

ORIGIN OF AMORPHOUS RIMS ON LUNAR SOIL GRAINS; Thomas J.

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In a recent paper, Keller and McKay [1] have challenged the generally accepted idea that the ~50nm amorphous rims on lunar soil grains are the result of solar wind (SW) ion damage [2]. They instead propose that these rims are almost entirely impact-derived rock vapor deposits (based on compositional differences between grain rims and interiors observed in Apollo 11, 16 and 17 silicate soil particles), and conclude that SW radiation effects are of minor importance relative to vapor deposition. A decisive test of this hypothesis should be provided by a study of the surfaces of ilmenite (FeTiO_3) in mature lunar soils, since this mineral (not investigated by Keller and McKay) is compositionally distinct from silicates and constitutes only a minor fraction of the regolith. Specifically, the vapor deposition model implies that any amorphous rims observed on ilmenites should be dominantly silicate vapor deposits.

To test this prediction, we have performed complementary noble gas and TEM studies of 7 ilmenite grains (90-125 μm) separated [3] from the mature lunar soil 71501 (with a modal ilmenite abundance of 8% [4]). The grains were imbedded in resin and partially sliced with a diamond-blade ultramicrotome to produce sections thin enough (70 nm) for study in the TEM. The remainder of each grain was then individually analyzed for noble gases using the the same laser extraction techniques as in a recent study [5] of 90 ilmenites from 71501. All of the grains in the present study are rich in SW gases (0.04 - 0.4 ccSTP $^4\text{He/g}$) and have He and Ne concentrations and Ne isotopic ratios within the range observed in the much larger ilmenite suite. The interiors of the grain sections are heavily shattered by the slicing, but portions (tens of μm) of the outermost surface of the grain immediately adjacent to the embedding resin are frequently preserved to a depth of 1-2 μm . This allows for comparative elemental analysis of the surfaces exposed to SW and the unexposed ilmenite beneath them. We performed energy dispersive X-ray analyses of the grain surfaces (73 analyses) and near-surface interiors (49 analyses) with a 20 nm, 200kV electron beam, using a Noran detector sensitive to elements with $Z \geq 5$.

The interior analyses reveal substantial Mg and minor Cr substitution for ferrous iron in these ilmenites ($\text{Mg/Ti}=0.04\text{-}0.17$; $\text{Cr/Ti}=0.01$), but $(\text{Fe}+\text{Mg}+\text{Cr})/\text{Ti}$ is unity within analytical uncertainty. Compared to the interior composition, the outermost 50nm of surface is typically enriched in Mg, Al, Si, S and Ca. These excess abundances are displayed in Fig. 1 as the mean difference between surfaces and interiors in terms of atomic ratios relative to Ti. Titanium is chosen as the reference element because its atomic abundance is less than that of all of the other major elements in 71501 [6] and because it is the dominant cation in ilmenite. Not included in the figure are analyses of surface glass splashes (which comprise at most a few percent of the surface and thus are not representative of the bulk surface composition). In Fig. 1 the ilmenites are ordered by increasing abundance of surface Si, the most abundant excess element. It is evident that the excess elements are far less abundant than Ti (mean excess $/\text{Ti} < 0.2$), so that the surfaces are compositionally similar to ilmenite. In the sense that the surfaces of the ilmenites are dominated by Ti, as opposed to Si and the other major elements in the bulk soil, the idea that vapor deposits entirely constitute the amorphous rims on lunar grains is seen to fail. On the other hand, the present work shows that there is indeed some vapor contamination of grain surfaces, as revealed by the element excesses. Within analytical uncertainty, the mean Mg/Si and Al/Si ratios in the excess are identical to those in the bulk soil [6] and to the ratios measured in the surface glass splashes. On this basis, it is reasonable to ascribe these excess surface elements to contamination by impact-generated rock vapor. Sulfur, on the other hand, is surface-enriched by

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an order of magnitude relative to the bulk soil, consistent with the observations of Keller and McKay [1]. Based on the surface abundances of Mg, Al and Si, all of the calculated excesses are probably low by 3-5% due to Ti that may have accompanied these elements in the vapor deposits, but this does not affect the conclusion that the surface composition of the ilmenites is essentially that of the interior, except for minor rock vapor contamination.

The surfaces of all of the ilmenites, regardless of degree of vapor contamination, are disordered to depths of 30-80nm as revealed by high resolution imaging and convergent beam diffraction. In addition to amorphous regions, the surfaces typically have randomly oriented ilmenite crystallites (<10nm) that are presumably the result of surface recrystallization. In the most contaminated grain (ILM6) there are also surface blebs (20-50nm) of metallic Fe, most likely formed by reduction of impact vapor iron on contact with the SW hydrogen-saturated grain surface. We may plausibly attribute the surface disorder of the ilmenite grains to SW ion damage, since the surface concentration [5] of SW He inferred for the most gas-rich ilmenites in 71501 is up to 5×10^{-3} ccSTP/cm², equivalent to a flat target He fluence of 10^{17} atom/cm². Simulation experiments [2] show that such fluences produce severe radiation damage in ilmenite, consistent with our observations. To our knowledge this is the first observation of SW ion damage in ilmenite. Thus, not only do the present results reject the vapor deposition model for the origin of lunar grain amorphous rims, but they also give new evidence in favor of the SW ion damage model.

Returning to the discussion of Fig. 1, we note that, on the average, there is a 10% deficiency of Fe relative to Ti in the ilmenite surfaces compared to their interiors. Vapor addition of Ti to the grain surfaces cannot account for this, since Fe should be at least twice as abundant as Ti in vapor generated from the bulk soil [6]. Detailed investigation of the disordered grain surfaces, the crystalline interiors and the region between them revealed no reservoir for this missing Fe. Given that Mg/Si and Al/Si in the surface vapor deposits are unfractionated relative to the bulk soil, we are forced to conclude that the Fe has been preferentially removed. Whether this occurred on the lunar surface or during the heavy liquid separation used to isolate the ilmenite [3] remains to be determined.

REFERENCES: [1] Keller L. and McKay D. (1993) *Science* **261**, 1305; [2] Bibring P. *et al.* (1974), *EPSL* **22**, 205. [3] Benkert J. *et al.* (1993), *J. Geophys. Res.* **98**, 13,147; [4] Heiken G. and McKay D.(1974), *Proc. 5th Lun. Sci. Conf.* v.3, 843; [5] Nichols R. *et al.* (1994) *Geochim. Cosmochim. Acta* **58**, in press; [6] LSPET (1973), *Science* **182**, 659.

Figure 1:

