DESTRUCTION OF BIOMARKERS WITHIN Mg-CHLORIDES BY ENERGETIC ELECTRONS, RELEVANT TO MARS AND EUROPA. Alian Wang, Alexander S. Bradley, and Yuanchao Yan, Dept. Earth & Planetary Sciences and McDonnell Center for Space Sciences, Washington University in St. Louis (alianw@levee.wustl.edu).

Introduction: The preservation of residual evidences of biological activities, i.e., biomarkers, at planetary surface and shallow subsurface is critical that would ultimately determine if a planet can be attributed to be habitable or even habited through landed missions and planetary sample returns.

Since the two Viking landers in 1970s', the exploration missions to Mars have found various evidences, on favorable environmental conditions that could support the habitability in the early history of Mars [1-2]. In addition, the digging and trenching operations made by landers and rovers on Mars, plus the orbital imaging of the "light-toned" matter excavated by impacts [3-5], have suggested a potentially life-friendly subsurface (when filled with hydrous salts and even H_2O ice), which could keep high relative humidity (RH), thus might help the preservation of biomarkers.

At martian surface, various harsh environmental conditions, e.g., the large ΔT, extremely low RH, the high dose of UVC and galactic cosmic ray, all have negative impact on the preservation of biomarkers.

Furthermore, we suggest another process that could add a negative impact, i.e., the electrostatic discharge (ESD) induced by martian dust activities (dust storm, dust devil, and grain saltation). Energetic electrons were known to be a major threat for the preservation of organic compounds at Europa surface [6]. The energetic electrons generated during Mars dust activities can cause even further damages. Because these electrons would collide with martian atmospheric molecules (CO_2, N_2, Ar, O_2, H_2O), to generate lots of more complex free radicals including charged ions, neutral atoms/molecules at excited states [7], and secondary electrons to induce chain reactions [8]. The chemical reactions caused by them, *the* ***multiphase redox plasma chemistry***, can happen in Mars atmosphere and between atmosphere and surface.

During previous electrostatic discharge (ESD) experiments conducted in a Mars chamber [9-11], simulating a medium strength ESD when compared with the modeled strengths of ESD-TDD (*Townson dark discharge*) and that of ESD-NGD (*normal glow discharge*) [12], we detected the simultaneous generation of CO_2^+, CO^+, O_I, H_{III}, H_{II}, OH, Ar_I, N_2, N_2^+ by *in situ* plasma emission spectroscopy (not excluding O_2, NO, and O^+ because of the overlapping of plasma lines used for detection), as well as O_3 by UV and mid-IR spectroscopy. Judged by the generation of CO_2^+ and H_{III}, the electron kinetic energy is > 17.19 eV, at least, in our experimental setting [11].

Furthermore, a set of experiments conducted by a team at Denmark [13,14] simulated the silicate grain saltation on Mars. They observed plasma glows (i.e., ESD-NGD), and detected the generation of hydrogen peroxide (H_2O_2) and hydroxyl radical (·OH).

What would be the impact of those free radicals and energetic electrons on the preservation of martian biomarkers?

How the degree of impact would be affected by the type of biomarkers and by their bury depth?

What would be the waste species produced by the plasma chemical reaction?

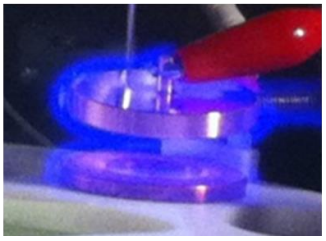
What would be the isotopic signatures dictated by this type of plasma chemistry?

These are some of many relevant questions that need to get answered, for the mission with *in situ* Mars organic matter detection (ESA-ExoMars), the Mars sample returns (NASA-Mars2020 and MSR, CNSA-Mars 2020 and MSR), and for the analysis of returned samples from Mars.

We started a set of experiments trying to address these questions. Our experiments are different from the experiments of Denmark team made on bacterial endospores [14, relevant to the forward contamination]. ***We aimed to evaluate the effect of plasma chemistry on the preservation of Mars relevant biomarkers.***

Samples Selections: For the preliminary experiments, we selected to start with the mixtures of Mg-chloride salts and a biomarker. Mg-salts were selected purposely to be relevant to Mars and also to Europa. A Mg-chloride (not Mg-sulfate) was selected firstly, to avoid the complication from sulfur compound. In order to study the effect of ESD generated OH to biomarker preservation, both $MgCl_2.6H_2O$ and $MgCl_2$ were used. The selection of salts further benefited from the fact that ESD experiments on both were conducted previously [15]; the Raman, Mid-IR, VNIR spectral features of Mg-chlorides were published [16]; and their stability field including phase boundary for deliquescence was understood [17].

Figure 1. electrodes and plasma

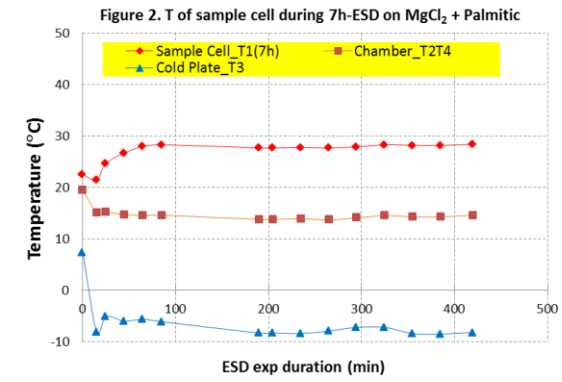


We selected palmitic acid (C_{16} saturated fatty acid) as an organic biomolecule for these experiments. Fatty acids of this size are widespread in bacterial and eukaryotic organisms. This fatty acid forms a simple starting material with which to investigate interactions between organic compounds and the free radicals generated by ESD.

ESD experiments: The electrostatic discharge (ESD) experiments were conducted in a Mars chamber (the PEACh, [9]). The chamber was first evacuated to $3x10^{-2}$ mbar to remove the air and then was filled with pure CO_2. The atmospheric pressure was kept at 3 ± 0.1 mbar during ESD experiments. We used two parallel copper electrodes (35 mm diameter) in PEACh to generate ESD in *normal glow discharge* (NGD) regime, with an electric current of 22 mA through the electrodes. This current corresponds an electron flux density of 1.43×10^{20} electrons per (second*m^2), which is about 10^4 times lower than the modeled electron flux for NGD type of ESD, but 10^4 times higher than the modeled electron flux for TDD type of ESD [12]. Both NGD and TDD are anticipated to occur during dust actives on Mars, although no actual measurement was made on Mars, hitherto [18, 19].

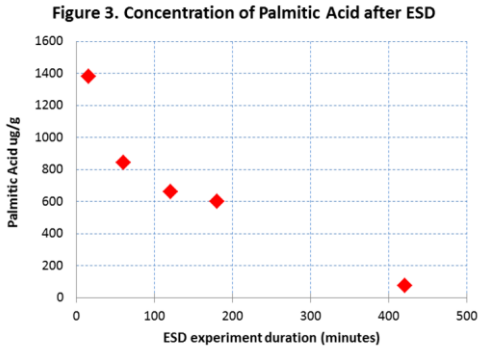
The Mg-chlorides were grounded and sieved, and a grain size range of 88 µm > d > 63 µm was selected to mixed with palmitic acid, at molar concentrations of 1 mmol of palmitic acid per mol of salt (0.1 mole%) in both mixtures. For each ESD experiment, about one gram of mixture was put into a fused SiO_2 cell of 20 mm diameter and 5 mm depth. The sample cell is placed inside of the lower electrode, facing the energetic electrons from upper electrode, and is entirely enveloped by the ESD generated plasma (Figure 1). Five ESD experiments at durations of 15 min, 1 hour, 2 hours, 3 hours and 7 hours were run for each of two mixtures.

For the purpose of evaluating the *pure effect* of plasma chemistry on the preservation of palmitic acid in Mg-chloride, and to minimize the temperature induced degradation, we kept the temperature of sample cell < 30°C during these two sets of ESD experiments [20]. Figure 2 shows the temperature profile during a 7 hours ESD on $MgCl_2$ mixed with palmitic acid.



Analyses: The top layer of a sample (~ 90-100 mg) and the rest of sample (700-800 mg) were removed, separately, from the sample cell after each ESD experiment. The samples were then suspended in HPLC-grade water to dissolve most of the salt, and extracted three with dichloromethane. The extracts were pooled, concentrated under a stream of N_2, and then transesterified to fatty acid methyl esters by reacting with a mixture of acetyl chloride in methanol. Samples were then analyzed by gas chromatography-mass spectrometry, with methyl decanoate used as an internal standard for quantitation.

Concentration of palmitic acid from the top layer shows an exponential decrease with time, with a half-life of approximately 100 minutes (Figure 3). No other GC-amenable organic compounds were detected in samples with low palmitic acid concentrations, suggesting that these compounds were transformed to a gas phase (CO or CO_2) or to another phase that was not detected by gas chromatography.



Conclusion and future works: Destruction of palmitic acid within $MgCl_2$ by a medium strength ESD process was observed. We will continue this set of tests on different types of biomarkers mixed with different salts, with variable conditions in ESD.

Acknowledgments: NASA SSW-80NSSC17K0776, and ICEE-2 NNH18ZDA001N

References: [1] Grotzinger et al., *Science*, 2013; [2] McLennan et al., *Science*, 2014; [3] Mellon et al., *JGR*, 2009; [4] Wang and Ling, *JGR*, 2011; [5] Byrne et al., *Science*, 2009; [6] Johnson & Quickenden, *JGR*, 1997; [7] Atreya et al., *Astrobiology*, 2006; [8] Jackson et al., *JGR*, 2010 [9] Sobron and Wang, *JRS*, 2012; [10] Wu et al., *EPSL*, 2015; [11] Wu et al., *EPSL*, 2018; [12] Delory et al., *Astrobiology*, 2006; [13] Bak et al., *EPSL*, 2017; [14] Bak et al., *Astrobiology*, 2019; [15] Wang et al., *abs#6117 for 9th Mars;* 2019; [16] Shi et al., *JRS*, 2019; [17] Wang et al., *Icarus*, 2019; [18] Farrell et al., *Acta Astronautica*, 2000 [19] Harrison et al., *Space Sci. Rev*, 2016. [20] Yan et al., *this volume*, 2020.