Observation and analysis of in situ carbonaceous matter in Nakhla: part II

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The search for indigenous carbon components on Mars has been a challenge. The first attempt was the Viking GC-MS in situ experiment which gave inconclusive results at two sites on Mars [1]. After the discovery that the SNC meteorites were from Mars [2], [3-5] reported C isotopic compositional information which suggested a reduced C component present in the martian meteorites. [6 & 7] reported the presence of reduced C components (i.e., polycyclic aromatic hydrocarbons) associated with the carbonate globules in ALH84001. Jull et al. [8] noted in Nakhl there was an acid insoluble C component present with more than 75% of its C lacking any $^{13}$C, which is modern-day carbon. This C fraction was believed to be either indigenous martian or ancient meteoritic carbon. Fisk et al. [9, 10] have shown textural evidence along with C-enriched areas within fractures in Nakhl and ALH84001. To further understand the nature of possible indigenous reduced C components, we have carried out a variety of measurements on martian meteorites. For this presentation we will discuss only the Nakhl results.

Interior samples from the Nakhl SNC meteorite, recently made available by the British Museum of Natural History, were analyzed. Petrographic examination [11, McKay et al., this volume] of Nakhl showed evidence of fractures (~0.5 μm wide) filled with dark brown to black dendritic material [Fig. 1] with characteristics similar to those observed by [10]. Iddingsite is also present along fractures in olivine. Fracture filling and dendritic material was examined by SEM-EDX, TEM-EDX, Focused Electron Beam microscopy, Laser Raman Spectroscopy, Nano-SIMS Ion Microprobe, and Stepped-Combustion Static Mass Spectrometry. Observations from the first three techniques are discussed in [11].

**Nano-SIMS Ion Microprobe** studies of the C-bearing fractures, containing the optically dark dendritic material, show direct correlation between C and N abundances. Ion abundances for epoxy are distinct from those of the dendritic material [Fig. 2].

**Laser Raman Spectrometry** was utilized to examine the optically dark dendritic material prior to stepped-combustion [Fig. 3]. Samples of the epoxy were examined along with the 100 - 150 μm diameter cores. Individual 3 - 5 μm size regions within the cores were analyzed in the 1000 - 2000 wavenumber (cm-1) region. Bands observed include: 1868, 1705, 1500, 1450, 1435, 1385, 1350, 1267, 1147, 1076 and 1045 wavenumber (cm-1) [Fig. 3]. This is the first report of an apparent complex mixture of carbonaceous components associated with Nakhl dendritic material and iddingsite.

**Stepped Combustion Static Mass Spectrometry** analysis is capable of distinguishing different C- and N-bearing components present along with their C and N isotopic compositions. Analysis of epoxy blanks along with cored samples bearing the opaque carbonaceous-rich materials were analyzed. Three distinct components were detected in Nakhl. A low-temperature C component released below 300°C was predominately terrestrial contamination with an isotopic composition of ~22 to ~24‰. A reduced C-bearing component with isotopic compositions of ~16.1‰ to ~18.4‰ to ~20.2‰ to ~19.4‰ was measured for the 400°, 450°, 500°, and 550°C temperature intervals, resp. Possible presence of a pre-terrestrial secondary carbonate with an isotopic composition of ~+5‰ was released at T > 550°C, but this phase is also similar to operational blanks. The isotopic composition of the reduced C-component was identical to values ~18 to ~20% reported by [8] and [12]. However, our C analysis is the first isotopic measurement of directly imaged high molecular weight carbonaceous components in Nakhl. Previous measurements were from bulk Nakhl samples with no direct observation of the C-bearing phases. N isotopic composition associated with the reduced C-component was ~+5‰.

This is the first report correlating fracture-fill material in Nakhl, iddingsite and optically dark dendritic material, with reduced carbonaceous components. The source of these components can be interpreted as produced by different possible processes: (a) C introduced during a carbonaceous-rich impactor on Mars 600,000 to 700,000 years ago [13] -- this impact may have produced the fractures in Nakhl where iddingsite resides; or, (b) these C-bearing components may be products of biogenic activity and introduced by groundwater into the fracture features in Nakhl [14].

**References:**
Fig 1. Optical views of Nakhla polished thin sections (above). Left: iddingsite veins in olivine. Isotopic analyses were performed on this region. Right: cpx region containing optically dark, dendritic features (red box) (see complementary abstract by McKay et al., this volume, for chemical composition). NanoSIMs analyses were performed on this region.

Fig 2. NanoSIMs analyses of epoxy and dendritic vein-filling material (above) showing that both are composed of carbon with distinctly different CN⁻/C⁻ ratios. NanoSIMs maps (right) of dendritic material show the distribution of C⁻ and CN⁻ ions.

Fig 3 (Left). Laser raman spectra of carbonaceous vein-filling material (red), CPX substrate (green), and epoxy embedding material (blue). Vein-filling material appears to contain a complex mixture of carbon compounds with isotopic composition C = -18 to -20‰.