Title

Catalyst: Radiation Effects on Volatiles and Exploration of Asteroids and the Lunar Surface

Journal

Chem, 4(1)

ISSN

1925-6981

Authors

Orlando, Thomas M
Jones, Brant
Paty, Carol
et al.

Publication Date

2018

DOI

10.1016/j.chempr.2017.12.004

Chem

CellPress

CATALYSIS

Catalyst: Radiation Effects on Volatiles and Exploration of Asteroids and the Lunar Surface

Thomas M. Orlando,[1,2,*]
Brant Jones,[1] Carol Paty,[3]
Micah J. Schaible,[1]
John R. Reynolds,[1]
Phillip N. First,[2]
Stephen K. Robinson,[4]
Valeria La Saponara,[4]
and Esther Beltran[5]

Prof. Thomas Orlando is currently a professor in the Georgia Institute of Technology (GIT) School of Chemistry and Biochemistry and an adjunct professor in the GIT School of Physics. He serves as director of the GIT Center for Space Technology and Research and as principal investigator (PI) of the NASA Solar System Exploration Research Virtual Institute Center on Radiation Effects on Volatiles and Exploration of Asteroids and Lunar Surfaces (REVEALS). Prof. Carol Paty and Dr. Esther Beltran are deputy PIs, and Dr. Brant Jones and Prof. Stephen Robinson are science theme leaders. Orlando, Jones, Paty, and Schaible focus on understanding radiation effects on the regolith and the solar-wind formation of volatiles. Profs. Valeria La Saponara, John Reynolds, and Robinson focus on mitigating health risks by developing nanocomposites for spacesuits and habitats. Prof. Phillip First explores 2D materials for radiation detection. Collectively, the efforts will help facilitate future human exploration of near-Earth destinations.

Recent space-exploration missions to a number of solar-system objects, including the Moon, Mars, Mercury, and near-Earth asteroids (NEAs), have revealed a wide variety of physical conditions that give rise to a diverse assortment of chemical environments and molecules. Because some of these objects are currently under consideration by NASA as strategic destinations for future human exploration missions, a more complete description of their respective surface conditions is desirable for mitigating human risk factors and determining the availability of *in situ* resources. Without an appreciable atmosphere, each of these potential destinations is constantly being bombarded by radiation from solar wind, galactic cosmic rays, and hypervelocity micrometeorite impacts from local (circumplanetary) or interplanetary sources.[1] Ionizing radiation (IR) and micrometeorite impactors can deposit, transport, alter, and even produce volatiles, such as water and methane, in the surface materials of such bodies. Relevant to possible human exploration of these airless bodies, IR is known to produce DNA damage that is most likely linked to cancer susceptibility, neurodegenerative disorders, developmental abnormalities, inflammatory responses, and accelerated and/or premature aging.[2] Thus, the constant radiation assault presents obvious life-threatening and program-limiting health risks for humans, and these must be understood, quantified, and mitigated by the development of effective shielding materials, real-time radiation-detection systems, and radiation-hardened human habitats and spacesuits. Given that ionization and the inelastic scattering of secondary low-energy electrons (LEEs) contribute significantly to radiation damage in materials and living cells,[3] the use of nanoscale and 2D materials that scavenge LEEs effectively is required for both monitoring and mitigating IR damage.

IR and micrometeorite bombardment of airless bodies can produce volatile resources for *in situ* utilization during an extended human mission. As shown in Figure 1, surface processing of solar-system bodies lacking protective atmospheres or magnetospheres—more generally referred to as space weathering—occurs when photon or charged-particle radiation and meteorite impacts modify the chemical and physical makeup of the dust, rocks, and ice that constitute the uppermost layer of the surface, called the regolith. If the incoming projectile is an electron, photon, or light ion, the energy deposition is primarily via electronic excitations and can lead to the breaking and rearrangement of chemical bonds and the removal of surface species through a process generally referred to as electronic sputtering. The interaction between solar protons and the regolith can lead to implantation, reactive scattering, and possibly the production of simple volatiles (e.g., water and methane). These, along with additional volatiles deposited by cometary or meteorite impacts, can be trapped and sequestered in the near-surface and polar regions of the lunar and NEA surfaces. The presence of significant abundances of water and methane would provide invaluable *in situ* resources for future human exploration missions.

Studies pertaining to the physical interaction of water have directly measured the binding energy and sticking probability on the lunar regolith and determined that the rate of water thermal desorption is high, such that only a small distribution of molecules have binding energies greater than the interactions expected from a traditional multilayer ice system. A simple Arrhenius model using the measured binding energies has revealed that molecular water will not persist on the sun-lit side of the Moon over a lunar day even at high latitudes (areas of less solar flux) as a result of high

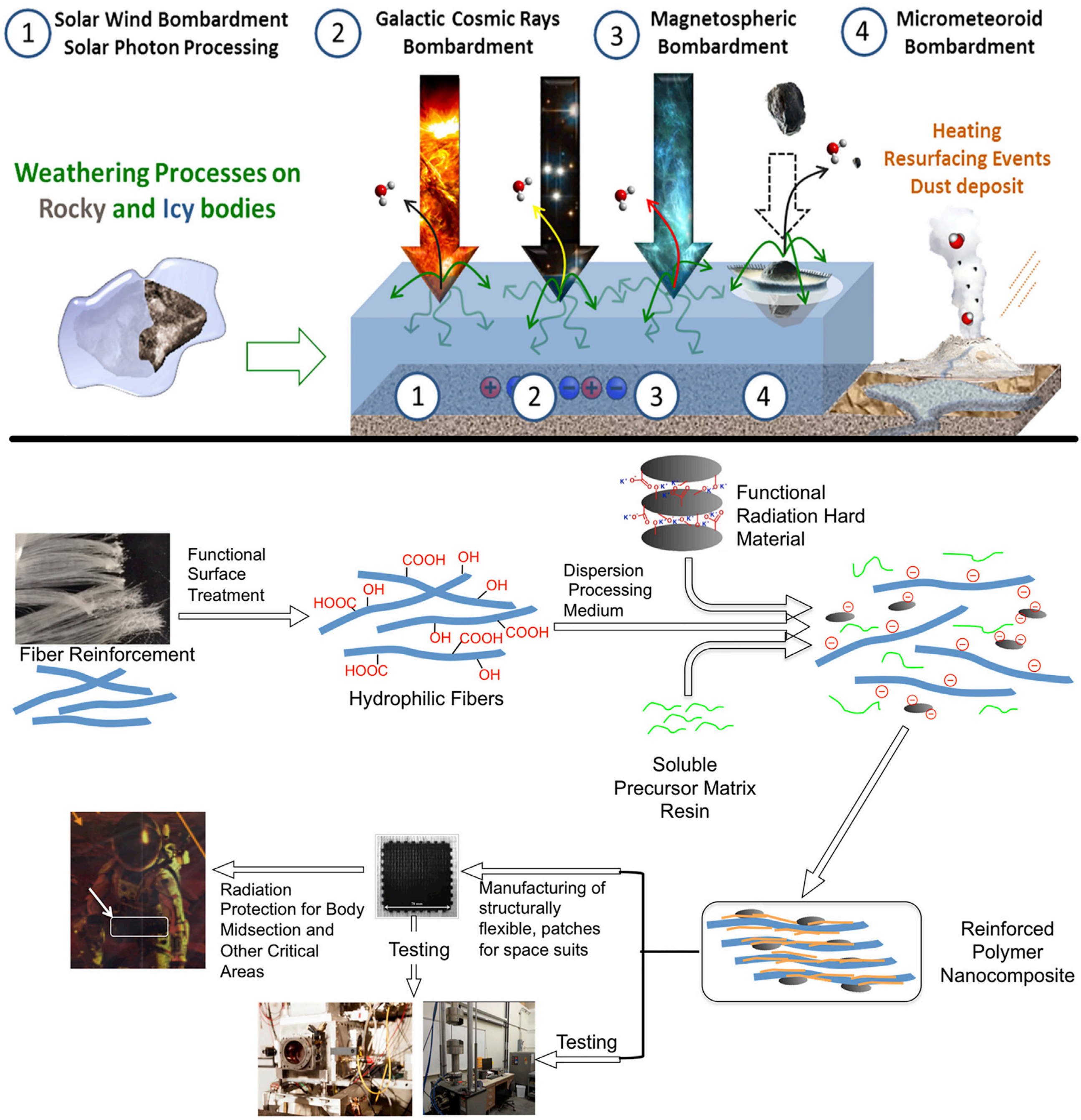

Figure 1. Overview of Research to Be Conducted by the REVEALS Investigation Team

(Top) Primary mechanisms of space weathering within the solar system; these include bombardment with solar wind, galactic cosmic rays, magnetospheric particles, and micrometeoroids. The formation of water and methane on airless bodies via solar wind will be investigated. Adapted with permission from Bennett et al.[1] Copyright 2013 American Chemical Society.

(Bottom) Process of forming and testing fiber-reinforced polymer nanocomposites as spacesuit patches with potential electrical conductivity, thermal conductivity, and radiation-hardness control.

thermal-desorption rates.[4] This impedes the buildup and persistence of surficial water on the sun-lit side of the Moon surface and on the surfaces of airless bodies whose temperatures exceed 150 K.

The interaction between electrons and photons and the regolith leads to electron-stimulated desorption and photon-stimulated desorption, respectively. These are known to contribute to the Moon glow and the migration of volatiles. Additionally, photoelectron emission tends to cause the day-side surface to charge positively, whereas solar-wind electron absorption on the night side leads to a negative charge buildup. In regions of obstructed plasma flow, such as the trailing plasma wake behind a body and within terminator craters, the solar-wind ion trajectories are diverted into the wake region via large negative potentials that develop across the plasma-void boundary.[5] This wake E-field makes surfaces charge even more strongly negative in relation to the unaltered plasma flow.[6] In unobstructed regions, the solar-wind plasma interacts directly with the surface. Experimental work has shown that interactions between the ~keV H^+ ions (protons) and the lunar regolith simulant can produce chemically bound hydroxyl (–OH), thus suggesting a potential solar-wind-induced formation mechanism for water precursors.[7] The chemically bound –OH groups cannot dissociate and recombine to form water, hydrogen, etc., under normal thermal conditions as a result of the high activation barrier. However, it has been demonstrated that molecular water is released from minerals with saturated –OH terminal sites and defects at high temperatures. This occurs by a process known as recombinative or associative desorption and involves the thermally activated reaction of two –OH groups that are in close proximity to one another. This reaction produces and releases water while healing the defect caused by the missing oxygen atom. In addition, the process can also result in the formation of molecular hydrogen, particularly if one of the neighboring defect sites is a hydride. Recombinative desorption in silicates typically requires a temperature of at least 450 K, well above the ambient temperature of the sun-lit side of the Moon or the surfaces of NEAs. Only regolith or minerals containing certain metal oxides (i.e., TiO_2, Fe_2O_3, etc.) allow recombinative desorption below 450 K. Thus, under the thermal conditions of lunar and NEA surfaces, recombinative desorption from minerals containing mostly silicates does not contribute significantly to the formation of water. However, during meteorite impacts, the temperature of the regolith can locally reach $\sim 10^4$ K depending on the velocity of impact, thus driving recombinative desorption and the formation of simple volatiles, such as water and methane.

The lunar surface is known to contain a wide range of organic molecules. Methane has been observed within both the lunar regolith[8] and the lunar exosphere.[9] More complex organics have also been observed *in situ* by the Lunar Crater Observation and Sensing Satellite (LCROSS), which detected infrared absorption bands attributed to various saturated hydrocarbons.[10] Even the ubiquitous tar resulting from the radiolysis of organic molecules has been detected in the lunar regolith.[11] How these molecules came to be under such harsh and isolated conditions is a question that has yet to be answered definitively. The delivery of organics via meteorites and interplanetary dust particles seems reasonable given the frequency of impacts on the Moon[12] and the fact that extraterrestrial organics have been identified on a variety of meteorites. Additionally, experiments have shown that large complex organics can be formed upon the energetic processing of volatile ice mixtures,[13] and a parallel avenue for production could be the exposure of ices to ionizing radiation in the form of galactic cosmic rays. As pointed out recently,[14] galactic cosmic rays will easily deposit 10 eV per molecule within a relatively (geologically) short time into the ices (water, carbon monoxide, and methane) that exist in the permanently shadowed regions of the Moon. Lastly, volatiles such as methane could have been produced during the period of lunar geological activity through a Fischer-Tropsch-type process via the conversion of carbon monoxide and hydrogen gas into saturated hydrocarbons. However, the relative importance of the different formation mechanisms for organic molecules on the surfaces of airless bodies is largely unknown.

In addition to needing *in situ* resources, human exploration missions beyond near-Earth orbit require a validated approach to addressing astronaut health risks due to radiation. Most human experience in spaceflight has been in low Earth orbit (LEO)—in fact, only about 0.5% of total human spaceflight time has occurred beyond LEO, during the Apollo lunar missions. In these future operations, real-time radiation monitoring will be especially critical given that astronauts can be far from radiation shelter in the event of a dynamic solar event. Now, with six decades of LEO experience behind us, planning for long-duration missions beyond LEO is a national priority. One of the chief technical barriers to feasible distant-destination missions by humans is space radiation and the ability to predict and monitor the radiation absorbed by astronauts on a real-time and mission-integrated basis. Although the deep-space radiation environment is reasonably well characterized, radiation-protection materials for human habitats and spacesuits have not been fully developed or characterized, and real-time radiation monitors remain in their infancy. For example, several types of real-time radiation monitors currently utilized on the International Space Station have produced inconsistent results, and they are not integrated with spacesuits.

Current spacesuit designs have single-function layers—including pressure garments, air bladders, and restraint layers—along with thermal cooling, insulation, and micrometeoroid protective layers. These multilayer laminates limit the astronauts' dexterity. Moreover, radiation protection is limited to short-term exposure within a protective environment (Earth's magnetic field) and is therefore not adequate for human exploration missions beyond near-Earth orbit. New materials to facilitate and improve radiation protection are an essential component of being able to work and live safely in a deep-space environment. Design drivers of novel spacesuits should therefore include multifunctional, lightweight materials with optimal mobility and flexibility, robust radiation protection, and high durability, as well as provide special protection for particularly vulnerable human organs and engineering systems for critical operability. In light of these requirements, materials composed of a polymer-matrix composite reinforced with a combination of materials that control mechanical integrity, electrical properties, and radiation hardness are being developed and tested within the NASA Radiation Effects on Volatiles and Exploration of Asteroids and Lunar Surfaces (REVEALS) program. This process, shown schematically at the bottom of Figure 1, demonstrates how a processable resin matrix precursor can be combined with modified fibers and fillers that incorporate electrical transport and radiation protection. The process uses fiber surface functionality to control polarity and induce strong bonding interactions at material interfaces during processing. These interactions will utilize the ability of polar filler materials to be formed directly into composites. Ultimately, these composite materials will be formed into flexible sheets and patches that can bring multifunctionality to spacesuit applications.

All human extraterrestrial missions will benefit from improvements in, and development of, new radiation-detection technologies in order to provide essential redundancy. Recent studies have dedicated special attention to the exposure of the human central nervous system to radiation because of its effects on human performance, cognitive effects, and late degenerative tissue processes. In addition to the development of new spacesuit materials, new 2D and topological materials for portable, organ-specific radiation-detection devices are needed. The quickest approach involves optimizing an existing graphene field-effect transistor and determining the device suitability for both pulse-counting and passive radiation detection. In parallel, changes in electronic properties and electrical conduction, which are induced by the irradiation of 2D and topological materials, will be monitored. Technologically advanced 2D materials, such as graphene, will be used for creating a prototype device and associated methodologies. The technological path established by this prototype will be leveraged for other promising materials, resulting in a reduction of the risk of human radiation exposure for missions beyond near-Earth orbit.

In summary, experimental and theoretical efforts to address solar-wind irradiation and micrometeorite bombardment will reveal a level of detail regarding radiation processing and space weathering of the Moon, Phobos, Deimos, and NEA surfaces necessary for future human mission planning. To date, no program has systematically examined all of the non-thermal channels related to radiation processing of these human exploration targets. Moreover, human radiation risks and mitigation approaches for long-duration deep-space missions are only partially understood and are the subject of a variety of ongoing and long-term NASA and international-partner studies. Therefore, focused efforts should also be on the development and testing of new 2D materials, active radiation dosimetry, and the operationally practical integration of these results into extravehicular-activity spacesuits and crewed vehicle mobility on distant surfaces.

ACKNOWLEDGMENTS

Radiation Effects on Volatiles and Exploration of Asteroids and Lunar Surfaces (REVEALS) is supported by the NASA Solar System Exploration Research Virtual Institute cooperative agreement number NNH16ZDA001N.

1. Bennett, C.J., Pirim, C., and Orlando, T.M. (2013). Space-weathering of solar system bodies: a laboratory perspective. Chem. Rev. *113*, 9086–9150.
2. Hoeijmakers, J.H.J. (2009). DNA damage, aging, and cancer. N. Engl. J. Med. *361*, 1475–1485.
3. Alizadeh, E., Orlando, T.M., and Sanche, L. (2015). Biomolecular damage induced by ionizing radiation: The direct and indirect effects of low-energy electrons on DNA. In Annual Review of Physical Chemistry, *Volume 66*, M.A. Johnson and T.J. Martinez, eds. (Annual Reviews), pp. 379–398.
4. Poston, M.J., Grieves, G.A., Aleksandrov, A.B., Hibbitts, C.A., Dyar, M.D., and Orlando, T.M. (2015). Temperature programmed desorption studies of water interactions with Apollo lunar samples 12001 and 72501. Icarus *255*, 24–29.
5. Halekas, J., Bale, S., Mitchell, D., and Lin, R. (2005). Electrons and magnetic fields in the lunar plasma wake. J. Geophys. Res. Space Phys. *110*, A07222.
6. Farrell, W., Stubbs, T., Halekas, J., Killen, R., Delory, G., Collier, M., and Vondrak, R. (2010). Anticipated electrical environment within permanently shadowed lunar craters. J. Geophys. Res. Planets *115*, E03004.
7. Schaible, M.J., and Baragiola, R.A. (2014). Hydrogen implantation in silicates: the role of solar wind in SiOH bond formation on the surfaces of airless bodies in space. J. Geophys. Res. Planets *119*, 2017–2028.
8. Abell, P.I., Eglinton, G., Maxwell, J.R., Pillinger, C.T., and Hayes, J.M. (1970). Indigenous lunar methane and ethane. Nature *226*, 251–252.
9. Hodges, R.R. (2016). Methane in the lunar exosphere: Implications for solar wind carbon escape. Geophys. Res. Lett. *43*, 6742–6748.
10. Neish, C.D., Bussey, D.B.J., Spudis, P., Marshall, W., Thomson, B.J., Patterson, G.W., and Carter, L.M. (2011). The nature of lunar volatiles as revealed by Mini-RF observations of the LCROSS impact site. J. Geophys. Res. Planets *116*, E01005.

11. Thomas-Keprta, K.L., Clemett, S.J., Messenger, S., Ross, D.K., Le, L., Rahman, Z., McKay, D.S., Gibson, E.K., Gonzalez, C., and Peabody, W. (2014). Organic matter on the Earth's Moon. Geochim. Cosmochim. Acta *134*, 1–15.

12. Speyerer, E.J., Povilaitis, R.Z., Robinson, M.S., Thomas, P.C., and Wagner, R.V. (2016). Quantifying crater production and regolith overturn on the Moon with temporal imaging. Nature *538*, 215–218.

13. Herbst, E. (2017). The synthesis of large interstellar molecules. Int. Rev. Phys. Chem. *36*, 287–331.

14. Crites, S., Lucey, P., and Lawrence, D. (2013). Proton flux and radiation dose from galactic cosmic rays in the lunar regolith and implications for organic synthesis at the poles of the Moon and Mercury. Icarus *226*, 1192–1200.

[1]School of Chemistry and Biochemistry

[2]School of Physics

[3]School of Earth and Atmospheric Sciences

Georgia Institute of Technology, Atlanta, GA, USA

[4]Department of Mechanical and Aerospace Engineering, University of California, Davis, Davis, CA, USA

[5]Florida Space Institute, Orlando, FL, USA

*Correspondence:
thomas.orlando@chemistry.gatech.edu

http://dx.doi.org/10.1016/j.chempr.2017.12.004

CATALYSIS

Reaction: Chemistry Driven by the Harsh Space Environment

William M. Farrell[1,*]

Dr. Bill Farrell is a plasma physicist at NASA's Goddard Space Flight Center. He is a co-investigator on the Cassini mission to Saturn and the Parker Solar Probe mission. He is also principal investigator of the DREAM2 Center for Space Environments (http://ssed.gsfc.nasa.gov/dream/), which examines the exosphere formation, radiation effects, and plasma interactions of the Moon and other airless bodies. Dr. Farrell has authored or co-authored over 200 journal articles on various aspects of space science, including the hydroxylation at the Moon, the curious plasma effects within the Enceladus plume, and the possibility of electricity generated in Martian dust devils.

Orlando et al.'s description of the exciting REVEALS (Radiation Effects on Volatiles and Exploration of Asteroids and Lunar Surfaces) program highlights a new opportunity to garner a further understanding of the surface chemistry that occurs on exposed airless bodies such as the Moon and asteroids. As described therein, the bodies become chemically active via their interaction with the various elements of the harsh space environment. This driving energy, which effectively "animates" the surface at the atomic and molecular scales, includes solar radiation, space plasmas (solar wind), energetic charged particles, and high-velocity impacts. REVEALS joins a set of expert partners in expanding the science and exploration connection under the umbrella Solar System Exploration Research Virtual Institute. Our DREAM2 (Dynamic Response of the Environments at Asteroids, the Moon, and Moons of Mars) team is part of this umbrella institute.

In 2011, NASA released the Vision and Voyages Planetary Decadal Study, which featured a scientific emphasis on understanding the manufacturing and sequestering of volatile species at all planetary bodies throughout the solar system—feeding into the overarching assessment of habitability. Although we generally don't think of the Moon, asteroids, and the moons of Mars as being "volatile-rich" bodies, in the last few years there has been a renewed emphasis on the water, carbon, and hydrogen systems at these bodies.

This emphasis is especially true for the Moon, where in 2009 the Lunar Crater Observation and Sensing Satellite (LCROSS) impact mission directly observed a water-rich plume originating from the floor of the permanently shadowed Cabaeus crater. Besides water, various hydrocarbons were also inferred to be in the plume. The Lunar Reconnaissance Orbiter (LRO), which has been orbiting the Moon since 2009, has mapped out regions of surficial water frost and also of deeper hydrogen-rich deposits at locations within shadowed polar craters known to be extremely cold.[1] However, the locations of the surface frost and deeper deposits do not spatially co-align, suggesting possibly different sources and separated systems.

Adding to the intrigue, separate infrared instruments each detected hydroxyl at mid-latitudes at the Moon in association with O–H molecular stretch at $2.8\ \mu\text{m}$. This surface hydroxyl was reported to have a diurnal variation, which suggests that the hydrogen is weakly bound and thus dynamic.[2] Adding to the dynamic aspect of the surface, copious amounts of methane were reported to be released at the dawn terminator as the surface rotates into sunlight.[3] The processes for creating these species are currently unknown, but surface chemical reactions involving solar-wind protons and carbon are high on the list of suspected mechanisms.

These two observations have dramatically changed the way we look at the lunar surface: we now consider the plasma-activated, oxide-rich regolith as a chemical-conversion surface that processes incoming solar wind and meteoric material and emits products such as H_2 and methane back into the lunar atmosphere (commonly called a collisionless exosphere).

The Surface Response

The large-scale response of the surface to the environmental drivers, shown in Figure 1, is the formation of a collisionless exosphere consisting