

CHARACTERIZING THE MECHANISMS FOR THE PRESERVATION OF ORGANICS AT THE PAINTED DESERT: LESSONS FOR MSL, EXOMARS, AND MARS 2020. E.Z. Noe Dobrea^{1,2}, A.C. McAdam³, C. Freissinet³, H. Franz³, I. Belmahdi³, M.R. Hamersley⁴, C.R. Stoker², B. Parker⁵, K. Ja Kim⁶, D.P. Glavin³, F. Calef⁷, and A.D. Aubrey⁷. ¹Planetary Science Institute (eldar@psi.edu), ²NASA/ARC, ³NASA/GSFC, ⁴SOKA University, ⁵Petrified Forest National Park, ⁶Korea Inst. of Geoscience and Mineral Resources, ⁷NASA/JPL.

Introduction: The Painted Desert of northern Arizona forms part of the ca. 215 My old Triassic Chinle formation, and consists of thick (ca. 100 m) layers of colorful bentonitic mudstones interbedded with sandstones and limestone formed by fluvial and lacustrine deposition [1]. Trapped in some of these layers is organic carbon derived from Late Triassic flora and fauna that were rapidly buried in the prograding beds and floodplains of the fluvio-lacustrine system present at the time [2,3].

The spectral and morphological character of the Painted Desert appear analogous in many ways to that of the Al-phyllsilicate bearing units identified on the plains units at Mawrth Vallis and Western Arabia Terra, Mars. Both regions present evidence for fluvial activity and have thick Al-phyllsilicate sequences containing Al-smectites, kaolins, hydrated silica, and jarosite [4-8]. These similarities make the Painted Desert a potential geological and compositional martian analog. Here, we are interested in understanding how the chemistry and textural character of these units may play a role in the preservation of organic compounds.

Organic compounds show high affinities to clay minerals, where interlayer binding acts as a sequestration mechanism for the sorption of organics onto phyllosilicates. Amino acids in particular demonstrate extremely strong sorptive properties with clay minerals [9,10]. Additionally, low O₂ concentrations at the time of burial are conducive to preservation over long timescales [11,12,13]. Smectites from the Painted Desert experienced rapid burial after deposition, and O₂ concentrations are thought to have been low. Hence, the preservation in these layers is expected to be high.

Past work: A past pilot study, performed at the Petrified Forest National Park (PFNP), focused on identifying correlations between organic content and rock-type and tonality of the host rock. The PFNP is found in the Painted Desert and its members belong to the Chinle Formation. Analyses of samples showed that the preservation of organic compounds varied strongly from layer to layer [14,15]. Although some of the dark mudstone layers of the Blue Mesa Member (BMM) did show a much stronger propensity for preservation of organics than the overlying sandstones of the Petrified Forest Member (PFM), other equivalently dark mudstones in the BMM did not exhibit any enhancement in organics beyond those found in the PFM sandstones. Correlations between organic content and mudstone tonality were also found to be weak. However, it was noted during the study that jarosite ap-

peared to be present wherever enhanced organic concentrations were found.

In addition to the in-situ identification of jarosite in organic-rich units, we also detected jarosite in remote sensing hyperspectral imagery of the region using AVIRIS. The jarosite was found to be correlated to dark-toned layers of the Purple Grey Formation (PGF).

In this follow-up study, we sought to obtain a more complete sampling of the units exposed at the PFNP to better establish the correlation between organic preservation and jarosite. We measure the concentration of organics in different layers of the Chinle formation using techniques available to MSL in order to establish a framework for the interpretation of MSL observations. Here, we report on findings from our latest field activity, performed in the spring of 2015.

Field Work and sample collection: Fieldwork was performed at the PFNP with the intent of sampling many of the members exposed within the park's boundaries. We targeted sequences of dark/light bentonite as well as units where jarosite had been identified in aerial hyperspectral imagery.

Field work focused on site characterization and sample collection. Site characterization involved a study of the rock textures, grain size, cementation, and mineralogy for each facies, with emphasis on comparison of the units that preserve organics to the units where organics have been lost due to silicification. Where possible, we identified sedimentary and diagenetic features. Grain size distribution was assessed to constrain mode of emplacement.

Organics-clean sample collection was performed using protocols developed during a previous field expedition. To minimize organic contamination, the glass vials and all materials used to store and handle the samples were previously pyrolyzed at 500 °C overnight. Samples were collected from 30 cm within outcrops exposed on steep-sided slopes (>60°) to reduce the chance of modern contamination by downward water percolation and root penetration from plants. Nitrile gloves were worn and replaced often and sampling instruments were rinsed in acetone and wiped down with clean fiberglass wipes to remove organics and any adhered material from previous sites. Pyrolyzed silica powder was brought to the field and taken through as many of the sample processing steps as possible to serve as a procedural blank.

Sample analysis:

Composition and chemistry: Mineralogy was assessed using VNIR spectroscopy and x-ray diffraction

(XRD), and chemistry was assessed using x-ray fluorescence (XRF) techniques in order to establish a geochemical setting for the samples, to distinguish between different types of alteration, and to allow the development of a coherent geological interpretation.

Total Organic Carbon, Nitrogen, and Stable Isotope Measurements: Total carbon (and, following carbonate acidification, organic carbon), nitrogen content and stable isotopic composition was quantified by micro-Dumas combustion followed by isotope ratio mass spectrometry. Carbonates were removed by two-stage acidification with 2 N HCl, followed by desiccation in a vacuum centrifuge. Samples were weighed into tin capsules for analysis.

EGA and GCMS analysis: SAM-like evolved gas analysis mass spectrometry (EGA) analyses were performed using a Setaram LabSys Evo instrument coupled to a Pfeiffer OmniStar mass spectrometer. Powdered rock samples were loaded into cleaned sample cups and placed into the oven. SAM-like helium pressures (~25 mb) and gas flow conditions (~0.8 sccm) were used. Evolved gases were monitored for compounds between 2-300 AMU as samples were heated at 35°C/min from ~50°C to ~1000°C. The organics content analyses were performed on a gas chromatograph coupled to a mass spectrometer (GCMS), by direct pyrolysis of the sample and by extraction-derivatization to reach the more complex and refractory organics. GCMS experiments were run using a commercial pyrolysis unit coupled to the injector inlet of a GCMS instrument. Powdered samples from the Painted Desert were heated inside a quartz boat at temperature steps of 300°C, 450°C, 600°C, and 800°C under helium carrier gas flow. Volatile organics released from the samples were pre-concentrated using the built-in CDS pyroprobe Tenax and glass bead trap held cooled to <10°C. Hydrocarbons adsorbed by the trap were then carried to the GC column inlet under He carrier gas flow after rapid heating of the trap to 300°C, followed by detection by electron impact quadrupole mass spectrometry. Some of the organic-rich samples were also extracted by heating directly in a mixture of MTBSTFA and dimethylformamide (DMF) prior to pyrolysis GCMS analysis to target amino acids, carboxylic acids, and other derivatized species.

Results: The layers exposed at the PFNP are dominated by Al-smectite-rich bentonite mudstones, some of which exhibit evidence for illitization. Shales and sandstones also occur in sequences associated to the PFNP, and are dominated by quartz. Jarosite and dark calcite-rich nodules occur embedded within some of units in association with organic-rich materials (see below).

TOC measurements indicate that all samples contain some degree of organic carbon. Sequences of light- and dark-toned mudstones do not exhibit a clear

correlation between TOC and rock tonality, suggesting that organic carbon does not necessarily play a role in the darkening of the rocks. The highest concentrations of organic carbon are found in association with the jarosite-bearing samples and the calcite nodules, irrespective of rock type. In particular, jarosite-rich rinds that encased dark, calcite-rich nodules were found to be rich in organics relative to the surrounding sandstone or mudstone matrix.

Preliminary EGA analysis of our samples show CO₂, SO₂, H₂O evolutions, as well as peaks in EGA traces associated with organic fragments. Some of the mudstone samples produce H₂O evolutions consistent with dehydration and dehydroxylation of a smectite, which demonstrates the SAM EGA's ability to help constrain sample phyllosilicate compositions. GCMS analysis shows that samples which evolved a lot of SO₂ were richer in organics variety, indicating a strong correlation between organic preservation and sulfur minerals (e.g., sulfates). Extraction via water-propanol + MTBSTFA derivatization was found to be the most efficient procedure for analysis of organics content of the Painted Desert samples.

Discussion: Although the identification of organics in the ancient fluvial sediments of the PFNP is not particularly surprising, the apparent lack of correlation in organic concentration and rock type is somewhat perplexing, as one expects organics to be better preserved in mudstones than in sandstones. This suggests that additional parameters must be taken into account when considering the preservation of organics. The detection of organics in association with jarosite precipitates points to a mechanism of preservation that is of high interest to MSL, Exomars, and Mars 2020. These results are especially compelling, particularly in light of the recent identification of organics by MSL/SAM in the jarosite-bearing Murray mudstone samples [16,17]. Additional analysis of the jarosite-rich samples will hopefully allow us to establish a genesis for the sulfate as well as a mechanisms for entrapment and preservation of these ancient organics.

References: [1] Allen (1930). *Amer. J. Sci.* doi:10.2475/ajs.s5-19.112.283 [2] Demko *et al.* (1998) *Geology*. [3] Ash and Creber (2003) *Paleontology* 43. [4] Bishop *et al.* (2008) *Science* 321. [5] Noe Dobrea *et al.* (2010), *J. Geophys. Res.* [6] Noe Dobrea *et al.* (2009) *Lunar Planet. Sci.* 40 # 2165 [7] Farrand *et al.* (2009) *Icarus* 204 [8] Noe Dobrea *et al.*, (2011) *Mars Journal*, 6. [9] Keil *et al.* (1998) *Geochim. Cosmochim. Acta* 62. [10] Zaia, (2004) *Amino Acids* 27. [11] Keil *et al.* (2004) *Mar. Chem.* 92. [12] Schroeder (1974) PhD thesis. UCSD. [13] Farmer and DesMarais, JGR 1999 [14] Noe Dobrea *et al.*, (2011) *MSL 5th Landing Site Workshop*. [15] Noe Dobrea *et al.* (2015) *AbSciCon 2015 #7762*. [16] Eigenbrode *et al.* (2015) AGU. [17] Freissinet *et al.* (2016) *LPS XLVII*.