

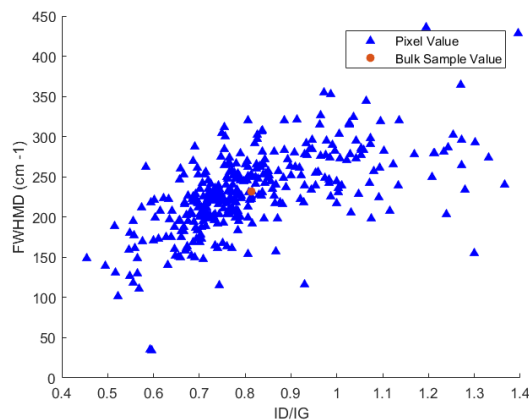
**TRACKING THERMAL HISTORY OF CHONDRITIC PARENT BODIES VIA RAMAN SPECTROSCOPIC ANALYSIS OF PAH CONTENTS** J. M. Young<sup>1</sup>, T. D. Glotch<sup>1</sup>, and M. Yesiltas<sup>1</sup> <sup>1</sup>Stony Brook University – Department of Geosciences – 255 Earth and Space Sciences, Stony Brook, NY 11790 (jordan.young@stonybrook.edu)

**Introduction:** The study of polycyclic aromatic hydrocarbons (PAH) in meteorites, specifically from a spectroscopic standpoint, has received a great deal of attention [1, 2, 3] primarily due to the effects of temperature on the spectral properties of PAHs. The main Raman spectral features of PAHs are the disordered and graphitic (D and G) carbon bands, which are the representations of vibrational modes resulting from edge defects in a graphene/PAH structure and C—C bonds within a PAH molecule respectively. The D and G bands occur at  $\sim 1350\text{ cm}^{-1}$  and  $\sim 1575\text{ cm}^{-1}$ , in a Raman spectrum, respectively. The exact positions of these bands, as well as other spectral parameters such as the band full-width half maxima (FWHM), are sensitive to structural and compositional changes associated with the thermal metamorphism of their host chondritic parent bodies. Thus it stands to reason that portions of a chondritic parent body's thermal history can be gleaned from observing the spectral features of PAHs in collected chondrites [4, 5].

The study of the thermal history of chondritic meteorite via Raman spectroscopy in the recent past has mainly focused on the spectral characteristics of PAH contents in various carbonaceous chondrites, specifically those in the petrologic type range of 3.0-3.9 [4,5,6,7]. This is due to the relatively large carbon contents of those meteorites. Unequilibrated ordinary chondrites (UOCs) have also received particular attention. UOCs only include the ordinary chondrites of petrologic type 3 that have experienced low thermal metamorphism. However, there has been little study of the equilibrated variety of ordinary chondrites (petrologic type 4-7), likely due to a markedly lower carbon budget than UOCs and their carbonaceous chondrite counterparts. Due to being the majority of collected falls [8], and measurable PAH contents, ordinary chondrites present an opportunity to conduct a comprehensive study of the thermal alteration of meteorites as recorded by the spectral properties of their PAH contents. As such, the purpose of this study is to observe the spectral properties of PAH materials in ordinary chondrites via Raman spectroscopy. Through these observations, we should be able to better understand the link between spectral parameters, petrologic type, and peak metamorphic temperature.

**Methods:** This study was conducted using a WiTEC alpha300R confocal Raman imaging system, coupled with a 512 nm Nd:YAG laser. A 50x (NA .80)

objective was used to view samples. Several spatially separated 2-D intensity distribution maps were collected from each sample. These intensity distribution maps were spatially separated in order to gauge the homogeneity of carbonaceous components within a given sample. This was done in order to avoid possible bias stemming from heterogeneity within the overall population of carbonaceous materials in a chondrite sample. These maps were collected using laser power of 1.3 mW, image areas of  $50 \times 50\ \mu\text{m}$  and an integration time of 0.1 s in order to minimize the occurrence of sample damage by heating. For a collected 2-D intensity distribution map, each pixel has an associated Raman spectrum. In order to gain an accurate understanding of the bulk spectral features of the carbonaceous component of the sampled chondrites, several hundred spectra associated with pixels of high intensity for the Raman bands of interest (D & G) were extracted from the maps. These raw spectra were then fit using the 2-Lorentzian band fitting method in order to extract useful spectral parameters (peak position, FWHM, and band intensity). Collected spectral parameters from these pixels were then averaged to yield a bulk value for a given sample, as shown in Figure 1.

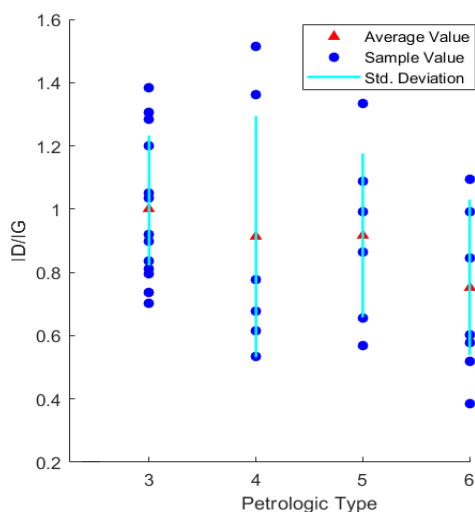


**Figure 1.**  $\text{FWHM}_D$  vs.  $I_D/I_G$  for individual pixel spectra; Average bulk sample value also plotted

**Samples:** We analyzed ordinary chondrites samples that encompass the known lithological types (H, L, and LL) and have petrologic types with a range of 3.15-6. The meteorites sampled are: Bishunpur (LL3.15), Krymka (LL3.2), GRO 95658 (LL3.3), ALH 78119 (LL3.5), DAV 92302 (LL3.6), QUE 93050 (LL4), ALH 78109 (LL5), ALH 84081 (LL6), Mangwendi (LL6), Hallingeberg (L3.4), ALH 85070

(L3.6), Khohar (L3.6), Mezo-Madaras (L3.7), ALH 85033 (L4), Mckinney (L4), Tennesilm (L4), ALH 81017 (L5), Barwell (L5), ALH 85017 (L6), Bruderheim (L6), Clovis (no. 2) (L6), Colby-Wisconsin (L6), WSG 95300 (H3.3), ALH 77299 (H3.7), ALH 77221 (H4), Ranchapur (H4), ALH 77012 (H5), Limerick (H5), ALH 77288 (H6) Kernouve (H6), Tieschitz (H/L3.6), and Bremervörde (H/L3.9)

**Results:** The average spectra of PAH materials from each of the chondrite samples have been normalized to the amplitude (intensity) of the G-band. This is done to better compare the similarities of spectral line-shapes with large disparities in spectral intensity. This removes biases in collected spectra arising from variation in the number of observed PAH molecules counts in differing chondrite samples. Normalizing the amplitude of the D-band by the G-band gives way to the parameter  $I_D/I_G$ . This parameter can be used as an indicator of the bulk structure of the observed carbonaceous materials. Decreasing values of the  $I_D/I_G$  ratio are the result of a strengthening of the G-band relative to the corresponding D-band, which can be an indication of an increasingly graphitic nature of the carbonaceous material. Therefore the  $I_D/I_G$  may be a useful tracer of alteration history. As such,  $I_D/I_G$  values have been plotted against petrologic type in Figure 2



**Figure 2.**  $I_D/I_G$  vs. Petrologic type; Individual sample values plotted with average values for petrologic types 3-6

Individual values of the  $I_D/I_G$  ratio vary widely within a given petrologic type, which makes it difficult to discern any existing trend. The average values of the samples in a given petrologic type (Figure 2), show a trend of decreasing  $I_D/I_G$  values with increasing petrologic type from type 3 to type 6. Other spectral parameters, namely  $FWHM_D$ ,  $FWHM_G$ ,  $\omega_D$ , and  $\omega_G$

were also collected and will be likewise be used in order to uncover spectral changes associated with alteration.

**Discussion:** As the petrologic type of the ordinary chondrite class increases it is widely held that the nature of the carbonaceous material within a given ordinary chondrite becomes more graphitic. As carbonaceous materials are progressively heated and bonds are broken due to relatively high thermal energy, carbon rings of PAHs are more likely to form the most stable mineral phase of carbon under those conditions. In the context of a chondritic parent body setting, low pressures and high temperatures make graphite and multi-ringed graphene-like PAH derivatives quite stable. As seen in Figure 2, petrologic type averages for  $I_D/I_G$  ratio decrease with increasing petrologic type. This suggests that on average, thermal alteration can be tracked by understanding how graphitic a population of carbonaceous molecules is. However, high variability in  $I_D/I_G$  values within a given petrologic type makes it difficult to understand the thermal history of individual chondrite samples. This is made evident by the observation that several samples belonging to petrologic type 3 have  $I_D/I_G$  values equivalent to or lower than bulk values for petrologic types 4-6. Similarly, many samples are belonging to types 4-6 register values above the average value for petrologic type 3 samples. The observed variation in individual values with respect to the average petrologic type value may be the result of varying degrees of thermal alteration. However, it may also be dependent on the oxidation-reduction environment. Graphene has been observed to have relatively large values of the  $I_D/I_G$  parameter when oxidized. Conversely,  $I_D/I_G$  values are markedly lower in reduced graphene derivatives [9]. Variable chemical compositions, resulting in variable oxidation environments, of fluids that interacted with ancient chondritic parent bodies, may be the root cause of the variability observed in  $I_D/I_G$  within this study's sample set. The observation of heteroatom carbon ring species within PAH materials corroborates the idea that precursorial parent materials of PAHs had variable oxidation states, which could complicate our understanding thermal histories of chondrites. If thermal history has been convoluted in this way, any effects due to chemical interaction need to be resolved in order for  $I_D/I_G$  to be a useful thermal alteration tracer.

**References:** [1] Sephton et al. (2002) *PSS*, 50, 711–716. [2] Quirico et al. (2003) *MPS*, 38, 795–811. [3] Cloutis et al. (2016) *Icarus*, 274, 211-230. [4] Chanet al. (2015) *AbsciCon* [5] Cody et al. (2008) *EPSL*, 272, 446-455. [6] Ronal et al. (2016) *GECA*, 189, 312-337. [7] Homma et al. (2015) *JMPS*, 110, 276-282. [8] Hughes D.W. (1966) *Meteoritics*, 16, 269-281. [9] King et al. (2016) *NSR*, 6, 1-6.