

The provenance and formation of reduced carbon phases in Martian meteorites. A. Steele¹ F.M. McCubbin², M Fries³. 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 - NASA, Johnson Space Center, Mail Code KT, Houston Texas, 77058. USA.

Organic carbon compounds are essential building blocks of terrestrial life, so the occurrence and origin (biotic or abiotic) of organic compounds on Mars is of great significance. Indeed, the question of Martian organic matter is among the highest priority targets for robotic spacecraft missions in the next decade including the Mars Science Laboratory and Mars 2020. Several Martian meteorites contain organic carbon (i.e., macromolecular reduced carbon-rich material, not necessarily related to biota), but there is little agreement on its origins. Initial hypotheses for the origin of this organic carbon included: terrestrial contamination (1); chondritic meteoritic input (2); thermal decomposition of Martian carbonate minerals (3); direct precipitation from cooling aqueous fluids (4); and the remains of ancient Martian biota (5). Fourteen martian meteorites were analyzed using stepped-combustion isotope-ratio mass spectrometry, and they were reported to contain between 1 and 50 ppm of “crystalline” carbon that combusted between 600 and 1000°C (1,2). This temperature release range was interpreted by Grady et al. (1) as representing reduced magmatic carbon along grain boundaries or included within silicates. We report the results of present studies of 13 Martian meteorites and show the presence of reduced carbon in 12 of these meteorites that appear to show several possible formation mechanisms.

In the first case study on Martian meteorite ALH 84001 we demonstrate that the magnetite and a reduced macromolecular carbon (MMC) phase formerly interpreted as relic biosignatures may be formed through abiogenic processes [3,4,5]. However, debate continues as to whether these processes required elevated temperatures [4,5]. If elevated temperatures are required, a biologic origin for these features can be excluded, but if they are more likely to have formed at low temperatures, a biologic origin remains a possibility. One of the primary arguments against a high temperature origin was the absence of graphite in the magnetite-carbonate assemblages, due to the kinetic inhibition of crystalline graphite precipitation at low temperature [2, 3]. In this study, in-situ Confocal Raman Imaging Spectroscopy (CRIS) was used to image carbonate globules on fresh fracture surfaces of ALH84001,347 [4]. In addition, high resolution transmission electron microscopic (TEM) imaging and selected area electron diffraction (SAED) was conducted on magnetite particles extracted from dissolved ALH

84001 carbonate globules. These studies confirm, the presence of graphite associated with magnetite in the carbonate globules in ALH84001. This highly crystalline graphite was found in association with magnetite in the rim of a carbonate globule in ALH84001. Furthermore, insoluble magnetically separated residue extracted from dissolved ALH 84001 carbonate globules analyzed by TEM showed graphitic carbon with morphologies varying from amorphous (MMC) to highly crystalline particles, filaments, and mesoporous shells bound to clumps of magnetite. The shells revealed a disordered turbostratic graphite micro-texture consisting of polycyclic-aromatic platelets surrounding more ordered graphite layers. The structure of this micro-texture were confirmed by SAED via the characteristic d-spacings for hexagonal graphite of 3.35Å (8). The range of graphite morphologies and their presence within carbonates were confirmed by the ordered and disordered (D and G band respectively) features within the Raman spectra and maps. This close association of graphite with magnetite formed on Mars is unambiguous evidence that the graphite is not the result of terrestrial contamination. The nature and presence of these graphite morphologies in the globule rims within the carbonates and associated with the magnetite suggest the presence of an indigenous high temperature nano-crystalline reduced carbon component in this meteorite as suggested by Jull et al [6].

In the second study, Confocal Raman Imaging Spectroscopy (CRIS) was used to study microphenocrysts of oxides (spinel-group minerals) included in olivine and pyroxene grains in twelve Martian meteorites including samples of the recent Tissint meteorite fall and NWA7034. We identified MMC in twelve of these meteorites associated with small (2-20µm) chromite-rich grains that are ubiquitous as mineral inclusions within olivine and / or pyroxene grains in these meteorites. Any MMC found to be incompletely enclosed within its silicate host (i.e. in cracks, grain boundaries, at the surface of the sample, or associated with weathering or contaminating phases) was treated as contamination and discounted from this study. All of the MMC reported was located at least several microns below the undisrupted surface of the observed thin section and occurred in association with chromite-rich microphenocrysts. The association of MMC with spinel was consistent in recent falls (Tissint, Zagami) as well as older finds (DaG 476, SAU 019) and is un-

likely to be terrestrial contamination. We therefore conclude that the trapping of this carbon-enriched melt in the mineral host likely led to the early saturation in a C-O-H fluid-phase in the melt inclusion. Importantly, the C:H ratio of the trapped melt would be greater than the parental melt as H-species diffuse much more rapidly through the melt than C-species thus setting the stage for subsequent MMC and PAH production and enrichment in the inclusion as the host olivine cooled and trapped melt crystallized. Furthermore, if the mantle source for these meteorites contained graphite early saturation in a C-bearing fluid phase could occur regardless of the boundary-layer effects at low degrees of partial melting. The amorphous nature of the MMC, and the presence of PAHs in the MMC (2) containing assemblages indicate that the MMC precipitated in contact with the oxides as an insoluble organic carbon phase whose presence was therefore sensitive to the redox state of the magma. It has been hypothesized that the Martian mantle is graphite saturated and that the oxygen fugacities of the mantle sources for the Martian meteorites are buffered by fluids in the C-H-O system. Significant amounts of hydrogen occur in Martian magmatic source regions, indicating that if the Martian mantle is graphite saturated, mantle fluids would have likely contained significant C-O-H components. The Tissint meteorite shows similar MMC / spinel features as the other meteorites with a $\delta^{13}\text{C}$ of -17.8 ± 1.89 and ~ 14 ppm of reduced carbon. Combining all these studies shows that igneous Martian rocks could contain up to $\sim 20 \pm 6$ ppm of reduced carbon with an average $\delta^{13}\text{C}$ of $\sim -19.8 \pm 4.3\%$. Therefore, it is not possible to assign a definite value to the concentration and isotope value of Martian organic carbon, however, this and previous studies indicates an indigenous and isotopically light carbon phase in these meteorites [1,2].

Finally we conducted an in depth study of the Tissint meteorite using a number of in-situ and bulk techniques. The basis of this study was the analysis of inclusions within maskelynite phases of the Tissint meteorite. 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 were 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 that 1) anhydrite 2) magnetite and 3) Ni containing pyrrhotite 4) montmorillonite were present. NanoSIMS analysis of the inclusions showed the presence of C and N as well as Cl, P and S within these inclusions. 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 was not present) and peaks indicative of C=C, C=O as ketone and carboxy groups, C-O-H as enol and carboxy groups, and possibly aliphatic carbon. The organic carbon phases show strong isotopic evidence for their Martian origin, for example a large positive δD value of features associated with organics in the region of $\sim +3500$ ‰. Furthermore there is a release of nitrogen containing organics above 600°C , at which temperature $\delta^{15}\text{N}$ is $\sim +40$ ‰. These results show unambiguously that Mars has an inventory of organic carbon and nitrogen containing molecules that are produced via simple abiotic hydrous chemistry with known mineral catalyst assemblages. Furthermore, graphite was found in the matrix of Tissint associated with a black glass phase that was formed during impact.

These studies when combined show 4 possible pools of reduced carbon on Mars. 1) impact generated graphite in Tissint, 2) secondary hydrothermal generated graphite in ALH 84001, 3) primary igneous reduced carbon in 12 Martian meteorites associated with spinels 4) primary hydrothermally formed organic carbon / nitrogen containing species in the Tissint meteorite. These studies show that Mars has produced reduced carbon / organic carbon via several mechanisms and reveal that the building blocks of life, if not life itself, are present on Mars.

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