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## Scanning micro-raman spectroscopy on carbon-rich residues of primitive chondrites: A tool for chondrite classification and stardust analysis

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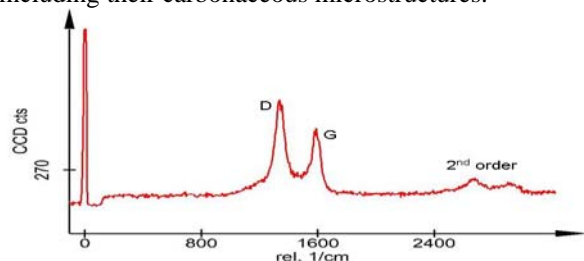
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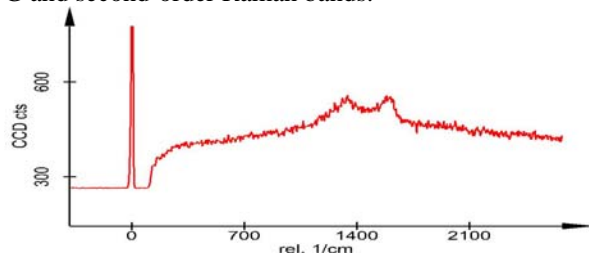
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**SCANNING MICRO-RAMAN SPECTROSCOPY ON CARBON-RICH RESIDUES OF PRIMITIVE CHONDRITES: A TOOL FOR CHONDRITE CLASSIFICATION AND STARDUST ANALYSIS** H. Busemann<sup>1</sup>, C. M O'D Alexander<sup>1</sup>, M. Fries<sup>2</sup>, L. Nittler<sup>1</sup> and A. Steele<sup>2</sup>, <sup>1</sup>Department of Terrestrial Magnetism, <sup>2</sup>Geophysical Laboratory, Carnegie Institution of Washington, 5241 Broad Branch Road, Washington DC 20015, USA. (busemann@dtm.ciw.edu).

**Introduction:** Organic matter in primitive meteorites may have mostly been formed in the interstellar medium [e.g. 1-3]. After formation of the solar system these molecules have been incorporated into the parent bodies of the various primitive meteorites [2]. Subsequent aqueous alteration and thermal metamorphism have altered the - initially similar - set of compounds including their carbonaceous microstructures.



**Fig. 1a.** Raman spectrum (Allende1, image 1) with D, G and second-order Raman bands.

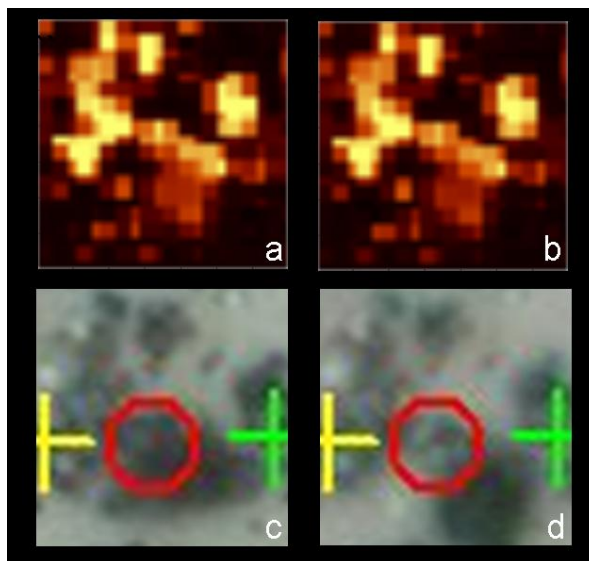


**Fig. 1b.** Raman spectrum (Murchison1, image 6) with increased background due to photoluminescence.

Raman spectroscopy is a sensitive tool to analyze the microstructure and graphitization of carbonaceous material [e.g. 4-6]. This will be important for the characterization of returned STARDUST samples. Single crystal graphite shows a first-order Raman shift relative to the exciting wavelength ("G" band) at  $\omega_G = 1582 \text{ cm}^{-1}$  (Fig. 1). Disordered finite-sized microcrystallites exhibit a "D" band at  $\omega_D \sim 1360 \text{ cm}^{-1}$  and additional peaks, e.g. close to the G band at  $\sim 1600 \text{ cm}^{-1}$ . Depending on the degree of crystallinity, various parameters such as the peak height ratio  $I_D/I_G$  or the area ratio  $A_D/(A_D+A_G)$ , the relative positions of the bands  $\omega_D$  and  $\omega_G$  and the half widths  $\Gamma_D$  and  $\Gamma_G$  may be useful for characterizing the analyzed material [6]. Quirico et al. [7] used Raman spectroscopy to relate the petrographic classification of unequilibrated ordinary chondrites with the structural state of the carbonaceous

matter, represented by the parameter pairs  $\Gamma_D-\omega_D$  and  $I_D/I_G-A_D/(A_D+A_G)$ .

We discuss here Raman spectroscopy of high purity organic residues. Compared to the examination of mm-sized matrix grains [7], this may have the advantage of being more representative. A residue samples the organic matter from large amounts of meteoritic rock ( $\sim$ g). Almost pure carbonaceous matter may reduce effects of photoluminescence and improves the Raman photon yield. We describe initial tests in order to establish a protocol that will be used to assess relative metamorphic grades of more than 35 well characterized residues from CI, CV, CO, CM, CR, LL, H and E chondrites. These results will be presented at the meeting.



**Fig. 2.** This Allende image ( $7 \times 7 \mu\text{m}$ ) consists of  $20 \times 20$  spectra. Regions with large D-bands (a) and G-bands (b). Scanned particles before (c) and after (d, not re-focused) analysis, as seen through eye view camera. The yellow and green crosses aid to estimate the particle size, the red circle indicates the image center.

**Experiment:** We used a new scanning Laser-induced Confocal Raman microscope WiTec  $\alpha$ -SNOM and analyzed aliquots ( $\sim$ mg) of residues residing on microscope glass slides (Table 1). The following parameters have been applied: Laser excitation wavelength 532 nm (frequency-doubled YAG), output laser

power <22 mW, mostly <8 mW at a spot & average pixel size of ~360 nm (using a 100x SWD objective), acquisition time per spectrum 1-5 s, spectral resolution  $4.56 \text{ cm}^{-1}$ , sample temperature  $20^\circ\text{C}$  (in air). The D and G bands were fitted with Lorentzian profiles and the background with a second-order polynomial. We discarded spectra that show large uncertainties (>25% for I and >50% for  $\Gamma$ ), usually those with large photoluminescence effects and those taken on sample-poor areas. We have analyzed aggregates up to  $40 \times 40 \mu\text{m}$  in size, but also regions with particles  $\ll 1 \mu\text{m}$ .

**Table 1.** The analyzed samples and peak height ratios.

sample	agent	# spectra (# images)	$I_D/I_G$ (avrg. $\pm$ s.d.)
Allende1	HF/HCl	6319 (9)	$0.79 \pm 0.20$
Allende2	CsF	8507 (8)	$0.84 \pm 0.04$
Murchison1	CsF	8656 (8)	$0.36 \pm 0.08$
Murchison2	(bulk)	384 (1)	$0.285 \pm 0.013$

**Results:** Typical Raman spectra with D, G and second-order bands are given in Fig 1. Fig. 1b shows the effect of photoluminescence. The background subtraction can mostly account for these effects. The two Allende residues obtained by demineralization with HF/HCl [8] and CsF [9] do not significantly vary in the averaged D and G band parameters (Table 2). The HF/HCl residue shows merely a larger variability in the data. Hence, Cs that potentially remained from the demineralization does not lead to a significant increase of the background. The most important  $\Gamma_D$  values are remarkably similar for Murchison bulk and the residue, indicating that the residues are representative for the bulk meteorites (Table 2). Similarly, the  $\Gamma_D$  values for the Allende residues agree with  $\sim 65 \pm 11 \text{ cm}^{-1}$  obtained for the bulk [7].

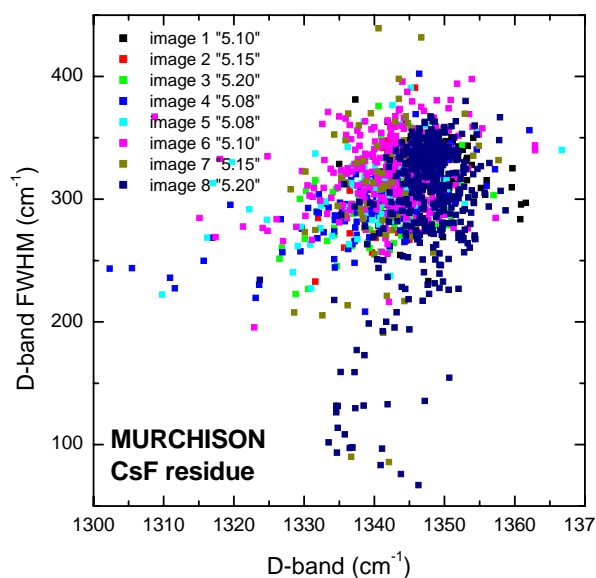
The most striking observation is the difference of  $\Gamma_D$  and  $\Gamma_G$ . Murchison's values are much higher than those for Allende (Table 2). This may reflect the history of the CM2 chondrites in being essentially unheated. On the other hand, the low  $I_D/I_G$  ratio for Murchison (Table 1) implies a high metamorphic grade [6]. The metamorphic sequence found in [7] shows however that the  $I_D/I_G$  ratio alone can not be used to non-ambiguously parameterize the metamorphic history. The D and G peak positions appear surprisingly uniform throughout all experiments (Table 2).

The Raman microprobe technique has often been referred to as "non-destructive". Nevertheless, although the laser power was set to the lowest practical values, often some carbonaceous material was ablated and small grains and fragile material was even lost. In general, however, modest variations in the laser power

do not yield varying results (Fig. 3) indicating that the measurement itself does not falsify the results. This is supported by the agreement between the results obtained for the carbon in bulk samples and residues. The difference observable in Fig. 2c and d (large particle in the lower right) is due to a movement of the particle.

**Table 2.** Average peak centers  $\omega$  and widths  $\Gamma$  for the D and G bands (in  $\text{cm}^{-1}$ , s.d., samples as in Table 1).

sample	$\omega_D$	$\Gamma_D$	$\omega_G$	$\Gamma_G$
All1	$1342 \pm 6$	$87 \pm 12$	$1588 \pm 8$	$67 \pm 6$
All2	$1343 \pm 5$	$76 \pm 8$	$1593 \pm 4$	$66 \pm 4$
Mur1	$1344 \pm 8$	$308 \pm 44$	$1588 \pm 5$	$109 \pm 12$
Mur2	$1354 \pm 6$	$307 \pm 28$	$1596 \pm 3$	$88 \pm 9$



**Fig. 3.** The D-band as measured on several areas of the Murchison residue. A slight variation of the laser power (see legend, arbitrary units) does not alter the results.

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**References:** [1] Sephton M. E. (2002) *Nat. Prod. Rep.* 19, 292-311. [2] Alexander C. M. O'D. et al. (1998) *Meteorit. Planet. Sci.* 33, 603-622. [3] Botta O. and Bada J. L. (2002) *Surv. Geophys.* 23, 411-467. [4] Tuinstra F. and Koenig J. L. (1970) *J. Chem. Phys.* 53, 1126-1130. [5] Wang Y. et al. (1990) *Chem. Mater.* 2, 557-563. [6] Wopenka B. and Pasteris J. D. (1993) *Am. Mineralogist* 78, 533-557. [7] Quirico E. et al. (2003) *Meteorit. Planet. Sci.* 38, 795-811. [8] Busemann H. et al. (2000) *Meteorit. Planet. Sci.* 35, 949-973. [9] Cody, G. D. et al. (2002) *GCA* 66,1851-1865.