NANOSIMS ANALYSIS OF ORGANIC CARBON FROM MARS: EVIDENCE FOR A BIOGENETIC ORIGIN.

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Introduction: Mars orbit and rover missions have brought us numerous lines of evidence for past or even extant existence of water on Mars. Studies of Martian meteorites, the only available rocks from Mars, also suggest a wet Mars at least in the early history. These observations promise discovery of life on Mars. However, there are few hints for existence of Martian life. Detection of methane in Martian atmosphere by the Mars Express orbiter [1] has revived exploration of life on Mars. However, question of Martian methane is still up in the air [2]. Tissint is a new witnessed Martian meteorite fall, supplying us with unique fresh samples to study the paleoenviroment and search for evidence of possible life on Mars. We find a carbon component in Tissint, filling fractures in silicates with another few inclusions in shock-induced melt veins. Laser micro-Raman spectra of the carbon component indicate a kerogen-like matter, similar to those reported in "*magma inclusions*" in other Martian meteorites [3]. We analyzed the elemental ratios of H, N, O, F, Cl, S and P to C, and the isotopic compositions of C, N and H using the nanoSIMS 50L. The results clearly favor a biogenetic origin.

Results: Tissint is an olivine-phyric shergottite that experienced heavy shock metamorphism with several melt veins (< 160 μm wide), highly fractured silicates and dissociation of olivine [4,5]. A carbon component was found in two petrographic settings in polished sections of Tissint. Most of the carbon component fully fills fractures in olivine and pyroxenes in several regions (Fig. 1a,b). It is noticed that around the main carbon-veins (<10 μm wide), countless thin cracks and cleavages are also filled with the same carbon component (Fig. 1a,b). This appears obvious in the nanoSIMS element images (Fig. 1c). In addition, several carbon inclusions (<6 μm) were found in the shock-induced melt veins in Tissint (Fig. 1d), NWA 6162 and NWA 856 [5].

Laser micro-Raman spectra of the carbon component exhibit a broad G-band centered at 1580 cm^{-1} and a smaller D-band at 1346 cm^{-1}, similar to kerogen in carbonaceous chondrites [6]. The centered D-band positions and the full width at half maximum (FWHM) of the carbon matter plot within the range of the reduced organic carbon component in other Martian shergottites [3]. Furthermore, a sharp peak at 1327 cm^{-1} was detected in some areas of the organic carbon enclosed in the shock melt veins, evidencing the diamond T_{2G} mode, pointing to formation by a shock event. This discovery confirms the independent observations in Tissint and other shergottites [5].

The elemental ratios of H, N, O, F, Cl, S and P to C of the organic carbon are distinctly higher than the graphite standards we used, but comparable with the coal working reference. In addition, the organic carbon is even more Cl-, F-rich than the coal reference.

The $\delta^{13}C_{VPDB}$ values of the organic carbon are very light, varying from (1σ) -13.3±2.1 ‰ to -33.6±1.9 ‰, with an average of -21.1±5.3 ‰. This is the first measurement of C isotopic compositions of possible organic matter from Mars. With the coal working reference (δD= -147 ‰, δ^{15}N= 3.0±0.2‰), the δD values of the organic carbon vary from +324 ‰ to +1183 ‰, except for 4 grains (-51 ‰ ~ +6.7 ‰), and the δ^{15}N values are -12.9 ‰ ~ +17.3 ‰ with an average of 4.4±8.4 ‰.

Discussion: This is the first discovery of confirmed organic carbon deposited in fractures in a Martian rock. Based on the laser Raman spectra, the organic carbon is distinct from graphite, but is similar to kerogen from carbonaceous chondrites [6] and reduced organic component reported in "*magma inclusions*" in other Martian basalts [3]. The petrographic settings of the organic carbon point to the following formation episodes: (1) Eruption of the igneous rock of Tissint to the subsurface of Mars; (2) After a long period of residence (> Ma), the igneous rock was impacted by an asteroid, highly fractured the rock and inducing partial melting; (3) Hereafter, the host rock of Tissint was infiltrated by organic-bearing fluids; (4) Organic carbon deposited from the fluid; (5) A second asteroid hit the same site, partially melting the organic carbon-bearing host rock and producing the shock-melt veins. The presence of the organic carbon inclusions in the shock melt veins set a clear lower limit of formation time for the organic carbon. The Raman T_{2G} band at 1327 cm^{-1} in some areas of the organic carbon inclusions indicates conversion to diamond by the shock event, similar to the observations in samples of Tissint and other shergottites [5]; (6) Finally, a third asteroid impacted the igneous rock again, launching Tissint into an Earthcrossing orbit at 0.7±0.3 Ma [7]. In addition, petrographic textures of the high-pressure polymorph assemblages in these Martian meteorites strongly suggest multiple shock events [5], consistent with the above scenario of the organic carbon.

The $\delta^{13}C$ values of the organic carbon (-13.3 ~ -33.6 ‰, average -21.1±5.3 ‰) strongly indicate a biogenetic origin (Fig. 2). The difference between $\delta^{13}C$ values of the organic carbon and Martian atmospheric CO_2 ($\delta^{13}C$= -2.5±4.3 ‰) [8] is comparable with biotic carbon (-20~ -40 ‰) and the atmospheric CO_2 (-7 ‰). If referred to ALH 84001 carbonates ($\delta^{13}C$= +27 ~ +64 ‰) [9], the organic carbon is even more lighter, in comparison with the lower $\delta^{13}C$ values of terrestrial carbonate (-5 ~ +5 ‰). The δD values (+324~+1183 ‰, except for 4 grains with normal compositions) are lower than that of the Martian atmospheric water, probably due to dilution by the D-poor water from depth. This is expected for cold and arid Martian surface that may have characterized for over 3 billion years [10]. In addition, the lower $\delta^{15}N$ values than the Martian atmosphere (634±60 ‰) [7] indicate a different N reservoir.

The petrographic setting of the organic carbon, filling the crack and cleavage space, is consistent with a biogenetic origin, but cast doubt on igneous origin as proposed for the reduced organic component in the alleged intact "*magma inclusions*" [3], which didn't show presence of any C-O-H fluid or voids within the inclusions. In fact, the alleged "magma inclusions" consist predominantly of one or more chromite grains [3], different from the typical feldspathic glass-bearing magma inclusions in olivine in Tissint and lherzolitic shergottites [11].

$\delta^{13}C$ values of carbonaceous chondrites (-4.8 ~ -22.0 ‰) [12] overlap with those of the organic carbon. However, impact of carbonaceous chondrite-like asteroids would destroy its own organic materials. In fact, no any relics of chondritic materials were ever reported in shergottites. It is also unlikely to extract the unsolvable organic carbon from impacting carbonaceous chondrites and fill the crack and cleavage space.

Graphite can precipitate from fluid via reaction of CO_2+CH_4. However, the organic carbon in Tissint is kerogen-like instead of graphite based on the Raman spectra. This is confirmed by its high concentrations of H, N, O, Cl, F, S and P.

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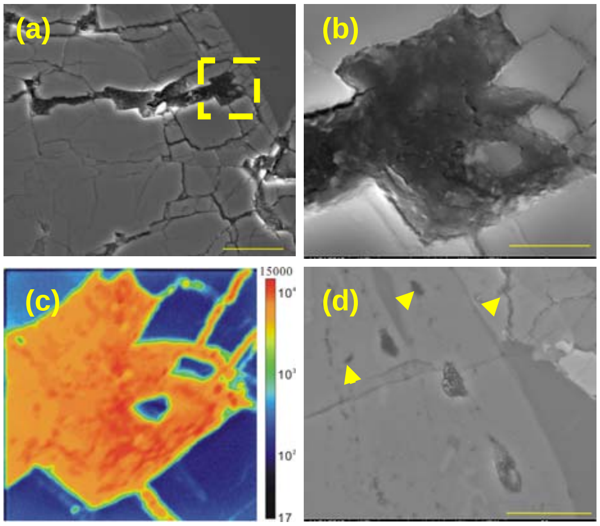

Fig. 1. SEM and nanoSIMS images of the organic carbon in Tissint. (a) Filling up cracks, scale bar of 20 µm; (b) High magnification of inset, scale bar of 4 µm; (c) C mapping of nanoSIMS, showing the fine cleavages filled with the organic carbon too; (d) Enclosed in the shock-induced melt vein, the smaller grains (arrows) are also the organic carbon. Scale bar of 20 µm.

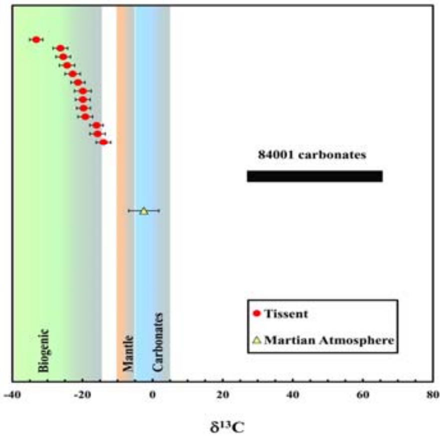

Fig. 2. $\delta^{13}C$ values of the organic carbon, in comparison with those of Martian atmospheric CO_2 [8] and ALH 84001 carbonate [9]. The analyses of the organic carbon arrange in a sequence of $\delta^{13}C$ decreasing upwards. The ranges of different origins of terrestrial carbon are given for reference.