Determining the correlation between mineral surface defect sites produced via mechanical alteration and their capability to generate reactive oxygen species

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NASA and commercial space exploration missions beyond low Earth orbit are likely to become more commonplace going into this century. On these missions, humans will be exposed to various space hazards that have the potential to significantly impact their health. Travel to other planetary bodies puts future explorers at risk for being exposed to planetary regolith. The Moon's surface is composed of a layer of fine particles that consists of 20% grains that are <20 µm in diameter.[1] Inhalation of such particulates is evidenced to lead to inflammation of respiratory tissues which can result in the development of bronchogenic carcinoma (lung cancer).[2] Apollo astronauts reported that lunar dust tore the top layer of their suits and jammed controls in their module. The astronauts also acquired symptoms such as headaches, fever, and nausea which was attributed to the inhalation of lunar dust.[3] The generation of reactive oxygen species (ROS) by mineral powders upon contact with water is considered the primary reason inhaling these dusts is deemed hazardous. Previous work has shown mineral composition as an important criterion for ROS generation. Mafic (i.e., Fe and Mg rich) minerals generate a larger amount of ROS compared to felsic (i.e., Si, Al, K, and Ca rich) minerals.[4,5] Our work has shown that minerals such augite, forsterite, and diopside generate about five times as much ROS compared to minerals such as quartz, feldspar, labradorite, and bytownite. Accordingly, it is possible that human activity on the lunar mare will pose a greater dust-exposure related health risk than in the highlands. Our previous work has investigated the role of Fenton reaction in the generation of hydroxyl radical (·OH), a highly reactive ROS species, which forms by the reaction of dissolved hydrogen peroxide and ferrous iron (Fe^{2+}).[6] This work relied on electron paramagnetic resonance (EPR) spectroscopy combined with a spin trapping compound (5,5-dimethyl-1-pryrroline-N-oxide, or DMPO), which has proven to yield reliable concentrations of hydroxyl radical in mineral-water slurries. While these experiments have provided valuable information on the relative ROS producing capacity of relevant mineral phases, the underlying chemical reactions responsible for the generation of ROS remain speculative. The precise chemical reactions between surface sites and aqueous species requires further investigation. To determine what defect sites are generated on mineral surfaces during mechanical pulverization, we are employing X-ray photoelectron spectroscopy (XPS), a technique that is sensitive to the surface speciation of solid materials. XPS spectra of freshly-ground mineral samples and ground samples exposed to air for increasing periods of time are being compared to determine what surface species are primarily responsible for the generation of reactive oxygen species in

[1]Heiken, G. et al. (1975), *Rev. Geophys. Space Phys.* 13, 567-587. [2]Aust, A. E. et al. (1995), *Chem. Rev.* 95, 97-118. [3]Science Beta, National Aeronautics and Space Administration, 2005 Electronic media. [4]Turci, F. et al. (2015), *Astrobiology.* 15, 371-380. [5]Hurowitz, J. A. et al. (2007), Earth Planet. Sci. Lett. 255, 41-52. [6]Hendrix, D. A., Hurowitz, J. A. (2017), Measurement of the Hydroxyl Radical Generation of Powdered Minerals Analogous to those on the Lunar Surface. Abstract, NASA Human Research Program Investigators' Workshop.

solution. We anticipate that our work will lead to a greater understanding of the surface-mediated mechanisms that lead to ROS production.

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