strongly influence mineral reflectance properties [1,2]. In addition to their implications for optical properties, surface features on regolith grains have provided useful clues to the basic thermal, chemical and radiation history of regoliths.

Ilmenite in the lunar regolith. Recent transmission electron microscope (TEM) studies have confirmed that silicate grains in the sub-20 μm fraction of lunar soils contain amorphous rims that likely formed by condensation of locally derived impact vapor [3]. These studies found no analogous rim deposits or coatings on ilmenite, but observations were limited by the low concentration of ilmenite relative to silicates in the bulk soils studied. We have re-examined ilmenites hand-picked from the sub-20 μm fraction of both submature and immature lunar soils and found that a large fraction do have outer margins that are highly altered and may contain vapor deposited material. The ilmenite rims have features that are also substantially different from those observed in silicates, and which we believe are influenced by solar radiation effects and subsolidus reduction, in addition to vapor deposition.

Samples and methods. Ilmenite grains 5 to 20 μm in diameter were hand picked from the sub-20 μm fraction of lunar soils 10084 ($I_s/\text{FeO}=48$), 67701 ($I_s/\text{FeO}=39$) and 61221 ($I_s/\text{FeO}=9.2$) [4]. The grains were prepared for TEM study by ultra-microtomy techniques that have been described elsewhere [3]. In addition to a combination of conventional and high-resolution imaging techniques, the TEM work utilized energy-dispersive X-ray spectroscopy (EDS) with light-element capabilities to perform chemical analyses at scales of 10-50 nm.

Results. The majority, but not all, of the ilmenites exhibit continuous outer rims 60 to 120 nm thick, which are shown to be nano-crystalline by selected-area electron diffraction (SAED). The average grain size within the rims is estimated to be between 4 to 10 nm, with a uniformly dense microstructure. Almost all rims show a 25-40% depletion in their atomic fraction of Fe relative to the grain interior. The very outer 10-50 nm of the rim contains Si (1.5-4.7 at.%), Al (0.4-1.4 %), Ca (0.4-0.8 %), and S (0.3-0.5 %) in various proportions; none of these elements occur in grain interiors.

SAED patterns confirm that nanocrystalline ilmenite makes up a portion of the rim material, but additional phases are required by the rim chemistry. We have noted two morphologically distinct types of crystallites within the rims. Type M crystallites are 8 to 10 nm in diameter with spherical or slightly elongate rounded shapes. Possibly due to interference from surrounding matrix their EDS analyses show a range of Fe/Ti ratios, although many show major Fe and minor Ti. The Type M grains are probably Fe metal, although some may also be small grains of ilmenite. The second class of rim components, Type R grains, occur as platelets 1 to 2 nm wide and 8 to 10 nm long, oriented parallel to the (001) basal plane of the ilmenite. Because they are less than 2 nm wide the platelets have been difficult to identify from EDS analyses or microdiffraction, but their crystallographic orientation and shape is identical to that of

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coarser precipitates of TiO₂ (rutile) known to form both in reduced and oxidized ilmenites [5]. Type R grains are typically highly concentrated in the outer 50 nm of a rim, with their concentration decreasing gradationally towards the interior of the ilmenite. In addition to Type M and R grains within the rims, the outer surfaces of some rims are decorated with spherical grains that we have positively identified as Fe metal. These are distinguished from Type M grains in that they are larger (10 to 20 nm in diameter) and occur as isolated blebs that protrude above the rim's outer surface.

Discussion. We believe the rims formed at least partly by alteration of the ilmenite grain's outer margin, rather than as deposited material. In particular the Type R grains are most reasonably interpreted as precipitates that formed within the original ilmenite, and along with the Type M grains represent the replacement of the ilmenite's original outer margin with a polycrystalline assemblage. This interpretation, however, does not account for the enrichments in Si, Al, Ca and S observed in the outer 5 to 10 nm of most rims. These elements would tend to indicate the presence of some type of thin surface deposit. In a few ilmenite grains we have been able to resolve a distinct, thin outer surface layer 2 to 5 nm thick, which may be the source of the anomalous elements. An interpretation of the Si and S in the rims as being derived from vapor deposition processes is consistent their known volatility [6], as well as with their presence in coatings on silicate grains now thought to be vapor deposits [3]. Ca and Al, although more refractory, should also occur in vapor deposits because they are major components of soil that is completely vaporized by micrometeorite impact.

The ilmenite rims differ from those on silicate grains in that they are *not* amorphous and, with the exception of their outer surface layers, differ in composition from their host grains only with respect to being Fe depleted. Although additional confirming evidence is needed, the phase assemblage within the rims appears to contain rutile and some Fe metal in the form of the type M grains. Both are established products of ilmenite reduction at 900-1000°C under H gas in the laboratory [7]. An alternative, low-temperature, reduction mechanism may be related to reactions discussed by [8] and [9], in which H⁺ implantation by the solar wind causes *in situ* reduction.

An origin for the rims as the product of solar wind effects is consistent with the gradational nature of the rim alteration, but it is clear that their formation involved processes other than just radiation damage *per se*. As noted above, one of these processes involved the formation of a Si-enriched surface layer by vapor deposition. The surface blebs of Fe metal are distinctly coarser in grain size than the bulk of the ilmenite rim, and these may have formed when the grain's very outer margin was reduced in episodes of short duration, higher temperature heating. Such episodic heating may account for the Fe loss from the ilmenite rims by volatilization. Alternatively the Fe metal component might have been volatilized over time due to diurnal solar heating, which can produce temperatures of 100-120°C on the lunar surface.

The fact that ilmenites appear to have a thinner layer of vapor-deposited material relative to regolith silicates may be because the ilmenite surface is more *reactive*, and experiences volume changes, lattice strains and recrystallization associated with *in situ* reduction. Such processes may make ilmenite a less receptive substrate for acquiring and retaining vapor deposits.

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