

**SPECTROSCOPIC STUDY OF BIOSIGNATURES IN CLAY-RICH SEDIMENTS: IMPLICATIONS FOR MARTIAN ASTROBIOLOGICAL EXPLORATION.** C. Che<sup>1</sup>, S. Parvez<sup>1</sup>, and T. D. Glotch<sup>1</sup>, <sup>1</sup> Department of Geosciences, Stony Brook University, Stony Brook, NY 11794 (Email: congcong.che@stonybrook.edu)

**Introduction:** Clay minerals have been observed to be abundant and varied on Mars and most of them are associated with ancient Noachian terrains [1-2]. It has been suggested that on Earth, clays are considered very important for habitability and organic preservation [3-4]. Studies of Earth's carbon budget indicate ~68% of organics are stored in clays and shales of Earth's crust [5]. Clays have high surface areas and as a result, organic carbon content in clays is relatively high due to adsorption processes [4, 6]. It also has been suggested that if organics and clays form synchronously, the preservation of biosignatures may be more resistant to weathering processes, due to the chemical equilibration between organics and sedimentary rocks [4, 7]. Previous studies suggest that long-term preservation of microbial biosignatures on Mars may occur in rapid burial processes in fine-grained clay-rich sediments, as anaerobic conditions due to quickly reduced porosity and permeability may slow the degradation of organics [3-4].

Geologic analysis of the clay mineral deposits near Mawrth Vallis indicates that they are early-to-mid Noachian in age and were likely deposited in a sedimentary environment [8]. The clay-bearing deposits are part of a set of layered rocks (>600 m thick) that contain interbedded, buried craters. If life ever existed on Mars, its record is likely to be found in sedimentary rocks that achieved kilometer-scale thicknesses and are rich in clay minerals. Here we examine organic matter stored in terrestrial clay-rich sediments using the techniques described below, to gain insights into the potential formation or preservation conditions of biosignatures in clay-rich sediments, and aid the search for biosignatures on Mars.

**Samples and Methods:** For this work, 43 organic-rich clay-bearing samples were selected [Table 1]. The sample suite studied here includes oil shales, red shales, grey shales and black shales.

The analytical techniques used in this work include visible and near infrared (VNIR) reflectance, mid-infrared (MIR) attenuated total reflectance (ATR), MIR emissivity, MIR reflectance, and Raman spectroscopies. X-ray diffraction (XRD) measurements were conducted in order to clarify the mineralogy of each sample. Of these measurements, VNIR reflectance and MIR emissivity spectral results can be used in future Mars data analysis studies. The MIR reflectance results are complementary to emissivity, as the spectral features associated with organics often occur within a low signal-to-noise (SNR) region

(1600-1800  $\text{cm}^{-1}$ ) in emissivity spectra. Raman spectroscopy is highly sensitive to spectral features due to organic materials and was selected for Mars 2020 rover. The results of these fundamental analytical measurements in the laboratory are crucial for enhancing the ability to detect possible biosignatures on Mars.

**Results:** *Determination of total organic carbon (TOC)* TOC analyses were conducted on powdered bulk samples using the loss on ignition method [9]. TOC values of studied samples vary from 0.02 (wt.%) to 38.31 (wt.%).

Table 1. TOC of selected samples\*

Sample ID/name	TOC (wt.%)						
Grey Shale	7.20	11663-61	6.09	75092	4.13	Oil Shale #3	23.40
Red Shale	2.47	117710-20	3.24	117730-27	2.97	Oil Shale #4	7.06
Oil Shale #1	12.30	85919	25.25	23582	3.94	Oil Shale #5	8.28
Oil Shale #2	16.61	113654-238	11.75	115812-235	0.59	76681-9	3.51
716813-40	0.58	87987-2	2.11	109579-29	3.77	109579-35	3.76
23584	5.05	88829-8	3.11	59128	7.85	117710-19	3.23
38176	5.61	117710-18	2.52	117797-46	2.68	91483-150	3.28
59146	4.20	59182	3.75	88829-59	7.60	117787-50	2.02
61641	1.94	59199	3.94	91483-151	0.37	117710-17	3.63
75904	9.21	91461-1	0.02	85921	22.53	91483-152	4.29
76813-116	3.10	74721-32	38.31	113723-19	3.04		

\*Oil shale, red shale, and grey shale were purchased from Fisher Scientific. All other samples are black shales acquired from the Department of Mineral Sciences at Smithsonian Institution.

*Acquisition of ATR spectra* Figure 1 shows ATR spectra of black shales with different levels of TOC. For samples with higher TOC value, we see evidence for organics in two peaks at ~2850 and ~2950  $\text{cm}^{-1}$  that are assigned to aliphatic C-H stretching modes and minor peaks in 1600-1800  $\text{cm}^{-1}$  that are due to C=O stretching modes [10]. The ATR spectral features associated with organic matter could be identified when the TOC value is higher than 6% (wt.).

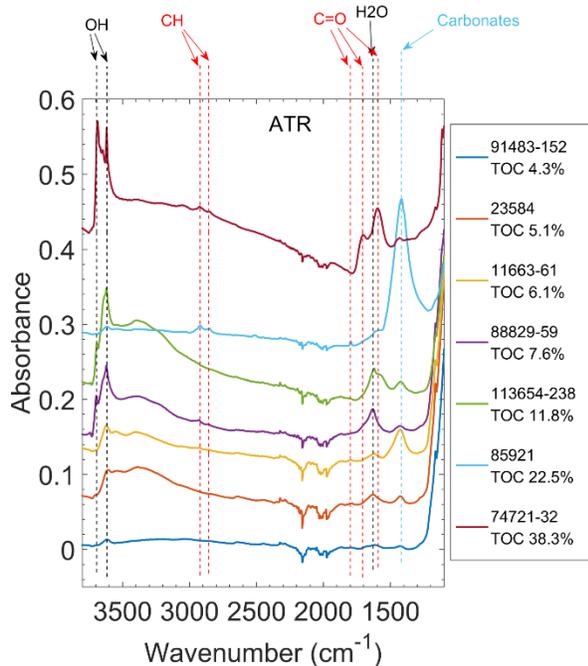


Figure 1. Selected ATR spectra of black shale samples with different levels of TOC.

**Acquisition of MIR reflectance spectra** Figure 2 shows the MIR reflectance spectra of several shale samples with different level of TOC. Overall, the spectra are dominated by Si-O stretching features near  $1000\text{ cm}^{-1}$  and Si-O bending features near  $500\text{ cm}^{-1}$  [11]. The strong features at  $\sim 1400\text{ cm}^{-1}$  are associated with carbonates. Minor C=O stretching features could be observed in the  $1800\text{--}1600\text{ cm}^{-1}$  range when the TOC value is significantly high (38.31%).

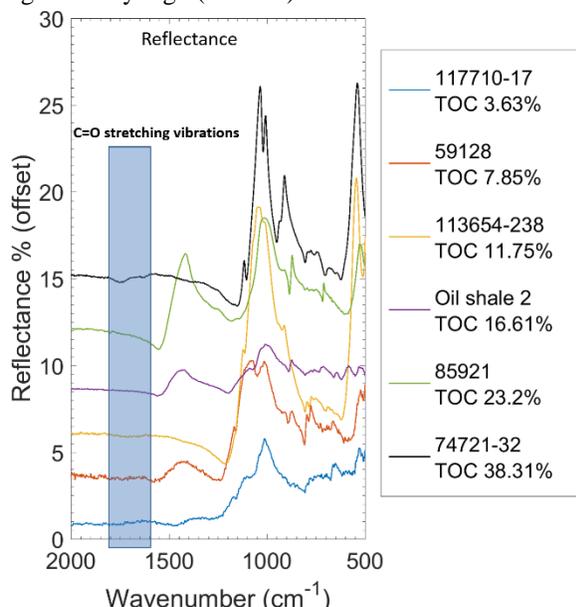


Figure 2. Selected MIR reflectance spectra of shale samples with different levels of TOC values.

**Acquisition of Raman spectra** Figure 3 shows Raman spectra of shales with different levels of TOC. Carbon was identified by characteristic disordered (D) band at  $\sim 1350\text{ cm}^{-1}$  and ordered (G) band at  $\sim 1610\text{ cm}^{-1}$  [12]. From the results, Raman spectroscopy is significantly more sensitive to organic matter than infrared spectroscopy. Different shapes and positions of D and G bands might be indicators of different alteration environments of carbon [13].

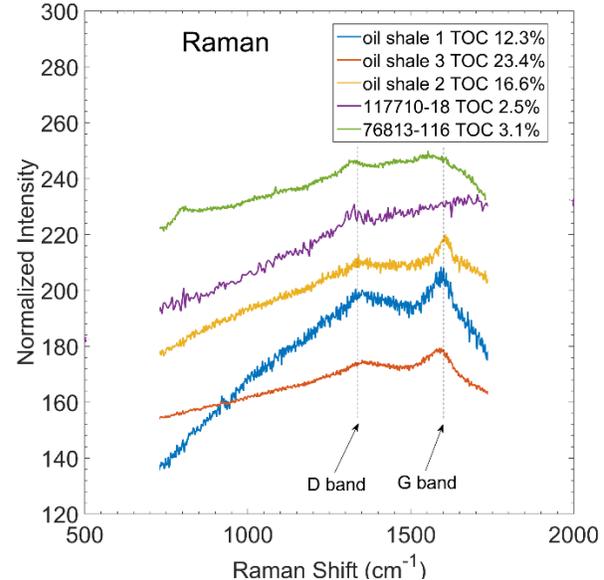


Figure 3. Raman spectra of selected shale samples with different levels of TOC values.

**Discussion:** The results indicate spectroscopy is a powerful tool for detection of organic features, and organic feature detection with spectroscopy may be dependent on TOC level. Raman spectroscopy is more sensitive to organic matter than IR spectroscopy.

**References:** [1] Poulet et al. (2005), *Nature* 438, 623-627. [2] Bibring et al. (2005), *Science* 307, 1576-1581. [3] Farmer and Des Marais (1999), *J. Geophys. Res.* 104, 26977-26995. [4] Summons et al. (2011), *Astrobiology* 11, 157-181. [5] Des Marais (2010), the 4th MSL Landing Site Workshop. [6] Kaiser and Guggenberger (2003), *Eur. J. Soil Sci.* 54, 1-18. [7] Hedges and Keil (1995), *Mar Chem* 49, 81-115. [8] Michalski and Noe Dobrea (2007), *Geology* 35, 951-954. [9] Heiri et al (2001), *J. Paleolimnol* 25, 101-110. [10] Marshall et al. (2006), *Vib. Spectrosc.* 41, 182-189. [11] Bishop et al. (1994), *Clays Clay Miner.* 42, 701-715. [12] Steele et al. (2007), *Meteorit. Planet. Sci.* 42, 1549-1566. [13] Steele et al. (2012), *Science* 337, 212-215.

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