

# Space weathering on airless planetary bodies: Clues from the lunar mineral hapkeite

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Physical and chemical reactions occurring as a result of the high-velocity impacts of meteorites and micrometeorites and of cosmic rays and solar-wind particles are major causes of space weathering on airless planetary bodies, such as the Moon, Mercury, and asteroids. These weathering processes are responsible for the formation of their regolith and soil. We report here the natural occurrence of the mineral hapkeite, a Fe<sub>2</sub>Si phase, and other associated Fe-Si phases (iron-silicides) in a regolith breccia clast of a lunar highland meteorite. These Fe-Si phases are considered to be a direct product of impact-induced, vapor-phase deposition in the lunar soil, all part of space weathering. We have used an *in situ* synchrotron energy-dispersive, single-crystal x-ray diffraction technique to confirm the crystal structure of hapkeite as similar to the structure of synthetic Fe<sub>2</sub>Si. This mineral, hapkeite, is named after Bruce Hapke of the University of Pittsburgh, who predicted the presence and importance of vapor-deposited coatings on lunar soil grains some 30 years ago. We propose that this mineral and other Fe-Si phases are probably more common in the lunar regolith than previously thought and are directly related to the formation of vapor-deposited, nanophase elemental iron in the lunar soils.

The formation of regolith and soil on airless planetary bodies, such as the Moon, Mercury, asteroids, is the result of processes virtually nonexistent on Earth. The physical and chemical changes that occur to the materials at the surfaces of such airless bodies are collectively known as “space weathering” and are mainly caused by impacts of meteorites, micrometeorites, and galactic/cosmic and solar-wind particles, in the deep vacuum of space. Since the cessation of major bombardment by large asteroid-size bodies on the Moon ( $\approx 3.8$  billion years ago), the micrometeorite impacts have been the major agents in modifying the upper few centimeters of the lunar regolith. Interplanetary micrometeorites consist of minute grains (mostly 10–150  $\mu\text{m}$ ) that can be traveling at velocities well over 100,000 km/hr, imparting tremendous kinetic energy to the surfaces they hit. The major effect of larger impacts is the crushing and pulverizing of rocks and minerals (comminution), thereby, decreasing their grain size. Many micrometeorites, on the other hand, have sufficient energy to effectively flash-melt the silicate rock particles, splashing the melt onto other grains, which are thereby aggregated together by the quenched melt (glass). These small pieces of comminuted rock, mineral, and glass fragments, cemented with impact-melt glass, are called agglutinates, which impart a unique property to the soil.

Although the returned Apollo samples revealed that lunar samples contain small amounts ( $\ll 1$  wt%) of elemental iron (Fe<sup>0</sup>) as a primary phase, the “soil” (<1-cm portion of the regolith) contained at least 10 times more Fe<sup>0</sup>, but almost entirely of submicroscopic size (cf., ref. 1 and references therein). Impacts of meteorites that contain extralunar metallic Fe could potentially contribute to this excess Fe<sup>0</sup>, but of the  $\approx 1$  wt % metallic Fe in mare soils, it is estimated that only a small fraction of the large native Fe is of meteoritic origin (2), and almost none of the submicroscopic metal is. The indigenous lunar origin of submicroscopic metal grains was also supported by their low Ni/Fe ratio. In addition, the limited range in  $\delta^{56}\text{Fe}$

isotopic compositions of a CM2 chondrite sample and iron meteorites (3) compared with the  $\delta^{56}\text{Fe}$  compositions of lunar soils have been used as an argument against significant net-Fe addition by meteoritic contribution (4). Thus, the majority of the Fe metal grains in the lunar soil can be assumed to be of indigenous origin, something inherent in the transition of rocks into soils.

It has been amply demonstrated that the outer 60–200 nm of the rims of most lunar soil grains contain a myriad of minute (typically, <10 nm) metallic Fe grains dispersed in an amorphous glassy matrix (cf., ref. 5 and references therein). Similarly, the agglutinitic glass also contains these minute grains. This metallic Fe has been variously called single-domain, nano-phase, superparamagnetic, and submicroscopic Fe<sup>0</sup>, all emphatic of the small size of these grains that are within the rims of soils and in agglutinitic glass that cements the soil aggregates. The formation of this nanophase elemental Fe<sup>0</sup> (np-Fe<sup>0</sup>) is related to space weathering.

In this study, we report on the occurrence of a lunar mineral Fe<sub>2</sub>Si and other associated Fe-Si phases in a lunar meteorite of a highland-regolith breccia, Dhofar 280. We have conducted single-crystal x-ray diffraction by using an *in situ* synchrotron x-ray diffraction technique to confirm the crystal structure of the Fe<sub>2</sub>Si phase. This mineral has been named hapkeite, after Bruce Hapke, who predicted almost 3 decades ago the presence of impact-induced np-Fe<sup>0</sup> in the lunar regolith and its possible effect on spectral reflectance.

## New Mineral and Other Iron Silicides

Grains of three new Fe-Si phases (Table 1), 2–30  $\mu\text{m}$  in size, were discovered in the highland regolith breccia, Dhofar 280.<sup>†</sup> This rock is a lunar meteorite discovered in the Dhofar region of Oman in January 2000, and its preliminary mineralogical and petrologic description was presented by Anand *et al.*<sup>‡</sup>

A regolith-breccia clast in Dhofar 280 contains numerous small (0.5–10  $\mu\text{m}$ ) opaque metal grains, similar to metal in an agglutinitic, glass-rich soil. The matrix is mainly composed of feldspathic material, compositionally similar to plagioclase glass. In reflected light, some of these fine-grained opaque minerals appeared to have a slight tarnish (Fig. 1). The largest grain of this type is  $\approx 35$   $\mu\text{m}$  in size with numerous smaller ones distributed throughout the breccia clast. Further inspection with an electron microprobe revealed that such tarnished metal grains were actually compounds of iron silicides. In most cases, the Fe-Si phases exhibit complex intergrowths of two or more phases at submicrometer levels, which pose difficulty in measuring the compositions of individual phases. However, in the largest grain, it was possible to identify and measure the composition of two

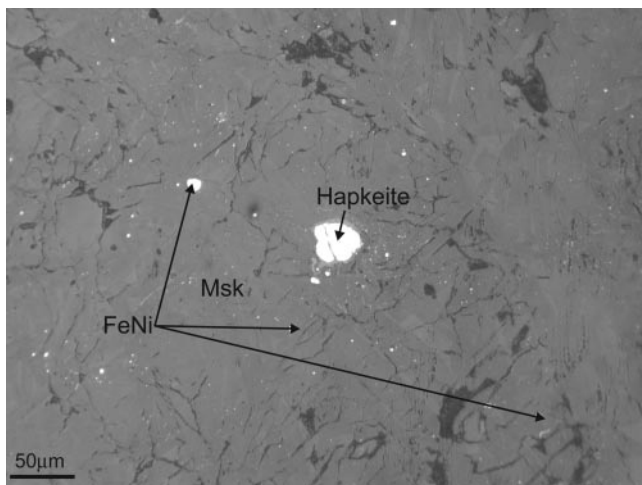
Abbreviation: np-Fe<sup>0</sup>, nanophase elemental Fe<sup>0</sup>.

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<sup>‡</sup>Anand, M., Taylor, L. A., Nazarov, M. A., Shu, J., Mao, H. K. & Hemley, R. J., 34th Lunar Planetary Science Conference, March 17–21, 2003, Houston, 1818 (abstr.).

<sup>§</sup>Anand, M., Taylor, L. A., Patchen, A. D., Cahill J. T. & Nazarov, M. A., 33rd Lunar Planetary Science Conference, March 11–15, 2002, Houston, 1653 (abstr.).

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**Fig. 1.** Reflected-light image of an area in the regolith clast in Dhofar 280, showing distribution of FeNi metal and Fe-Si metal grains in a feldspathic matrix, Msk, Maskelynite.

separate phases. The bigger grain is  $\text{Fe}_2\text{Si}$  in composition (this is the one we have named as hapkeite), whereas the smaller grain is FeSi. Fig. 2 shows backscatter electron and x-ray elemental maps of this grain. In general, >95 wt% of this mineral is composed of Fe and Si, with only minor amounts of Ni, P, and Cr. However, x-ray elemental maps also reveal “hotspots” of Ti and P-rich areas in this grain (4.6 and 15 wt%, respectively). A third iron-silicide,  $\text{FeSi}_2$  in composition, was also discovered in this meteorite (Table 1). This discovery constitutes a previously unreported occurrence of Fe-Si phases in lunar rocks. The FeSi and  $\text{FeSi}_2$  phases have been named previously as fersilicite and ferdisilicite, respectively (6).

**Table 1.** Chemical composition of Fe-Si phases

	$\text{Fe}_2\text{Si}$ (5)*	FeSi	$\text{FeSi}_2$
	hapkeite	fersilicite <sup>§</sup>	ferdisilicite <sup>§</sup>
Wt %			
Fe	75.3 (2) <sup>‡</sup>	65.9	46.1
Si	18.4 (5)	31.1	49.0
Co	0.12 (5)	0.16	0.00
Ni	3.14 (12)	1.27	0.21
P	1.85 (46)	0.30	1.87
Cr	0.37 (5)	0.21	ND <sup>¶</sup>
Total	99.2 (2)	99.0	97.2
At %			
Fe	63.4	50.7	31.3
Si	30.8	47.6	66.2
Co	0.09	0.12	0.00
Ni	2.51	0.93	0.13
P	2.82	0.42	2.30
Cr	0.33	0.17	—
Total	100	100	100

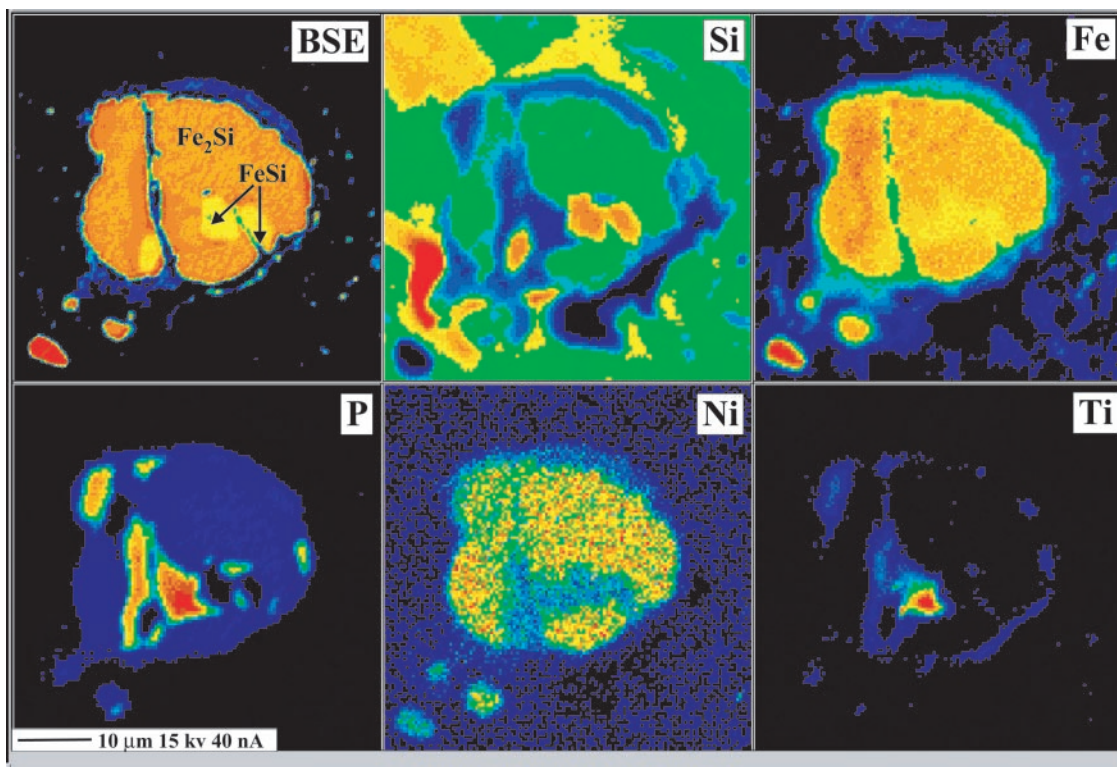
\*Average of five analyses.

<sup>‡</sup>The numbers in parentheses are standard deviations in the last digit.

<sup>§</sup>Ref. 6.

<sup>¶</sup>ND, not determined.

Single-crystal x-ray diffraction study, following the procedure of Chen *et al.* (7), has further established the lattice parameters and cubic structure of the  $\text{Fe}_2\text{Si}$  phase (Table 2). A close resemblance exists between the natural and synthetic  $\text{Fe}_2\text{Si}$  phases (8) and confirms the previously unreported occurrence of mineral hapkeite in a natural sample. It appears from the literature that there is some ambiguity about assigning a crystal structure to the synthetic  $\text{Fe}_2\text{Si}$  phase. It has been suggested to



**Fig. 2.** Backscatter electron (BSE) and x-ray elemental maps of hapkeite. Intergrowths of FeSi phase are seen in the lower part of hapkeite.



**Table 2. Single-crystal data for Fe-Si**

$d_{\text{measured}}$	$d_{\text{calculated}}$	$hkl$	$d_{\text{synthetic}}^{\dagger}$
2.831	2.83	100	2.821
2.000	2.001	110	1.988
1.631	1.634	111	1.625
1.415	1.415	200	1.406
1.267	1.266	210	1.256
1.157	1.155	211	1.149
1.000	1.0005	220	0.9953

Crystal system: cubic

Space group:  $Pm\bar{3}m$  (221)

Cell parameters:

$$a = b = c = 2.831 \text{ (4) \AA}$$

$$\alpha = \beta = \gamma = 90^\circ$$

$$V = 22.69 \text{ (64) \AA}^3$$

Because of the nature of our single-crystal x-ray technique, we do not have accurate intensity data because the x-ray beam covered slightly different areas while rotating the sample.

<sup>†</sup>Ref. 8.

be similar to the CsCl structure, wherein, on first approximation, Fe is thought to occupy one site and  $\text{Fe}_{0.33}\text{Si}_{0.66}$  occupies another site through statistical distribution (8). The possibility of supercell structure is likely with this configuration of atoms, but this will necessitate further refinement of the  $\text{Fe}_2\text{Si}$  structure.

The only other Fe-Si minerals reported previously from meteorites are suessite,  $\text{Fe}_3\text{Si}$ , as described from an ureilite (9) and perryite,  $(\text{Ni,Fe})_5(\text{Si,P})_2$ , in enstatite achondrites (10). In terrestrial rocks, Essene and Fisher (11) reported the occurrence of similar Fe-Si compounds in the glassy areas of Winans Lake fulgurites (lightning-produced fusion products) from southeastern Michigan.

### Formation of Fe-Si Phases

The presence of hapkeite and various other Fe-Si phases in Dhofar 280 indicates extreme reducing conditions, whether on the Moon or on an asteroid. If from a meteorite, these phases may have an origin similar to that postulated by Keil *et al.* (9) and Wasson and Wai (10). FeNi Metal grains in enstatite chondrites are also known to contain up to a few percent of Si (12). Inasmuch as they do occur in a fragmental lunar breccia, such an extralunar origin is possible.

Badjukov\*\* and Badjukov and Petrova<sup>††</sup> conducted experiments on shock effects of hypervelocity impact of iron metal projectiles into a silica target. These authors reported the reduction of  $\text{SiO}_2$  to Si metal accompanied by oxidation of metallic iron to FeO. An appreciable amount of Si (up to 2 wt%) was found dissolved in melted kamacite material. However, the iron-silicide compounds that we have studied in Dhofar 280 contain a significantly larger amount of Si (up to 50 wt%) along with Fe and are dispersed in a feldspathic matrix. Thus, a prohibitively large quantity of Fe-metal-rich meteorite is required for the formation of iron-silicides of the present study. However, the enrichments of Ni and P in the Fe-Si phases can be interpreted as a meteoritic contribution, because lunar rocks are significantly depleted in these elements. Therefore, the presence of extralunar, meteoritic material in the soil is to be expected. However, some indigenous mechanisms are required to explain the formation of iron-silicides in the lunar meteorite, Dhofar 280. It is important to note that the Fe-Si phases in

Dhofar 280 only occur in the lunar regolith-breccia clast that has not undergone significant high-temperature metamorphism subsequent to its initial formation, as witnessed by the abundant, minute Fe-metal grains (<1–2  $\mu\text{m}$ ).

In the Winans Lake fulgurites, Essene and Fischer (11), based on thermodynamic calculations, proposed that temperatures in >2,000 K and reducing conditions approaching those of  $\text{SiO}_2$ -Si buffer were needed to form coexisting metallic and silicate liquids. Furthermore, the thermodynamic data also suggested that coexistence of metallic Si and Fe require strong gradients of up to ten orders of magnitude in terms of oxygen fugacity. Therefore, some transient, ultrahigh-temperature events such as a lightning strike on Earth or impact vaporization of lunar soil are ideal mechanisms for the formation of Fe-Si compounds. In Winans Lake fulgurites, carbon compounds in the form of charred tree roots were found closely associated with the glass containing the Fe-Si compounds. These were believed to have provided a strong-reducing environment conducive to the formation of Fe-Si phases. However, additional mechanisms such as vaporization of oxygen during a boiling process and formation of nitrous oxide gases were also considered to have possibly aided in the overall reduction process. From 50 to 200 ppm of C (13) and similar amounts of H are present in the lunar soil as solar-wind-implanted particles, but this will probably be insufficient to provide strong reducing conditions needed for the formation of Fe-Si phases. Notwithstanding, they may aid in the overall reduction process. Since the impact events on lunar surface may involve temperatures in excess of normal igneous melt temperatures (i.e.,  $\gg 2,000^\circ\text{C}$ ), thermal dissociation of a melt into elemental species can occur in the vapor phase. Subsequent rapid cooling will lead to condensation of Fe-Si compounds in various stoichiometries, as seen in the present case. We suspect that vaporization and condensation may play the dominant role in the formation of iron silicides on the Moon.

We propose a scenario for the indigenous lunar formation of iron silicides that involves melting and vaporization of lunar soil by micrometeorite impact. As mentioned earlier, works of Keller and McKay (5) and Wentworth *et al.* (14) have shown that the surfaces of many lunar-soil particles consist of thin (60–200 nm) patinas and rims. Of the various morphologic types, the inclusion-rich rims contain abundant np- $\text{Fe}^0$  randomly dispersed inclusions or as distinct layers embedded in an amorphous silica-rich matrix. Most of this np- $\text{Fe}^0$  is from the vaporization of FeO from impact-melted soil in which  $\text{Fe}^0$  rapidly condenses onto the surface of soil particles dispersed within the silica-rich glass. Furthermore, a critical observation is that the inclusion-rich rims are compositionally distinct from their host grains and typically contain accumulations of elements, not indigenous to the host (5), and such rims are formed largely by the deposition of impact-generated vapors, with a contribution from the deposition of sputtered ions.

In our opinion, little consideration of the role of  $\text{SiO}_2$  in the vapor phase has been made. We suggest that the  $\text{SiO}_2$  in the vapor dissociates further to  $\text{SiO}^{2+}$  and  $\text{Si}^0$ . Thermodynamic calculations for a transient ultratemperature event (11) have suggested that it is possible that the  $\text{Fe}^0$  in the vapor combines with various proportions of  $\text{Si}^0$ , also in the vapor, and condenses as small Fe-Si grains (Fig. 3). Several experimental investigations studying vaporization processes of lunar samples (15, 16) have demonstrated the occurrence of higher partial pressures of relatively more volatile elements, such as Na, K, O, and Fe, above the melted silicate substrate. These same studies showed that Si also behaves as a volatile element and has significantly higher partial pressures above the silicate melt (16). Since Na, K, and O are highly volatile elements, and since the first two are generally present in very minute quantities in the lunar soil, thermal vaporization essentially causes complete loss of these elements from the lunar atmosphere (e.g.,

\*\*Badjukov, D. D., 21st Lunar Planetary Science Conference, March 12–16, 1991, Houston, pp. 36–37 (abstr.).

<sup>††</sup>Badjukov, D. D. & Petrova, T. L., 22nd Lunar Planetary Science Conference, March 18–22, 1992, Houston, pp. 41–42 (abstr.).

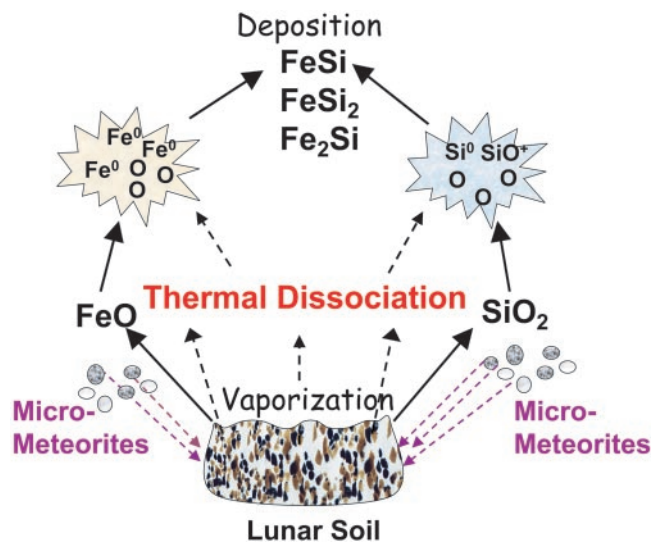


Fig. 3. Cartoon illustrating the formation of iron-silicides on the Moon.

ref. 16). The lower escape velocity on the Moon further facilitates the loss of most volatile species present in the vapor phase. In contrast, Fe and Si (with lesser volatility, i.e., higher sticking coefficient, than Na, K, and O) may recombine from the vapor phase and form various Fe-Si compounds, such as those found in Dhofar 280.

#### Formation of Nano-phase Metallic Fe<sup>0</sup>

To understand the genetic significance of the new Fe-Si phases, we will briefly review the current understanding about the formation of np-Fe<sup>0</sup> in the lunar regolith, because iron silicides and np-Fe<sup>0</sup> may be more closely related in origin than previously thought. In addition, such phases may also play a dominant role on the optical properties of the lunar soil as seen through remote-sensing data.

**Hydrogen Reduction.** The paradigm in lunar science for the past 30 years has been that the abundant np-Fe<sup>0</sup> grains in agglutinitic glass is the result of autoreduction in impact melts (cf., ref. 17), represented by the reaction:



However, several issues with this scenario have not been resolved, such as the lack of evidence for H<sub>2</sub>O in lunar soils, expected as a natural by-product of the supposed hydrogen-reduction reaction of FeO.<sup>§§</sup> In addition, laboratory simulations of space-weathering processes using pulsed laser beams have shown that the presence of H<sup>+</sup> is not a requirement for the formation of np-Fe<sup>0</sup> (18, 19).

**Sputtering and Vapor-Phase Deposition.** Sputtering by solar-wind particles and impact-induced vaporization by micrometeorite impacts are the two other mechanisms that have been implicated in the formation of np-Fe<sup>0</sup> in the amorphous rims of lunar soil grains (e.g., refs. 16 and 20). The relative contributions of the two mechanisms, however, have been contentious<sup>§§</sup> (21, 22). Although the production of amorphous rims on lunar soil grains had long been assumed to be a result of solar-wind irradiation

damage (23), recent investigations using transmission electron microscopy have revealed that rims of soil grains are not homogeneous and contain a variety of different morphologies and chemical compositions (5). It has been shown that vapor deposition on individual soil grains probably plays a major role compared with the solar-wind sputtering and ion damage in producing the ubiquitous patinas and rims that contain silica-rich, amorphous glass with embedded np-Fe<sup>0</sup> (5, 14, 21). Similarly, a larger proportion of the np-Fe<sup>0</sup> signal in the lunar soil, in particular, in the finest size fractions, is attributed to the surface-correlated, vapor-deposited np-Fe<sup>0</sup>, which increases as the surface area to volume ratio increases (24).

Bruce Hapke (20) was the first person to predict the presence of vapor-deposited elemental Fe as coatings on lunar soil grains. However, it took 20 years (21) before this prediction was confirmed. In this vapor-deposition scenario, on impact melting of lunar soil, some silicate melt is also vaporized, selectively releasing its most volatile elements into the vapor phase. Solar-wind sputtering may also play a role in the production of vapor phases. However, the latter mechanism could be potentially more important in the space weathering on asteroid surfaces. In addition to volatile elements such as S, Na, and K, FeO and SiO<sub>2</sub> can also vaporize, where FeO can undergo further dissociation to elemental Fe<sup>0</sup>. Volatilized Fe<sup>0</sup> and SiO<sub>2</sub> condense on the surfaces of many soil particles and form thin, amorphous glass layers that contain np-Fe<sup>0</sup> (5). Moreover, np-Fe<sup>0</sup> occurs on both ferrous-poor and ferrous-rich mineral and silicate-glass grains in near equal proportions (25).

It was the discovery of these np-Fe<sup>0</sup> particles on the rims on most particles of mature lunar soil that has permitted the explanation of the spectral reflectance properties of surfaces on airless bodies, such as the Moon, within the Solar System. Recall that it was Hapke's research team (e.g., refs. 16 and 26) that first suggested the deleterious effects that such space weathering should have on the reflectance spectra of lunar soils. However, it remained for Pieters *et al.* (27, 28) to characterize the effects of the np-Fe<sup>0</sup>, especially in the smallest-size fraction, on the optical properties of lunar soil. The results of the Lunar Soil Characterization Consortium, a group of lunar scientists concentrating on the physical and chemical properties of lunar soils, have provided considerable data that relate the calibration of the spectra of the soils to the ground truth of what is actually in the soils for application to the methods of remote compositional analysis (24, 28, 29).

Thus, if the np-Fe<sup>0</sup> and the new Fe-Si phases are, indeed, the result of impact-produced vaporization of lunar soil components, it is predicted that many of the small, micrometer-sized Fe<sup>0</sup> metal grains occurring in lunar soil may well contain Si<sup>0</sup> and Fe-Si phases.

#### Summary

The existence of np-Fe<sup>0</sup> and Fe-Si phases in a regolith-breccia clast of Dhofar 280 is a signature of space-weathering processes that operate on the lunar surface. The generally accepted view that the majority of the np-Fe<sup>0</sup> forms as a result of impact-generated melting of solar-wind-saturated soils has recently been questioned (30). It has been speculated that the majority of np-Fe<sup>0</sup> and Fe-Si phases were formed by vapor deposition and subsequent reworking of the soil.<sup>¶¶</sup> Similar observations based on Fe isotope studies of lunar soils supports this new paradigm (4). We predict that the Fe-Si phases are more prevalent in lunar soils than originally thought. Discovery of the mineral happeite, and other associated Fe-Si phases in Dhofar 280, highlights the importance of space-weathering processes operating on airless

<sup>§§</sup>Taylor, L.A., Rossman, G.R. & Qi, Q., 26th Lunar Planetary Science Conference, March 13–17, 1995, Houston, pp. 1399–1400 (abstr.).

<sup>¶¶</sup>Bernatowicz, T. J., Nichols, R. H. & Hohenberg, C. M., 25th Lunar Planetary Science Conference, March 14–18, 1994, Houston, pp. 105–106 (abstr.).

<sup>¶¶</sup>Taylor, L. A., The Moon Beyond 2002: Next Steps in Lunar Science and Exploration, September 12–14, 2002, Taos, NM, 3022 (abstr.).

bodies, such as the Moon, and their significance in unraveling spectral reflectance data.

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