ASSESSING ORGANIC CONTENT OF SEDIMENTS WITH REFLECTANCE SPECTROSCOPY: ANALYSIS OF NATURAL SAMPLES AND LABORATORY MIXTURES. H. H. Kaplan and R. E. Milliken¹, ¹Brown University, 324 Brook St., Providence, RI 02912 (Hannah_Kaplan@Brown.edu).

Introduction: Visible - near-infrared reflectance spectroscopy is a technique used to obtain remotely-sensed information on the mineralogical composition of planetary surfaces, but the near-infrared region can also be used to detect organic compounds (C-H bonds and functional group bonds) [1]. However, in order for reflectance spectroscopy to reach its full potential in the detection of organics on Mars or for the study of organic-bearing meteorites [e.g. 2], it is necessary to better constrain detection limits in fine-grained materials and sediments.

Organics and clays have long been linked in terrestrial sedimentary environments. Observations and experiments have confirmed the link, but determining causation from this correlation has proved difficult [3, 4]. Clay deposits on Mars have been discussed in great detail as possible hosts of organic material and, clays are known to be important components of some carbonaceous chondrites. This has led us to focus on clay-organic mixtures in this study.

Fundamental C-H vibrations occur between 3 and 4 µm (3333 to 2500 cm⁻¹), a wavelength region that has been used to quantify C-H₂ and C-H₃ bonds in carbonaceous chondrites using transmission spectra [2]. Using the strength of absorption features in reflectance spectra to quantify organics is not as straightforward, particularly for intimate, multi-component mixtures [5]. Low albedo (a common characteristic of meteorites and some planetary surfaces) is also known to have a disproportionately strong weakening effect on absorptions in reflectance spectra [6,7], complicating detection limits of organics in dark materials.

The purpose of this study is to build a foundation for the quantification of organic content in clay-rich sedimentary samples using reflectance spectroscopy. The influence of clay mineralogy, albedo, water content, and other properties are considered for both natural samples and synthetic mixtures.

Methods: Natural sedimentary samples from multiple location were ground into powders of <45 µm and reflectance was measured from 0.35 to 25 µm using ASD and FTIR spectrometers. The organic make-up and geologic setting of these samples has been reported previously by [8].

Synthetic mixtures of pure, solid organic compounds and clay mineral standards were weighed out and mixed by hand. The clay minerals used were montmorillonite (SAz-1) and kaolinite (KGa-1) and the organic compounds were hexamethylbenzene (C₆(CH₃)₆) and sodium stearate (CH₃(CH₂)₇O₂Na).

Spectral analysis of both natural and laboratory samples involves using a convex hull fit to approximate and remove the spectral continuum over the wavelength region of 3.1 to 3.6 µm. Band depth values were then calculated at the wavelength of interest. Reflectance spectra were also converted to single scattering albedo (SSA) and analyzed in a similar manner.

Results: Natural Samples: There is no single, unifying relationship between total organic carbon (TOC) in a sample and the band depth of organic absorptions that fits all natural samples. Instead, samples with low albedo or a strong 3 µm H₂O absorption fall on a different trend line than brighter and less hydrated samples. Multiple regression confirms that TOC, albedo, and hydration are significant predictors of band depth. Samples from the same location have similar albedo, hydration, and TOC, effectively causing quantification to be dependent on provenance.

Synthetic Mixtures: Initial lab mixtures show band depth increasing with organic content (in wt. %). This relationship becomes more linear when viewed in SSA rather than in reflectance (Fig. 1). The 3.38 µm C-H₃ absorption is consistently weaker in both hexamethylbenzene and sodium stearate mixtures; the 3.41 µm absorption, due to C-H₂ bonds, is stronger. The ~3.38 µm feature is consistently shifted to shorter wavelengths in the mixtures with hexamethylbenzene.

Bright, relatively unaltered natural samples from the McArthur Fm. in Australia and Green River Fm. in the USA show a striking similarity to the laboratory mixtures as seen in Fig. 1. Where the SSA band depth versus TOC plot for natural samples remains linear even at high TOC values, the trend line of the laboratory mixtures flattens out at higher TOC values.

The two organic compounds show distinct differences in band depth vs. TOC when mixed with the same clay mineral (Fig. 2a). Mixtures using different clay minerals, but the same organic compound do not show a noticeable difference in band depths (Fig. 2b).

Discussion: Although both hydration and albedo are significant predictors of band depth, albedo is clearly more dominant, as noted in previous studies of low-albedo clay mixtures [6]. The choice of one CH₃- and one CH₂- dominated organic compound is meant to verify the band assignments in this wavelength region. Although hexamethylbenzene theoretically contains no CH₂ bonds, it still has a strong 3.41 µm absorption, complicating our initial assignments. Interestingly, the natural samples we studied all have a similarly shaped triplet with absorptions at 3.38, 3.41, and
3.50 µm, which is not mirrored by the shapes of the absorptions of either of the pure organics.

The band depth versus TOC slope for the synthetic mixtures decreases with increasing TOC, suggesting the organic absorptions are becoming saturated. Although SSA should show increased linearity compared to reflectance, we still see logarithmic trends. For similar or higher TOC values, the natural samples appear to exhibit a linear trend in SSA. These trends may arise from intrinsic differences between the physically mixed and natural samples, where in the latter the organic matter can be incorporated into the structure of the inorganic host material at a sub-micron scale [4]. However, the trend of decreasing slope is less convincing for the sodium stearate mixture (at 3.33-3.38 µm) due to large uncertainties for the highest TOC sample.

The error bars in Fig. 2a represent variation from multiple measurements of the same mixture. The small spot size (1-2mm) of the FTIR used in this study may be sensitive to small differences in the distributions of organic particles during different measurements, resulting in significantly different band depths for the same mixture. Although it is easy to measure this as a change in band depth for the same TOC value, in reality, the TOC of the sample within the beam would be different.

**Conclusions and Future Work:** This work represents an initial basis for quantifying organic content from reflectance spectra. If this type of spectroscopy is to be used for detection of organics in meteorites or on the surface of Mars, it will be important to understand how different properties of the sediment influence organic detection limits and quantification. Of these properties, albedo is a key controlling factor that can likely be assessed with laboratory mixtures.

Future work will focus on laboratory methods that allow us to control for specific variables including adding a darkening component, assessing different means for making homogenous mixtures at low TOC values, and the effects of different inorganics and organics. This work will ultimately lead to more accurate quantification of organic matter with reflectance spectroscopy using methods that can be employed by rover or lander-based instruments.

**Fig 1:** Natural samples (bright, unaltered, fine-grained) from the McArthur Fm. and Green River Fm. are compared with laboratory mixtures of kaolinite with two different pure organic compounds. The non-linear shape of the laboratory mixture trend lines may be due to saturation of these absorption features.

**Fig 2:** a) Comparison of hexamethylbenzene and sodium stearate when mixed with kaolinite and b) a comparison of the same organic compound mixed with two different clays. These figures suggest that organic composition has a strong effect on the organic absorptions in reflectance spectra, but the influence of clay mineralogy is weak or non-existent.