

MECHANISMS FOR PRESERVATION OF ORGANICS IN JAROSITE AT THE PAINTED DESERT.

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Introduction: Phyllosilicate and sulfate deposits are widely observed on Noachian and Early Hesperian terrains on Mars, and the association of similar ancient terrestrial deposits with high concentrations of organics makes these martian deposits viable and attractive targets in the search for organics. Here, we examine sediments from a Mars-analog material, the Painted Desert sediments, to investigate the mechanisms of organic preservation in fluvio-lacustrine systems.

The Painted Desert of northern Arizona consists of 215 My old, interbedded layers of mudstones, sandstones, and limestone deposited in a fluvio-lacustrine and deltaic environment [1]. Trapped in some of these layers is biogenic organic carbon that was rapidly buried in the prograding beds and floodplains of the system [2,3].

The spectral and morphological character of the Painted Desert appears analogous in many ways to that of the Al-phyllosilicate-bearing units at Mawrth Vallis, Mars. Both regions present evidence for fluvial activity and have thick Al-phyllosilicate sequences containing Al-smectites, kaolins, hydrated silica, and jarosite [e.g. 4]. These similarities make the Painted Desert a potential geological and compositional martian analog. We seek to understand the mechanisms for organic preservation in ancient clay and sulfate-rich Mars-analog sediments.

Previous Work: In a previous study, we focused on relationships between organic content, rock-type, and color of the host rock [5]. We found typical concentrations of a few tens of mg C/kg in smectite deposits and C:N ratios between 1 and 10. The latter are lower than would be expected for terrestrial flora, indicating either diagenetic loss of C or allochthonous sources of N during diagenesis. We also found organic-rich (>300 mg C/kg) pieces of dark calcite (interpreted as calcified wood) coated by a jarosite rind and embedded in the clay beds. We noted the contrast with silicified logs that were embedded in sandstone-rich layers.

Additional field expeditions identified high organic carbon concentrations (500-1500 mg C/kg) in jarosite-bearing mudstones targeted via remote sensing, in dark calcite nodules, in jarosite precipitates coating the calcite, and in sandstones encasing these nodules. Low organic carbon content (ca. 30 mg C/kg) was found in the jarosite-free clay beds and in the silicified wood. In general, we found neither host rock tonality nor grain size to be a good predictor of organic content.

GCMS and EGA analyses provided greater insight into the presence and distribution of organics.

Organic fragments evolved at the same temperatures of gas releases (SO₂, H₂O, CO₂) that result from mineral decomposition at high temperatures, suggesting that some organics were trapped within sample minerals. Data from GCMS flash pyrolysis to 900°C indicated the presence of aromatics with up to three rings. Subsequent water/isopropanol extraction of the organic content of the sample followed by MTBSTFA derivatization, allowed measurement of the most refractory organic molecules present in the samples: numerous amino acids were detected, in addition to carboxylic and dicarboxylic acids, alcohols, aliphatics and other complex molecules [6].

Current work: In the current phase of the project, we seek to understand the mechanisms by which jarosite precipitates and encases organic material in our samples. Given the evident preservation of organics in jarosite precipitates, we subsampled the jarosite-encased organic nodule identified in the first field season. We performed spectral and XRD analyses of the subsamples, and also sent the samples out for sulfur isotopic analysis.

Results: Spectral and XRD measurements show a clear mineralogical trend as a function of depth into the sample, with the outermost layers being dominated by gypsum, followed by jarosite, followed by chalcocopyrite. Deeper, we found graphite in association with oxidative alteration products of pyrite, namely chalcocopyrite, goethite, rozenite, and melanterite. Sulfur isotopic analysis is still forthcoming.

Discussion: The identification of chalcocopyrite in the transition zone between the jarosite rind and the graphite (interpreted here as wood that has been permineralized to graphite); and identification of oxidative alteration products of pyrite in association with the graphite, suggests a chemical microenvironment conducive to ion mobilization within an organic acid-rich cool aqueous solution and later diagenesis. The detection of organics in association with jarosite precipitates points to a mechanism of preservation that should be of high interest to MSL and future missions, especially in light of the recent identification of organics by MSL/SAM in the Murray mudstones [7,8].

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