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**Article** *in* Spectroscopy Letters · October 2011

DOI: 10.1080/00387010.2011.610417

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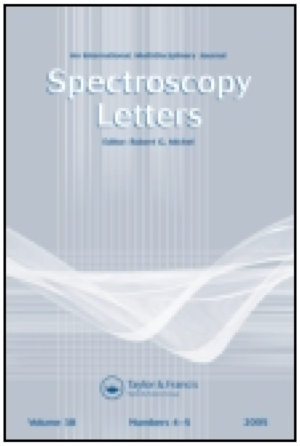

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lstl20

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To cite this article: M. R. Ammar, E. Charon, J.-N. Rouzaud, J. Aleon, G. Guimbretière & P. Simon (2011): On a Reliable Structural Characterization of Polished Carbons in Meteorites by Raman Microspectroscopy, Spectroscopy Letters, 44:7-8, 535-538

To link to this article: http://dx.doi.org/10.1080/00387010.2011.610417

*Spectroscopy Letters*, 44:535–538, 2011
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ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010.2011.610417

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# On a Reliable Structural Characterization of Polished Carbons in Meteorites by Raman Microspectroscopy

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**ABSTRACT** Polished section of Acapulco meteorite was used for the structural examination of graphitic matter by Raman microspectroscopy. The polishing process was shown to be necessary for the samples, where carbon matter is embedded in metallic phases. However, this process is known to drastically change the Raman spectrum, inducing unacceptable errors in the intrinsic structural characterization of these carbon materials. The deconvolution of spectra shows that the G-band width, related to the only bond stretching of sp$^2$ atoms, gives real structural information, even on polished carbon, whereas the common intensity ratio $I_D/I_G$, which is too sensitive to polishing process, has to be avoided.

**KEYWORDS** graphitized carbon materials, polishing, Raman microspectroscopy

## INTRODUCTION

Carbon is one of the most abundant chemical elements in the universe. Regardless of its anthropogenic or natural origin (terrestrial and extraterrestrial), the carbon multiscale organization (structure, nanostructure) is a fingerprint allowing the researcher to reconstruct its formation conditions. Therefore, structural examination is very important to better constraining some parameters such as precursor nature, the metamorphism degree, and particularly the maximum temperature it has undergone.[1–2] Raman spectroscopy has become a popular tool for the structural characterization of the carbon matter. Indeed, some differentiated meteorites, such as acapulcoites and lodranites, contain little amount of small carbon inclusions associated with metallic opaque phases. Micro-Raman spectroscopy, with its high spatial resolution ($\sim 1\,\mu$m), appears to be a more appropriate and powerful technique than X-ray diffraction and Transmission Electron Microscopy for characterizing and monitoring the full range of the structural states present in such carbon materials, from perfectly crystalline ones to amorphous ones. The intensity ratio $I_D/I_G$ has frequently been used as a reliable quantitative parameter of the structural order such as the determination of the mean "crystallites" diameter,[3–5] the estimation of the maximum metamorphic temperature for natural carbons,[6] or the

This submission was presented during the CORALS-2 Meeting on Micro-Raman Spectroscopy and Luminescence Studies in the Earth and Planetary Sciences, which was held between May 19 and 21, 2011, in Madrid, Spain. This is an invited paper for a special CORALS-2 GEO-SPECTROSCOPY issue of *Spectroscopy Letters.*

Received 27 June 2011;
accepted 19 July 2011.

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assessment of the $sp^3$ content.[7] However, the field lacks reliable quantitative analyses for carbon in meteorites where polishing is necessary to discriminate by the reflection mode the opaque minerals as carbons and metals, prior to performing Raman acquisition.

## OBJECTIVE

The objective of this work is to examine the use of Raman parameters in the study of carbons in meteorites previously polished and how to extract the intrinsic structural information from Raman spectra drastically modified by the effect of the polishing.

## MATERIALS AND METHODS

Polished section of the Acapulco meteorite was used for the structural examination of the graphitic matter. This meteorite (1914 g) fell in 1976 at Guerrero, Mexico, and was obtained from the famous collection of meteorites belonging to the laboratory of mineralogy and cosmochemistry at the Natural History National Museum (MNHN) of Paris, France. The characterization was performed by Raman microspectroscopy (InVia Renishaw device). The spectra were collected under a microscope (×50 objective), and a circular polarization of the excitation laser (514.5 nm) was used. The Raman-scattered light was dispersed by a holographic grating with 1800 lines/mm and detected by a Charge Coupled Device (CCD) camera. Very low incident power (~2 mW) was used to avoid local heating and graphitization effect.[8]

Quantitative Raman parameters were obtained from the deconvolution of Raman spectra by the conventional fitting procedures (Wire 3.0 program (Renishaw)), after using a linear baseline and Voigt function. The output parameters are the band position, intensity, full width at half maximum (FWHM), and integrated area of all the bands (D, D', and G). An additional band between D and G was required to perfectly fit Raman spectra.[9]

## RESULTS AND DISCUSSION

Figure 1 shows optical photography performed on polished surface of the Acapulco meteorite in the reflection mode. This acapulcoite-differentiated meteorite belongs to the achondrite group. It is made of a mix of mafic silicate minerals (Olivine, Pyroxene, and Plagioclase) and opaque metallic phases (Chromite, Kamacite, and Troilite). Among all these phases, very few and small amounts of carbon inclusions can be recovered (see the encircled region in Fig. 1). In order to observe them by reflected light, a careful polishing process was absolutely necessary prior to performing Raman analysis.

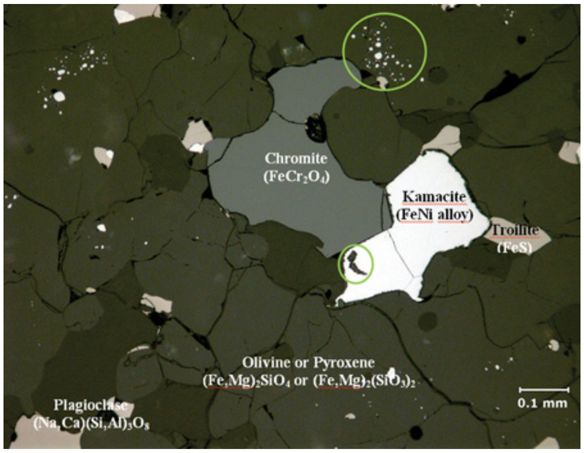

**FIGURE 1** Reflected light micrograph of the Acapulco meteorite showing some carbon inclusions (encircled regions) among silicates and metallic phases. (color figure available online.)

Figure 2 displays a first- and second-order Raman typical spectrum of the acapulcoite carbon obtained with the excitation laser energy at 2.41 eV (514.5 nm wavelength). Their most prominent features are the so-called "G-band" (for graphite) appearing at 1582 cm$^{-1}$, the D-band at about 1350 cm$^{-1}$, the D'-band at about 1620 cm$^{-1}$, and the G'-band at about 2700 cm$^{-1}$.

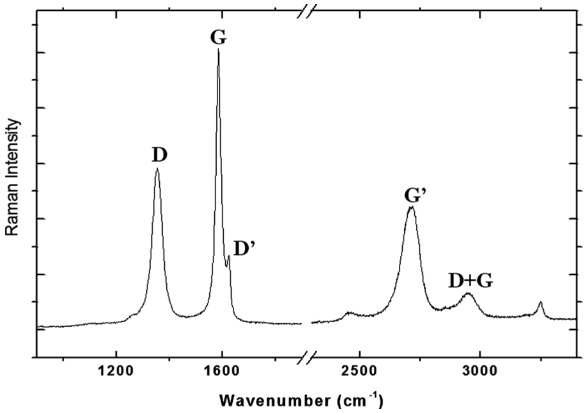

**FIGURE 2** Raman spectrum of the carbon in Acapulco meteorite showing the main Raman features taken with the excitation laser energy (wavelength) of 2.41 eV (514.5 nm).

The G band is the doubly degenerate phonon mode ($E_{2g}$ symmetry) at the Brillouin zone center that is Raman active for $sp^2$ carbon networks. It is defined as a C-C stretching mode (i.e., stretching within the carbon rings that make up the basal planes of graphitic materials). It is known to change in position and width with disorder in graphitic materials. The D and D' bands are defect-induced Raman features, and the intensity ratio $I_D/I_G$ has widely been used for characterizing the defect quantity in such materials (e.g., allowing the determination of the crystallites size $L_a$). However, the polishing process was shown to drastically modify the Raman spectrum (remarkable growth of the D band) with the important consequence in the misestimation of the original degree of graphitic structure ordering.[9–11]

Geologists prefer to study carbonaceous samples, in situ in their rock matrix, based on a mineralogical and petrographical approach by using optical microscopy. In presence of opaque minerals, the observations have to be performed by reflected light on polished sections. Geologists have successfully solved the problem of polishing artifacts by focusing the laser beam either on the subsurface continuations of polished grains or on the grains of interest placed below polished transparent phases.[11] However, such alternatives become impossible for carbon components in meteorites located mainly among opaque phases, and particularly metallic minerals. Additionally, our previous study, performed on polished anthracene-based coke, has shown that the polishing-induced changes in the upper surface of the graphitic carbon cannot be viewed as an increase of a real intrinsic disorder but rather for the change of the resonance conditions giving rise to the D-band increase. It was previously demonstrated that the G-band width ($FWHM_G$), which is the only symmetry-allowed phonon peak in carbon-based materials, and known to be characteristic of the local structural order, remains almost unchanged, while the intensity ratio exhibits a drastic change upon polishing and obviously present a remarkable heterogeneity.[9]

Figure 3a shows an optical micrograph of the graphitized carbon in contact with metal in the

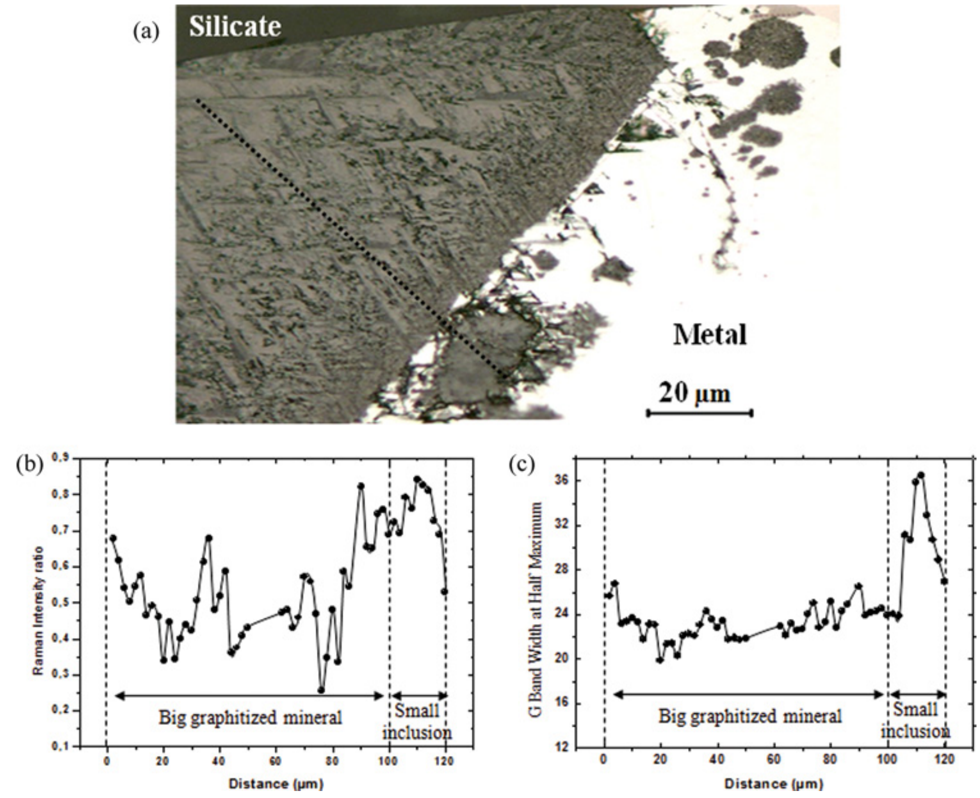

**FIGURE 3** (a) Micrograph (reflected light) of the graphitized carbon (light grey) located between silicate (dark grey) and metallic opaque phases (white). (b) Results of the deconvolution of Raman spectra along the analyzed dotted line: The calculated Intensity ratio of D-band relative to the G-band from Raman spectra. (c) Full width at half maximum of the G band. (color figure available online.)

Acapulco meteorite studied. Raman characterization was performed across the various sample areas (dotted line). Figure 3b and 3c present the deconvolution parameters: the intensity ratio $I_D/I_G$ and $FWHM_G$, respectively. The intensity ratio $I_D/I_G$ (Fig. 3b) along the analyzed line with 2 μm step, displays clearly that this parameter is suggesting a disordered carbon (high value of the intensity ratio) and an apparent structural heterogeneity since this ratio ranges from 0.25 to 0.84. However the G-band width (Fig. 3c), which is the only contribution of $sp^2$ atoms, does not provide biased information on the real intrinsic structural disorder degree, highlighting a clear structural difference between the big carbon mineral (0–100 μm), with a narrow G band characteristic of a highly graphitized carbon, and the small carbon inclusion (100–120 μm) exhibiting larger G band attributed to a lower degree of graphitization. All these observations have been confirmed by the transmission electron microscopy at high resolution performed in thin sections prepared in situ by the focused ion beam technique (not shown here).[12]

Our previous study, performed on varying graphitization degree of anthracene-based coke, shows linear behavior between the intensity ratio and the G-band width, and this correlation was described by the following function:

$$\mathrm{FWHM}_{\mathrm{G\ band}} = 14 + 35\frac{I_D}{I_G}\,(\mathrm{R}^2 = 0.99)$$

Thus, the use of this relationship permits the researcher to predict the expected intensity ratio, which gives a relatively low value (~0.25) for the large carbon mineral, suggesting the high graphitization degree, that is, far from the disordered carbon suggested by the $I_D/I_G$ ratio recorded on the polished carbon.

## CONCLUSIONS

The polishing process is absolutely necessary for an accurate optical observation of the meteorite samples in reflected light, to first discriminate the carbon inclusions generally embedded in metallic phases, prior to performing Raman analysis. The classical $I_D/I_G$ intensity ratio appears to be particularly sensitive to the surface preparation of the graphitic samples and then provides wrong and random information about the intrinsic structural disorder. Consequently, it must be proscribed. By contrast, the G-band width, which is the only symmetry-allowed phonon peak, easily provides reliable quantitative information on the intrinsic structural order and the details completely missing by the polishing effect. Therefore the use of this reliable parameter is highly recommended.

## ACKNOWLEDGMENTS

The authors thank the laboratory of mineralogy and cosmochemistry at the Natural History National Museum (MNHN) of Paris for providing the Acapulco meteorite.

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