Towards the development of an automated instrument for determining oxidative reactivity of lunar dust during moon exploration activities.

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Introduction: NASA, ESA and other space agencies are planning to undertake a new Moon exploration activity conducted by human crews in the near future. These projects aim to advance the ability of human beings to live and work in extreme environments and will constitute a formidable opportunity to answer several crucial questions about the evolution of the Solar System. Artemis Program, involves further landings on the Moon and, eventually, the creation of a surface outpost that will assure a consistent and lasting human presence on the Moon. A prolonged interaction of humans with the lunar environment constitutes an unknown, which requires to conceive strategies aimed at minimizing any potential risk. One of the most alarming aspects is the possible toxic outcomes that a prolonged exposure to lunar dust could induce in humans.

During the Apollo Program, the astronauts that landed on Moon surface were exposed to lunar dust as a result of crew member entry into the lunar modules with spacesuits covered with lunar dust from extravehicular activities (EVA). After exposure, the NASA astronauts experienced a variety of acute upper respiratory tract symptoms. On the other hand, these exposures were too short (just few days at most) to expect any significant findings from the point of view of pulmonary effects.[1,2]

The physico-chemical determinants of terrestrial particulate toxicity (including asbestos, quartz, volcanic ash and urban particulate matter) have been the focus of considerable research efforts and, in part, clarified. The toxic potential of a particle is determined by several features rather than one specific property. Three main factors play a key-role in the toxic outcomes induced by a given particulate: size and shape, surface reactivity and bio-persistence.[3] Regardless to the other factors, potential to cause lung disease is strongly linked to the chemical reactivity of mineral dusts, especially the formation of free radicals. The difference in toxicity is correlated to differences in the free radical content of the mineral, and is confirmed by carefully performed .animal studies.[4] Particle-derived free radicals associated to cell-derived reactive oxygen species (ROS) and reactive nitrogen species (RNS) cause oxidative stress in surrounding cells, which is exacerbated if the antioxidant defenses are depleted.

On the other hand, the physico-chemical properties of the lunar dust, and therefore its toxicity, could differ substantially from those observed with toxic terrestrial particulates. Regardless of dust grain morphology and mineralogical aspects, the radiation environment of the Moon is expected to have a significant impact on the chemical reactivity of lunar dust, and, therefore, is expected to influence finally pulmonary toxicity. None of the lunar samples exist in a pristine state that preserves the peculiar reactive chemical conditions that are believed to be present on the lunar surface.

Previous investigations indicates that mineral dusts and the parent materials from which mineral dusts are derived are sensitive to irradiation, including components of space radiation, such as high-energy protons.[5-10] The effects of radiation on these materials may induce electronic defects, ion implantation and degradation effects, all of which are indicative of bond breakage in the materials. Moreover in micro/hypogravity environment the risk of inhalation increases due to the reduced gravity-driven sedimentation. Actual lunar samples, returned to earth during the Apollo era, have been subjected to radiation treatment as well, and show evidence of chemical changes that could have significant toxicity implications in the lungs. In situ measurements are needed to provide an accurate quantitative assessment of the chemical reactivity of lunar dust, as it actually exists on the lunar surface. Furthermore, in situ measurements will serve as a reference point to study also the mechanisms involved in the lunar dust surface reactivity in terrestrial laboratories and to understand their potential pulmonary toxicity. A fully automated approach allows continuous detection of the chemical reactivity of lunar dust, since human exploration extends to previously unexplored sites.

Terephthalate (TA) assay is proposed here as a feasible and easy-to-perform chemical method to assess the overall oxidative reactivity of lunar dust, to be employed for in situ investigations. TA assay is based on the conversion of the terephthalate anion (TA, non-fluorescent) to 2-hydroxyterephthalate (TA-OH, strongly fluorescent) upon exposure to ROS.[2] A previous study carried out by some of us on buffered aqueous suspensions of JSC 1A vf lunar simulant

evidenced that TA was converted to TA-OH also redox active metal ions (e.g. ferryl-state Fe^{IV}).[11]

Prospective Experimental design: Thanks to its chemical simplicity, TA assay can be scaled up from lab scale to automated space instrument. TA probe, as well as the oxidized form TA-OH, is stable with time but requires an aqueous medium to solubilize reagents and suspend dust. Clearly, experiments to be operated in an aqueous environment may represent a challenge in space. The wet environment needed for this assay may however be provided by a hydrogel buffer, which is impregnated with TA (TA-patch, figure 1). The patches for the TA are prefilled with hydrogel and terephthalate, and sealed. The seal is spring-loaded and can be removed (figure 1a) immediately before putting the patch over the sample (figure 1b). The cap of the patch is transparent for UV (325nm) such that the terephthalate oxidized to TA-OH can be excited and the fluorescence signal at 425nm be detected. The fluorescent response TA-OH can be read by an optical microscope through a transparent container that is inserted over the sample (λ_{ex} =312 nm, λ_{em} = 426 nm, figure 1b).

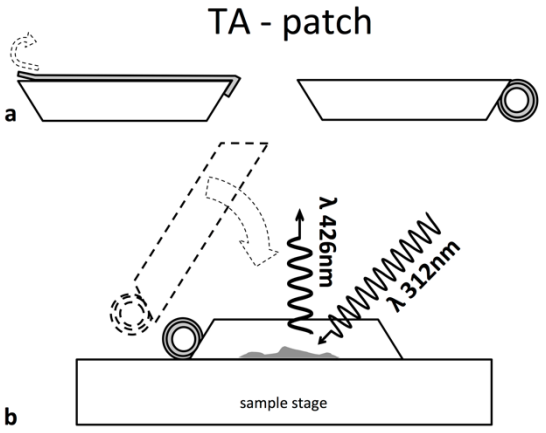

Figure 1: description of the TA patch proposed for TA assay a) removal of the seal from the TA patch before contacting it with the sample; 2) the TA patch is contacted with the sample and the TA-OH produced can be excited and the fluorescence detected thanks to the transparent container.

The optics necessary to perform the fluorescence measurement can be easily obtained and are inexpensive. A lunar dust sample is obtained from the lunar surface and deposited in a lunar powder distribution system. The equipment may allow to test the reactivity of the sample under different atmosphere. Operating under inert atmosphere conditions will give information on the dust activity in its pristine state, when first contact with human lungs, skin and mucosae may occur. Simulating a habitat-like atmosphere (in the presence of oxygen and water) can provide information on the passivation kinetics of surface reactivity of lunar dust in oxidative environment. The determination of the reactivity decay kinetics can be particularly important to define the necessary period and useful treatments to mitigate the hazard of lunar dust. In situ measurements are designed to provide critical data so that lunar dust samples can be manipulated appropriately in subsequent and more complex laboratory studies, including wider physical-chemical characterization, *in vitro*, and *in vivo* toxicological screenings.

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