RAMAN SPECTROSCOPY OF HEATED SYNTHETIC, TERRESTRIAL, AND EXTRATERRESTRIAL CARBON - IMPLICATIONS FOR THE METHOD? R. Visser[1], T. John[1] and G. Senges[2], [1]Freie Universität Berlin, Department of Mineralogy, Malteserstraβe 74-100, 12249, Berlin, Germany. (robbin.visser@fu-berlin.de). [2]Freie Universität Berlin, Department of Chemistry, Fabeckstraβe 34-36, 14195, Berlin, Germany.

Introduction: Raman spectroscopy allows for a labor evasive, quick, and non-invasive analysis of the sample material at a high spectral resolution. Ever since a relationship between the physics of Raman spectroscopy and the irreversible structural changes with temperature on carbon was described, a method to estimate peak temperatures started to develop [1]. The first carbon thermometer was a calibration between the Raman spectra of terrestrial rocks calibrated to the known temperature of these rocks [2]. Following up on this work, many calibrations have been produced, focusing mainly on different fitting methods and variations in temperature range (e.g., [3], [4]). The structural changes of carbon in carbonaceous chondrites have also been used to determine the maturity of meteorites ([6], [7]). Additionally, peak temperature correlations for chondrites by [5] has been established and has been used in an extensive peak temperature study of carbonaceous chondrites and volatile-rich clasts by [6]. However, all these studies are based on empirical correlations and a critically examination of the reliability of this method to indeed determining peak temperatures is still lacking an experimental approach.

In fact, when spectra of terrestrial samples and extraterrestrial sample are compared, some significant inconsistencies appear (Fig. 1). At temperatures higher than 500 ºC terrestrial samples have a graphitic structure with a dominant G-band and virtually no D1-band in terrestrial samples. Spectra at a similar temperature in carbonaceous chondrites however, show a dominant D1- and G-band as well as the presence of a D3- and D4-band which is surprisingly similar to spectra of roughly 300 ºC in terrestrial samples.

In this study we aim to resolve the reason behind these strong 'apparent' differences among the structures of terrestrial and extraterrestrial carbon developed at a given temperature. We perform heating experiments on synthetic, terrestrial, and extraterrestrial carbon to determine correlation between carbon structures and absolute temperatures. Not only does this limit the uncertainty which comes with calibrations based on estimated temperatures obtained by other methods (e.g., Phase relations, Fe-Mg diffusion, C isotopes), it will additionally enable us to determine: i) the effects of heating time (kinetics), ii) the influence of the starting material on the structure at higher temperatures, and iii) the implications of different formation and or alteration environments on the evolving structure of carbon.

Methods: For the start of this experiment synthesized organic carbon is heated in a vacuum glass tube to 400 ºC for 2, 4, and 6 weeks to determine the equilibration temperature of the material. After the equilibration temperature is established different samples of the same carbonaceous material will be heated with temperature steps of 100 ºC to cover the temperature range from 0-600 ºC. The subsequent measurements are performed with a Horiba ISA Dilor Labram micro confocal Raman spectrometer with 532.15 nm Nd:YAG laser at the Freie Universität Berlin. After the analyses of synthetic carbon, similar tests will be performed with extracted terrestrial carbon and extracted carbon from carbonaceous chondrites. Additionally 14 carbonaceous chondrites (CV3; Allende, Axtell, Grosnaja, Vigarano, Mokoia, Kaba, Leoville, CO3.2; Kainsaz,, CR2; Renazzo, CM2; Murray, Murchison, Cung; Tagish Lake, CI; Orgueil, Ivuna) are going to be analyzed for their Raman spectra and will be used to construct new accurate calibration of the thermometer.

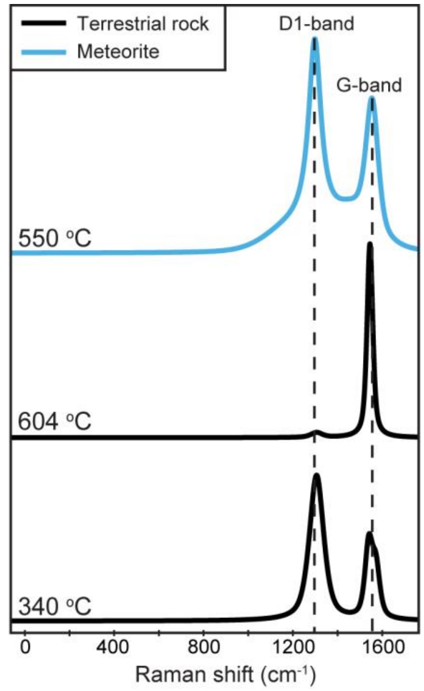

Fig. 1: *Three examples that show the differences between Raman spectra of carbon from carbonaceous chondrites and terrestrial rock. The meteorite used in this specific example was Allende [8] and the terrestrial rocks were from [4].*

Results and Discussion: Preliminary results show that the equilibration time for 400 ºC is most likely larger than 80 hours. However, a change in the spectrum could already be detected. After 80 hours on 400 ºC the Raman spectrum was similar to that of both terrestrial and extraterrestrial carbon correlated to 100-150 ºC. Additional analyses regarding the equilibration time and step-wise heating are currently being prepared and the first results are expected soon. Future work and interpretation on these measurements could give more insight in the differences between the synthetic, terrestrial and extraterrestrial carbon, but also the effect on the environment and what the presence of fluids might have on the structure and timing when heated. Finally, the most important question regarding the effect on the timing of heating will be answered. Since prolonged heating on a low temperature might result in a structure that is now associated to higher peak temperatures than is actually reached. This could then result in misinterpretations of the peak temperatures experienced by many rocks and meteorite used in a large amount of studies.

References: [1] Tuinstra F. and Koenig J. L. (1970) *JU. Chem. Phys., 53,* 1126–1130. [2] Beyssac O. et al. (2002) *J. Metamorph. Geol., 20, 859-871.* [3] Aoya M. et al. (2010) *J. Metamorph. Geol., 28, 895-914.* [4] Kouketsu Y. et al. (2014) *Isl. Arc, 23, 33-50.* [5] Bonal L. et al. (2006) *Geochim. Cosmochim. Acta, 70, 1849-1863.* [6] Busemann H. et al. (2007) *Meteorit. Planet. Sci., 42, 1387-1416.* [7] Homma Y. et al. (2015) *J. Mineral. Petrol. Sci., 110, 276-282.* [8] Visser R. et al. (2018) *Geochim. Cosmochim. Acta, 241, 38-55.*

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