PRESERVATION OF BIOMARKER AND ALIPHATIC CARBON SIGNALS ON HIGHLY IRRADIATED ORGANIC MATTER BEARING PLANETARY BODIES.

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Introduction: The detection and characterization of organic matter on planetary bodies, such as Ceres and Mars, has been achieved both through remote spectroscopy [1] and through direct, on site, sampling and analysis [2]. The remarkable SAM analysis suite on the Mars Curiosity rover, in particular, was designed to assess organic matter composition at a molecular level and thus is capable, in principle, of examining any occurrences of biomarker compounds or alteration products that would be indicative of life processes [2,3]. The difficulties of carrying out such analyses include low carbon contents [4], reactive and oxidative sample matrices, and high surface cosmic ray irradiation levels on candidate bodies such as Ceres [5], or Mars, where near surface radiation doses are in the Megagray (MGy) range that readily degrade organic species [6,7]. While many useful model compound radiolysis studies have been carried out, the most radiation resistant organic compounds are certain hydrocarbons, and these have not been well characterized for durability under planetary body irradiation conditions in complex matrices. The impacts of irradiation on organic matter in terrestrial settings are well studied, with applications to petroleum system chronology [8,9] and the recent discovery that radiolysis of sedimentary organic matter produces carbon isotopically depleted methane as a byproduct [10,11]. Here, we assess the impact of high radiation dosage (MGy) on the durability of biomarker hydrocarbons in organic matrices and, based on inferences from terrestrial petroleum systems, speculate on more optimal candidate localities and protocols for detection of novel biomarker signals on other worlds.

Methods: The approach has already been detailed elsewhere [8]. Briefly, crude oils without their solution gas were submitted to gamma ray irradiation from ^{60}Co decay, up to an accumulated radiation dose of 10 MGy. ^{60}Co decays to ^{60}Ni, generating mainly two gamma ray photons at 1.33 and 1.17 MeV, respectively. Analytical techniques such as GC-MS and NMR [8], FTICR-MS [9], and gas analysis [10] were used to investigate the impacts of radiolysis at molecular and bulk chemical property levels. Similar approaches are being used to study sulphate and other mineral radiolysis effects.

Terminology: The term hydrocarbon is used inconsistently in both the planetary geology/astronomy literature and also in the organic geochemical literature. Even in the petroleum industry it is used inconsistently and often in a colloquial rather than chemical context. For precision, we will use the term hydrocarbon here, to mean a chemical species consisting solely of the elements hydrogen and carbon. More complex organic matter containing hydrogen and carbon as well as other elements, and containing abundant alkyl carbon structural elements, we will refer to as ACROM (alkyl carbon rich organic matter).

Results and Discussion: Identifying life markers in chemical and isotopic records from sampled material, or spectroscopic signals of planetary bodies is difficult. Even if biological signals were originally present, several processes, including radiolysis, attenuate signals, complicating analysis. If organic matter of biological origin was generated on a planetary body, diagenetic processes at shallow depths would quickly remove reactive species through cross reaction or mineralization, leaving only more refractory species behind. Further, if sediments containing biomarker structures were buried through tectonic processes, then thermal maturation of the organic matter would also result in production of more refractory species as products such as hydrocarbons.

Even if carbon-based life on an alien world was fundamentally different from that on Earth, hydrocarbons are likely stable end products of organic matter alteration. It also seems plausible that alien carbon-based biochemistry would encode structural specificity in its products as a result of life's information copying mandate. Thus, structurally specific hydrocarbons are a plausible choice for seeking organic life markers in organic matter containing environments on planetary bodies. Even if the biochemistry is not known, structural specificity is a good indicator of biological origin with prior examples, such as the discovery of hopanoids from analysis of hydrocarbons in crude oils, before recognition of the biosynthetic pathways and products in organisms [12]. Structurally specific hydrocarbons are prime targets for analysis.

Crude oil, produced by microbial and thermal alteration of biomass, is a very plausible model for studying biomarker resistance to radiation in ACROM environments. Biomarkers in crude oil are found at concentrations from sub-ppm to thousands of ppm. In a large study of radiation impacts in petroleum basins, biomarkers were quantitated by GC-MS, after crude oils were irradiated, at gamma radiation doses up to 10 MGy, equivalent to near surface irradiation at weakly shielded planets such as Mars. High dose irradiation results in degradation of all hydrocarbon and non-hydrocarbon species to complex products, with aromatic hydrocarbons and thioaromatic compounds being most refractory and large alkanes, including the classical terrestrial biomarker isoprenoid, hopanoid and steroid hydrocarbons, being degraded faster [8]. Figure 1 shows the impact of gamma irradiation on C30 hopane concentrations in two crude oils. The hopane concentration decreases sub-linearly with increasing radiation dose but even at 10 MGy, substantial C30 hopane remains. At this level of radiation doses, radiation alone is unlikely to remove all biological signatures from organics, and possibly, readily detectable levels of biomarkers may be found even after ~several 10s of MGy of gamma irradiation. If biomarker signals are absent in samples irradiated up to these dose levels, then one might conclude that either biomarkers were never present originally or other processes than radiolysis have destroyed them. We note, however, that radiolysis may produce oxidative species in the presence of water or oxygen bearing complexes such as oxyanions and we are investigating how these matrix-impacted settings impact biomarker stability. We report early results on sulphate radiolysis. We note that complex products of radiolysis included ^{12}C enriched methane, showing a 30-40 per mil fractionation factor, indicating isotopically light methane can be readily derived from radiolysis of alkylated organic matter and is not exclusively indicative of biological activity [10].

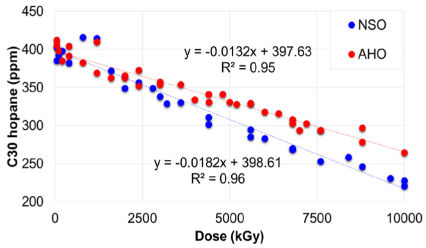

Figure 1: C30 Hopane concentrations in two crude oils during gamma irradiation (after [8]).

Sampling of seeping plume fluids is being tasked with the search for life markers on Enceladus and other bodies [13]. Hydrocarbon-rich material can also find its way to the surface of Earth in the form of focused seeps in terrestrial petroleum systems and as a complementary approach to analysis of geologically targeted spot samples, sampling of likely fluid seepage sites could provide focused access to larger scavenged volumes of the better protected subsurface and might potentially improve opportunities for detection of life signals.

Remote spectroscopic observation of planetary bodies has been used to confirm the presence of ACROM. De Sanctis and co-workers [1] used data returned by the Dawn spacecraft to suggest detection of an organic absorption feature at 3.4 µm wavelength on Ceres. This signature is likely characteristic of aliphatic organic matter (ACROM), and Figure 2 shows that this infrared absorption feature appears quite resistant to change during irradiation of crude oils up to 10 MGy. Although unclear what compound mixtures generate such a signal in other planetary bodies, our results show that the bulk signature may persist even after long-term exposure to high dosage of radiation.

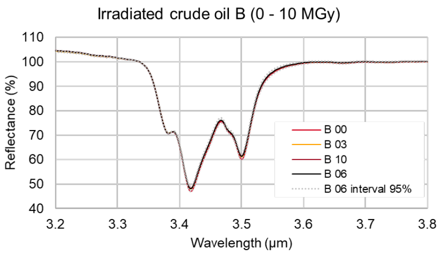

Figure 2: Variation in absorption spectra of crude oils in the 3.2-3.8 µm region shows little impact of radiation dose. B03 represents data after 3MGy. B06 95% dashed line represents replicate confidence interval.

Conclusions: Biomarker hydrocarbons and spectroscopic indicators of alkyl carbon in ACROM appear somewhat refractory under gamma radiolysis at ambient conditions in organic matrices.

Acknowledgments: We thank the NASA Mars Exploration Program for support of the MSL project and for useful discussions with that group. We acknowledge the support of the Project Rip van Winkle staff and sponsors for the radiolysis studies.

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