

THE EFFECTS OF PROTON IONIZING RADIATION ON ORGANIC MATTER IN MARTIAN SURFACE SEDIMENTS.

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Introduction: One aim of the Mars Science Laboratory (MSL) mission is to search for organic molecules in sediments at Gale Crater using the Sample Analysis at Mars (SAM) instrument suite for detection. Chlorinated hydrocarbons have been detected in the Sheepbed mudstone and their presence is consistent with a martian origin [1], but it is unclear what sources and processes are responsible for their presence. Organic matter deposition and preservation on Mars are presumed to be largely governed by Earth-like processes, yet there is no terrestrial analog (natural or simulated) for the radiation conditions at the surface. Other studies have explored the direct effects of UV and gamma radiation on organic molecules, e.g. [2-3]. Here, we present preliminary results on the effects of high-dosage, high-energy proton radiation on one type of sedimentary organic matter (kerogen) in a simulated analog sediment. The addition of chlorinated salts and moisture were tested for their influences on molecular abundances as observed using SAM-like techniques.

High energy protons account for the largest fraction of nuclear particles in GCRs (85-90%), which make up the bulk of ionized particles reaching the surface. 200 MeV protons were chosen for this study to approximate the greatest flux of the proton spectrum, consistent with RAD in situ measurements [4].

Methods: A thermally mature kerogen isolate was added to the mixture of NAu-1 nontronite and forsterite. Five wt% kerogen was used to insure adequate detection of molecular signals, though this quantity far outweighs the parts per million levels expected under most hypothetical circumstances (deposition from interplanetary dust particles or kerogen from processed biomatter) for Mars. Analogs with no salt addition, 1 wt% of sodium chloride, and 1 wt% calcium perchlorate with and without additional 1 wt% water were irradiated. Sediments were packed 4-cm deep glass vessel at $\sim 1.5 \text{ g/cm}^3$. After irradiation, 1-cm depth aliquots were separated for analyses.

All samples were irradiated to achieve cumulative doses up to 500 kGy, which have been modeled using GEANT4 [5] indicating an equivalent ~ 8 Myr of exposure (or ~ 2 Myr exposure using constants comparable to the 78 ± 30 Myr exposure age of Cumberland at Sheepbed [6]). Evolved gas analysis (EGA) of kerogen-bearing samples involved heating samples in 0.9 ml/min at 0.5 b He to thermally desorb and cleave molecular components. Analytes were transferred at 270 °C and directly detected by a mass spectrometer. Sam-

ples were heated at 75 °C for 25 min to desorb most surface water, then heated at 35 °C/min to 1050 °C. Benzene, naphthalene, methylene, and alkyl fragments (represented by C_7H_{15}), and chlorobenzenes were monitored for changes.

Results: Irradiation (63-500 kGy) of dry analog materials containing kerogen induced little change in product abundances attesting to the refractory nature of the organic material and the relatively inert chemistry of the matrix. The addition of water and chlorinated salts drastically changed the products released from the kerogen, amplifying release of products only in the presence of perchlorate with no additional water. Ongoing analyses are exploring the changes in other products to help deconvolve the chemical reactions resulting from radiolysis and heating.

Conclusions: These results indicate that the effect of radiation on refractory organic matter is highly dependent on the chemistry the host matrix. Such refractory organic matter may be difficult to detect via SAM-like techniques without first being chemically broken down by natural or analytical processes. Oxychlorine phases, which may be ubiquitously distributed in surface materials, may make the structure of large macromolecules more labile and support the production of small molecular components. Such a process would support habitability by making small organics accessible to microbes during periods of surface irradiation. It also would support detection by SAM-like techniques; however, it is unclear at what rate and for how long such alteration of macromolecules may occur. Further, individual molecular products from the alteration of macromolecules are expected to persist at the surface at different rates. The full pathway of organic alteration at the surface is complex but perhaps critical to understanding carbon cycling on Mars and implications for habitability.

References: [1] Freissinet, C. et al. (accepted) *JGR*. [2] Court et al. (2006) *GCA*, 70, 1020-1039. [3] Stalport (2009) *Astrobio*, 9, 543-549. [4] Mathiae et al. (in prep). [5] Pavlov et al. (2012) *GRL*, 39, L13202. [6] Farley et al. (2014) *Science*, 343, 1247166-1.

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