THE EFFECTS OF SHOCK AND RAMAN LASER IRRADIATION ON THE MATURITY OF ORGANICS IN MARTIAN METEORITES. A. C. O'Brien[1], L. J. Hallis[1], A. Steele[2], L. Daly[1] and M. R. Lee. [1]School of Geographical and Earth Sciences, University of Glasgow, Glasgow, G12 8QQ, UK (a.obrien.1@research.gla.ac.uk) [2]Geophysical Laboratory, Carnegie Institute, Washington D.C., USA.

Introduction: Macromolecular organic carbon (MMC) occurs as inclusions within igneous minerals and has been found in several martian meteorites (both in falls and finds) e.g. [1-3]. These MMC inclusions consist primarily of polycyclic aromatic hydrocarbons, which enclose magnetite crystals (e.g., Figure 1). MMC can be identified by its characteristic Raman D and G peaks at ~1350 cm^{-1} and ~1580 cm^{-1}, respectively [1]. These organic compounds are of astrobiological interest since such molecules can be a key component in the synthesis of amino acids [4]. The inclusions are unlikely to be terrestrial in origin since they are completely enclosed in magmatic minerals and occur below thin-section surfaces [1]. This organic material is also spectroscopically distinct from epoxy resin (Figure 2), reinforcing the argument that MMC is not a terrestrial contaminant.

Fig. 1 A plane polarised transmitted light image of a spray of MMC enveloping a magnetite inclusion in Tissint

The origin of the organics is currently unclear: they may be indigenous to the martian mantle [1] or could be exogenous and have been deposited on the planet's surface, post accretion, by carbonaceous chondrite meteorites [3]. Recent analysis has also shown these MMC inclusions are similar to organics discovered by the Mars Science Laboratory in 2018 [5].

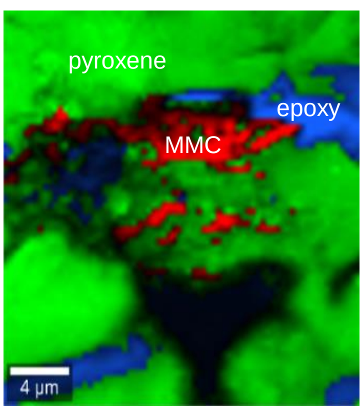

Fig. 2 Raman map of MMC inclusion in Tissint; epoxy, pyroxene and MMC are shown in blue, green and red, respectively.

Characterising MMC and determining its origin will therefore inform our understanding of the martian, and potentially interplanetary, carbon cycle. Results will also support mission science undertaken by MOMA (Martian Organic Material Analyser) onboard ESA's ExoMars rover and SHERLOC (Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals) onboard NASA's Mars 2020 rover.

Here, we discuss how some martian organic material may be affected by shock during meteoritic ejection, as well as during analysis by Raman spectroscopy, a crucial method used for its detection. We focus primarily on Tissint, a martian meteorite that was seen to fall in 2011 [6], since terrestrial contamination has been kept to a minimum.

Methods: MMC-bearing regions were identified and analysed using Confocal Raman Spectroscopy at the Geophysical Laboratory, Carnegie Institute, Washington D.C. These regions were extracted using a FEI dual beam Ga-F Focused Ion Beam scanning electron microscope (FIB-SEM) at the University of Glasgow. Scanning transmission X-ray microscopy X-ray absorption near-edge structure spectroscopic (STXM XANES) analyses were carried out at Diamond Light Source, UK, to identify functional groups in the organics.

Results and Discussion: Raman spectroscopy identified MMC in thin sections of Tissint, Northwest Africa (NWA) 8159 and Sayh al Uhaymir (SAU) 008. *Immature Organics:* Some areas of immature carbon were found in Tissint and SAU 008, whereby the initial Raman spectra did not have clear D and G peaks. When the Raman laser was continually focused on a spot in these areas for > 30 seconds distinct D and G peaks formed under laser heating (Figure 3), indicating that

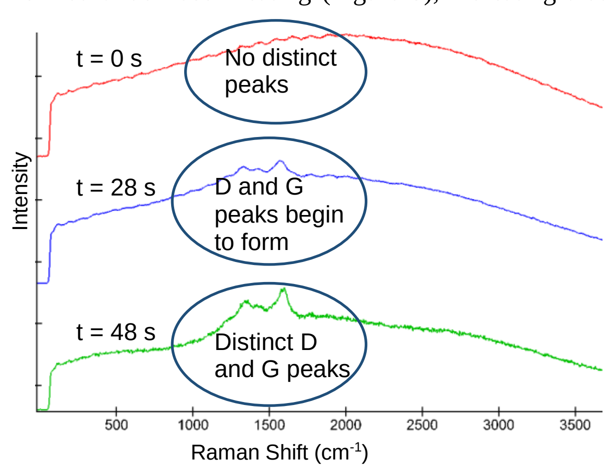

Fig. 3 Extract of time series Raman spectra of labile organic material in Tissint. The Raman laser was focused on a single point, 1 µm below the thin section surface. 20 successive spectra were acquired over a 48 second period. Initially, only fluorescence was observed, with D and G peaks forming under laser heating, indicating increasing maturation of the organics with time. No epoxy peaks are present.

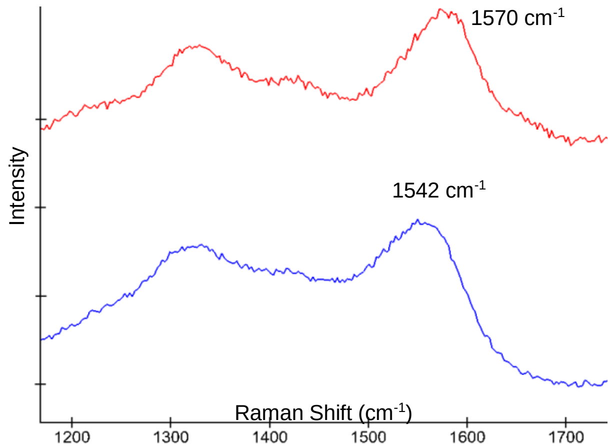

Fig. 4 Variation in the position of the G peak centre observed within a single Tissint inclusion.

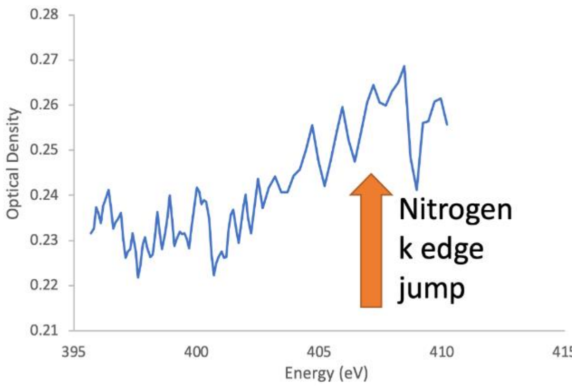

Fig. 5 Nitrogen K edge XANES data for a carbon-rich area in Tissint; the edge jump is indicated. Intensity of the signal is too weak to discern functional group peaks.

some of this martian material is labile. If confirmed the presence of immature / labile organic matter is an important step toward understanding less refractory phases in these meteorites, as they are more likely to contain amino acids and carboxylic acids than more mature MMC [7, 8].

G Band Peak Centre Shift: G peak centre positions in Tissint samples vary, within the same inclusions, as shown in Figure 4. Tissint is a highly shocked (albeit heterogeneously) martian meteorite [6], it is possible therefore that shock affects the ordering of MMC. Although this also may be due to heterogeneous nature of the MMC detected in these meteorites. [9]

XANES Data Analyses: STXM XANES analyses identified MMC in FIB sections of Tissint and NWA 8159 (see Figures 6 and 7). Nitrogen was also detected in association with MMC in Tissint.

Implications/Future Work: TEM analyses will give insight into the nature of the carbonyl group in NWA 8159 (Figure 6), as to whether it is amorphous or crystalline. This work will allow us to determine if the

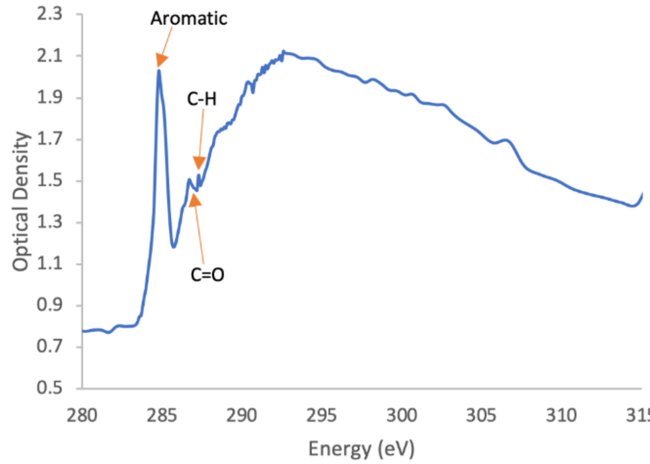

Fig. 6 Carbon K edge STXM XANES spectrum obtained from carbon rich area in a FIB-section in Tissint. Aromatic, C=O and C-H peaks are indicated.

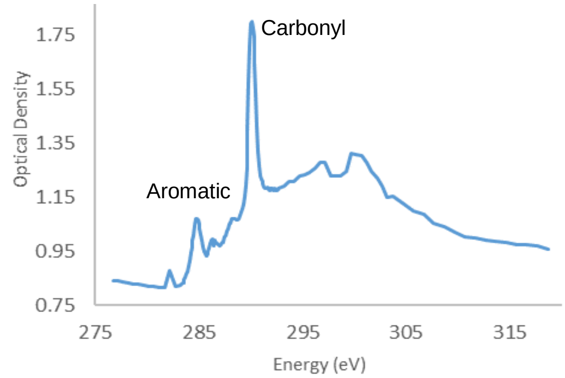

Fig. 7 Carbon K edge STXM XANES spectrum obtained for sample of NWA 8159. Carbonyl and aromatic peaks are indicated.

290.1 eV peak is due to carbonate or another carbonyl group.

In January 2018 hydropyrolysis will be performed on samples of Lafayette, Nakhla and Tissint (all fresh falls/finds) to remove MMC from the bulk rock host. This process will allow us to perform molecular and isotopic identification (via polynomics and GC-MS), and the technique also prevents maturation of labile MMC, such as that shown in Figure 3. The results of this work will be presented at the meeting.

References: [1] Steele A. et al. (2012) *Science* 6091, 337 [2] Sephton M. A. et al. (2002) *Planetary & Space Science* 50: 711-716. [3] Lin Y. et al. (2014) *Meteoritics & Planetary Science* 49: 12. [4] Shock E. L. & Schulte M. D. (1990) *Nature* 343: 728. [5] Steele A. et al. (2018) *Science Advances* 4:10 1-10. [6] Chennaoui Aoudjehane H. et al. (2012) H. *Science* 6108, 338. [7] [8] Summons R. E. et al. (2011) *Astrobiology* 11:157 Westall F. et al. (2015) *Astrobiology* 15:11 [9] Steele A. et al. (2016) *Meteoritics & Plan. Sci.* 51, 12