

Organic Carbon Inventory of the Tissint meteorite. Steele A¹., McCubbin, F. M²., Benning L.G.³., Siljeström S^{1,4}., Cody G¹., Goreva, Y⁵., Hauri, E. H⁶., Wang, J⁶., Kilcoyne, A.L.D⁷., Grady M⁸., Smith C¹¹., Freissinet C¹²., Glavin, D. P¹²., Burton A. S¹³., Fries, M. D¹⁴., Blanco J.D.R. ³, Glamoclija M¹., Rogers, K.L.¹, Mikhail, S1, Dworkin J¹². 1 - Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd, NW Washington DC, 20015 USA. 2 – Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico, 87131 USA. 3 – School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK. 4 – Department of Chemistry and Materials, SP Technical Research Institute of Sweden, 501 15 Borås Sweden. 5 – Department of Mineral Sciences, Smithsonian Institution, Washington, DC. 20013-7012 USA. 6 – Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd, Washington DC. 20015 USA. 7 – Advanced Light Source, 1 Cyclotron Road, MS 7R0222, LBNL, Berkeley, California 94720. USA. 8 - Centre for Earth, Planetary, Space and Astronomical Research. Open University, Milton Keynes, Walton Hall, Milton Keynes, MK7 6AA, UK. 9 - Université de Toulouse, UPS-OMP, IRAP, Toulouse, France. 10 - CNRS, IRAP, 9 Av. colonel Roche, BP 44346, 31028, Toulouse Cedex 4, France. 11- Department of Mineralogy, The Natural History Museum, Cromwell Road, London, SW7 5BD. U.K. 12 - NASA Goddard Space Flight Center, Greenbelt Road, Maryland 20771, USA. 13 - Catholic University of America, NASA Goddard Space Flight Center, 8800 Greenbelt Road, Greenbelt, Maryland, 20771, USA. 14 - Planetary Science Institute, 1700 East Fort Lowell, Suite 106, Tucson, Arizona, 85719 USA.

The fall of the Tissint meteorite has provided a unique opportunity to study a minimally contaminated piece of Mars for the presence of organic carbon. Martian organic carbon has been detected previously in igneous basalts and the carbonates of ALH 84001 [1-4]. Analysis using Confocal Raman Imaging Spectroscopy has shown the presence of inclusions in maskelynite that contain macromolecular organic material similar in its characteristics to that found in other Martian basalts [1-4]. Comprehensive description of the meteorite has shown that it is a geochemically depleted picritic shergottite that is very similar to EET 79001 [5]. It also contains a similar non-maskelynite black glass phase that closely resembles lithology C from EET 79001 [6]. The basis of this current study is the analysis of inclusions within maskelynite phases of the Tissint meteorite. Figure 1 shows 2-D Confocal Raman Imaging Spectroscopy (CRIS) mineral maps of a series of small 1 – 3 μm diameter dark spherical globules enclosed within maskelynite and associated with a large dark irregular feature at the maskelynite pyroxene border. Such features have been described in several meteorites including EET 79001 and DHO 019 [5,7]. Figures 1 B – G show CRIS maps of the area shown in Figure 1A and correspond to maskelynite, magnetite, apatite, pyroxene, pyrite and MMC, respectively and occur approximately 5.4 μm under the surface of the section. Raman mapping confirmed the presence of similar pyrite, MMC and magnetite rich assemblages in 18 maskelynite bound inclusions in Tissint. Transmission Electron Microscopy (TEM) and Energy Dispersive X-Ray spectroscopy (EDX) as well as Time of Flight Secondary Ion Mass Spectrometry (ToFSIMS) provided further confirmation of the mineral assignments used in Raman mapping.

To further elucidate the provenance of the minerals observed in this particular sample a section through one of these inclusions was prepared for high-resolution TEM (HR-TEM) and Scanning Transmission X-Ray Microscopy (STXM) analysis using Focused Ion Beam (FIB) milling. TEM images have been captured showing an inclusion surrounded by the host maskelynite but with the interface delineated by a series of empty, rounded, bubble-like features

and with additional voids inside the inclusion. EDX and Selected Area Electron Diffraction (SAED) confirmed the following mineral phases 1) anhydrite 2) magnetite and 3) Ni containing pyrrhotite were present. The small particle size in area 4 did not allow an unambiguous characterization. While the presence of magnetite was confirmed, the remaining Si, Al and Cl are in an as yet unidentified nano-phase that could possibly be Cl containing aluminosilicates.

Given the presence of the inclusions within impact formed feldspathic glass (maskelynite), it is difficult to constrain their petrologic history. The process of maskelynite formation can erase relict grain boundaries, and depending on the thermal history of the shock event, inclusions may or may not be completely melted and recrystallized during cooling (Stoffler 1986). These vesicles could have formed from a trapped fluid or melt that exsolved a vapor during cooling or they could have formed by dehydration of low temperature hydrous phases during shock-induced heating. Moreover, there are several possibilities that could explain the formation mechanism of both the inclusions and associated phase assemblage shown in Fig 2. These formation mechanisms include: 1) magmatic, 2) magmatic-hydrothermal, 3) impact emplaced melt pockets, and 4) low-temperature secondary aqueous alteration of late stage crystalline melt pockets. In scenario 1) the assemblage originated as a late-stage volatile-rich melt that was trapped within an igneous feldspar that exsolved a fluid and eventually vapor as the inclusion cooled and crystallized. The second scenario suggests a hydrothermal fluid that exsolved from the Tissint magma body during degassing and was trapped within a growing feldspar crystal and the fluid evolved and precipitated hydrothermal minerals over a large oxidation gradient and eventually exsolved a vapor at low pressure. Scenario three suggests that during an impact event, volatile-rich shock melted material was injected into the maskelynite, and the phase assemblage evolved during cooling in a similar manner to the formation of lithology C in EET 79001 and the black glass component in Tissint [5]. Finally in scenario 4, relatively low-temperature (i.e., <200°C) aqueous alteration produced the

low temperature mineral assemblage through weathering of a late stage crystallization pocket. The subsequent shock event that launched Tissint towards Earth erased those relict grain boundaries during maskelynitization, leading to minor degassing of the low-temperature alteration phases. Scenarios 1, 2 and 4 are pre-ejection events, with the ejection impact shock having an unknown effect on the assemblage. Scenario 3 solely derives from the effects of impact.

NanoSIMS analysis of the inclusions showed the presence of C and N as well as Cl, P and S within these inclusions (Fig 1H-L). STXM analysis of FIB sectioned inclusions analyzed by Raman and nanoSIMS showed a complex aromatic moiety containing no graphitic domains (a significant peak at 290.1 eV that is indicative of graphite is not present) and a significant portion of C=C, C=O as ketone and carboxy groups, C-O-H as enol and carboxy groups, and possibly aliphatic carbon.

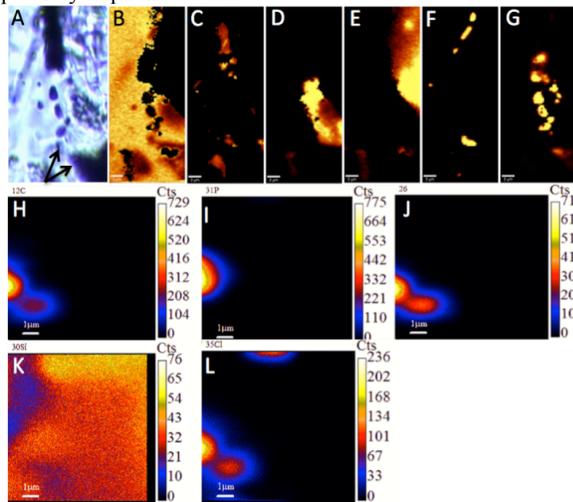


Figure 1. shows a combination of Light microscopy, Confocal Raman Imaging Spectroscopy (CRIS) and NanoSIMS analysis of small (2-3 micron) inclusions within the Tissint meteorite. A) Light microscopy of area of interest (dark globules are 2 – 3 μm in diameter). B – G are CRIS maps of B) glass, C) Magnetite, D) apatite, E) pyroxene, F) pyrrhotite, G) MMC. H to L are NanoSIMS maps of area in Fig 1A shown by arrows H) C^{12} , I) P^{31} , J) $\text{C}^{12}\text{N}^{14}$, K) Si^{30} and L) C^{13} .

The question then remains as to whether the signature of $^{12}\text{C}^{14}\text{N}$ from nanoSIMS is strongly indicative of organic carbon-nitrogen bonds (i.e. nitrile or amide), given the high spatial association of nitrogen to carbon. However, there is a small but real possibility that analytical artifacts, i.e. combination of C and N from other species such as SiN , NH_4^+ and PAHs to form CN^- during sputtering, as well as the presence of inorganic cyanides such as FeCN , CaCN , that could explain the observation. The question of organic nitrogen on Mars is one of paramount importance to possible prebiotic chemistry and is the next logical goal after the proof of organic carbon in the search for habitability. Firstly there is indirect evidence from the C:N ratio measured during stepped combustion for the temperature step between

600 and 800°C being similar to that measured in the nanoSIMS ($\sim 1:16$ C:N) (6). Unfortunately STXM data of the C 1S region does not resolve the possible CN peak at 286.7 eV (Cody et al., 2011). However, that is not proof of absence given the complexity of the spectra throughout the C 1S region. Analysis of the amino acid inventory of Tissint proved the presence of amino acids of terrestrial origin (SOM Fig 4). Since the amino acid extraction was from a bulk sample of Tissint, the contaminating amino acids may be tied to the presence of small grains of carbonate from the Moroccan soil where the meteorite landed and comprised ~ 1.5 ppm in total. ToFSIMS investigations shown in Figure 4 reveal the presence of CN^- (m/z 26.03) and CNO^- (m/z 42.02) associated with S and SO_2 , (within a mass accuracy of ~ 10 ppm) at concentrations well above background levels. Pyrolysis Gas Chromatography Mass Spectrometry (GCMS) studies are currently underway and the preliminary results appear to correlate nanoSIMS and ToFSIMS spatially resolved data that indicate that the Tissint meteorite has an inventory of organic carbon and nitrogen compounds indigenous to the meteorite. Whatever the formation mechanism of the mineral associated mineral assemblages it is clear that the presence of clays and sulfates within the inclusion favors a hydrothermal origin for the formation organic carbon and nitrogen species.

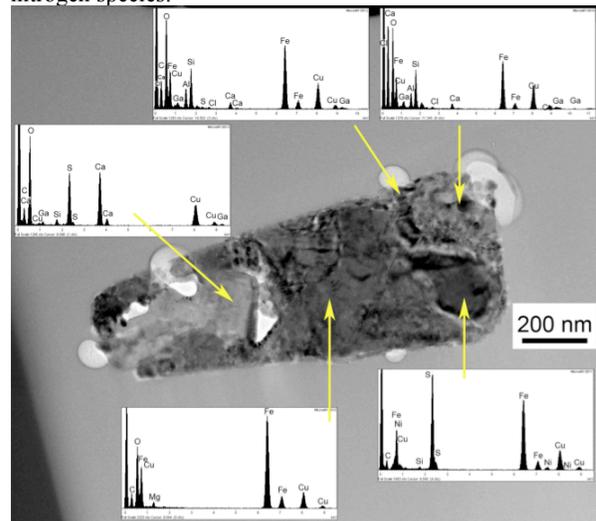


Figure 2. TEM image of inclusion milled from Tissint showing (from EDX data) anhydrite, magnetite, pyrrhotite, carbon as well as several vesicles surrounding and within the inclusion.

References: [1] C. Agee et al., *Science*. 3rd January 2013. [2] Steele et al., *Science* **337**, (6091) 212-215 (2012a). [3] Steele et al., *American Mineralogist* **97**, 1256-1259 (2012b). [4] Steele et al., *Meteoritics & Planetary Science* **42**, 1549 (2007). [5] H. C. Aoudjehane et al., *Science*. 11th October 2012, [6] L. A. Taylor et al., *Meteoritics & Planetary Science* **37**, 1107-1128 (2002). [7] L. Walton, P. J. Jugo, C. D. K. Herd, M. Wilke, *Geochim. Cosmochim. Acta* **74**, 4829 (2010).