NITROGEN-BEARING, INDIGENOUS CARBONACEOUS MATTER IN THE NAKHLA MARS METEORITE.
K. L. Thomas-Keprta[1], S. J. Clemett[1], S. Messenger[2], Z. Rahman[1], E .K. Gibson[2], S. J. Wentworth[1], D. S. McKay[3]; [1]Jacobs JETS Contract, NASA/JSC, Houston, TX 77058 (kathie.thomas-keprta-1@nasa.gov); [2] ARES, NASA/JSC, Houston, TX 77058; [3]Deceased, formerly ARES, NASA/JSC, Houston, TX 77058.

We report the identification of discrete assemblages of nitrogen (N)-rich organic matter entrapped within interior fracture surfaces of the martian meteorite Nakhla. Based on context, composition and isotopic measurements this organic matter is of demonstrably martian origin. The presence of N-bearing organic species is of considerable importance to the habitable potential and chemical evolution of the martian regolith.

Introduction: Carbonaceous phases have been identified in several martian meteorites by bulk analyses and/or chemical extractions. Such bulk studies do not constrain the form and relationship(s) of the organic phases with the host mineralogy. Moreover, it can be difficult to differentiate between indigenous and contaminant organics by bulk studies. To address this, we have undertaken an *in situ* analysis of freshly fractured, interior surfaces of the martian meteorite Nakhla.

Methods: The Nakhla samples used in this work were acquired from the British Museum of Natural History. Chips from Nakhla, split 15 were fractured under clean conditions using stainless steel tools. Fragments which revealed fresh interior fracture surfaces were then selected and immediately imaged optically before being lightly coated with ~1 nm Pt and characterized using field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDX) to identify C-rich regions. Figures 1A & 1B show one such C-rich feature from which two thin sections were subsequently extracted by focused ion beam (FIB) microscopy. One section was prepared for two-step laser mass spectrometry (μ-L^{2}MS) and NanoSIMS analyses, while the other (Fig. 1C) was thinned to electron transparency for characterization by scanning transmission electron microscopy (STEM) and EDX.

Results: Figs. 1A & 1B show a FESEM/BSE image of the C-rich feature on a freshly fractured surface of Nakhla. Yellow boxes indicate the location from which the transverse thin-sections were extracted by FIB. Fig 1C shows a bright-field STEM image of one of these sections in which the C-rich feature which appears as a thin layer ~8 × 0.5 μm in size. STEM/EDX spectra (Fig. 1D) show the carbonaceous region of interest (ROI) contains N, O, Si, Ca & S. The right side of the ROI also contains Na & K while the left side is enriched in Mn. EDX point spectra indicate N is present at significant amounts with estimates ranging from ~1 – 4 wt. % across the ROI. STEM/EDX mapping (Fig. 1E) shows Si is present as discrete 'hot spots' while the Mn appears uniformly distributed. High resolution imaging and selected area electron diffraction indicate the carbonaceous matter lacks ordering and appears amorphous with no evidence of any graphite or 'graphitic-like' phases. From our previous study [1], μ–Raman spectra demonstrate characteristic broad D– and G–band structures with Raman shifts of ~1375 and 1561 cm^{-1} indicating the presence of aromatic moieties. H isotopic imaging showed the ROI to be enriched in D with a δD of 306 ± 52‰ (1σ), strongly suggestive of a non-terrestrial origin.

Discussion: Nitrogen is recognized as one of the key building blocks of life and N-containing functional groups are present in virtually all biomolecules from amino acids to DNA. The observation of discrete assemblages of indigenous N-rich organic matter in a martian meteorite is thus relevant to the potential for Mars as a habitable environment. For N to be incorporated into organic species, it must first be reduced (*i.e*., $N_2 + 2e^- \rightarrow 2N^-$). On Earth this occurs by reduction of N_2 through biological fixation by nitrogenase enzymes [2]. However, unlike Earth, N_2 is only a minor component of the martian atmosphere and in the absence of a catalyst, abiotic reduction of N_2 is kinetically inhibited [3]. Although previous studies have shown nitrates (NO_x) have been detected in several Mars meteorites (EETA79001 [4,5], Nakhla [5], and Tissent [6]), in sedimentary deposits at Gale crater [7], and benzonitrile in extracted Nakhla organic matter [8], this is the first report of *in situ*, indigenous N-bearing organic matter in a Mars meteorite. μ-L^{2}MS organic measurements [*e.g*., 9] of the ROI are planned that will help determine how N was assimilated into this organic material; this technique is key to the *in situ* characterization of discrete organic molecules comprising the ROI. Coordinated NanoSIMS N and C isotopic measurements are also planned.

References: [1] Clemett *et al*. (2016) *LPSC* 47, Abst # 2379. [2] Varley *et al*. (2015) *Phys. Chem. Chem. Phys*. 17:29541-29547. [3] Brandes *et al*. (1998) *Nature* 395:365-367. [4] Kounaves *et al*. (2014) *Icarus* 229: 206. [5] Grady *et al*. (1995) *J. Geophys. Res. Planets* 100: 5449. [6] Aoudjehane *et al*. (2012) *Science* 338: 785. [7] Stern *et al*. (2015) *PNAS* 112: 4245-4250. [8] Sephton *et al*. (2002) *Planet. Space Sci.* 50:711-716. [9] Clemett *et al*. (2012) *LPSC* 43, Abst # 1659.

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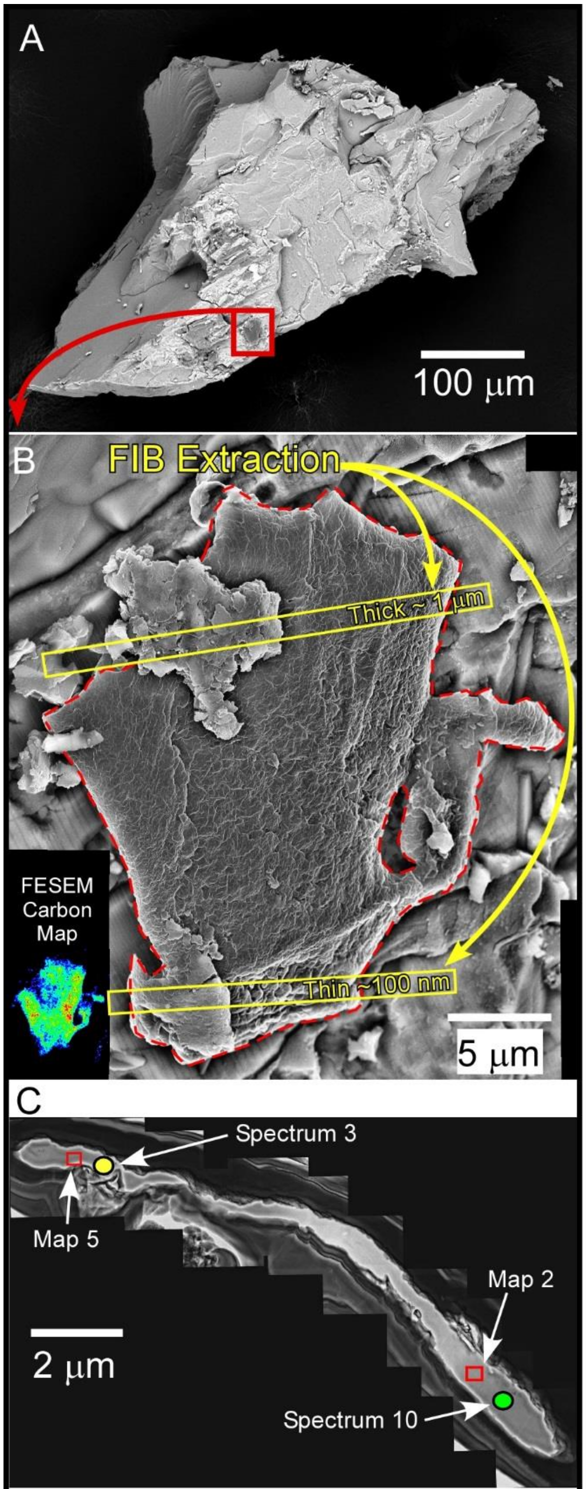

Figure 1. (**A**) BSE image of a freshly fractured grain from Nakhla,15. Region of interest (ROI) in the red box is C-rich. (**B**) Magnified BSE view of the ~ 15 x 20 μm C-rich ROI (outlined by the dashed red line) shown in (**A**). Locations of two extracted FIB sections are given by yellow rectangles. SEM/EDX C-map is shown on lower left. (**C**) TEM view of the C-rich ROI in the thin FIB section.

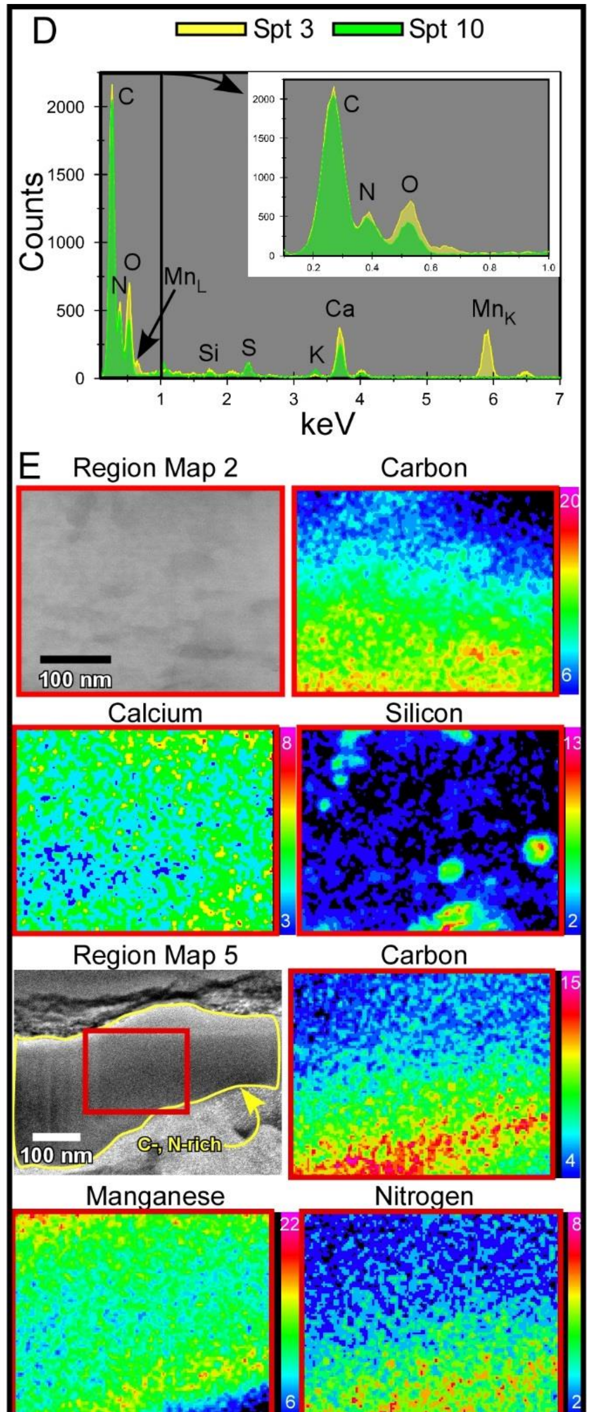

Figure 1, cont. (**D**) EDX spectra of C-rich regions (locations shown in **C**); C-rich matter contains N, O, Si, S, K, Ca and Mn (see insert). N ranges from ~1 – 4 wt.%.(**E**) TEM images (Region Map 2, bright field & Region Map 5, dark field) and corresponding EDX element maps of C-, N-rich feature (see **C** for map locations). Map 2 shows Ca is uniformly distributed while Si is present as 'hot-spots'. Map 5 shows relatively uniform distribution of Mn, other regions show Mn is heterogeneously distributed (not shown); C & N are spatially associated.