RADIOLYSIS PRODUCTS OF MACROMOLECULAR ORGANIC MATTER IN MARS-RELEVANT MATRICES. A. C. Fox[1], J. L. Eigenbrode[2] and, K. H. Freeman[1], [1]Pennsylvania State University, University Park, Pennsylvania, USA, [2] NASA Goddard Space Flight Center, Greenbelt, Maryland, USA

Introduction:

The Sample Analysis at Mars (SAM) instrument suite onboard the Mars Science Laboratory (MSL) rover detected organic carbon at two locations at Gale crater. Small, chlorinated hydrocarbons were found in the Sheepbed mudstone at Yellowknife Bay (*1*) and sulfurized hydrocarbons were found in lacustrine mudstones at the base of the Murray formation at Pahrump Hills (*2*). The source of these small hydrocarbons remains unclear, but are thought to be derived from larger, recalcitrant macromolecular organic matter, such as kerogen. Macromolecular organic matter could be due to biologic or geologic sources, or delivered to the surface via meteorite impact.

An estimated 2.4×10^8 g of reduced carbon is delivered to Mars by meteorites each year (*3*). This organic matter can be altered or destroyed by the harsh radiation environment on the Martian surface. Benner *et al*. (2000) predicted that meteoric, macromolecular organic matter exposed to UV radiation would produce low molecular weight organic acids via Fenton-like reactions. Subsequent laboratory studies have confirmed this hypothesis; however, UV radiation does not penetrate beyond the first several millimeters of Martian soil. In contrast, cosmic and solar radiation can penetrate up to two meters, affecting organic matter that is buried at depth (*4*). While UV radiation experiments have identified possible oxidation pathways and metastable organic intermediates of radiolysis of organic matter, similar studies using higher energy radiation or macromolecules have not been explored.

The primary purpose of this experiment was to determine if high energy radiation produced similar metastable products to UV radiation via Fenton-like reactions. Fenton reactions produce OH radicals by reactions with iron catalysts and oxygen bearing species, such as water (*6*). These radicals can then cleave bonds in macromolecules and recombine to form small organic acids. In the mechanisms proposed by Benner *et al.* (2000), benzoate, phthalate, and oxalate were the primary products of radiolysis of most meteoric organic matter. It is unclear if similar products would be produced by exposure to higher energy radiation, which is significantly more energetic that molecular bonds.

Here, we present the first study of radiolysis of organic macromolecules by high energy protons in Mars-relevant matrices. This study will aid in understanding the preservation of organic macromolecules at depths from which SAM-analyzed samples were acquired, ~2 cm below the surface that are exposed to higher energy radiation.

Methods:

To assess the effects of high-energy radiation on organic macromolecules, samples with Martian-relevant matrices and macromolecular organics were exposed to proton radiation.

Samples. Each sample contained a mineral matrix with 5 wt % of organic matter added. A subset of samples contained 1 wt % inorganic salts (NaCl, $CaPO_4$, or $CaSO_4$) and/or liquid water. Mineral matrices included fused silica (SiO_2), $CaSO_4$, or an analog mixture (olivine Fe_2SiO_4, nontronite $Na_{0.3}Fe_2(Si,Al)_4O_{10}(OH)_2 \bullet nH_2O$, and fused silica), referred to as "analog 1". Organic matter included 4 natural samples, Archean kerogen, Pony Lake fulvic acid, Green River shale, and Guaymas Basin and one standard solution containing pristine, phytane, sterane, n-heptadecane, stigmasterol, pyrene, phenanthrene, C14:0 fatty acid, C:18:1 fatty acid, L-alanine, L-serine, glycine, mellitic acid, benzoic acid, adipic acid referred to as Organic Mix.

Radiation and Analysis. After mixing, samples were placed in an ashed quartz-glass tube under 7 mbar of 99.999% Ar and flame sealed. Samples were irradiated using 250 MeV protons at Brookhaven NASA Space Radiation Laboratory. Samples received a cumulative dose of either 0, 63, 125, 250 or 500 kGys, representing Martian surface exposure of up to $\sim 7.6 \times 10^6$ yrs (*5*). Samples were extracted for low molecular weight organic acids by sequential extraction in 25 °C DI water then 95 °C DI water. Extracts were analyzed using ion chromatography mass spectrometry (Dionex ICS-2100 MSQ+). Compounds were separated on a AS11 guard and analytical column with a multistep gradient KOH eluent.

Results:

Each sample was analyzed for formate, oxalate, benzoate, phthalate, and citrate. Oxalate and formate were the only two organic acids detected at measurable quantities *(Figure 1).* Benzoate was added prior to radiation in all samples containing Organic Mix, so it is unclear if those samples produced additional benzoate; however, no other samples contained benzoate. No samples produced phthalate or citrate.

The formation of oxalate and formate depends on both the matrix and organic matter added *(Figure 1).*In equivalent samples (same organic matter added), analog 1 produced more organic acids than fused silica. Some analog 1 control samples (no organic matter added) produced organic acids, indicating organic matter was present in the matrix. Samples containing calcium sulfate as the primary matrix did not produce organic acids. The

addition of inorganic salts inconsistently affected organic acid production. In most cases $CaSO_4$ inhibits production, the effect for NaCl and $CaPO_4$ varies depending on other sample properties (i.e. matrix or organic starting material).

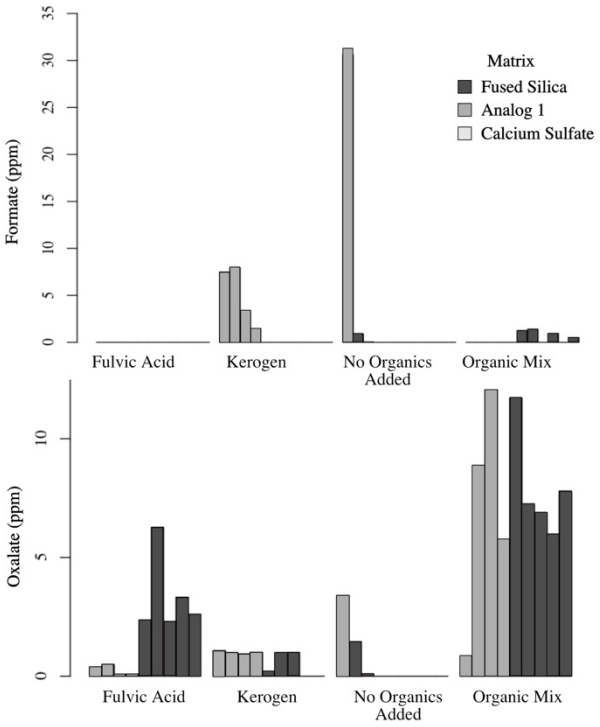

Figure 1: Oxalate and formate concentrations in dry samples that did not contain added salts. Calcium sulfate samples did not produce any organic acids.

Discussion:

Mars-relevant organic-mineral mixtures were irradiated with high energy protons to determine if Fenton-like reactions degraded organic macromolecules into organic acids. The results presented here do not support the formation of organic acids via Fenton-like reactions. While organic acids were produced, they differed from those predicted by Fenton reactions. More notably, organic acids were produced in samples that did not contain iron, a requirement for Fenton chemistry. Therefore, another mechanism is needed to explain these results.

Several authors have reported oxygen and hydroxyl radical production when semi-conductor surfaces (i.e. SiO_2 or TiO_2) are illuminated by gamma radiation (*7–9*) These radicals have been shown to produce organic acids from a variety of starting materials including chloroethane, HCN, and CH_4 in the presence of semi-conductor surfaces. We propose a mechanism similar to semi-conductor surface reaction is responsible for organic acid formation in our irradiated samples, not Fenton reactions. In our experimental sample suite, SiO_2 acts as the semi-conductor that facilitates OH radical production, although this process is less efficient for SiO_2 than TiO_2 or Al_2O_3 (*10*). It is possible that Fenton reactions are also occurring in iron bearing samples, which may explain the higher concentrations of organic acid samples in some analog 1 samples. However, the presence of Al_2O_3 in nontronite in the analog 1 mixture could also explain this discrepancy, because it is a more effective semi-conductor than SiO_2.

In Analog 1 control samples that did not have organic matter added, formate, benzoate, and oxalate were detected. Fused silica control samples produced small amounts of formate and oxalate. Blank DI water was run between every sample during IC-MS analysis and did not contain any target compounds. Therefore, the source of this contamination is likely organic material that was not removed despite careful pre-extraction and ashing.

Implications:

The work presented here attempts to identify possible metastable organic species produced by ionizing radiation in Martian soils. Unlike previous work, we focus on higher energy radiation effects, rather than UV, that penetrate much deeper into the Martian surface. These results can be used to help interpret data collected by SAM and future missions which drill below the Martian surface. Our results not only show that organic acids are produced, but are preserved for hundreds of thousands of years in silicate matrices rather than sulfates. Therefore, future missions should be equipped to measure organic acids (or salts) and future sampling should prioritize areas with primary silicates and low sulfate concentrations.

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