

DETECTION OF ORGANIC MATTER IN ANCIENT SEDIMENTARY ROCKS USING REFLECTANCE SPECTROSCOPY. H.H. Kaplan¹, R.E. Milliken¹, A.H. Knoll², T. Bristow³, M.E. Knowlton¹, ¹Brown University, Box 1846, Providence, RI 02912 (Email: *Hannah_Kaplan@brown.edu*), ²Harvard University, Cambridge, MA 02138; ³NASA Ames Research Center, Moffett Field, CA 94035.

Introduction: On Earth, organic matter (OM) is associated with a variety of sedimentary rock types that span the geologic record. Thus it is not surprising that sedimentary rocks on Mars have received attention in the search for OM beyond Earth. Certain depositional environments may be better at concentrating OM than others [1], and terrestrial experience informs us that OM can be sequestered during deposition of fine-grained sediments in sedimentary basins. Numerous studies have shown that clay minerals (clays) are particularly well suited for organic sequestration and preservation due to unique physical and chemical properties [2]. Detection of clays in various sedimentary deposits on Mars [3] has led to the consideration of such sites for *in situ* exploration.

The detection of clays in Gale Crater [4] was a key factor in its selection for the Curiosity rover landing site, and similar considerations will likely arise during site selection for the Mars 2020 rover, especially given the desire for the capability of *in situ* organic detection and sample caching. In this context, reflectance spectroscopy is a powerful tool as it is rapid, non-destructive, can be done remotely, and is capable of detecting organic compounds. Detection limits for OM with reflectance spectroscopy must be quantified if this method is to be used in the search for Martian OM. Moreover, these limits must be well constrained for non-idealized cases such as natural rocks in which the interplay of particle size, mineralogy, texture, porosity, and hydration state can affect strengths of absorption features.

This study represents a first step in assessing the detection of organic matter using reflectance spectroscopy in fine-grained sedimentary rocks. Here we present initial analysis of Proterozoic mudstones from a variety of locations and depositional settings. The relationship between bulk mineralogy and organic signatures is examined to establish a link between detectability of organic absorption features and mineral assemblages, focusing on the 1 – 6 μ m wavelength region.

Samples & Geologic Setting: *McArthur Basin.* Samples from the McArthur and Roper basins in Australia's Northern Territory preserve thick successions of Late Paleoproterozoic to Mesoproterozoic marine siliciclastic sediments. Shales in these basins are extensive and show little deformation or metamorphism [5]. The McArthur, Nathan and Roper groups have been sampled with seven drill holes, and facies definitions for six distinct depositional environments within this succession are discussed by [6].

Within the Roper Group, organic-rich shales of the Velkerri Formation (drill hole Urupanga-4) accumulated

in a deep water environment and are dominated by prokaryotic biomarkers [7]. The older Lynott Formation (drill hole Amoco 82/4) lies near the top of the McArthur Group and is comprised of dolomites, evaporates and subordinate shales formed when the basin was restricted [5, 8].

Doushantuo Formation. Neoproterozoic samples from a series of organic bearing (TOC up to 4wt%) marls and carbonaceous shales making up part of the Doushantuo Formation in South China may contain some of the oldest authigenic smectites (saponite) [9], suggesting burial and diagenesis have not managed to transform all of the original Mg-clay assemblage to illite or chlorite, though these phases are also present. Samples are from the Yangtze Gorges area, which may have been isolated from open water, and are described in detail by [9].

Methodology: Reflectance spectra were acquired for visible, near-, and mid-infrared wavelengths using a portable ASD FieldSpec3 (0.35 – 2.5 μ m) and a Nicolet iS50 FTIR (0.8 – 25 μ m). Data were collected for bulk rock powders dry sieved to <45 μ m for 46 McArthur Basin samples and 43 Doushantuo Fm. samples. Spectra from each instrument were scaled and spliced to provide a continuous spectrum from 0.35 – 25 μ m for each sample. An upper convex hull fit was used to model the spectral continuum, which was divided out of each spectrum over the wavelength region of interest. These continuum-removed spectra were used for modeling absorption features in Matlab with a linear mixing model based on library spectra of individual components and organic absorption features. Absorption band strength was also assessed to understand the relationship between organic content, mineralogy, and spectral features.

Preliminary Results: Absorptions in reflectance spectra are consistent with the mineralogy identified in previous studies (Fig. 1). Proterozoic clays are primarily illite or chlorite, likely the result of burial diagenesis and transformation of smectite, though saponites within the Doushantuo Fm. samples are an exception. A number of samples also exhibit evidence for possible kaolinite (features near 2.16 – 2.21 μ m). Roper Group samples exhibit clear illite absorption bands, as do samples from the underlying Nathan and McArthur Groups. Carbonate features are observed in all of the McArthur sample spectra (CO₃ vibrational bands near 3.4 μ m and 3.8 – 4.2 μ m); a few Roper Group samples also show weak carbonate features. A small proportion of samples (~25%) from both groups exhibit absorption bands due to Fe²⁺ and Fe³⁺-bearing phases in the 0.4 – 1.3 μ m wavelength region. Doushantuo samples contain saponite, mixed-layer smectite/chlorite, cor-

rensite and chlorite, with some samples exhibiting weak to modest carbonate bands.

The Proterozoic samples measured in this study that lack carbonates all exhibit weak to modest organic absorptions. The strength of these features varies non-systematically with depth both within and between drill cores for the McArthur basin samples. Known organic features at 3.38, 3.41, and 3.50 μm are present in the spectra, as well as a weak 3.48 μm feature, due to C-H stretching vibrations. However, carbonate absorptions overlap with C-H features at these wavelengths and can obscure the organic features entirely in samples with modest amounts of carbonate (Fig. 2). In samples with weak carbonate absorption bands, both organic and carbonate features can be seen in the ~ 3.4 μm region.

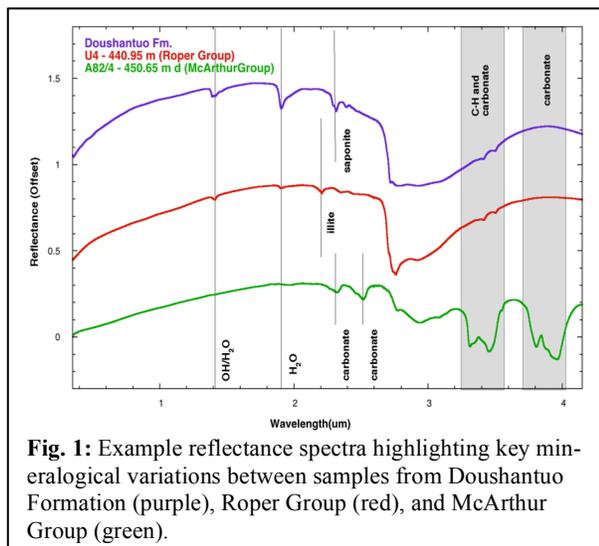


Fig. 1: Example reflectance spectra highlighting key mineralogical variations between samples from Doushantuo Formation (purple), Roper Group (red), and McArthur Group (green).

Discussion & Future Work: These results indicate OM detection with reflectance spectroscopy can be dependent on mineral assemblage. Carbonates can mask organic features, and ongoing analyses will determine exactly how much carbonate must be present for this to occur. Simple linear mixing models between carbonate and OM spectral endmembers also predict this outcome. Since not all organic absorptions overlap completely with carbonate features, it is likely still possible to detect OM in rocks with minor carbonate provided the spectra have a sufficient signal to noise ratio.

In contrast, clay minerals have no direct impact on the detectability of organic absorption features. The strength of the organic features, which is assumed to relate to organic abundance, does not vary systematically with clay type (e.g., illite vs. smectite) for the samples studied here, but additional study is warranted. However, all clay-bearing samples exhibit strong broad H₂O features from 2.6 – 4 μm on which the organic features are superposed. This will act to weaken organic features, possibly precluding their detection in highly hydrated samples. Martian (smectitic) clays may be

less hydrated than terrestrial counterparts due to local lower relative humidity, but these effects may be significant when attempting to detect OM in hydrated salts. Future work will focus on measuring a subset of samples under Mars-like T and RH conditions to assess the effects of hydration state on organic detection.

Assessing variations in OM content with bulk mineralogy is a first step, and additional measurements are underway to quantify these relationships. Specifically, total organic content will be measured for the samples discussed here to provide a direct link between absorption strength and OM content. This will help establish detection limits for both ancient clay and carbonate-bearing rocks, which are of direct relevance to Mars. Non-organic carbon content for the McArthur Basin samples will help constrain the upper limit on the amount of carbonate that needs to be present before organic features are no longer recognizable in reflectance spectra. SEM-EDS and bulk chemistry will be carried out on splits of select samples, and we will assess specifically the presence of Fe in silicate components to determine whether or not it may be reactive and thus impact organic preservation.

Reflectance spectroscopy is a promising tool for remote, non-destructive detection of organics in Martian rocks, but well-controlled experiments on samples relevant to Mars are needed to fully understand and quantify the complexities and detection limits associated with this technique. This work represents a first step in this process and will aid in our understanding of the relationships between mineralogy of fine-grained sediments and organic preservation potential.

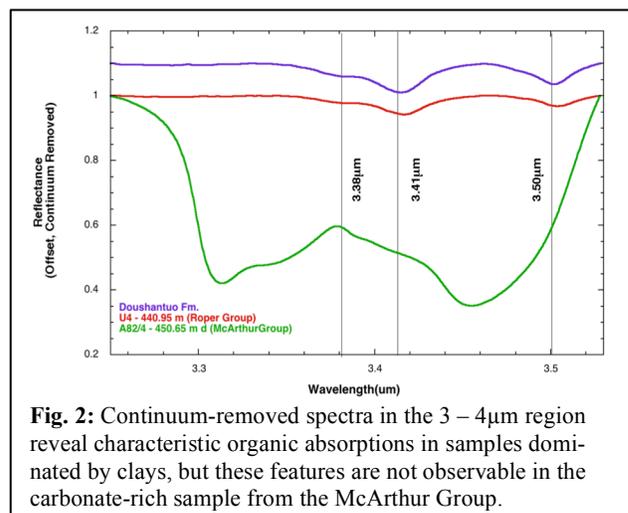


Fig. 2: Continuum-removed spectra in the 3 – 4 μm region reveal characteristic organic absorptions in samples dominated by clays, but these features are not observable in the carbonate-rich sample from the McArthur Group.

References: [1] Summons R. et al. (2011) *Astrobiology*, 11, 157-181; [2] Keil R. G. et al. (1994) *Nature*, 270, 549-552. [3] Poulet F. et al. (2005) *Science*, 438, 623-627; [4] Milliken R.E. et al. (2010) *GRL*, 37, L04201; [5] Johnston D. T. et al. (2008) *GCA*, 72, 4278-4290. [6] Abbott S. T. and Sweet I. P. (2000) *Aus. J. of Earth Sci.*, 47, 637-657. [7] Kendall B. et al. (2009) *GCA*, 73, 2534-2558. [8] Page R. W. et al. (2000) *Aus. J. of Earth Sci.*, 47, 431-459. [9] Bristow T. F. et al. (2009) *PNAS*, 106, 13190-13195.