The Chemical Reactivity of Lunar Dust Relevant to Human Exploration of the Moon

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I. SUMMARY

As NASA prepares to return to the Moon, a clear understanding of the chemistry of lunar dust is required to set the stage for extended duration lunar surface operations. All aspects of the unique environment of the Moon—micrometeorite bombardment, UV light exposure, solar wind radiation, solar particle event radiation and galactic cosmic radiation—influence the mineralogy of the Moon, and are believed to impart a high degree of chemical reactivity to lunar dust. While the basic structure and composition of lunar dust is well known, little is known about its chemical reactivity, which could have significant implications for astronaut health and *in situ* resource utilization needed for lunar habitat development. This white paper advocates development of a comprehensive effort to understand the chemical reactivity of lunar dust by carrying out a combination of ground based studies, focusing on UV and solar radiation effects on lunar dust, together with development of instrumentation to obtain *in situ* chemical reactivity information.

II. INTRODUCTION AND BACKGROUND

Formation and Composition of Lunar Dust. Lunar regolith, including the fine fraction of lunar dust, is a complex material, formed and modified by continuous micrometeorite impacts on the lunar surface. High velocity impacts induce "shock melting" and cause localized vaporization of lunar regolith which quickly re-condenses, resulting in agglutinates with high surface area, complex shapes, and sharp jagged edges (Figure 1).

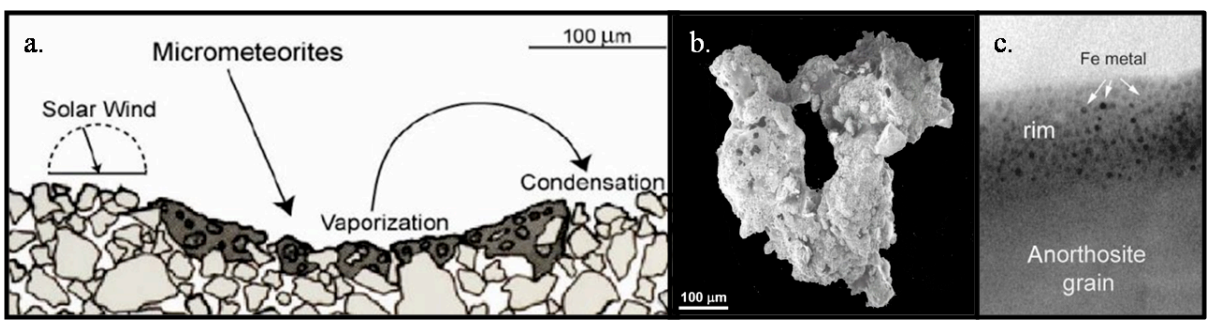

Figure 1. a) Micrometeorites impacts cause shock-melting of lunar regolith, which results in vaporization and re-condensation. b) Particle of lunar regolith showing sharp, jagged edges, as viewed by electron microscopy. c) Lunar dust contains nano-scale size deposits of metallic iron ("nanophase iron"). Images courtesy of Lawrence Taylor and David McKay.

The bulk chemical composition of lunar dust varies across the lunar surface, but is about 50% SiO_2, 15% Al_2O_3, 10% CaO, 10% MgO, 5% TiO2 and 5-15% iron (Table 1), with lesser amounts of sodium, potassium, chromium, zirconium. Trace amounts of virtually all elements, ranging from the ppb level to the ppm level, can be found in lunar dust. The iron component consists of both iron oxide and nanoscale deposits of fully reduced metallic iron (termed "nanophase iron"), the latter being a form of iron not present in terrestrial minerals (Wentworth, 1999).

Apollo Era Studies—Minerology. Immediately after lunar rock and dust samples were returned to Earth from the Apollo era missions, mineralogical characterization, physical/mechanical characterization and chemical analysis of these samples were carried out. Minerological studies revealed that lunar rock consists of pyroxene, plagioclase, ilmenite, olivine, with rare grains of

cristobalite, tridymite, chromite kamacite, taenite and trolite (Agrell, 1970). Analysis of lunar fines (down to the micron size range) revealed an increasing proportion of glassy material with smaller particle size, consistent with the understanding that lunar regolith undergoes shock-melting as a result of micrometeorite bombardment.

Sample	SiO_2	Al_2O_3	TiO_2	FeO	MgO	CaO	Na_2O	K_2O	MnO
Lunar: 10019	41.1	13.7	8.25	15.7	7.86	11.9	0.93	0.14	0.22
Lunar: 10022	43	13	7	16	8	12	0.54	0.12	0.23
Lunar: 70161	40.34	11.6	8.99	17.01	9.79	10.98	0.32	0.08	0.23
Lunar: 64501	53.63	12.77	3.47	13.37	3.57	9.2	0.73	1	0.2
Lunar: 14053	48	12	1.5	16	8.4	12	0.38	0.14	0.29

Table1. Major chemical constituents of lunar dust.
The metal content is arbitrarily designated as the metal oxide.

Apollo-Era Studies—Ultraviolet Light Exposure. Lunar scientists of the Apollo era recognized that a full understanding of the chemistry of lunar dust required an understanding of UV and other radiation effects on lunar dust. Indeed, several key experiments were carried out, shortly after the first Apollo specimens were returned to Earth. Exposure to UV light (xenon-mercury lamp), for instance, caused changes in the optical properties of lunar dust (reflectance spectra, absorption spectra), possibly related to changes in the oxidation state of iron (Hapke, 1970). Control experiments in which lunar dust was heated only (without UV light exposure) revealed no changes in the optical properties of lunar dust (Hapke, 1970). Additional studies of energetic photon effects done with X-rays showed that the absorption spectrum was affected in the 4.5 eV energy range of the spectrum, again suggesting changes in iron chemistry. Some reversibility of these changes was documented by re-examination of these specimens many hours after x-radiation was carried out, although detailed passivation studies were not performed.

Apollo-Era Studies—Solar Wind Radiation. Irradiation of Apollo 11 lunar dust samples with low energy protons, to mimic the solar wind, resulted in changes in the visible and IR reflectance spectrum, indicating changes in the chemistry of lunar dust, of similar magnitude to the effects of UV exposure (Hapke, 1970).

Apollo-Era Samples – Today. As documented by Grossmen in 1970 the vacuum seals of the sample containers containing pristine Apollo 11 lunar dust sample leaked. This information and similar reports from other scientists have raised a concern of the pristine nature of the lunar samples, especially for the purposes of chemical reactivity and toxicity analysis. Efforts to "reactivate" lunar dust are clearly necessary.

Pulmonary Toxicity Studies—LADTAG. In preparation for the return of astronauts to the Moon, the Lunar Airborne Toxicity Assessment Group (LADTAG) is working to characterize the pulmonary toxicity of lunar dust, which is widely recognized to constitute the number one risk to the health of astronauts related to lunar dust. From studies of silica toxicity (human epidemiological studies, mineral chemistry studies and animal studies), it is well recognized that chemical reactivity plays a key role in the toxicity of crystalline silica (Porter, 2002; Shoemaker, 1995; Fubini, 2003). Freshly-fractured silica, which can be created by certain dry-mining

operations causes a particularly severe form of silicosis, *acute silicoproteinosis* (Shoemaker, 1995). Patients with *acute silicoproteinosis* develop a lipid rich protein accumulation in the alveoli, which is fatal within several months to a few years. In this form of the disease, as in conventional silicosis, activation of lung macrophage cells and lung epithelial cells by surface radicals on the mineral surface is believed to be of central importance, followed by generation of macrophage-derived reactive oxygen species, which cause further inflammation, eventual scarring (fibrosis) and impairment of gas exchange within the lungs. Surface radicals are believed to interact with water and/or oxygen to produce hydroxyl radicals, superoxide anions and possibly hydrogen peroxide to trigger these processes. Indeed, fresh-fractured silica, which is more potent at generating aqueous radicals, causes the most potent form of silicosis (Fubini, 2003). This mechanism is likely to be important for lunar dust because of its high concentration of silica. The fact that most of the lunar dust silica is glassy (non-crystalline), remains an unknown factor for the topic of biotoxicity, and, potentially for non-biological aspects of chemical reactivity. LADTAG recognizes that an understanding of the chemical reactivity of lunar dust—and in particular, how the lunar environment affects the chemical reactivity—is important for a comprehensive assessment of lunar dust pulmonary toxicity.

III. RATIONALE AND OBJECTIVES

Basic studies conducted during the Apollo era indicate that the lunar radiation environment affects the chemistry of lunar dust. These fundamental processes are also revealed by studies of analog materials, including terrestrial minerals and Martian soil (Viking and Phoenix missions). Because work that started in the Apollo era was never completed, large gaps in our understanding of the chemical reactivity of lunar dust remain. The work advocated by this white paper would seek to fill these gaps.

Overall Goal: ***To carry out a comprehensive study of the chemical reactivity of lunar dust, focused on the effects of Moon-relevant radiation, to support NASA's plans for human exploration of the Moon.***

Objective #1: *To characterize the effects of UV irradiation on the chemical reactivity of lunar dust.* Recent data suggests that UV wavelengths down to the Lyman-Alpha line can change the chemistry of lunar dust (Abbas, 2007; Tranfield, 2009).

Objective #2: *To characterize the effects of solar radiation on the chemical reactivity of lunar dust.* Solar protons represent the largest fluence of particle radiation incident on the Moon, and may alter the surface chemistry of lunar dust.

Objective #3: *To characterize the effects of solar particle event radiation on the chemical reactivity of lunar dust.* Episodic solar particle events, which deliver brief, high exposure of energetic protons to the lunar surface, may result in changes to the surface chemistry of lunar dust, above and beyond that caused by other radiations.

Objective #4: *To characterize the effects of galactic cosmic radiation on the chemical reactivity of lunar dust.* Constant bombardment of the lunar surface by high energy protons and heavy ions may have an effect on the chemical reactivity of lunar dust, above and beyond the effects of lower energy, higher fluence radiation, and should be studied along with other radiation effects.

Objective #5: *To develop a small lightweight instrument for determining the chemical reactivity of lunar dust in situ.* A payload for determining the *in situ* chemical reactivity of lunar dust would validate ground-based studies of lunar dust chemical reactivity. Such an instrument could be part of a lunar precursor mission or be used as an astronaut-deployed device for characterizing lunar dust at sortie and habitat sites, as part of a comprehensive lunar exploration program.

IV. APPROACHES

Objectives #1 and #2: To support a comprehensive examination of UV radiation and solar wind effects on lunar dust, development of a vacuum chamber with the capability for delivering simulated solar wind radiation (1-3keV protons) and full-spectrum UV radiation would be appropriate. One such device is conceptualized in Figure 2. The concept is to closely mimic lunar conditions including the deep vacuum of the Moon (10 –12 torr), a wide range of temperatures, and UV radiation and solar wind protons, both singly and in combination.

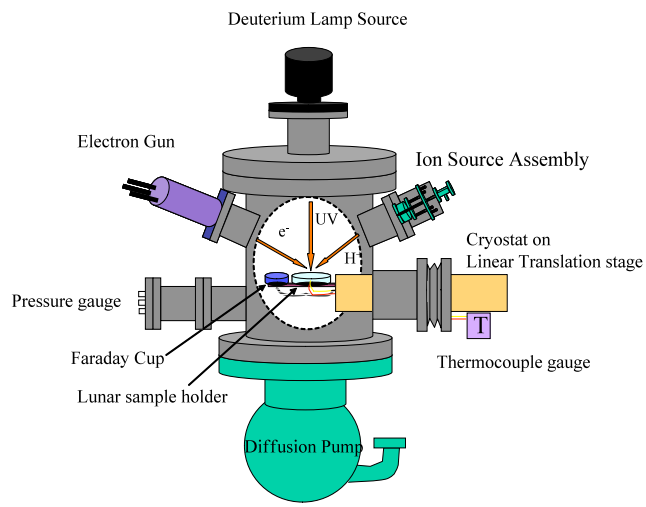

Figure 2. Conceptual Solar Wind and UV Exposure Test Chamber. An ion pump will simulate the hard vacuum of the Moon, and a thermal control system will allow a wide range of lunar-relevant temperatures to be examined. The lunar dust samples will be agitated to achieve "mixing," to ensure that all surfaces are exposed to the solar wind. The set-up includes independent sources for subjecting the lunar soil to photons, electrons, and hydrogen ions under solar wind conditions. The chamber is of high vacuum construction and capable of operation at pressures as low as 10^{-10} torr. An ion gun assembly ionizes molecular hydrogen and accelerates it to energies between 0.3 and 3 keV. A velocity discriminator within the assembly removes H_2^+ and H_3^+ ions so that the beam produces an ion flux composed entirely of protons. An electron flood gun would provide electron flux in the range of 50-1500eV, comparable to solar wind, and would neutralize charging from the ion beam. UV Photon flux could be provided by a deuterium lamp, coupled by a magnesium fluoride window, to permit studies of deep UV wavelengths

Analytical Modalities. In order to evaluate the effects of UV exposure and solar wind exposure, a number of analytical modalities could be employed, as described below.

1) Fourier Transform-Infrared Spectroscopy. Provides detailed information about changes in the chemistry of lunar dust, after exposure to radiation. Can be directly coupled to the vacuum chamber, to permit monitoring during the process of radiation exposure, as well as monitoring of time-dependent decay of activated states after radiation/UV exposure is turned off.
2) GC/MS. A useful tool for analysis of gases that may be introduced into the irradiation chamber after lunar dust specimens are irradiated. The interaction of habitat gases with lunar dust may have implications for habitat design.

3) Electron Spin Resonance (ESR). For evaluation of free radicals (dangling bonds) that may be generated by lunar dust radiation. By analogy to silica, free radicals may be of particular importance for lunar dust pulmonary toxicity. ESR has been used successfully to demonstrate free radicals in silica, which correlate with increased toxicity.
4) Terephthalate Assay (TA). The application of the TA for characterization of lunar dust chemical reactivity was pioneered by Drs. Wallace and Jeevarajan at JSC (Wallace, 2009). TA measures hydroxyl radical generation when lunar dust is exposed to water.
5) Calorimetry. Calorimetry is a valuable tool for determining enthalpies of reactions between two or more chemicals, and may be especially helpful for characterization of reactions between lunar dust and habitat gases (oxygen, nitrogen, water, etc.).
6) Thin-film technology. Thin-film technology uses metals with adsorbed surfaces for detecting specific types of chemical reactions, and, in some cases, may provide information that is complementary to more conventional chemical analyses.

Objective #3: *To characterize the effects of solar particle event radiation on the chemical reactivity of lunar dust.*

To study the effects of solar particle event radiation on the chemical reactivity of lunar dust, we would advocate using the Loma Linda University synchrotron facility. This NASA funded facility provides protons at energies up to 250MeV, and can simulate solar particle events. By using a mechanical energy modulation system reduced proton energies (mimicking the lower-energy component of the SPE-spectrum) can be supplied to the target sample. The strategy is to move rapidly from one energy level to the next, in 10MeV increments, so that the full energy spectrum of SPE protons can be delivered. The system can be thought of as a multiplexing system that provides a time-averaged "solar particle event" proton radiation of the correct energy spectrum. To carry out irradiations under vacuum conditions, the mineral specimen can be placed in a section of beam-line tubing, with a special window to admit the proton radiation. Once radiation exposure is complete, the section of beam-line tubing can be removed from the beam-line, with vacuum maintained, so that the specimen can be transported back to other facilities for analysis. No charge for beam time for NASA-funded investigators.

Objective #4: *To characterize the effects of galactic cosmic radiation (GCR) on the chemical reactivity of lunar dust.*

The fluence of GCR is lower than the solar radiations, but it is highly penetrating, and can alter the structure and potentially the chemistry of lunar dust. Apollo studies, for example show clear evidence of particle tracks, with associated local disruption of grain structure. The NASA Space Radiation Laboratory at Brookhaven National laboratory can deliver GCR protons and high Z, high E (HZE) particles, so that the effects of these types of radiation on lunar dust can be studied.

Figure 3. The beam line at the NSRL is suitable for irradiation of mineral specimens.

Objective #5: *To develop a small lightweight instrument for determining the chemical reactivity of lunar dust in situ.*

The ground-based studies outlined in this white paper would provide information about the types of chemical reactivity that lunar dust may exhibit, as a result of the lunar radiation environment. A valuable extension of these ground-based studies would be the development of a small lightweight instrument that could be carried to the Moon to analyze the *in situ* chemical reactivity of lunar dust. The instrument will use one or two of the analytical modalities described above to 1) determine the chemical reactivity of pristine lunar dust, and 2) to determine the passivation rate of the chemically reactive state upon exposure to a habitat-like environment. To accomplish these goals, the instrument would need to collect a small sample of lunar material; divide the sample into fractions with similar particle size and mass; contain the experiment in a pressurized compartment for a duration of 24 – 48 hours and, ultimately, communicate the data back to Earth.

IV. IMPLICATIONS AND SYNERGIES

A comprehensive understanding of the chemical reactivity of lunar dust is critical to support a sustained human presence on the Moon. The most immediate benefit of these studies would be to improve the evaluation of the pulmonary toxicity of lunar dust. By using activated lunar dust that most closely matches *in situ* activation, LADTAG scientists will be able to perform follow-on animal experiments that yield more accurate toxicity estimates.

The implications of lunar dust chemical reactivity extend well beyond the field of human health. Virtually all scenarios for an extended presence on the Moon call for the use of lunar regolith and lunar dust as a resource to support the development of an outpost. Applications may include the use of lunar dust to support the growth of edible plants, to support the development of bioregenerative life support systems and other closed-loop systems, and to pave the way for bio-geoprocessing applications. In some cases, the chemical reactivity of lunar dust may be an asset, which can be exploited to carry out beneficial chemical reactions. Lunar dust particles, with their high surface area and structural inhomogeneities, may serve as catalysts to support gas-phase or liquid-phase chemistry applications.

Finally, an understanding of the chemical reactivity of lunar dust will provide fundamental geoscience knowledge that may help us to understand other airless planetary bodies, such as near-Earth asteroids and other moons.

V. REFERENCES

Abbas, M.M., D. Tankosic, P.D. Craven, J.F. Spann, A. LeClair, E.A. West, 2007. Lunar dust charging by photoelectric emissions. Planetary and Space Science, vol. 55, issues 7-8, p. 953-965.

Agrell, S. O., Scoon, J. H., Muir, I. D., Long, J. V., McConnell, J. D., Peckett, A., 1970. Mineralogy and petrology of some lunar samples, science 30, vol. 167. no. 3918, p. 583-586.

Fubini, B., Hubbard, A., 2003. Reactive oxygen species (ros) and reactive nitrogen species (rns) generation by silica in inflammation and fibrosis. Free Radical Biology & Medicine, vol. 34, no. 12, p. 1507–1516.

Grossman, J. J., Ryan, J. A., Mukherjee, N. R., and Wegner, M. W., 1970. Surface properties of lunar samples, Science 30, vol. 167. no. 3918, p. 743-745.

Hapke B. W., Cohen, A. J., Cassidy, W. A., and Wells, E. N., 1970. Solar Radiation Effects in Lunar Samples. Science 30, Vol. 167. no. 3918, pp. 745 – 747.

Porter, D. W., Barger, M., Robinson, V. A., Leonard, S. S., Landsittel, D., and Castranova, V., 2002. Comparison of low doses of aged and freshly fractured silica on pulmonary inflammation and damage in the rat. Toxicology 175, 63–71.

Shoemaker, D.A., Pretty, J.R., Ramsey, D.M., McLaurin, J.L., Khan, A., Teass, A.W., Castranova, V., Pailes, W.H., Dalal, N.S., Miles, P.R., et al., 1995. Particle activity and in vivo pulmonary response to freshly milled and aged alpha-quartz. Scand J Work Environ Health, 21 Suppl 2:15-8. Press, New York.

Tranfield, E., J. C. Rask, W. T. Wallace, C. McCrossin, K. Kuhlman, D. Loftus, 2009. Chemical activation of lunar dust specimens and simulants, NASA Lunar Science Institute conference, abstract and poster.

Wentworth, S.J., Keller, L.P, McKay, D.S., Morris, R.V., 1999. Space weathering on the moon: patina on Apollo 17 samples 75075 and 76015, Meteor Planet Sci, 34,593-603.