

**QUANTIFYING ORGANIC CONTENT WITH REFLECTANCE SPECTROSCOPY: APPLICATIONS TO CARBONACEOUS CHONDRITES AND PLANETARY SURFACES.** H. H. Kaplan<sup>1</sup>, R. E. Milliken<sup>1</sup>, G. M. Luo<sup>2</sup>, <sup>1</sup>Brown University, Dept. of Earth, Environmental, and Planetary Sciences, Providence, RI 02912 ([Hannah\\_Kaplan@Brown.edu](mailto:Hannah_Kaplan@Brown.edu)). <sup>2</sup>MIT, Department of Earth, Atmospheric and Planetary Sciences, Cambridge, Massachusetts, USA

**Introduction:** Reflectance spectroscopy is a non-destructive method that can be used to remotely detect both organic compounds and minerals at visible – infrared (VIS-IR) wavelengths at laboratory, field, and orbital scales. Multiple VIS-IR reflectance spectrometers will be used to determine the surface composition of C-type asteroids on JAXA’s Hayabusa2 and NASA’s OSIRIS-REx missions. These spectrometers specifically target the ~0.5 – 4  $\mu\text{m}$  wavelength region to detect carbonate, phyllosilicate, sulfate, Fe-oxide and primary silicate minerals as well as organic compounds, with the goal of answering questions about the thermal history, formation of organic compounds, and the distribution of water on carbonaceous chondrite parent bodies [1, 2].

Organic matter (OM) in carbonaceous chondrite (CC) meteorites is found adsorbed to/closely associated with phyllosilicate minerals, which is also common in terrestrial sedimentary rocks, or as discrete nanoglobules [4]. These associations may give rise to diagnostic vibrational absorptions, and indeed, studies of terrestrial samples have previously attempted to quantify OM in soils, sediments, and oil shales using reflectance spectroscopy, typically by employing principal components or partial least squares data analysis techniques [5,6].

In this study, bulk rock samples and their kerogen separates are analyzed to better understand how to interpret and quantify organic signatures that may be observed in reflectance spectra of meteorites or acquired by current and future asteroid missions. We use natural clay and organic-bearing terrestrial samples as a starting point for assessing a variety of spectral models, in part because these samples are abundant and because the fine-grained components are commonly mineralogically simpler compared with the matrix of C1 and C2 chondrites. This work will provide a foundation for measurement and analysis methods that can be applied in the future to more precious and limited carbonaceous chondrite meteorite samples.

**Methods:** Samples used in this study are clay-rich Mesoproterozoic shales (McArthur basin, Australia) that show little evidence of metamorphism/deformation and are rich in organics, including prokaryotic biomarkers [7]. Bulk rock samples ( $n = 33$ ) from multiple drill cores were ground to  $<45 \mu\text{m}$  particle size and reflectance spectra were acquired with an ASD FieldSpec3 (0.35 – 2.5  $\mu\text{m}$ ) and Thermo iS50 FTIR spec-

trometer (1.5 – 25  $\mu\text{m}$ ) to provide continuous reflectance values from 0.35 – 25  $\mu\text{m}$ . Kerogen was separated from 13 samples and measured using the same methods. Total organic carbon (TOC) was measured with an Elemental Analyzer (EA) for each bulk rock sample.

The bulk rock powders were also measured with a Bruker D2 phaser X-Ray Diffractometer (XRD) from  $2 - 70^\circ 2\theta$ , with a  $0.02^\circ$  step size and 3 s/step integration time. Modal mineralogy is estimated using Rietveld refinement on the XRD patterns. Minerals included in the model are based on those known to occur in the basin and are included only if they significantly decrease the RMS error of the fit.

Qualitative and quantitative spectral analyses were performed on the original and continuum removed reflectance spectra, including band depth and band area measurements. A Hapke-based radiative transfer model [8] was also carried out for a subset of samples, which includes converting reflectance spectra to single scattering albedo (SSA) and fitting the data with end-member mineral and kerogen spectra to estimate mineral and organic contents. These mineral/organic abundances were then compared to the XRD and EA results (i.e. independent measures of mineralogy and organic content). Spectral analysis using a partial least squares technique was also carried out and results are likewise compared to the independent measurements.

**Results:** Spectra of isolated kerogen typically show strong triplet absorptions near 3.4  $\mu\text{m}$  due to aliphatic C-H bonds. Aromatic bonds also give rise to a weaker absorption near 3.2  $\mu\text{m}$  (Fig. 1). As the H/C ratio of the kerogen decreases, the spectrum becomes flatter and darker and evidence of organic absorptions disappears from both the kerogen and bulk rock spectra. Spectra of the bulk rock powders have a consistently weaker 3.4  $\mu\text{m}$  triplet feature than is observed in the corresponding kerogen spectra and the 3.2  $\mu\text{m}$  ‘aromatic’ absorption is often not present.

Spectra of the bulk rock samples also exhibit strong absorptions due to OH/H<sub>2</sub>O at 2.8 and 2.95  $\mu\text{m}$ . XRD results for these samples indicate that OH is mainly found in the clay minerals illite, muscovite, and kaolinite with a minor amount in an iron-oxide/hydroxide phase; these are also the minerals that are most likely physically associated with OM. CC meteorites, on the other hand, have a broader absorption at 2.8 - 2.9  $\mu\text{m}$  due to a mineral assemblage that includes serpentine,

smectitic clay minerals, and other hydrated alteration phases (Fig. 1). The CC meteorite spectra also display evidence of the organic triplet near 3.4  $\mu\text{m}$ , despite being  $\sim 10 - 30\%$  darker than the McArthur Basin samples.

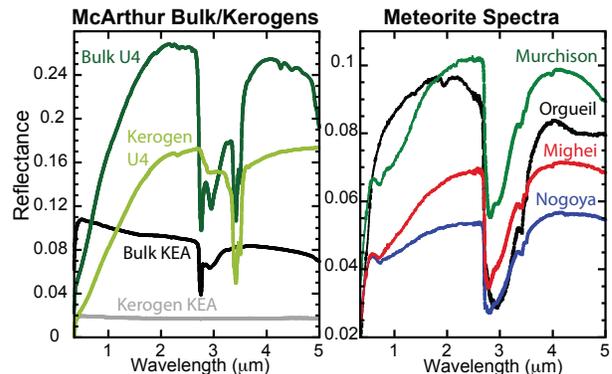
**Spectral Modeling.** Preliminary modeling shows promise for quantifying organic carbon using reflectance spectroscopy. Using 8 spectral endmembers in the Hapke model, spectra of bulk rock powders are fit reasonably well from  $\sim 2-4 \mu\text{m}$  (Fig. 2). Additionally, there is a strong linear correlation between organic abundance (wt. % kerogen) estimated from the spectral fit and the measured TOC values (Fig. 3).

**Discussion and Conclusions:** Detailed analysis of natural, well-characterized organic-bearing samples is an important step towards assessing reflectance spectroscopy as a rapid, non-destructive technique for quantifying the organic content of meteorites and planetary surfaces, particularly in cases where there is little or no *a priori* information. We show that although mineralogy, albedo, and water content have a significant effect on the strength of organic absorptions, it is still possible to model the overall spectral shape of clay and organic-bearing samples using appropriate mineral and organic endmembers. Organic contents predicted from spectral models are strongly correlated to TOC, demonstrating that reflectance spectroscopy is a viable method for quantification of mineralogy *and* organic content, particularly for samples with moderate to high H:C ratios.

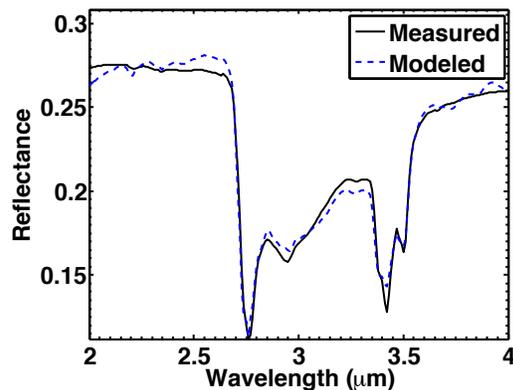
However, the amount of kerogen currently predicted from the spectra is  $\sim 2.25$  times greater than the measured TOC. This is likely due to the presence of significant amounts of phases that are largely non-absorbing at these wavelengths (e.g.,  $\sim 40-60$  wt.% quartz+feldspar); such factors may not be as important for spectra of CC meteorites. XRD-derived estimates of modal mineralogy for these samples will allow us to better estimate TOC as a weight percent of the spectrally-sensitive phases, but early results indicate points in Fig. 3 will be shifted much closer to the 1:1 line after this correction. Ongoing work is focused on applying these spectral modeling techniques to terrestrial samples that are better mineralogical analogs to C chondrites (e.g., Mg/Fe-serpentine-bearing samples) as well as actual organic-bearing CC meteorites.

**References:** [1] Pilorget, C. and Bibring, J -P. (2013) *Planetary Space Sci.*, 76, 42-52. [2] Libourel, G. and Corrigan C. M. (2014) *Elements*, 10, 11-17. [3] Matthewman R. et al. (2013) *Astrobiology*, 13, 324-333. [4] Pearson V. K. et al. (2002) *Meteoritics & Planet. Sci.* 37, 1829-1833. [5] Chang C. W. et al. (2001) *Soil Sci. Soc. Am. Journal*, 65, 480. [6] Washburn K. E. et al. (2015) *Energy & Fuels*, 29, 4264-4271.

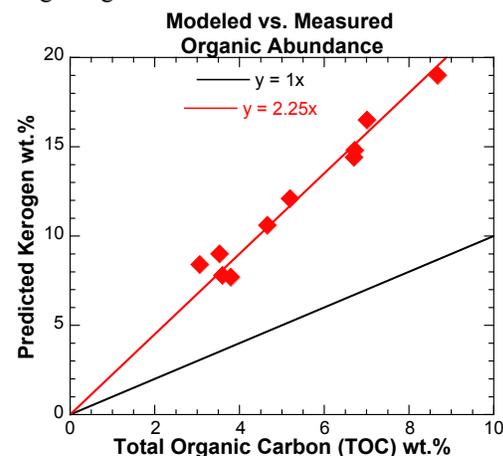
[7] Johnston D. T. et al. (2008) *GCA*, 72, 4278-4290. [8] Hapke, B. (1993), *Cambridge University Press*, 455pp.



**Figure 1:** (left) Example spectra for kerogen and bulk rock powders from McArthur basin. Carbon in KEA is graphitized. (right) Example CC meteorite spectra from RELAB database for comparison.



**Figure 2:** Example spectrum and model fit for McArthur basin sample. Hapke model uses 8 end members, including a kerogen spectrum, to fit the 2 – 4  $\mu\text{m}$  wavelength region.



**Figure 3:** Measured TOC vs. modeled kerogen abundance showing linear relationship.