

DETECTION OF ORGANICS IN FINE GRAINED SEDIMENTS USING NEAR-INFRARED REFLECTANCE SPECTROSCOPY. H. H. Kaplan¹, R. E. Milliken¹, A. H. Knoll², ¹Brown University, Box 1846, Providence, RI 02912 (Email: Hannah.Kaplan@brown.edu), ²Harvard University, Cambridge, MA 02138

Introduction: With the discovery of a habitable environment on Mars by MSL [1], future missions will focus on searching for additional habitable environments and the detection of biosignatures, including organic compounds. The work presented here represents the initial results in an ongoing effort to assess the detection limits and quantification of organic matter in fine-grained sediments using reflectance spectroscopy and implications for this method in Mars exploration.

Reflectance spectroscopy is a remote, rapid, and non-destructive technique that can be employed in an active or passive mode, making it useful for a variety of laboratory, field, and orbital applications. In addition to being used for mineral identification, reflectance spectroscopy at near-infrared (NIR) wavelengths, particularly in the 3 – 4 μ m region, can be used to detect organic compounds. Therefore, it is a powerful technique for in situ rover-based analyses as well as lab-based studies of valuable organic-bearing samples such as carbonaceous chondrites. This study seeks to answer fundamental questions about organic detection using reflectance spectroscopy, with a current focus on fine-grained sediments and applications to rover-scale observations on Mars.

Carbon-hydrogen bonds give rise to absorption features near 3.3 – 3.6 μ m, and by analyzing the variation in these features in natural samples we aim to understand (1) the lower limits of detection for organic matter with this method, (2) the relationship between these absorption features and the organic carbon content of the sample, and (3) the impact of mineral assemblages on detection of organic compounds. The latter is important because spectra of carbonates, for example, exhibit absorptions that overlap with organics, thus complicating detection of C-H absorptions.

Samples and Methodology: Over 180 samples have been measured that span a range of sedimentary depositional environments, mineralogy, albedo, and total organic carbon (wt.% TOC). The geologic context, and often the organic content, of these samples have been described in previous studies [e.g. 2, 3, 4]. The majority of samples are Proterozoic shales (1.5 Ga) in which the organic matter is predominantly insoluble, such as the McArthur/Roper Group samples discussed here [5]. In contrast, Eocene (50 Ma) samples from the Green River Fm. were also studied and contain up to 17 wt.% immature organic carbon [6]. The mineralogy of all samples is dominated by clay minerals, carbonates, and/or Fe-oxides.

Spectra of bulk rock powders (<45 μ m particle size) were collected for wavelengths from 0.35 – 2.5 μ m with an ASD FieldSpec3 and from 0.8 – 25 μ m with a Nicolet iS50 FTIR. Select samples that contain carbonate were treated with HCl following the methods of [4] and spectra of the carbonate-free powders were also acquired. Total carbon (TC) and TOC were measured with an NC2100 Elemental Analyzer, and the difference between the two measurements provides an estimate of total inorganic carbon (TIC), which is assumed to be primarily associated with carbonate minerals.

An upper convex hull is fit to the spectral region of interest and divided from the sample spectrum to remove the spectral continuum. Absorption band depths of the continuum-removed spectra were measured for the organic absorption feature at 3.38 μ m. Recent work has shown that transmittance spectra of carbonaceous chondrites in the ~3 μ m region can be modeled with Gaussian curves [7]. We use a similar method to fit the organic region in our spectra with a series of Gaussian and Lorentzian curves. Band centers are fixed based on known absorption features related to C-H and carbonate vibrations and amplitude for each curve is allowed to vary. Nonlinear least squares minimization is used to determine the best fit. In addition to Gaussian/Lorentzian modeling, a Hapke model is used to convert reflectance spectra to single scattering albedo (SSA) in order to minimize nonlinear effects associated with multiple scattering [8]. This step also allows us to test if SSA provides better quantitative estimates of TOC than the original reflectance spectra.

Results: All of the 180 samples measured thus far exhibit organic absorption bands near ~3.4 μ m, though the strength of the bands is highly variable. The lowest TOC sample contains 0.08 wt.% organic carbon and exhibits clear C-H absorptions, indicating the detection limit of organic matter with reflectance spectroscopy is below this value for natural fine-grained samples. However, organic absorption bands in spectra for some samples with higher TOC are overpowered by large carbonate absorptions, making organic matter detection difficult. Exceptions are the Green River samples, whose spectra exhibit both carbonate and organic absorptions.

There does appear to be a relationship between band depth (or Gaussian/Lorentzian amplitude) and TOC when samples are grouped by sequence (i.e. samples from the McArthur Group follow a clear trend). This relationship is linear when using SSA re-

ther than reflectance and is shown for the McArthur Group ($p < 0.0001$, $R^2 = 0.75$) and the Green River Fm. ($p = 0.0003$, $R^2 = 0.96$) samples in Fig. 1. The carbonate-poor McArthur Group shales exhibit a similar linear relationship to the carbonate-bearing Green River Fm. samples, though the trends are offset.

Spectra from this study can be fit with Gaussians or Lorentzians with residuals of less than 0.01 for both curve types (Fig. 2), and it is possible that a mixed Gaussian/Lorentzian model would further reduce residuals. For the samples with both carbonate and organic absorption features, 7-8 Gaussians are needed to fit all obvious absorptions (local minima). Band depth is expected to go to zero when TOC is zero, but the presence of carbonate absorption features near $\sim 3.4 \mu\text{m}$ may have an effect on estimates of “organic” band depth. Therefore, the amplitude of the individual curve fits associated with C-H features likely provides a more accurate assessment of organic content than band depth from the original reflectance spectra.

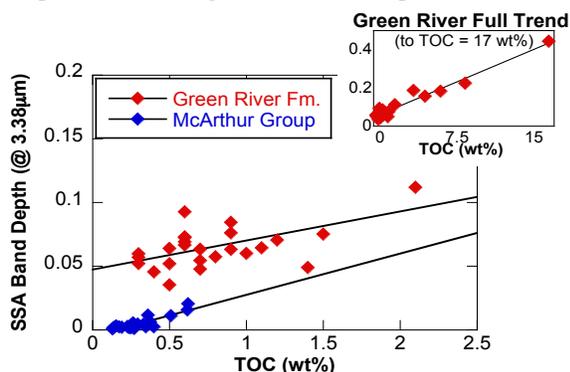


Fig 1. SSA band depth at $3.38 \mu\text{m}$ vs. TOC for McArthur Group and Green River Fm. samples. R^2 values for the trend lines are 0.75 and 0.96 respectively.

Discussion: Under lab conditions we are able to detect C-H absorptions at $\sim 3.4 \mu\text{m}$ in a sample with 0.08 wt.% TOC, a value that falls within the range of background levels expected to be present on the surface of Mars due to meteoritic organics [9]. Future work will focus on measuring samples with lower TOC values to obtain a true lower limit of detection for clay and/or carbonate-bearing samples.

Band depth (from SSA) versus TOC shows a statistically significant linear relationship, though different sample suites exhibit different trends. Age of samples, degree of diagenesis, maturity of organic matter, and mineralogy are all important, and ongoing work will assess how these factors may influence detection limits of organic compounds.

Albedo, in particular, may be important in controlling the slope of the trend line because organic-rich samples tend to be dark in color. The albedo of the Green River samples, for instance, decreases with in-

creasing TOC. It is known that band depths will become smaller as albedo decreases for samples of the same composition [10]. Therefore, the change in albedo with organic content may explain the lower slope in the Green River TOC vs. band depth plot, whereas the McArthur Group samples exhibit a slightly higher slope because they all have similar albedo.

The most significant effect of mineral assemblage on organic detection is the presence or amount of carbonate. Though apparently not abundant on Mars, carbonates are common components of fine-grained rocks on Earth and must be accounted for in terrestrial applications. There is no absolute value at which carbonate absorptions overpower organic absorptions, but rather the relative amount of carbonates and organics control organic detection limits.

NIR reflectance spectroscopy has clear potential as a rapid and non-destructive method for detecting and quantifying organic content, as well as mineralogy, in sediments and sedimentary rocks. By exploring the relationship between measured TOC and absorption feature strength in reflectance spectra this work will provide a foundation for understanding the quantitative applications of this method on the surface of Mars.

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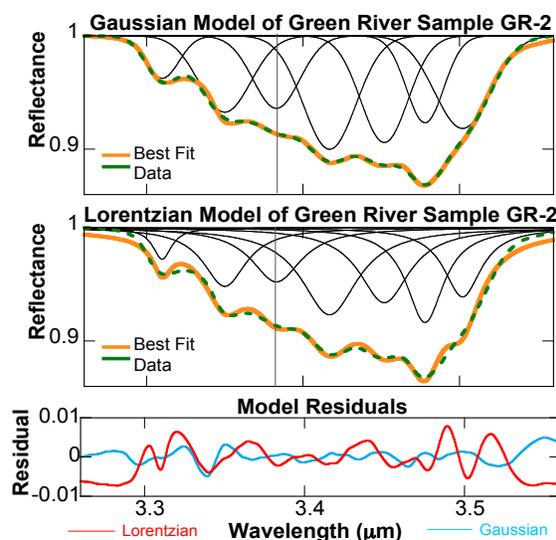


Fig. 2 Gaussian and Lorentzian fits for Green River sample GR-2. Each Gaussian/Lorentzian is centered on a known carbonate (3.35, 3.31, 3.42, 3.45, and $3.47 \mu\text{m}$) or C-H (3.38, 3.41 – overlaps 3.42, and $3.50 \mu\text{m}$) absorption feature. The $3.38 \mu\text{m}$ band center is shown with a gray line.