

**Key Points:**

- Macromolecular organic material bombarded with high-energy protons produced organic acids
- Radiolysis products did not depend on mineral matrix or organic starting material
- Organic acids were possibly produced by radicals formed by interactions with semiconductor surfaces

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## Radiolysis of Macromolecular Organic Material in Mars-Relevant Mineral Matrices

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**Abstract** The fate of organic material on Mars after deposition is crucial to interpreting the source of these molecules. Previous work has addressed how various organic compounds at millimeter depths in sediments respond to ultraviolet radiation. In contrast, this study addressed how high-energy particle radiation (200-MeV protons, simulating the effect of galactic cosmic rays and solar wind at depths of <4–5 cm) influences organic macromolecules in sediments. Specifically, we report the generation of organic-acid radiolysis products after exposure to radiation doses equivalent to geological time scales (1–7 Myr). We found that formate and oxalate were produced from a variety of organic starting materials and mineral matrices. Unlike ultraviolet-driven reactions that can invoke Fenton chemistry to produce organic acids, our work suggests that irradiation of semiconductor surfaces, such as TiO<sub>2</sub> or possible clay minerals found on Mars, forms oxygen and hydroxyl radical species, which can break down macromolecules into organic acids. We also investigated the metastability of benzoate in multiple mineral matrices. Benzoate was added to samples prior to irradiation and persisted up to 500 kGys of exposure. Our findings suggest that organic acids are likely a major component of organic material buried at depth on Mars.

**Plain Language Summary** Organic molecules are the building blocks of life and could provide some of the best evidence for the presence of life on early Earth. The search for evidence of life beyond Earth has focused on detecting these molecules. Missions to Mars have been equipped to detect them, and small molecules have been found, although they cannot be definitively tied to life. The lack of complex molecules may reflect Mars' harsh radiation environment. Unlike Earth, Mars lacks a magnetic field and experiences high radiation, which can penetrate below the surface and can alter or destroy organic material. We exposed complex organic molecules in different mineral matrices to high-energy radiation to determine how these molecules are altered. We found that complex molecules break down into smaller organic acids when exposed to high-energy radiation. Furthermore, we found that the same products were produced when different initial organic sources were mixed with a variety of rock types. Therefore, to look for unaltered organic molecules, future missions will have to study samples that have not been exposed to radiation.

### 1. Introduction

#### 1.1. Organic Material on Mars

The preservation and detection of organic material on Mars is critical to our understanding of Mars' ability to host life throughout time. Chemical signatures encoded in organic material provide information on ancient ecologies if life existed in the past and, in the absence of life, provide clues about the environmental and thermal history of Mars.

Detecting organic material is a central goal of the Mars Exploration Program (MEPAG, 2015), but this goal is complicated by evidence for oxidizing Martian soils (Oyama & Berdahl, 1977; Zent & McKay, 1994). Various oxidizing species have been proposed to explain the high soil reactivity, including superoxide ions (Yen et al., 2000), hydroxyl and oxygen radicals (Benner et al., 2000), and perchlorate intermediates (Carrier & Kounaves, 2015; Quinn et al., 2013). These reactive species likely form by interactions with ionizing radiation. The lack of a magnetic field and thin atmosphere exposes the Martian surface to high doses of ionizing electromagnetic (e.g., ultraviolet [UV] and  $\gamma$ ) and particle (i.e., proton, neutron, and higher mass atoms) radiation that can oxidize organic matter directly or through reactions with secondary oxidants (Hassler et al., 2014; Patel et al., 2002).

Despite a hostile environment, there is evidence for organic material at several locations on Mars. The Sample Analysis at Mars instrument onboard the Mars Science Laboratory (MSL) Curiosity Rover detected chlorinated hydrocarbons indigenous to the ~3.5-Ga lake sediments at Yellowknife Bay, Gale crater (Freissinet et al., 2015). Other aliphatic, aromatic, and sulfur-bearing hydrocarbons that were detected in lake sediments studied at Pahrump Hills are thought to be derived from larger macromolecular structures that aided their preservation (Eigenbrode et al., 2018). Other potential indications of indigenous organic matter are indirect and are observed as thermal evolution of CO<sub>2</sub> and CO observed during Sample Analysis at Mars' evolved gas analysis and are in part attributed to decarboxylation and decarbonylation of organics in samples from diverse rocks and aeolian sediments in Gale crater (Ming et al., 2014; Sutter et al., 2016), which may also explain CO<sub>2</sub> observed by the Viking GCMS (Biemann et al., 1976). Chloromethanes (Navarro-González et al., 2010) and chlorobenzene (Guzman et al., 2018) detected in Viking data may also be Martian carbon signals, but terrestrial sources have not been definitively excluded. Additionally, reduced carbon phases including graphite, polycyclic aromatic hydrocarbons, and macromolecular phases with diverse synthesis mechanisms have been detected in Martian meteorites (Steele et al., 2016). These observations together indicate that Martian organic matter is present in different preservation states but the sources and alteration processes affecting these organics are not well constrained.

### 1.2. Alteration of Organic Material by Ionizing Radiation

Unlike Earth, Mars lacks a magnetic field and is therefore bombarded by ionizing radiation that can alter organics. Previous work has employed a range of UV,  $\gamma$  rays, and X-rays to study the effect of ionizing radiation on organic material. Of these, the majority of studies concerning organic matter preserved on Mars have focused on the effect of UV radiation. Studies on the survivability of amino acids (Poch et al., 2013; Stalport et al., 2009; ten Kate et al., 2005), carboxylic acids (Stalport et al., 2009), PAHs, and urea (Poch et al., 2014) exposed to varying doses of UV radiation revealed that long-term exposure to UV radiation (<10 years on Martian surface) completely degraded organic material. Stalport et al. (2009) also found that exposure to UV led to the formation of metastable compounds that survived on longer time scales than the initial compounds.

Stalport and colleagues' work supports an idea originally introduced by Benner et al. (2000) to explain the lack of organics detected by the Viking missions. Benner et al. predicted that UV-driven, Fenton reactions of meteorite-delivered organics would produce organic acids as a metastable intermediate. Although traditionally an aqueous reaction, Fenton reactions degrade organic material by producing OH radicals from H<sub>2</sub>O<sub>2</sub> in the presence of an iron catalyst. Hydroxyl radicals then react with organic material, likely via H abstraction, to form new degradation products (Pignatello et al., 2006). The predicted organic acids are largely nonvolatile and were likely invisible to the Viking gas chromatograph-mass spectrometer. Laboratory studies have shown that the rate of formation of organic acids outpaces their destruction by a factor of 10<sup>3</sup>, suggesting these molecules can persist on long time scales (Benner et al., 2000; Lamrini et al., 1998). Based on an influx of  $2.4 \times 10^8$  g/year of reduced carbon and 1-m mixing depth, Benner et al. predicted organic acid concentrations of  $\approx 500$  ppm. While Benner et al.'s estimate did not account for processes that remove organic acids, to fall below Viking detection limits (approximately tens of ppb) over 99% of organic acids would have to be destroyed. Benner's hypothesis was further supported by more recent work that suggests solid oxalic acid is stable on the surface of Mars and may be present in reinterpreted Viking, Phoenix, and MSL data (Applin et al., 2015).

Benner et al. invokes Fenton chemistry that requires exposure to UV radiation (3–100 eV), which can only penetrate the first several millimeters of Martian soil (Cockell & Raven, 2004). In contrast to UV, other forms of ionizing radiation, such as galactic cosmic and solar rays, are predicted to penetrate up to 2 m of Martian soil (Hassler et al., 2014; Pavlov et al., 2012). Understanding how organic matter in rocks, regolith, and aeolian sediments is altered by ionizing radiation below the Martian surface (2–200 cm deep) is crucial to interpreting data from current and future missions. In situ samples analyzed by the MSL and Viking missions were collected at depths of 5–10 cm, and the ExoMars rover will have the ability to drill up to 2 m (Grotzinger et al., 2012; Oyama & Berdahl, 1977; Vago et al., 2006).

At depths relevant to MSL (~5 cm), contributions from solar rays are minimal (Hassler et al., 2014; Pavlov et al., 2012). Galactic cosmic rays are primarily composed of high-energy protons (87%) that span energies from 10 to 1,000 MeV (Benton & Benton, 2001). Their high energy allows them to cleave bonds

indiscriminately within the Martian soil profile creating a highly reactive environment. Studies investigating the effects of  $\gamma$  radiation on macromolecular organic material have found destruction of organic material via cross-linking, oxidation, and bond scission accompanied by increases in aromaticity of remaining organic material (Brown & Weiss, 2003; Court et al., 2006; Schäfer et al., 2009). Similar results were reported for nucleobases that were destroyed after exposure to  $\gamma$  radiation (Ertem et al., 2017). From these results, it is unclear if metastable species can form or persist below the Martian surface (2–200 cm) or if organic material would be completely destroyed.

Here, we report metastable products formed from radiolysis of macromolecular organic species exposed to high-energy protons (200 MeV). We irradiated mixtures of recalcitrant organic material and Mars-relevant minerals for cumulative doses up to 500 kGy, representing ~6.6 million years at the surface of Mars. The focus of this study was to determine if organic acids are produced due to interactions with high-energy protons. Using these data, we aim to determine the likely metastable products below the Martian surface and constrain how long these products persist in different mineral matrices.

## 2. Materials and Methods

### 2.1. Samples

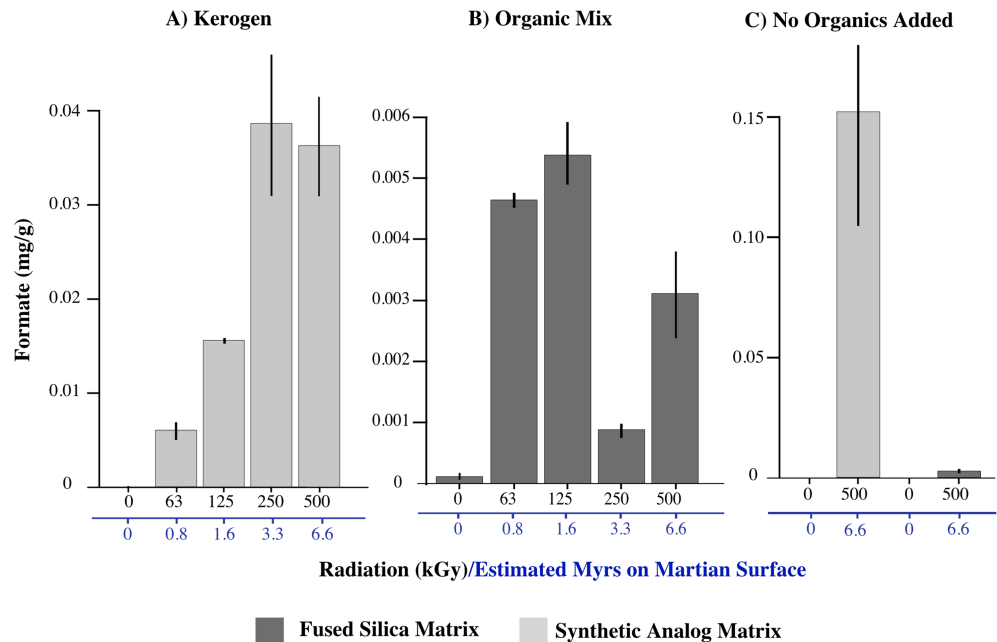
Mineral matrices included fused silica ( $\text{SiO}_2$ ),  $\text{CaSO}_4$ , or a synthetic analog mixture. The analog included 50% olivine sand ( $(\text{Fe}, \text{Mg})_2\text{SiO}_4$ ) and 50% nontronite ( $\text{Na}_{0.3}\text{Fe}_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , Nau-1; Clay Mineral Society). The olivine sand was acid washed, rinsed profusely to remove the acid, and dried. Organics in the sand and fused silica were ashed (i.e., combusted in air at 550 °C for 8 hr). The sample was then powdered in an ashed stainless steel ball mill and sieved to  $<250 \mu\text{m}$ . The nontronite was pre-extracted with a series of solvents to remove preexisting organic matter. A subset of samples contained 1 wt% of inorganic salts, either  $\text{CaSO}_4$ ,  $\text{CaCl}_2\text{O}_8$ , or NaCl. Minerals were chosen based on observations from the Mars Reconnaissance Orbiter CRISM instrument (Mustard et al., 2008).

Organic material included either 5 wt% of an Archean kerogen isolate described in detail in Eigenbrode and Freeman (2006), Pony Lake fulvic acid, or 50 ppm of a standard solution referred to as organic mix. The organic mix consisted of 50 ppm of pristine, phytane, sterane, n-heptadecane, stigmaterol, pyrene, phenanthrene, C14:0 fatty acid, C18:1 fatty acid, l-alanine, l-serine, glycine, mellitic acid, benzoic acid, and adipic acid. These organic materials were chosen to represent different types and different chemical states of sedimentary organic material common in the terrestrial geologic record. All solid materials including any solid organics were mixed at low speed in a ball mill. In some cases, water or organic solvents were used to evenly distribute organic material in the mineral matrix. Homogenization was achieved by mixing samples in a rotary evaporator while drying the samples at 50 °C, 10 mbar.

Organic removal from minerals was not complete, and some molecules were detected in control samples that did not have added organic material. Specifically, formate and oxalate were detected in the synthetic analog and fused silica control samples, and benzoate was detected in fused silica control samples. Nonirradiated control samples had concentrations near detection limits (~100 ppb), and irradiated control samples had significantly higher concentrations. Deionized water samples run during extraction and analysis were free of these compounds, and this suggests the acids were present in the synthetic analog and fused silica matrices. The increase in background organic acid signal in control samples after irradiation indicates that the source material of the organic acids was altered by high-energy proton exposure (Figures 1 and 2).

### 2.2. Radiation by High-Energy Protons

After mixing, samples were packed to  $1.6 \pm 0.1 \text{ g/cm}^3$  density in an ashed quartz-glass cuvette, then purged under 99.999% Ar and covered with ashed aluminum foil held in place by Kapton tape with acrylic adhesive on the outside of the vessel. Samples were irradiated using 200 MeV protons at the Indiana University Cyclotron Facility. Proton energy was chosen based on the predicted energy profile for inbound protons to Mars (Heynderickx et al., 2004) and is in reasonable agreement with Radiation Assessment Detector (RAD) measurements on MSL (Ehresmann et al., 2014). Samples received a cumulative dose of either 0, 63, 125, 250, or 500 kGys. The RAD instrument measured the galactic cosmic ray dose rate at 76 mGy/year (Hassler et al., 2014), so these experiments represent up to  $\sim 6.6 \times 10^6$  years on the Martian surface. This exposure age estimate assumes that the single 1.25-mm quartz glass cuvette wall that the proton beam



**Figure 1.** Formate concentration in all sample combinations where it was detected: (a) synthetic analog and Archean kerogen isolate, (b) fused silica and organic mix, and (c) control samples for synthetic analog and fused silica.

penetrates has negligible effects on the exposure age estimate for the sample and that proton cumulative dose for the experiments is comparable to the long-term effects of the full spectrum of radiation that make up the dose rate monitored by RAD.

### 2.3. Organic Acid Extraction and IC-MS Analysis

Samples were extracted for low-molecular-weight organic acids and analyzed using ion chromatography mass spectrometry (IC-MS). One gram of each sample was mixed with 5 ml of deionized, ultrapure water (pH = 6.5) and agitated for 2 hr. The liquid extract was separated from the sample by centrifugation for 15 min at 5,500 RPM. This procedure was repeated with 95 °C DI water, to remove larger organic acids, for a total extraction volume of 10 ml. Previous work reports between 85% and 95% recovery for the reported organic acids extracted from clayey-loamey soils (Mimmo et al., 2008).

The extracts were concentrated to 5 ml and run on a Dionex ICS-2100 MSQ+. Column choice, eluent concentration, and MSQ parameters were chosen to detect acetate, formate, benzoate, oxalate, phthalate, and citrate, which represent a range of common organic acids and products predicted by Benner et al. (2000). Compounds were separated on a 2 mm AS11 guard and analytical column with a multistep gradient of KOH (0.5 mM 0–6 min, 5 mM 6–18 min, and 38.3 mM 18–22 min). Control samples without added organic material were run on a Dionex ICS-5000+ Q Exactive with the same analytical column and eluent concentration gradient.

No organic acids were detected in calcium sulfate-containing samples. This is likely the result of the extraction method, where hydration of calcium sulfate produced sulfuric acid, which oxidized organic material. Therefore, calcium sulfate results are not reported.

		Radiation (kGy)					
		0	63	125	250	500	
Organic Material	A) Fused Silica	Control Samples	–	–	–	–	✓
	Organic Mix	✓	✓	✓	✓	✓	
	Fulvic Acid	✓	✓	✓	✓	✓	
	Kerogen	–	✓	–	✓	✓	
Organic Material	B) Synthetic Analog	Control Samples	✓	–	–	–	✓
	Organic Mix	✓	✓	✓	✓	✓	
	Fulvic Acid	✓	✓	✓	✓	✓	
	Kerogen	✓	✓	✓	✓	✓	

**Figure 2.** Oxalate presence and absence charts for (a) fused silica and (b) synthetic analog samples. Check marks indicate positive detection, minus symbols indicate no detection, and gray boxes indicate those conditions were not tested.

Positive identification of target compounds met three criteria. First, peaks eluted  $\pm 1$  min of the average retention time for the given organic acid standard. IC-MS analysis produced both an ion chromatogram and a mass spectrum. For the second criterion, there must be a peak in both the ion chromatogram and mass spectra of the target mass. Third, the ratio of peak areas between the ion chromatogram and mass spectra had to be in the same range as the standards. Due to mass interferences from silica at  $m/z = 60$ , acetate could not be identified and therefore is not reported. IC-MS detection limits for the target compounds was 100 ppb. Each analysis set was bracketed by standards. The values for formate and benzoate standards fell within  $\pm 20\%$  for each analysis set. Uncertainty for each sample was determined by the standard deviation of two runs of and fell within  $\pm 20\%$  for formate and benzoate.

### 3. Results

Of the target compounds, only formate and oxalate were detected in irradiated samples. Concentrations of formate are reported in Figure 1. Formate was detected in two samples, fused silica and organic mix and synthetic analog and kerogen (Figure 1). In the case of the fused silica and organic mix samples, a small amount of formate was detected in the nonirradiated control sample. However, irradiated samples showed an order of magnitude increase of formate, suggesting radiation led to additional formate production. There was no detection of formate in the synthetic analog and kerogen control sample, consistent with the breakdown of kerogen to formate. The detection of formate in irradiated control samples without added organic material suggests that this formate may be the product of an unknown contaminant, rather than kerogen or organic mix. However, formate was not detected in any other samples (i.e., fulvic acid, Green River shale) nor samples containing added additional inorganic salts, indicating these materials either promoted the destruction or inhibited the production of formate.

Due to coeluting peaks and low concentrations, oxalate abundance could not be reliably quantified, a presence/absence chart is given in Figure 2. Oxalate was detected in all synthetic analog samples, including the nonirradiated control samples and a subset of samples with added inorganic salts. Therefore, it cannot be assumed that oxalate was produced from radiation-driven mechanisms. However, oxalate was not detected in the fused silica and kerogen nonirradiated control sample but was detected in the irradiated fused silica and kerogen samples. This indicates that oxalate can be produced by radiation-driven processes. It is possible that oxalate was produced in other samples by radiation-driven processes, but subsequent work that can quantify oxalate in these samples is needed to test this theory.

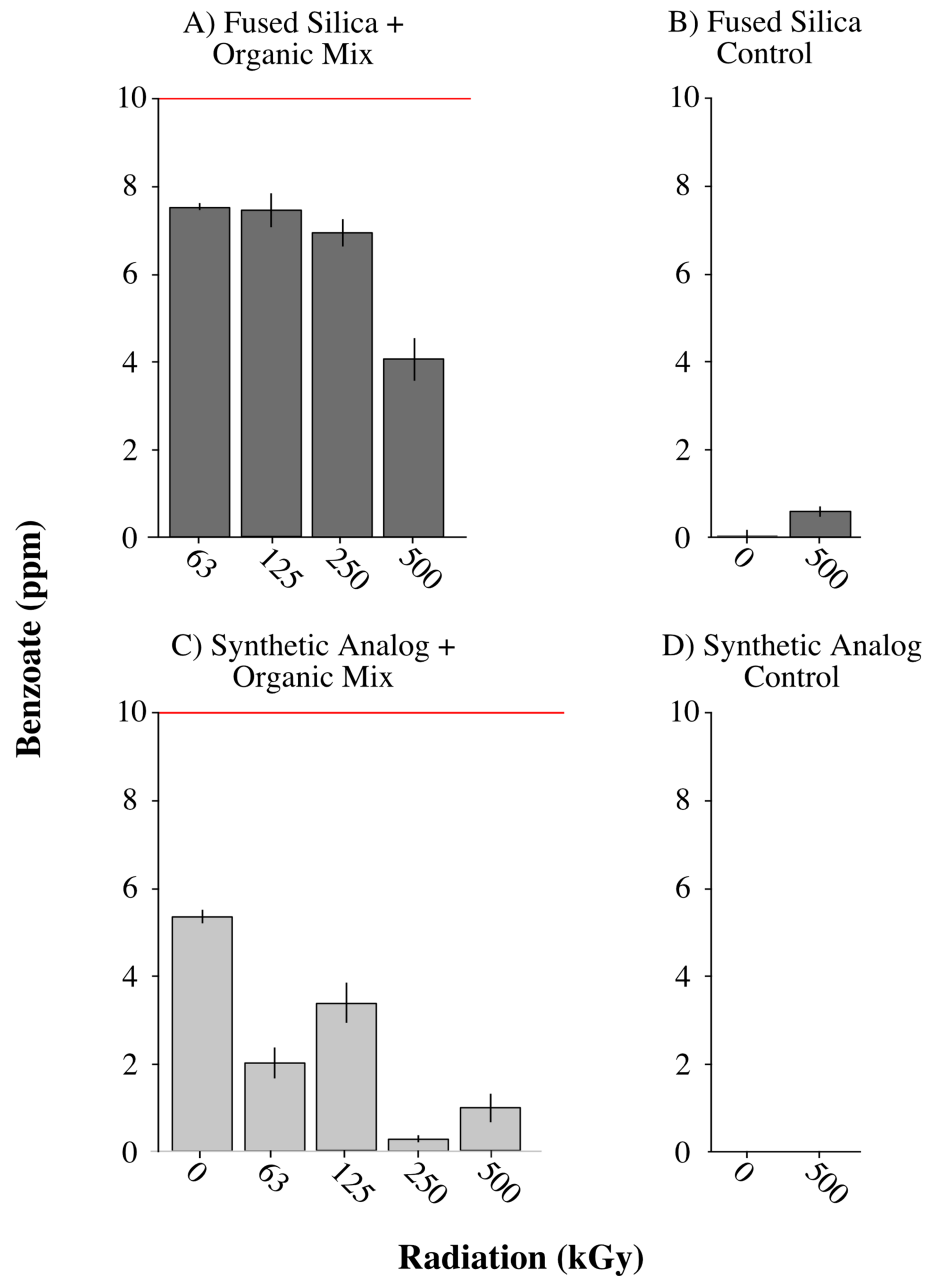
Benzoate was detected in samples containing the organic mix, of which benzoate was a component. The addition of 10 ppm of benzoate prior to irradiation in these samples allows a comparison of different matrices to protect organic acids from radiolysis. Figure 3 shows benzoate concentrations in analog and fused silica samples at different cumulative doses. Extraction of benzoate from the nonirradiated control samples shows that extraction is more efficient in fused silica, 77%, than synthetic analog samples, 58%. Figure 4 shows the relationship between benzoate concentration and radiation dose. More benzoate persisted in fused silica samples compared to analog samples.

### 4. Discussion

The presence of formate and oxalate coupled with the loss of benzoate suggests that organic acids are simultaneously created and destroyed by processes driven by high-energy protons. Mechanisms of production and destruction rely on interactions between mineral surfaces and high-energy protons to produce radicals that can both break down larger organic matter and combine to form small organic molecules.

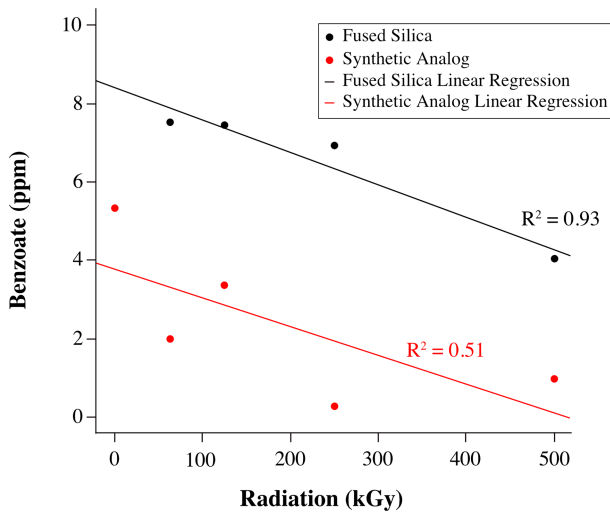
#### 4.1. Organic Acid Formation

Organic acids were detected in irradiated samples that were not detected prior to exposure to high-energy protons. Therefore, interactions between macromolecular organics, the mineral matrix, and high-energy protons formed formate and oxalate. Previous authors have reported similar results. Mao et al. (1991) reported organic acids were produced from irradiation of chloroethanes on  $\text{TiO}_2$  semiconductor surfaces. Formate and oxalate were produced when pyridine and quinoline were irradiated with  $\text{TiO}_2$  nanoparticles (Chu et al., 2018).



**Figure 3.** Benzoate concentration in (a) fused silica and organic mix, (b) fused silica control, (c) synthetic analog and organic mix, and (d) synthetic analog control. Red lines on panels a and c indicate the starting concentration of benzoate prior to irradiation; no benzoate was detected in the synthetic analog control. Error bars show the standard deviation of two analyses.

To predict where organic acid production is likely on Mars, we must understand the mechanism. Studies of UV-driven organic acid formation invoked Fenton chemistry as the dominant mechanism. Generally, Fenton reactions occur when photons interact with iron (or other redox sensitive elements) and hydroxyl species to form hydroxyl and oxygen radicals (Pignatello et al., 2006). This reaction is unlikely in fused silica samples because they lack mentionable iron. The only possible iron source would be from powdering in a stainless-steel ball mill. Any iron contribution would likely be small and should not contribute significantly, suggesting Fenton reactions are not the primary driver of radical production in fused silica samples.



**Figure 4.** Benzoate concentration as a function of radiation dose for organic mix samples. Fused silica and organic mix samples are shown in black, and synthetic analog and organic mix samples are shown in red. Linear regressions were performed for both matrices, and  $R^2$  values are displayed on the chart.

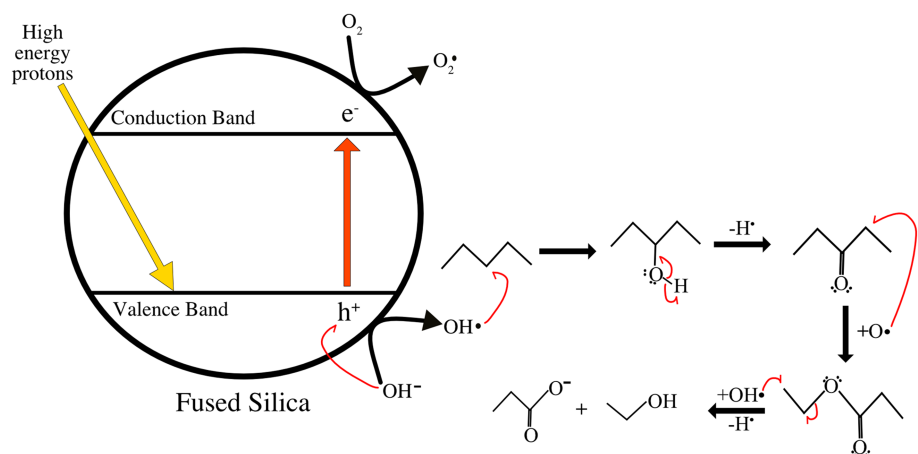
Alternatively, organic acid formation could be driven by the irradiation of semiconductor surfaces. Prior work has observed that silica particles exposed to  $\gamma$  radiation produced hydrogen atoms, which are attributed to radiolytic homolysis of hydroxyl impurities on the silica surface via reaction (1).



In reaction (1), high-energy particles excite electrons to higher energy levels in the conduction band, leaving behind positive “holes” in the valence band. The decoupled electrons and holes get trapped at surface defects. Adsorbed species can then either scavenge trapped electrons or donate an electron to a hole (Zhang et al., 1997). Interactions with trapped electrons or holes result in either radical formation or oxidation (Thomas, 2005; Zacheis et al., 1999).

We propose a similar mechanism for formate and oxalate production in fused silica samples, illustrated in Figure 5. High-energy protons excite electrons in the valence band of the silica surface splitting an electron-hole pair. The electron ( $e^-$ ) and positive hole ( $h^+$ ) become trapped at surface defects in semiconductors. On Mars, possible semiconductors include oxide minerals such as  $\text{TiO}_2$  or  $\text{Al}_2\text{O}_3$  (Baird et al., 1976) and clay minerals (Bish et al., 2013). Hydroxyl and oxygen species present in the Martian soil due to the radiation driven breakdown of hydrated clays (Vaniman et al., 2014), oxide minerals (Gebicki & Gebicki, 1993), or salts such as perchlorate (Hecht et al., 2009; Quinn et al., 2013) can form radicals by interacting with trapped species, which then break down macromolecular organics to produce organic acids. The diversity of starting organic materials both in previous studies and reported in this study suggest that many oxidation reactions can lead to organic acid production.

Synthetic analog samples contain iron-bearing minerals. The presence of redox-sensitive elements can facilitate Fenton reactions, which may be the dominant mechanism for organic acid production in the analog samples. However, semiconductor surface interactions may also be present because nontronite can behave as a semiconductor. Clay minerals have a smaller band gap between their valence and conduction band, allowing electrons to be excited to the surface more easily. As a result, nontronite is potentially a more effective semiconductor surface than fused silica that yields increased radicals relative to fused silica (Thomas,



**Figure 5.** Proposed formation mechanism for organic acids in samples containing fused silica. High-energy protons excite valence band electrons to separate electron-hole pairs. These electrons and positive holes ( $h^+$ ) get trapped at surface defects and can interact with oxygen and hydroxyl species to form radicals. Radicals can then form organic acids via a general oxidative pathway, shown here for pentane interacting with a hydroxyl radical.

2005). It is not possible to determine which mechanism, either Fenton reactions or irradiation of semiconductor surfaces, is primarily responsible for organic acid production in synthetic analog samples from this data set. Future work could determine the role of surface-mediated reactions by measuring changes in organic acid production with nontronite surface area.

Alternatively, radicals can be produced by the breakdown of oxides exposed to ionizing electromagnetic radiation. Gamma radiation can generate reactive oxygen species that can break down proteins in aqueous solutions (Gebicki & Gebicki, 1993) and is likely responsible for perchlorate production in chlorinated ices or aqueous oxide solutions (Kim et al., 2013; Schuttlefield et al., 2011). While we cannot rule out this mechanism contributing to radical production in fused silica and analog samples, previous work has shown that radical production on SiO<sub>2</sub> is a function of particle's surface area. The dependence on surface area suggests radicals are produced by surface-mediated reactions rather than the breakdown of SiO<sub>2</sub> (Zhang et al., 1997).

#### 4.2. Metastability of Organic Acids in Different Matrices

Benner et al. (2000) suggested the rate of organic acid formation was significantly faster than their rate of destruction by UV radiation, allowing them to exist on the surface of Mars. It is unclear if similar formation and destruction rates can be expected for organic acid synthesis driven by high-energy protons. This work provides a direct test of benzoate's survival to bombardment with high-energy protons for a range of radiation doses.

In analog and fused silica matrices, exposure to radiation caused benzoate to be lost (Figure 3), potentially degraded to CO<sub>2</sub>, or incorporated into new organic phases. Benzoate decreased linearly ( $R^2 = 0.93$ ) with increased radiation exposure in fused silica samples. This is consistent with increased radical production at higher cumulative radiation dose, which led to higher benzoate loss (Figure 4). Analog samples do not show a strong linear relationship to radiation dose. The reason for the lack of trend in these data is unclear. Possible explanations include (1) multiple formation and destruction mechanisms competed (i.e., Fenton chemistry and surface reactions), (2) differences in the surface area of nontronite grains caused inconsistent production, or (3) experimental uncertainty masked a trend.

Fused silica samples had higher benzoate concentrations at all radiation doses. This could be the result of a less-efficient extraction of benzoate in synthetic analog samples, evidenced by the poor recovery in the non-irradiated synthetic analog and organic mix sample. Extraction in the fused silica and organic mix control sample had a recovery of 77%, consistent with previous reporting. Alternatively, the higher benzoate concentrations and lower formate concentrations could be due to fewer radicals produced in fused silica samples. These observations further support that analog samples experienced both Fenton reactions and semiconductor surfaces interactions to produce radicals. As a result, both rates of production and destruction of organic acids are increased in synthetic analog samples.

Despite enhanced losses, benzoate persisted in most matrices and radiation doses. Measurements from the RAD on the MSL Curiosity rover show that 500 kGys is roughly equivalent to 6.6 Myrs at the Martian surface (Hassler et al., 2014). Future work should further investigate the relative rates of the production and destruction of organic acids demonstrated here in order to determine if organic acids are likely metastable products beneath the Martian surface that have been exposed to high-energy protons for millions of years.

### 5. Conclusions

We found bombardment of macromolecular organics with high-energy protons common to the Martian cosmic ray spectrum produced organic acids in fused silica and analog matrices. Our results are consistent with previous UV radiolysis studies that found organic acids to be a major radiolysis product. We proposed an alternate mechanism of formation for radical production that does not invoke Fenton chemistry and therefore does not require redox sensitive elements. Taken together, these studies indicate that organic acids are likely a major component of present-day Martian organics at and below the surface. Furthermore, we demonstrated that organic acid products were not dependent on starting material or mineral matrix, suggesting they cannot record information about the source organic material. Based on this work, samples will have to be taken at depths that are not exposed to high-energy protons in order to learn more about the Martian organic sedimentary record that are not altered by ionizing radiation.



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