RAMAN SPECTROSCOPY STUDY OF LASER-INDUCED THERMAL EFFECTS ON CARBONACEOUS METEORITE. A.G. Dall'Asén, M. Zakariya, C. Bock, R. Kayastha, Department of Physics and Astronomy, Minnesota State University-Mankato, Mankato, MN 56001, USA. E-mail: analia.dallasen@mnsu.edu.

Introduction: Raman spectroscopy has been used extensively on meteoritic samples since it is a nondestructive tool that provides information about their structure and mineralogical composition [1-3]. These properties can give valuable clues about planet formation [4]. However, the power of the laser excitation source used in this technique can alter the properties of the samples due to thermal effects [1,5]. In this work, the laser-induced thermal effects produced on the carbonaceous chondritic meteorite Northwest Africa 6603 (NWA 6603) were studied in detail by analyzing the Raman spectra parameters of the minerals found in the inclusions and matrix of the sample as a function of the laser excitation power. These thermal effects were correlated with the topography of the irradiated regions by analyzing their changes using optical microscopy.

Sample, Experimental Methods and Data Analysis: A fragment of carbonaceous chondritic meteorite NWA 6603 (CV3, found in Morocco in 2006, 1.9961 g) was studied using Raman spectroscopy and optical microscopy as a function of the Raman spectroscopy laser excitation power. No sample preparation was required for none of the experimental techniques employed in this work.

Low- and high-resolution Raman spectroscopy measurements were carried out to study the structural and mineralogical composition of the sample. These measurements were performed at room temperature using a micro-Raman spectroscopy system with a 532-nm excitation source, a laser spot of ~3 µm and power range of 1-19.3 mW on the sample. Raman spectra were taken from numerous regions of selected inclusions and surrounding matrix using a 1-s integration time and 100 accumulations to obtain high signal-to-noise ratios. The laser power was increased in increments of ~1 mW. After reaching the highest power, this was brought back to ~4.7 mW, which provided high signal-to-noise-ratio spectra using a low power density, to examine possible permanent alterations produced in the irradiated regions. The obtained Raman spectrum peaks were fitted using Gaussian functions to determine their position (ω), full width at half maximum (FWHM, Γ), area (A) and intensity (I). The fitting parameters were used to identify the mineralogical composition of the selected regions, and to compare the spectra obtained for the different laser powers.

Optical micrographs of the studied regions were taken before and after irradiating them with the different laser powers to inspect the surfaces of the inclusions and surrounding matrix, and to evaluate if any topological changes were produced. The micrographs were taken using an optical microscope at several magnifications (from 50 to 1000X). These optical images were correlated with the corresponding Raman spectra.

Results and Discussion: Graphitic carbon, olivine (forsterite), pyroxene (enstatite), hematite and gehlenite were the main minerals identified in the analyzed regions. Figure 1 shows representative high-resolution Raman spectra of the materials found from one of the regions as a function of the laser excitation power.

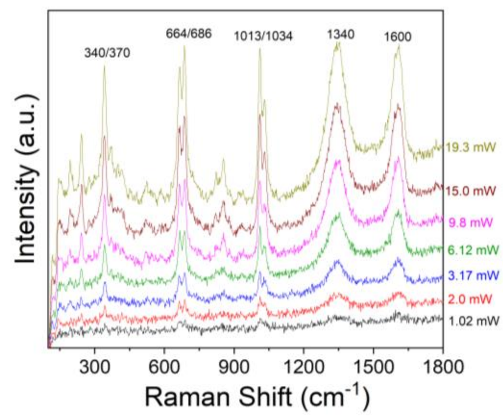

Figure 1. Representative Raman spectra of the materials found from one of the studied regions (matrix of inclusion 3, spot 1) of carbonaceous chondrite NWA 6603 as a function of the laser excitation power. For clarity, only the spectra of a few studied powers are shown. The numbers indicate the main peaks of enstatite (340 to 1034 cm^{-1}) and graphitic carbon (1340 and 1600 cm^{-1}).

Most of the Raman parameters of these minerals were affected by the laser excitation power to a great or lesser extent. In general, the Raman shift ω of the peaks decreased with the laser power, which can indicate rearrangements of molecular structure toward other family members (e.g., from forsterite to fayalite, in the case of olivine). In most of the cases, the FWHM Γ of the peaks increased with the laser power which can suggest an amorphization of the material (e.g., from graphitic carbon to amorphous carbon). The area ratio of two main peaks increased or decreased with the laser power depending on the material (e.g., graphitic carbon and forsterite, respectively). As an example, Figure 2 shows the change observed for the parameters

ω, Γ and area ratio (A_{824}/A_{855}) of the two main peaks of forsterite.

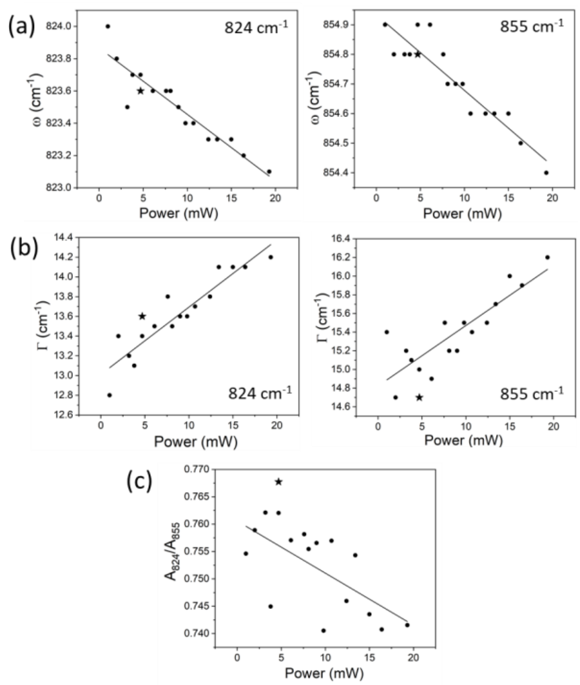

Figure 2. Raman parameters of the forsterite main peaks (824 and 855 cm^{-1}) found in one of the studied regions (inclusion 2, spot 2) as a function of the laser excitation power: (a) Raman shift (ω), (b) FWHM (Γ), and (c) area ratio (A_{824}/A_{855}) of the peaks. ★: 47-mW-power data points re-measured after irradiating the sample with the highest power.

After reaching the maximum power and bringing it back to ~4.7 mW, most of the analyzed regions presented some alteration in their Raman parameters (represented with a star in Figure 2). Figure 3 shows a comparison of the Raman spectra obtained from one of the regions (inclusion 1, spot 1) before and after irradiating the sample with a laser power of 4.7 mW, where is possible to distinguish a change of the Raman shifts and relative intensity of the enstatite and graphitic carbon peaks.

The studied regions were inspected using optical microscopy before and after they were irradiated. In general, no significant changes in the topography of these regions were found. However, it was possible to observe a clear topographical alteration of one of the regions (inclusion 1, spot 1), shown in Figure 4.

Therefore, these findings exhibited a strong evidence of the thermal effect induced by the excitation laser power on the materials found in the studied regions of the fragment NWA 6603 which must be considered to avoid alterations of physical and chemical properties of meteoritic samples. In addition, these results could be used to better understand the thermal effects produced in meteorites for implications of planet formation.

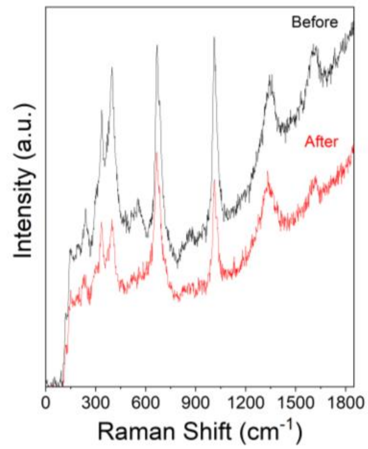

Figure 3. Raman spectra of one of the studied regions (inclusion 1, spot 1) for a laser power of ~4.7 mW: (a) before, and (b) after the region was irradiated with the used power range.

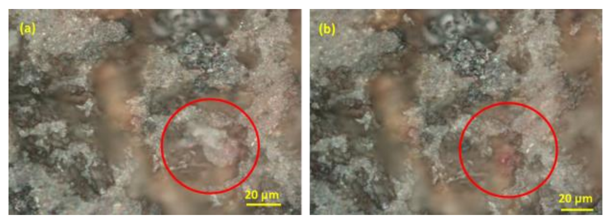

Figure 4. Micrographs of one of the studied regions (inclusion 1, spot 1) where a clear change in its topography was observed: (a) before, and (b) after the region was irradiated with the used power range. The red circles mark the area that was affected due to laser-induced heating.

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References: [1] Dall'Asén A. G. et al. (2017) *Spectrosc. Lett.*, 50, 417-425, and references therein. [2] Dall'Asén A. G. (2018) *49th LPSC*:2571-2572; (2019) *50th LPSC*:2897-2898, and (2020) *51st LPSC:*292-293. [3] Kayastha R. (2019) *NCUR Proceed. 2019*: 350-358. [4] Scott E.R.D. (2007) *Annu. Earth Planet. Sci.* 35:577-620. [5] Morishita et al (2011). *Spectrosc. Lett.* 44:459-463, and references therein.