Assessing OH* generation capabilities of lunar simulant and mineral phase lunar analogs in order to increase understanding of potential health hazards of future astronauts Donald A. Hendrix[1], Tristan Catalano[1], Joel A. Hurowitz[1], Hanna Nekvasil[1], Jamie Hsing-Ming Chang[2], Kevin Chen[2], and Bruce Demple[2]. [1]Department of Geosciences, Stony Brook University (donald.hendrix@stonybrook.edu), [2]Department of Pharmacological Sciences, Stony Brook University.

Introduction: Apollo astronauts were exposed to various quantities of lunar dust and reported that exposure induced allergy-like symptoms from which the term "Lunar Dust Hay Fever" was coined. Our work is focused on the assessment of reactivity, as measured by the concentration of hydroxyl radical (OH*) generated in solution by mechanically pulverized minerals and lunar simulants that are analogous to regolith materials found on the lunar surface. We have found that OH* generation is highest for iron-rich silicates (i.e. olivine, pyroxene) and lowest for iron-poor silicates (i.e. bytownite, labradorite) [1]. The observed reactivity is likely due to the exposure of surficial Si-O· which reacts with water to make hydrogen peroxide (H_2O_2) which then reacts with surficial Fe^{2+} to make OH* in a reaction otherwise known as the Fenton reaction [1]. Generalizing based on prior studies [1-2], the OH* generation of each mineral from greatest to least are as follows: olivine, augite, diopside, albite, bytownite, labradorite, and quartz. The OH* has been linked to DNA damage and lung cancer [3]. The oxygen in OH* has an oxidation state of (-1) instead of the usual (-2), hence its high tendency to react and oxidize any biomolecules it comes in contact with, including, e.g., DNA [3].

Statement of the Problem: Up to this point we have worked with terrestrial mineral phases and the lunar simulant Johnson Space Center-1A (JSC-1A). Terrestrial minerals, while similar to those found on the Moon, usually exhibit different chemistries than those found on the lunar surface, are frequently deficient in both Fe and Ca, and contain excess Na, K, and Mg [4]. The lunar simulant JSC-1A is a multi-mineral heterogenous mixture, which makes it difficult to pinpoint what minerals contribute to its observed reactivity. JSC-1A adequately replicates physical lunar soil properties (i.e. specific gravity, thermal/electrical properties) but does not adequately replicate the chemistries observed in lunar soils. Here, we describe new experimental research aimed at understanding the reactivity of analogue materials that more closely mimic the chemistry and mineralogy of lunar dust deposits, and account for some of the unique chemical changes that are induced by reductive space weathering processes.

Materials and Methods: We have acquired Lunar Mare Simulant-1 (LMS-1) and Lunar Highland Simulant-1 (LHS-1) from the Exolith Lab at the University of Central Florida. These simulants better replicate the lunar mineralogy of both mare and highlands regions and will give us a better understanding of the reactivity of lunar dusts from these regions. LMS-1 contains approximately 30% pyroxene, 25% glass, 20% plagioclase, and 4% ilmenite. LHS-1 contains approximately 75% plagioclase, 25% glass, and <1% olivine, pyroxene, and ilmenite [5]. These simulants are an improvement to the commonly used lunar simulant JSC-1A due to better replicating mineral abundances, but still exhibit some important chemical differences from lunar soils due to the differing formation conditions of terrestrial and lunar minerals.

One important difference is a lack of metallic nanophase iron ($np\text{-}Fe^0$), which is common in lunar soils due to space weathering. In an attempt to add metallic iron to the samples we have incorporated a simple reduction method described in Allen et al. [6]. We reduced approximately 3 g of JSC-1A, LMS-1, and LHS-1 in order to add metallic iron to the surface.
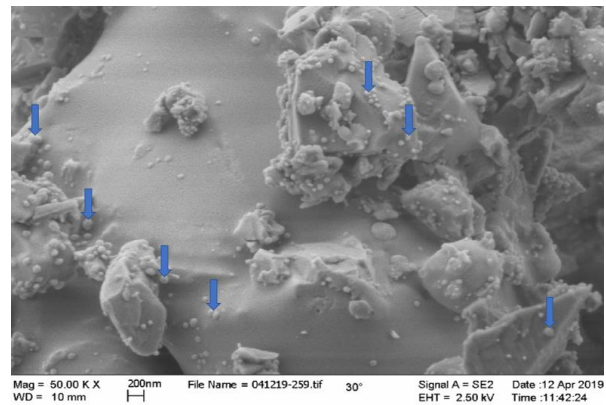

Mag = 50.00 K X   200nm   File Name = 041219-259.tif   30°   Signal A = SE2   Date :12 Apr 2019
WD = 10 mm   EHT = 2.50 kV   Time :11:42:24

Fig 1. Metallic iron blebs present in JSC-1A as indicated by the blue arrows.

As previously mentioned, the chemical compositions of readily accessible terrestrial minerals are not well-matched to those observed on the lunar surface. In addition, natural mineral samples are often affected by exposure to air and water. In order to bypass these issues, we have synthesized various olivine compositions as follows, Fa_0, Fa_{50}, Fa_{60}, Fa_{90}, and Fa_{100}. Olivine was chosen due to its simple chemical formula, it being relatively abundant on the lunar surface, its ease in synthesizing, and the fact that it is the most reactive silicate mineral we have measured to date. For reactivity analysis, all samples were hand-ground in an agate

mortar and pestle for 10 min and then analyzed for OH* radical generation by spin-trapping techniques described in [1].

Results: Upon reduction, our sample became darker and scanning electron microscopy (SEM) images showed the formation of metallic iron blebs on the surface of various grains (**Fig 1**). These metallic iron metal blebs were also observed by [6], which led us to conclude our reduction process was successful.

Our reduction experiments demonstrate that OH* generation increases for all reduced lunar regolith simulants, as shown in **Fig 2**. Reduced JSC-1A generates about double the OH* relative to non-reduced JSC-1A.
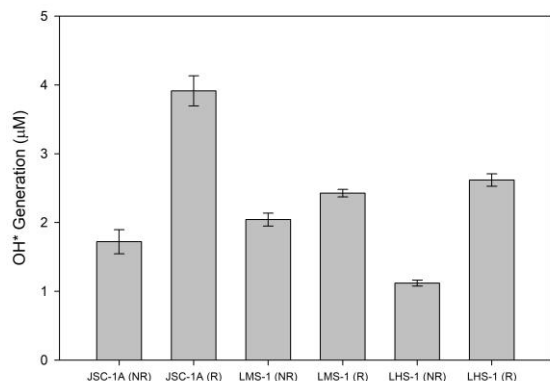

Fig 2. Reduction of lunar simulants leads to increases in OH* generation relative to non-reduced samples.

For synthetic olivine samples, the reactivity of both end members is low and that reactivity rises as both end members begin to deviate from each other. Reactivity rises until it hits a maximum at approximately 1.5 μM OH* for Fa_{50}. **Fig 3** shows how reactivity changes through the olivine solid solution members measured so far.
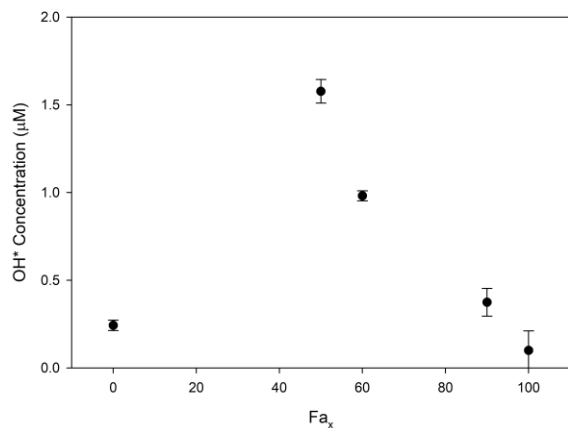

Fig 3. OH* generation vs. olivine composition (Fa_x). Endmembers generate a minimum of approx. 0.1 μM OH* and Fa_{50} generates approximately 1.5 μM.

Summary: Reduction of lunar simulants has shown that metallic iron leads to large increases in OH* generation, particularly for JSC-1A and LHS-1. We speculate that metallic iron participates in a Fenton-like reaction that leads to increased observed concentrations of OH*. Non-reduced LMS-1 is twice as reactive as non-reduced LHS-1. This is most likely due to more iron-rich silicates present in LMS-1 as it is a lunar mare simulant.

Our results for OH* generation across the olivine solid solution are intriguing; previous work has shown a strong correlation between FeO wt%. in silicates and OH* generation [1]. These findings seem to contradict previous results and indicate that other mechanisms besides the Fenton reaction may be at play. It is unclear what is contributing to both the reactivity of Fa_{50} and relative inertness of Fa_0 and Fa_{100}. It may be possible that crystal lattice effects may contribute to reactivity. Never the less this method of synthesizing olivine helps to understand how reactivity changes as a function of chemical composition within the same phase, and this method can also be applied for other minerals which would further our understanding lunar mineral reactivity.

Future Work: SEM images will be obtained of reduced LMS-1 and LHS-1 to verify if metallic iron metal blebs were formed. More olivine phases will be synthesized in order to complete the analysis of the olivine solid solution series (**Fig 3**). This will allow us to better understand the underlying mechanisms of reactivity and what else besides Fenton chemistry may be responsible for the observed peculiar reactivity trend for olivine.

References: [1] D. A. Hendrix et al. (2019) *GeoHealth* **3**(1), 28-42. [2] C.J. Horwell et al. (2003) *Environ. Res.* **93**(2), 202-215 [3] M. Dizdaroglu et al. (1991) *Arch. Biochem. Biophys.* **285**(2), 317-324. [4] E. Hill et al. (2007) *GeoHealth* **112**(E2). [5] D.T. Britt et al. (2019) ESF 2019, Abstract #NESF2019-082. [6] C.C. Allen et al. (1994) *J. Geophys. Res.* **99**(23), 173-185