

Martian Organic Synthesis by Electrochemical Reduction of Aqueous CO₂. A. Steele¹ L.G. Benning², R. Wirth², M. Fries³. ¹Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd, Washington DC 20015. asteel@carnegiescience.edu 2- Geo-Forschungs Zentrum (GFZ) Interface Chemistry group, Potsdam, Germany. 3- NASA JSC, Houston Tx.

Introduction: The source and nature of carbon on Mars has been a subject of intense speculation. This proposal seeks to expand on a successful Mars fundamental research proposal that enabled analysis of eleven Martian meteorites, spanning ~4.2 Ga of Martian history [1]. Ten of the meteorites contain macromolecular carbon (MMC) phases included within high temperature mineral phases, namely pyroxene and olivine hosted melt inclusions that contain mineral oxides and MMC. More recently analysis of the Tissint meteorite has shown the presence of organic carbon and nitrogen phases that again are coupled to the presence of spinel minerals (magnetite, ilmenite etc). However, in the case of Tissint there is a reservoir of organic carbon and nitrogen compounds that are found within feldspathic glass inclusions that does not appear to be associated with high temperature igneous processing [2].

It is the analysis of the organic material found in Tissint that led directly to the search, identification and characterisation of organic phases in the Cumberland mud stones by the Sample Analysis at Mars study recently published [3,4]. As part of this study several other Martian meteorites including Nakhla, Governador Valadares and NWA 1950 have been studied.

Methods;

Samples

Analyses were conducted on both thin sections and fresh fracture surfaces of the 3 meteorites in question. Samples of Nakhla were provided by Johnson Space center, Governador Valadares (GV) was supplied by N Boctor. 3Tissint by the University of New Mexico and the Natural History Museum London (Caroline Smith) and NWA 1950 was from Carnegie Institution of Washington.

Confocal Raman Imaging Spectroscopy (CRIS)

Raman spectra and images were collected using a Witec α -Scanning Near-Field Optical Microscope that has been customized to incorporate confocal Raman spectroscopic imaging. The excitation source is a frequency-doubled solid-state YAG laser (532nm) operating between 0.3 and 1 mW output power (dependent on objective), as measured at the sample using a laser power meter. Objective lenses used included a x100 LWD and a x20 LWD with a 50 μ m optical fiber acting as the confocal pin hole. Spectra were collected on a Peltier-cooled Andor EMCCD chip, after passing through a f/4 300mm focal length imaging spectrometer typically using a 600 lines/mm grating. The lateral resolution of the instrument is as small as 360 nm in air

when using the x100 LWD objective, with a focal plane depth of ~800nm.

Focused Ion Beam Milling (FIB)

Electron transparent TEM foils have been prepared by using the focused ion beam (FIB) system at GFZ Potsdam.

Soft Transmission X-ray Microscopy (STXM)

Two STXM beam lines located at beamline 5.3.2 at the Advanced Light Source, Lawrence Berkeley Laboratory and the IO8 beamline at DIAMOND were used for all analyses. Both C1S and N1S edges were scanned

Transmission Electron Microscopy (TEM)

EM analysis of the FIB prepared foils was performed with a TECNAI F20 X-Twin transmission electron microscope at GFZ Potsdam. The TEM was operated at 200 keV with a Schottky field-emitter as electron source.

NanoSIMS

Isotopic imaging was performed using the NanoSIMS 50L ion microprobe at the Department of Terrestrial Magnetism, Carnegie Institution of Washington. The selected area (In Figure 1) of the sample were first pre-sputtered using a 5-10nA Cs beam to remove surface contamination, and to sputter down through the sample until the area of interest was reached were exposed; an electron flood gun was used for charge compensation. We then utilized a 200pA primary beam of Cs ions focused to a diameter of 400 nanometers for obtaining isotopic images. Simultaneous detection and imaging of, ¹H, ²D and ¹³C, were obtained by rastering the primary beam over areas 15x15 microns starting at the surface of the section over the feature

Results

Organic phases were discovered by CRIS associated mostly with titanomagnetite and magnetite (but also pyrite and pyrrhotite phases in some cases) in all four martian meteorites analyzed. High-resolution transmission electron microscopy (TEM) images of these titanomagnetite / MMC associations, (which followed focused ion beam (FIB) extractions from the areas rich in MMC from CRIS analysis), revealed that in all cases across all meteorites MMC was associated with cracks in Ti rich magnetite that appear slightly to moderately corroded. Detailed imaging of some areas in Nakhla revealed that titanomagnetite grains showed a comb-like pattern of etching into the grain along exsolution lamellae (Steele et al., 2018). The titanomagnetite lamellae were closely interlinked with an amorphous carbon-rich phase (based on energy disper-

sive X-ray (EDX) analyses and CRIS mapping) that did not show any diffraction contrast.

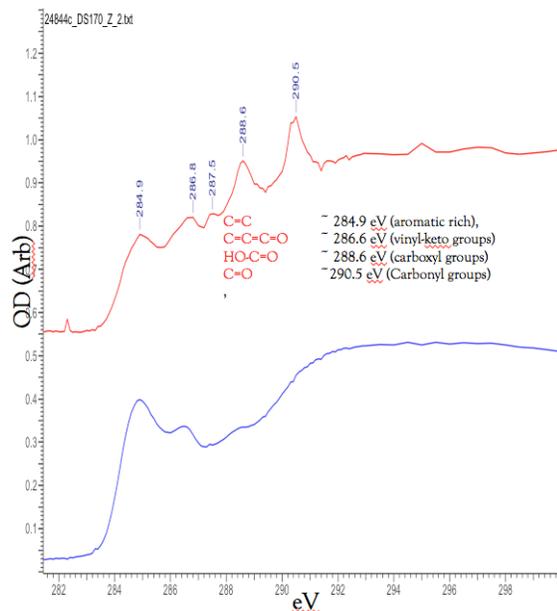


Figure 1. C1S STXM analysis of MMC in NWA 1950 (red) and thin section polymer (blue).

NanoSIMS analyses of hydrogen isotopes in the carbon-rich phases associated with similar alteration cracks in titanomagnetite laths in the Tissint meteorite result in an average δD of $\sim 3600 \pm 1000\%$. This value indicates that the hydrogen associated with the MMC in the Tissint meteorite is of Martian crustal origin and arises from a fluid pool that equilibrated with the martian atmosphere. The hydrogen isotopes (δD) of MMC in both Nakhla and NWA 1950 are $219 \pm 60\%$ and $98 \pm 20\%$ respectively, in areas that correlate to ^{13}C . These values exclude a terrestrial carbon contaminant source but are consistent with formation from a martian magmatic water source. Therefore, the Tissint meteorite appears to have incorporated atmospheric deuterium dissolved in near-surface brine, while the Nakhla and NWA 1950 MMC formed from a brine drawing from a magmatic source. Further evidence for the nature of the organic phases in these Martian meteorites comes from high resolution TEM and scanning transmission X-ray microscopy (STXM) analyses (Fig 1) [4].

STXM and EELS analyses reveals that the MMC is very oxygen rich containing a large percentage of carbonyl, carboxyl, and vinyl-keto groups as well as nitrile and pyrrole functionality of nitrogen. Soft Transmission X-ray Microscopy conducted on area containing thin section polymer and the MMC show two distinct carbon spectra, one indicative of thin section polymer and one showing a uniquely different molecular

bonding pattern. Peaks for the MMC area are 285eV (aromatic), 286.6 eV (C=C, C=O, C=N or nitrogen heterocyclic), 287.5 (aliphatic) and dominant peaks at 288.6 eV (carboxyl) and 290.5 eV (carbonyl) groups differ extensively from the mainly aromatic (285 eV) and 286.5 eV (C=C, C=O, C=N or nitrogen heterocyclic) group found in the thin section polymer (Steele:2018). These analysis are consistent with preliminary C and N edge STXM on MMC in the Tissint meteorite (Steele et al., 2018) i.e. carbon oxygen functional groups including C-O, C=O and COOH and carbon nitrogen analysis showing nitrile and pyrrole groups.

The spatial relationships between organic carbon, nitrogen and sulfur compounds as well as their intimate link to spinel-group minerals (i.e. titanomagnetite), sulfides and their alteration products and textures, requires a syntheses mechanism that is parsimonious with the presence of all of these molecules. The implications of the chemical associations shown in these meteorites are that a Cl-rich fluid (brine) reacted with magnetite, pyrrhotite, pyrite and titanomagnetite grains to initiate a galvanic cell. We hypothesize and will present evidence to show that the voltage and current produced during the corrosion process are in these circumstances enough to reduce aqueous CO_2 and N_2 to the range of organic molecules shown in this work and through extension discovered by the Curiosity on Mars [3].

Here we show that Tissint, Nakhla, GV, and NWA 1950 have an inventory of organic carbon and nitrogen species associated with fluid-mineral reactions, revealing secondary brine-rich fluid alteration processes. We advance the hypothesis that electrochemical reactions of spinel-group minerals and sulfides with such brine rich fluid, enable the electrochemical reduction of aqueous CO_2 to organic molecules. This is the first time a natural process for conversion of CO_2 to complex organics has been described in an environmental sample from another planet and has profound implications for the start of life on Earth as well as organic synthesis on Europa and Enceladus [4].

References:

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