EFFECTS OF SHORT-TERM THERMAL ALTERATION ON ORGANIC MATTER IN EXPERIMENTALLY-HEATED TAGISH LAKE OBSERVED BY Raman spectroscopy. Q. H. S. Chan¹, A. Nakato², M. E. Zolensky¹, T. Nakamura¹, Y. Kebukawa¹, J. Maisano³, M. Colbert³, and J. E. Martinez⁶, ¹ARES, NASA Johnson Space Center, Houston, TX 77058, USA (queeniechs@gmail.com), ²Kyoto University, Kyoto, 606-8502, Japan, ³Tohoku University, Miyagi 980-8578, Japan, ⁴Faculty of Engineering, Yokohama National University, Yokohama 240-8501, Japan, ⁵Department of Geological Sciences, Jackson School of Geosciences, The University of Texas, Austin, TX 78712, USA, ⁶Jacobs Engineering, Houston, TX 77058, USA.

Introduction: Carbonaceous chondrites exhibit a wide range of aqueous and thermal alteration characteristics, while some are known to demonstrate mineralogical and petrologic evidence of having been thermally metamorphosed after aqueous alteration [1]. This group of meteorites are commonly referred to as thermally metamorphosed carbonaceous chondrites (TMCCs), and their reflectance spectra show resemblances to that of C-type asteroids which typically have low albedos. This suggests that the surfaces of the C-type asteroids are also composed of both hydrous and dehydrated minerals [2, 3], and thus TMCCs are among the best samples that can be studied in laboratory to reveal the true nature of the C-type asteroids.

Although TMCCs are usually meteorites that were previously categorized as CI and CM chondrites, they are not strictly CI/CM because they exhibit isotopic and petrographic characteristics that significantly deviate from typical CI/CM. More appropriately, they are called CI-like and/or CM-like chondrites. Typical examples of TMCCs include the C2-ung/CM2TIV Belgica (B)-7904 and Yamato (Y) 86720 [4]. Thermal alteration is virtually complete in these meteorites and thus they are considered typical end-members of TMCCs exhibiting complete dehydration of matrix phyllosilicates [1, 4]. The estimated heating conditions are 10 to 10⁷ days at 700°C to 1 to 100 hours at 890°C, i.e. short-term heating induced by impact and/or solar radiation [5].

While the petrology and chemistry of TMCCs have only recently been extensively characterized, we have just begun to study in detail their organic contents. In order to understand how short-term heating affects the maturity of insoluble organic matter (IOM) in hydrous chondrites, we investigated experimentally-heated Tagish Lake meteorite using Raman spectroscopy, as the chemical and bulk oxygen isotopic compositions of the matrix of the carbonate (CO₃) poor lithology of the Tagish Lake (hereafter Tag) meteorite bears similarities to the TMCCs [6].

Samples and Methods: The CO₃-poor lithology of Tag (#11, renamed from MM47/66) was located with X-ray computed tomography at the University of Texas. Tomographic imaging was useful in identifying internal lithologic and mineralogical differences, which we used to decide where to make the initial slice into the sample and prepare thin sections. The initial samples were then characterized by scanning electron microscopy (SEM) with a Zeiss SUPRA 55VP field-emission SEM at the Structural Engineering Division, NASA JSC, to verify the CO₃-poor lithology based on elemental mapping and comparison to the XRCT images (Figure 1).

![Figure 1. (a) 3D rendering of Tag#11 produced from XRCT. (b) A slice image of Tag taken at the dashed line in (a). (c) SE image of region of interest indicated by arrows in (a,b). (d) Ca EDX map of (c).](https://ntrs.nasa.gov/search.jsp?R=20170000485 2019-05-26T06:46:00:00Z)

Selected subsamples (~100 mg) of the CO₃-poor lithology were subjected to heating experiments: (1) 600°C/1h, (2) 600°C/96h, (3) 900°C/1h, and (4) 900°C/96h. The samples were then studied with Raman spectroscopy at NASA JSC using a Jobin-Yvon Horiba LabRam HR Raman microprobe. At least 12 spectra were collected on the surface of each raw matrix grain (flattened between two glass slides) with a 514 nm excitation wavelength at 80x magnification and a spot size of ~1 μm. The laser power at the sample surface was ≤450 μW and the total acquisition time was 450s. The Raman band parameters were determined by simultaneous peak fitting to the two-peak Lorentzian and Breit–Wigner–Fano model [7] and linear baseline correction. Wavelength calibration against a silicon wafer sample was checked daily prior to sample analyses. Details of the Raman technique are given in [8, 9].

Results and Discussion: The mineralogy and texture of the Tag samples heated at 900°C show the closest resemblance to that of the strongly heated TMCCs due to the dehydration of hydrous minerals such as phylo-
silicates and formation of magnetite, and recrystallization back into anhydrous fine-grained (<100 nm) secondary olivine, pyroxene, Fe-Ni metal and troilite [6].

The Raman parameters of the unheated Tag vary from previous studies [10, 11], probably due to different analytical methods, the peak fitting algorithm, and/or sample heterogeneity due to the brecciated nature of Tag which contains two other major lithologies: CO$_2$-rich lithology and foreign clasts [12]. Nevertheless, the Raman parameters of the three adjacent unheated subsamples of the CO$_2$-poor lithology are comparable (Figure 2), indicating that the organic content is consistent within this lithology.

![Figure 2. Raman peak parameters (full width half-maximum [Γ] and peak positions [ω]) of the D bands, and the D/G peak intensity [I_D/I_G] selected spectra of Tag matrix.](image)

**Heating experiment.** A reduction in the intensity of the fluorescence background was observed after the samples were subjected to heating. A similar effect of heating on the fluorescence background has been observed for the thermally-altered CMs [e.g., 11]. The D band parameters show a clear correlation to the heating temperature, however heating duration only affects these parameters to a lesser extent. Decreases in the fluorescence intensity and the Γ$_D$ indicate that the IOM gains maturity through thermal annealing by losing hydrogen and heteroatoms to form polyaromatic structures. The ω$_D$ and Γ$_D$ of the heated (≥700°C) Y-86720 are ~1349 and ~245 cm$^{-1}$ respectively [10], which is placed between the 600°C and 900°C experiments on the ω$_D$ vs Γ$_D$ plot (Figure 2). The I_D/I_G ratio increases with heating, which indicates that graphitization has not been completed, as large-scale graphitization would have significantly reduced I_D/I_G. Our experimental data also indicate that the heating experiments have significantly led to the widening of Γ$_G$. However, this trend runs counter to that for meteoritic organics, where decreasing Γ$_G$ is associated with increasing metamorphism [10]. A decrease in Γ$_G$ (7–10 cm$^{-1}$) was associated with samples that were exposed to a longer heating duration (96h) (Figure 2), although the Γ$_G$ values are still at least 14 cm$^{-1}$ wider than the unheated samples. This indicates that Γ$_G$ is sensitive to short-term heating and the heating effects are rapid as shown by the difference between the Raman parameters of the unheated Tag and Tag heated for only 1h. Prolonged heating such as long-term parent body metamorphism could lead to a reduction in Γ$_G$, which could ultimately result in very low Γ$_G$ values once graphitization is completed. This explains the Γ$_G$ values observed for meteorites such as Y-86720 and PCA 91008 – their OM maturation do not follow the general trend observed for meteoritic IOM [10, 11], which supports an extensive but brief heating history that these meteorites have experienced after the aqueous alteration episode(s). The IOM maturation grade strongly depends on the time/temperature history.

**Conclusions:** We studied the experimentally-heated Tag with Raman spectroscopy. ω$_D$ and Γ$_D$ decrease with increasing temperature; Γ$_G$ first increases and then falls. Despite the chemical similarities between Tag and the extensively-heated TMCCs and the comparability of their D band parameters, a variation in G band parameters was only observed for the experimentally-heated (short-term) Tag but not the naturally metamorphosed Y-86720, which suggest that IOM maturity and graphitization is time dependent.

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