Vapor Deposits in the Lunar Regolith

L. P. Keller and D. S. McKay (*1*) present direct evidence, obtained by transmission electron microscopy, that widespread coatings were formed by deposition of impact-generated vapor on lunar regolith particles. Since the Apollo missions, we have emphasized the following points, which are based on theoretical calculations and on laboratory studies of the properties of evaporated silicate deposits and of lunar samples (*2*). (i) The mass of vapor generated by impacts on the lunar surface is comparable in magnitude to the mass of impact melt glasses; (ii) the physics of impact into a porous regolith requires that much of this vapor be retained in the soil rather than lost to space (as is widely believed); (iii) experimental coatings made from vaporized or sputtered lunar basalt contain abundant inclusions of submicroscopic, superparamagnetic metallic Fe; and (iv) this Fe may explain the magnetic signature, low albedo, reddened spectrum, and subdued absorption bands of lunar regolith.

Our conclusions have been generally rejected by the lunar geochemical community for two reasons: (i) there seemed to be no direct evidence for vapor deposits in Apollo samples (*3*), and (ii) it seemed that the lunar optical properties could be explained by the presence of impact melt glasses alone (*4*). However, advances in our understanding of the optical properties of glasses (*5*) and of light scattering by planetary regoliths (*6*), and now the direct detection of vapor deposits (*1*), show that these objections are not valid. Vapor phase transport is a major process on the lunar surface, and unless its effects are taken into account, the chemical, magnetic, and optical properties of the regolith cannot be understood.

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2. B. Hapke, *Moon* 7, 342 (1973); W. Cassidy and B. Hapke, *Icarus* **25**, 371 (1975); B. Hapke, W. Cassidy, E. Wells, *Moon* **13**, 339 (1975); B. Hapke, *Phys. Earth Planet. Inter.* **15**, 264 (1977); R. Baron *et al., Earth Planet. Sci. Lett.* **37**, 263 (1977); B. Hapke, in *Abstracts, 8th Lunar Science Conference* (Lunar and Planetary Institute, Houston, TX, 1977), part 1, p. 398.
3. As recently as last year, M. Cintala [*J. Geophys. Res.* **97**, 947 (1992)] argued that vapor deposits in the lunar regolith were either nonexistent or were so thin that their optical effects were negligible.
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Keller and McKay conclude (*1*) that the amorphous rims of approximately 500 Å on lunar dust grains are largely a result of impact-produced vapor deposits. This contrasts with previous work by Bibring *et al.* (*2*), who concluded that these rims result from solar wind (SW) ion damage. Keller and McKay base their conclusion on the observation of compositional differences between the rims and grain interiors of silicates. Setting aside for the moment the question of whether such compositional variation can also occur within a radiation damage model, a crucial test of the lunar vapor scenario should be provided by lunar soil ilmenite (not studied by Keller and McKay in their report), because it is compositionally distinct from silicates and is only a minor lunar soil component. Because vapor deposition and SW ion implantation affect all lunar soil grains, if the vapor deposit model is correct, it follows that any amorphous rims on ilmenite [$FeTiO_3$] grains must also be dominantly silicate vapor deposits. Alternatively, because ilmenites are more resistant to radiation damage than are silicates (*2*), if SW ion damage is important for ilmenites, it is at least equally important for silicates.

We have recently performed rare gas studies (*3*) of seven ilmenite grains (~100 μm) from the submature lunar soil 71501 that were partially microtomed for transmission electron microscopy (TEM) observation. All of the grains had SW rare gases and disordered rims with chemical compositions similar to those of the host ilmenite. Furthermore, the rare gas extractions from individual lunar ilmenite grains (*3*) yielded lower limits on SW He fluences to which grains from this soil were subjected. The measured values of up to 5×10^{-3} He ccSTP per square centimeter correspond to an equivalent flat target fluence of about 10^{17} He per square centimeter. Simulation experiments (*2*) showed that this fluence is large enough to produce severe radiation damage in ilmenite, as observed. The ilmenite surfaces are also contaminated by vapor deposits, as evidenced by enrichments in Mg, Al, Si, S, and Ca. The dominant vapor deposit species is Si, with an atomic abundance, however, that averages only 20% of that of Ti in the outer few hundred angstroms of the ilmenite grains. The disordered rims cannot, therefore, be pure vapor deposits, as advocated by Keller and McKay. Instead, they must represent SW-damaged layers with a composition that has been affected to only a limited extent by vapor contamination.

The marked rounding of rimmed silicate grains, observed by Keller and McKay (*1*), cannot be ascribed to vapor deposition because the amorphous rims and the material beneath them are rounded. This rounding reflects an efficient erosion process that can be triggered by SW ion sputtering ($E \approx 1$ keV/amu), but not by the "impact" of lunar vapor with a much lower energy (≈ 0.1 eV/amu). Simulation experiments of SW (*2*), which indicate that silicates are about ten times more sensitive to damage and sputtering than ilmenite, reproduce this rounding and "coating" effect. The critical fluence of SW ions needed to form amorphous rims on lunar silicates is two to three times smaller than the critical fluence required to round off their edges. Consequently, the well-rounded feldspars depicted in the report by Keller and McKay (*1*) necessarily contain a SW ion damage layer.

Other observations support the dominance of SW radiation damaged layers. First, the quantity of SW rare gases retained depends on the nature of the lunar mineral, with ilmenite being the most retentive (*4*). Thus, these gases cannot be implanted in silicate vapor deposits on ilmenite, consistent with our TEM observations. Second, thermal annealing experiments (*2*) indicate that the approximately 500 Å amorphous rims on lunar silicates anneal at the same temperature (≈800°C) as the fossil nuclear tracks registered in the same grains. The same annealing conditions were noted for damage layers of about 500 Å obtained with artificial SW. In contrast, artificial feldspar vapor deposits on silicates start recrystallizing at very low temperatures (≈300°C) and flake off at about 500°C (*5*). Thus, annealing experiments also indicate a radiation damage origin for the lunar amorphous coatings.

Our observations confirm that vapor deposits do alter the composition of lunar grain surfaces, but they also show that disordered rims on lunar grains must be largely ascribed to radiation damage. Moreover, unlike Keller and McKay, we do not expect that the composition of the SW damage layer will strictly match the composition of its host minerals because "recoil mixing" (6) can deplete this layer in light elements and especially because the SW damage layer on silicates is extremely reactive. For example, Dran *et al.* (7) showed that hydration rates can be up to 10^3 times higher than that of the undamaged mineral. Concommitant ejection of alkali metal ions in silicates loaded with SW-implanted hydrogen could, for example, provide an explanation for the alkali metal depletion in the lunar silicate rims observed by Keller and McKay (*1*).

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Response: Bernatowicz *et al.* do not present the same analyses on silicates as they do on ilmenites. They apparently assume that ilmenite behaves similarly to the silicates present in lunar soils—for example, that ilmenite acquires and retains vapor deposits with the same efficiency as do silicate grains. Christoffersen *et al.* (*1*), however, have shown that the surfaces of ilmenite grains are reactive in the lunar soil environment. Several processes operating in the lunar regolith serve to modify the surfaces of ilmenite grains, including the implantation of solar wind ions, in situ reduction, and vapor deposition. Christoffersen *et al.* showed that most ilmenite grains in their samples contained outer rims of up to 120 nm thick, where the host ilmenite had decomposed into a mixture of Fe metal and Ti-oxide grains. These reaction rims correspond to the "disordered" rims observed by Bernatowicz *et al.* (2) and are distinguished from their hosts by their microstructure and composition; all of the reaction rims analyzed are nanocrystalline (not amorphous) and show strong depletions in Fe (up to a 40% depletion of Fe relative to stoichiometric ilmentite). This Fe depletion cannot be the result of direct solar wind sputtering (for example, knock-on and ejection of Fe atoms) of ilmenite because such sputtering is essentially a surface phenomenon that removes surface atoms in proportion to their abundance (notwithstanding the outermost few nanometers where preferential sputtering may occur). Nor can it be ascribed to sputter deposition, because deposits formed by sputtering would be enriched in Fe, not depleted. The reaction rims probably result from the interaction of solar wind hydrogen with ilmenite, either directly during implantation or through subsequent heating of the ilmenite grains (*1*). This interaction would result in the reduction of Fe^{2+} to Fe^0, migration of Fe^0 to the grain surface, and loss of Fe^0 by vaporization. Thus, the surfaces of ilmenite grains are dynamic; they suffer significant mass loss and volume reduction. These data indicate that ilmenite should be avoided, not sought, as a test of the vapor deposition model, because ilmenite appears to be chemically reactive with solar wind hydrogen and this reaction greatly complicates the outer rims, obscuring other effects.

Table 1. Average compositions of amorphous rims on specific minerals in lunar soils 10084 and 78221 (in weight %)

Host mineral	Na_2O	MgO	Al_2O_3	SiO_2	S	CaO	TiO_2	FeO
Anorthite	0.1	3.5	20.1	53.4	0.7	9.7	4.0	8.5
Cristobalite	0.2	5.4	11.5	59.2	1.7	7.3	3.9	10.8
Olivine	0.6	8.8	15.5	47.6	0.4	8.8	3.6	14.7

The only truly amorphous material on the surfaces of the ilmenite grains is a thin rind of silicate material that is superimposed on the reaction rim. We agree that some proportion of the Na and K depletion observed in the rims might be accounted for by sputtering, as demonstrated experimentally by Hapke *et al.* (*3*). However, "recoil-mixing" cannot account for the gross chemical differences between most rims and their hosts. Rims on cristobalite (essentially pure SiO_2) contain major Mg, Al, Ca, Ti, and Fe (Table 1); these elements are foreign to cristobalite and so must have been deposited on the surfaces of grains by condensation of impact-derived vapors or by sputter deposition. Similar arguments can be made for the amorphous rims on olivine [$(Mg,Fe)_2 SiO_4$] grains, which contain major amounts of Ca, Al, and Ti (elements that are normally present in olivine at only trace amounts), and for rims on anorthite (An_{95-99}), which contains major Mg, Ti, and Fe (which are also present in trace concentrations in the host plagioclase). Overall, the average rim compositions are remarkably similar and are independent of the host grain mineralogy (Table 1). These data indicate that much of the "thickness" of amorphous rims consists of elements that are not indigenous to the host soil grains.

Whether there are "sputtering" or radiation effects superimposed on the vapor deposited material can be debated. We do not explicitly exclude the effects of radiation damage as a contributing factor to the formation of amorphous rims; we merely emphasize the major (and generally overlooked) role played by condensed vapors in the formation of amorphous rims on lunar soil grains.

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