

# Automated analysis of carbon in powdered geological and environmental samples by Raman Spectroscopy

Robert Sparkes<sup>1,2</sup>, Niels Hovius<sup>2,3</sup>, Albert Galy<sup>2</sup>, R. Vasant Kumar<sup>1</sup>, James T. Liu<sup>4</sup>

<sup>1</sup> Department of Materials Science and Metallurgy, University of Cambridge

<sup>2</sup> Department of Earth Sciences, University of Cambridge

<sup>3</sup> GFZ German Research Centre for Geosciences, Potsdam, Germany

<sup>4</sup> Marine Geology Department, National Sun Yat-Sen University, Taiwan

Corresponding author:

Robert Sparkes

[robert.sparkes@manchester.ac.uk](mailto:robert.sparkes@manchester.ac.uk)

+44 7763934347

Present address: School of Earth, Atmospheric and Environmental Sciences

University of Manchester

Oxford Road

Manchester

M13 9PL

Other authors:

[hovius@gfz-potsdam.de](mailto:hovius@gfz-potsdam.de)

[albert00@esc.cam.ac.uk](mailto:albert00@esc.cam.ac.uk)

[rvk10@cam.ac.uk](mailto:rvk10@cam.ac.uk)

[james@facmail.nsysu.com.tw](mailto:james@facmail.nsysu.com.tw)

## Abstract

Raman Spectroscopy can be used to assess the structure of naturally occurring carbonaceous materials (CM), which exist in a wide range of crystal structures. The sources of these geological and environmental materials include rocks, soils, river sediments and marine sediment cores, all of which can contain carbonaceous material ranging from highly-crystalline graphite to amorphous-like organic compounds. In order to fully characterise a geological sample and its intrinsic heterogeneity, several spectra must be collected and analysed in a precise and repeatable manner. Here we describe a suitable processing and analysis technique. We show that short-period ball-mill grinding does not introduce structural changes to semi-graphitized material and allows for easy collection of Raman spectra from the resulting powder. Two automated peak

38 fitting procedures are defined which allow for rapid processing of large datasets.  
39 For very disordered CM, Lorentzian profiles are fitted to five characteristic peaks,  
40 for highly-graphitized material three Voigt profiles are fitted. Peak area ratios and  
41 peak width (FWHM) measurements are used to classify each spectrum and allow  
42 easy comparison between samples. By applying this technique to samples  
43 collected in Taiwan following typhoon Morakot, sources of carbon to offshore  
44 sediments have been identified. Carbon eroded from different areas of Taiwan  
45 can be seen mixed together and deposited in the offshore flood sediments, and  
46 both graphite and amorphous-like carbon have been recycled from terrestrial to  
47 marine deposits. The practicality of this application illustrates the potential for  
48 this technique to be deployed to sediment sourcing problems in a wide range of  
49 geological settings.

50 **Keywords: Taiwan, Raman Spectroscopy, Sediment,**  
51 **Graphite, Typhoon Morakot, Grinding, Organic Carbon,**  
52 **Kerogen**

## 53 **Introduction**

54 Raman Spectroscopy is a precise tool for analysing the structure of carbonaceous  
55 material in geological,<sup>1, 2</sup> biogeochemical<sup>3</sup> and environmental samples.<sup>4</sup> The  
56 method targets individual carbon particles that can be finely dispersed, with  
57 variable structural ordering, making the measurement of a large number of  
58 spectra for a given sample a prerequisite for robust interpretation. Established  
59 methods acquire Raman spectra from thin sections, by passing the incident light  
60 through an overlying transparent mineral onto a carefully aligned graphite  
61 crystal, or directly from raw sediment grains or powders. This is followed by  
62 manual peak fitting of the collected data, which is time-consuming and limits the  
63 rate of work. This is not a problem for metamorphic studies, where only a few  
64 spectra are required, but hundreds or thousands of different spectra may be  
65 collected when analysing sedimentary rocks. Here we describe methods of  
66 sample preparation and peak fitting which facilitate rapid acquisition of Raman  
67 spectra and analysis of carbon structure for the benefit of geological and  
68 environmental applications. This involves short-period ball-mill grinding of solid  
69 rock or sediments which releases carbonaceous material without introducing  
70 structural changes, and automated peak fitting permitting objective analysis and  
71 comparison of many spectra without requiring manual intervention, yet allowing  
72 for checking of individual fitting results.

73 Whilst crystalline graphite is the thermodynamically stable form of carbon in the  
74 Earth's lithosphere,<sup>5</sup> its formation is kinetically hindered at Earth-surface  
75 conditions. Sedimentary organic matter transforms progressively to graphite  
76 through the loss of oxygenated functional groups, followed by aliphatic groups,  
77 and subsequent structural reorganisation<sup>3</sup> with the application of heat and  
78 pressure at depth within the Earth. However, once formed, graphite does not

79 revert easily to a disordered state. Beyssac et al.<sup>6, 7</sup> showed that heat is the  
80 main driving force for the crystallisation of graphite below Earth's surface. As  
81 burial depth increases, heat diffused from Earth's deep interior and from  
82 radioactive decay in the surrounding rocks provides the energy required to form  
83 graphite crystals. This is a gradual process, which is only completed when the  
84 temperature approaches 650°C, at lower temperatures carbon remains partially  
85 disordered, although a couple of exceptions have been reported. Firstly, CO<sub>2</sub>-rich  
86 fluid can deposit graphite during hydrothermal alteration at temperatures as low  
87 as 500°C,<sup>8</sup> and secondly, thin films of graphite can form on mineral faces at  
88 moderate metamorphic temperatures, leading to structural heterogeneity within  
89 a sample<sup>9</sup>. Crystallinity of graphite can be measured using Raman Spectroscopy;  
90 spectra from disordered carbon exhibit multiple broad peaks, especially at 1350  
91 and 1600 cm<sup>-1</sup>. With increasing crystallinity, these peaks are replaced by a single,  
92 sharp peak (full-width at half-maximum as little as 15 cm<sup>-1</sup>) at 1580 cm<sup>-1</sup>.<sup>1</sup> The  
93 degree of crystallinity, determined by comparing peak areas, has been correlated  
94 to the maximum temperatures experienced by the C-containing rock, as  
95 quantified by mineral assemblages.<sup>6</sup>

96 Complex geological settings, such as mountain belts, contain rocks that have  
97 experienced a wide range of peak temperatures. Upon erosion, these rocks yield  
98 carbon with a commensurate range of structures. Together with sediment,  
99 eroded carbon is conveyed by rivers from erosional source areas into  
100 depositional basins. During transport, river load is thoroughly mixed so that  
101 analysis of the full range of carbon structures present in a sediment sample  
102 allows the input of each carbon type to be investigated, and insight to be gained  
103 into the geological processes to which the source rocks and their erosional  
104 products have been subjected. Eroded highly-graphitized carbonaceous material  
105 can survive fluvial and submarine transport unaltered over 1000s of km, and be

106 re-deposited in new sedimentary formations,<sup>10</sup> while disordered and semi-  
107 graphitized material is more prone to oxidation en-route.<sup>11, 12</sup> In smaller  
108 systems where the transport distance is an order of magnitude shorter, loss of  
109 fossil organic carbon is less pronounced<sup>13</sup> so that the carbon inventory of basin  
110 deposits may be representative of the pattern of erosion in the sediment source  
111 area. The mountain island of Taiwan is an example of such a small system.

112 Taiwan is situated at 22-23 degrees North, within the Inter-Tropical Convergence  
113 Zone, at the convergent boundary between the Asian continent and the  
114 Philippine Sea plate. In 2009 Typhoon Morakot stalled over south Taiwan,  
115 precipitating up to 3600 mm of monsoon-supplied water in four days and causing  
116 extensive flooding and the mobilisation and export of large quantities of  
117 sediment.<sup>14</sup> The deposits of this exceptionally large event are rich in  
118 carbonaceous material spanning the full compositional breadth from terrestrial  
119 plant biomass to fully graphitized carbon. In order to systematically and  
120 efficiently determine the source of carbonaceous material in a large number of  
121 samples collected from Morakot's deposits and the geological formations from  
122 which these deposits were sourced, several methodological requirements must  
123 be met. The sample preparation method must ready different precursors such as  
124 bedrock, coarse-grained fluvial sediment and fine-grained offshore sediment for  
125 analysis in uniform fashion. The heterogeneous carbon species present in these  
126 samples must all be probed, with enough data collected to represent the  
127 population of carbon compounds within a single sample. Some of these carbon  
128 types may be present encased within rock fragments. Finally, having collected a  
129 large dataset there must be an automated processing system in place to analyse  
130 the spectra and report the results. In this paper we present a new method for  
131 automated analysis of carbon in powdered geological materials by Raman

132 spectroscopy, and review its use in an assessment of the sourcing of carbon  
133 during typhoon Morakot.

## 134 **Material and Methods**

### 135 **Sample acquisition**

136 Following typhoon Morakot, we have collected samples of flood deposits in the  
137 floodplain of the Gaoping River in SW Taiwan and from the shelf and submarine  
138 canyon offshore where the river had delivered material to the sea (Fig. 1). These  
139 samples represent the wide range of metamorphic grades and lithologies  
140 exposed in the Gaoping catchment, and allow investigation of metamorphic  
141 carbon from source to sink in a tectonically active setting following an extreme  
142 climatic event. They also contain a full range of particulate organic carbon in a  
143 diverse range of geological materials, offering a suitable opportunity to test the  
144 versatility and practicality of the new approach. Offshore core samples were  
145 collected by Taiwan Research Vessel Ocean Researcher 1, during sampling cruise  
146 number 915, using a box-coring process, in which a container of sediment is  
147 collected from the seafloor and separately cored after recovery. The exception is  
148 core K1, which was collected by driving a weighted tube directly into the sea  
149 floor. Cores were cut longitudinally and sub-sampled at centimetre resolution,  
150 and each sub-sample individually freeze-dried. Of this, a representative 5 g  
151 aliquot was collected at selected locations within the core. Meanwhile, samples  
152 of river sediments were taken beside the Gaoping main channel at the Pingtung  
153 Line railway bridge, and from two tributaries in Ligang Township. The western  
154 tributary drains mostly lowland areas and foothills underlain by sedimentary  
155 rocks of the Cholan and Tuokoshan formations. The eastern tributary drains  
156 mostly highland rock units exposed in the central mountain belt, although the  
157 location of sampling is within the lowland units.

158 The central mountain belt has been sampled extensively,<sup>15</sup> finding a range of  
159 graphite-bearing rock units. These units contain autochthonous partially  
160 graphitized material, with detrital highly graphitized crystals reported in the  
161 Hsuehshan Range and Backbone Slates.

162 The Cholan and Tuokoshan formations in Western Taiwan comprise marine to  
163 terrestrial sediments of Late Pliocene / Early Pleistocene age. Hand-specimen  
164 samples were collected from outcrops exposed in a riverbed to the east of  
165 Taichung city, along-strike from the Gaoping river basin. In each case, 50-300 g  
166 of solid rock were collected.

167 Bedrock and fluvial sediment samples were dried overnight at 80 °C after  
168 collection, to prevent microbial decay. Rock samples contrast with the individual  
169 sediment grains of the river, and fine mud of the offshore samples, providing a  
170 processing challenge in which each type of sample must be prepared  
171 equivalently to facilitate rapid acquisition of multiple Raman spectra of  
172 carbonaceous materials. This involves size reduction of coarser materials.

173 Investigations of the introduction of disorder to graphite crystals by grinding in  
174 air using an agate mortar found that grinding for many hours can introduce  
175 disorder peaks at 1350 and 1620  $\text{cm}^{-1}$ .<sup>16</sup> However, grinding periods of less than  
176 one hour did not significantly alter the Raman spectra of the graphite samples.

177 Similar work<sup>17</sup> corroborated this finding using Raman Spectroscopy, XRD and  
178 HRTEM to show that the crystallinity of high-grade graphite was unchanged after  
179 up to 120 minutes of grinding. Although neither of these papers considered  
180 changes in semi-graphitized or disordered precursor material, we have adopted a  
181 grinding approach to sample preparation in this study, and tested its effect on  
182 carbon structure. We ground dry sediment and rock samples in a PM-400 agate  
183 ball-mill grinder (Retsch) for 12 minutes at 250 rpm (sun wheel speed), the

184 standard procedure for preparation for geochemical analysis. Stainless-steel  
185 claddings on the grinding pots served to keep the material cool. After grinding  
186 the volume weighted mean particle diameter was 20  $\mu\text{m}$ , with median diameter  
187 of 9.2  $\mu\text{m}$ , as measured by a Mastersizer 2000 laser grain sizer (Malvern  
188 Instruments). The effect of this homogenization procedure on semi-graphitized  
189 material was assessed by comparison with un-ground equivalents, where dry  
190 sediments were placed directly onto glass slides.

## 191 **Raman Spectroscopy Techniques and Methods**

192 Graphitic carbon has been investigated using Raman spectroscopy for over 40  
193 years. Semi-graphitized materials produce a Raman peak at 1350  $\text{cm}^{-1}$ , the D1  
194 peak, which decreases in amplitude and width with increasing order.<sup>18</sup> This peak  
195 is sensitive to excitation frequency, lowering its Raman shift with increasing  
196 incoming wavelength.<sup>19</sup> To maintain comparability with previous studies on  
197 geological carbonaceous material,<sup>20</sup> we have also used a 514nm Ar-ion laser to  
198 collect spectra. A further three disorder peaks, D2, D3 and D4, appear in  
199 increasingly disordered carbonaceous materials. <sup>21</sup> <sup>22</sup> The 1620  $\text{cm}^{-1}$  D2 peak  
200 combines with and dominates the crystalline-graphite G peak (1580  $\text{cm}^{-1}$ ) in  
201 highly disordered material, forming a single "G band", while the D3 and D4 peaks  
202 are minor components which sit at 1500  $\text{cm}^{-1}$  and 1150-1250  $\text{cm}^{-1}$  respectively in  
203 the most disordered material.

204 Raman spectra from sediment cores were collected using Ramascope-1000 and  
205 InVia Raman spectrometers (Renishaw). One spatula ( $\sim 0.25$  g) of material was  
206 pressed between glass slides to produce a flattened sample area with 2 cm  
207 diameter. This removed the depth-of-field effect of the high-magnification lens,  
208 reducing the requirement to refocus the microscope, which dominates when  
209 sampling sediment directly. Within this sample area, 10-20 flakes of



210 carbonaceous material were usually visible using a 50 times magnification  
211 objective lens. Measurements were taken from each carbonaceous grain using a  
212 514 nm Ar-ion laser, set to 0.75 - 1.8 mW for 30 seconds to avoid damaging the  
213 target. The open-air exposure of the graphite grains, and surrounding sediments,  
214 minimizes thermal damage to the samples; no such damage was seen during the  
215 work. Raman shift was measured from 800 – 3200  $\text{cm}^{-1}$  using the “synchroscan”  
216 function.

## 217 **Peak Fitting**

218 Spectroscopic peaks are often fitted best using Voigt profiles, which are a  
219 combination of Lorentzian and Gaussian broadening behaviours. Gaussian  
220 profiles alone do not accommodate sufficient peak-broadening, while Lorentzian  
221 profiles can be excessively broad. A published peak-fitting method for semi- and  
222 highly-graphitized material fits Voigt profiles to three peaks: G, D1 and D2.<sup>7</sup> A  
223 linear baseline is removed from each sample, as background intensity tends to  
224 increase with Raman shift. This technique was calibrated for CM submitted to  
225 metamorphic burial temperatures above 360 °C.

226 Another published fitting procedure, designed for fitting of spectra from more  
227 disordered materials, fits Lorentzian profiles to five Raman peaks, covering  
228 typical ranges for G, D1, D2, D3 and D4.<sup>22</sup> In this procedure, Lorentzian profiles  
229 were chosen rather than Voigt profiles to reduce the degrees of freedom  
230 available when fitting, as the multi-parameter approach of Voigt fitting produced  
231 unstable fits for complex spectra. Increasingly disordered material has larger  
232 peak widths, for which the broad Lorentzian profile is a good match.

233 For this study, two automatic fitting routines have been created using the  
234 software “GNUPlot”. The first routine is based on the Voigt fitting procedure.<sup>7</sup>  
235 Three Voigt profiles are fitted, with a linear baseline. If required, non-linear

236 equations for the baseline could be incorporated, although tuning the baseline  
 237 for every individual spectrum removes some objectivity. Initial conditions are  
 238 provided by sampling relevant parts of the input spectra, namely the amplitudes  
 239 and locations of the G and D1 peaks. Initial D2 amplitude is also measured from  
 240 the input spectra. The width and location parameters are then allowed to vary  
 241 within certain ranges, defined in Table I, whilst amplitude is allowed to vary  
 242 without limit. The Voigt profile is defined as:

$$243 \quad V(x; \sigma; \gamma) = \int_{-\infty}^{\infty} G(x'; \sigma) L(x-x'; \gamma) dx' \quad (1)$$

244 where  $G(x)$  is a Gaussian function and  $L(x)$  is a Lorentzian function,  $\sigma$  is the  
 245 standard deviation of the Gaussian function and  $\gamma$  is the half-width at half-  
 246 maximum of the Lorentzian function. The Voigt function is computationally  
 247 complicated, and GNUPlot uses a rapid approximation of the Voigt profile,  
 248 accurate to one part in  $10^4$ .<sup>23</sup> Thus the function fitted is:

$$249 \quad f(x) = \sum_{i=peaks} area_i \times voigt(x-location_i, width_i) + mx + c. \quad (2)$$

250 The second routine fits five Lorentzian profiles.<sup>22</sup> As before, G, D1, D2, D3 and  
 251 D4 are initiated by reading from the input spectra, taking the highest amplitude  
 252 in a given range and correcting for a linear baseline. The peak amplitudes are  
 253 again free to vary unrestricted, while peak widths and locations are fixed within  
 254 certain ranges, as defined in Table II. The equation for fitting Lorentzian profiles  
 255 is:

$$256 \quad f(x) = \sum_{i=peaks} height_i width_i^2 / (x-location_i)^2 + width_i^2 + mx + c.$$

$$257 \quad (3)$$

258 Both of these procedures are able to fit spectra rapidly with minimal residual  
259 intensity (defined as the difference between the input spectra and the fit). The  
260 fitting procedure is iterated until the change in residual is less than  $10^{-9}$  of the  
261 total residual intensity. The advantage of using any automated procedure for this  
262 type of analysis is twofold. Firstly the analysis requires only computation time,  
263 spectra and analysis graphs can be produced automatically if new data is  
264 collected, or if it is decided to perform the peak analysis differently. Secondly,  
265 there is no bias introduced through operator-guided detection of peaks, each  
266 spectrum has been treated in exactly the same manner. Figure 2 shows the fits  
267 produced by these two procedures. Each fitting run generates a results figure  
268 showing the fitted peaks, fitting procedure and residual signal after fitting,  
269 allowing inspection of the accuracy of the procedure.

## 270 **Carbon Classification**

271 To resolve differences within populations of graphite and disordered carbon,  
272 samples can be characterised using a variety of parameters. The R1 and R2  
273 measurements, applied to Voigt-fitted spectra, characterise intermediate- and  
274 high-grade graphite very successfully, and have been calibrated for peak  
275 temperature using metamorphic petrology,<sup>6</sup> making the carbonaceous material  
276 geothermometer a useful tool.

$$277 \quad R1 = D1 \text{height} G \text{height} \quad (4)$$

$$278 \quad R2 = D1 \text{area} G \text{area} + D1 \text{area} + D2 \text{area} \quad (5)$$

$$279 \quad \text{Temperature} = -441 \times R2 + 645 \quad (6)$$

280 Whilst both ratios have been calibrated for temperature, R2 is the preferred  
281 metric. In samples where D1 is wide but has a low-intensity the R1 parameter

282 can show a reversed trend and it is also more sensitive to the accuracy of  
283 baseline corrections and D2 fitting. R2 is particularly effective at characterising  
284 highly-crystalline material, up to perfectly-graphitized crystals with T=645 °C.  
285 However, R2 measurements saturate above ~0.7 (metamorphic temperatures  
286 below ~330 °C). The RA2 measurement is applied to disordered materials with  
287 Lorentzian fits, but the temperature correlations are less certain.<sup>22</sup>

$$288 \quad \text{RA1} = \text{D1area} + \text{D4area} + \text{Garea} + \text{D1area} + \text{D2area} +$$
$$289 \quad \text{D3area} + \text{D4area} \quad (7)$$

$$290 \quad \text{RA2} = \text{D1area} + \text{D4area} + \text{Garea} + \text{D2area} + \text{D3area} \quad (8)$$

$$291 \quad \text{Temperature} = \text{RA2} - 0.270.0045 \quad (9)$$

292 Lastly, because it has been noted that empirically, increasingly disordered  
293 material tends to have a larger total-width,<sup>22</sup> the full-width at half-maximum  
294 (FWHM) of the G, D1 and D2 peaks were recorded (the total-width parameter).

295 The fitting procedures were calibrated by comparison with a collection of spectra  
296 with known metamorphic temperatures, fitted manually using the program  
297 “PeakFit®”,<sup>7, 22</sup> covering a wide range of carbon structures. Figure 3 shows  
298 cross-plotted results for R1, R2, RA1 and RA2, with very good agreement  
299 between the manual and automatic fits. For RA1 and RA2, automated fitting  
300 results are related to manual fits with a linear 0.95:1 relationship and R<sup>2</sup> values in  
301 excess of 0.925. For the Voigt procedure, R1 values correlate with a linear  
302 1.004:1 relationship and R<sup>2</sup> = 0.999, while R2 values have a 0.91:1 relationship  
303 and R<sup>2</sup> value of 0.991.

304 It is important that spectra are fitted with the appropriate procedure. Applying  
305 the Voigt fit to disordered material, or the Lorentzian fit to highly-graphitized  
306 material, leads to poor fits and incorrect parameterisations. In order to choose  
307 the correct procedure automatically, the following workflow was implemented. In  
308 the first instance, spectra were fitted with the Voigt procedure, as this is  
309 computationally more efficient and can fit graphitized carbon as well as low-  
310 temperature material, albeit with less precision. The results of this fit were  
311 analysed and if the R2 value was below 0.6, and either the D1 peak width below  
312  $120 \text{ cm}^{-1}$ , or the R1 value was less than 0.5, then the Voigt fit was accepted. If  
313 the fit had  $R2 > 0.6$ , or D1 width  $> 120 \text{ cm}^{-1}$  and  $R1 > 0.5$  (values chosen by  
314 inspection of a range of spectra), then a Lorentzian fit was applied. Whilst R2  
315 values of 0.65 or 0.7 can be collected from reasonably graphitized material, they  
316 can also be produced by very disordered material and thus the Lorentzian fit is  
317 applied. If the RA2 value calculated from this fit was greater than 2 (the  
318 maximum value measured in previous studies),<sup>22</sup> then the procedure reverted  
319 back to the Voigt fit. Finally, each spectrum was characterised using two  
320 parameters, the estimated metamorphic temperature as calculated from the R2  
321 or RA2 value (as applicable) and total-width (the sum of the G, D1 and D2 peak  
322 widths).

323 This workflow leads to the identification of three groups of spectra. Spectra from  
324 highly-graphitized material have a high R2 temperature, above  $360 \text{ }^\circ\text{C}$ . Partially  
325 graphitized and disordered materials both have low estimated temperatures, but  
326 the former has intermediate and the latter high total peak widths. Spectra fitted  
327 with the Voigt procedure have a temperature of more than  $360 \text{ }^\circ\text{C}$  and  
328 corresponding samples have experienced significant metamorphic conditions.  
329 Values of the total width parameter (G1 + D1 + D2 widths) vary, reaching up to  
330  $250 \text{ cm}^{-1}$  in these spectra. Those fitted with the Lorentzian procedure are less

331 metamorphosed – published RA2 values cover temperatures as low as 200 °C<sup>22</sup> -  
332 and in some cases are little more than charcoal or lignite-grade. The total width  
333 distinguishes between these two groups. By inspection of fitting results, low-  
334 grade metamorphic material has a total width less than 290 cm<sup>-1</sup> while spectra  
335 collected from lignite clasts in the Plio-Pleistocene of Taiwan have total widths up  
336 to 350 cm<sup>-1</sup>. By plotting measured total width against temperature, spectra from  
337 each sample fit into one of three carbon classes. Figure 4 shows a collection of  
338 spectra from sample K1-19, just offshore Taiwan, plotted in this fashion.

339 Whilst less precise than the temperature-correlated area ratios and an entirely  
340 empirical parameter, the total-width metric separates very disordered material  
341 from partially-graphitized carbon. The total-width metric is not associated with a  
342 particular solid-state physical phenomenon, but it was found to be the most  
343 effective means of characterising extremely disordered material. Several other  
344 possible characterisation parameters were investigated, such as peak location  
345 and individual peak widths, but none of these were chosen due to an inability to  
346 completely separate the various carbon types present in these samples. G peak  
347 location is one possible metric, but the presence of significant D2 peaks in  
348 disordered material can limit the relevance of the G peak position. The widths of  
349 individual peaks can only be used to characterise portions of the continuum of  
350 spectra, whilst the combination of all three peaks (G, D1 and D2) allowed  
351 variation across a wider range of spectra to be identified.

## 352 **Results and Discussion**

### 353 **Effects of Grinding and the utility of sample homogenization**

354 Whilst pure graphite has previously been shown to be robust in grinding and  
355 lengthy fluvial transport, the disordered and partially graphitized nature of the  
356 material found in the river sediment could have made it prone to damage during

357 grinding. To assess the effect of grinding on the structure and relative abundance  
358 of different types of carbonaceous material in our samples, we have compared  
359 results for ground and un-ground aliquots of samples KP2A and KP3B from the  
360 Gaoping River. Figure 5 shows a comparison of Lorentzian fitting results plotted  
361 as RA2 temperature against total width. Eight data points collected from  
362 powdered sediment have average temperature and total width values that lie  
363 within one standard deviation of the equivalent averages for five data points  
364 collected from the un-ground aliquot. Similarly, the results from sample KP3B  
365 show a matching clustering of spectrum properties for both raw and powdered  
366 materials. Both sets of spectra show a slight and statistically insignificant  
367 increase in total width after grinding, with little or no impact on the estimated  
368 temperatures. These results demonstrate that grinding has not introduced  
369 significant disorder into the samples, and we proceed assuming that this holds  
370 for all other samples in our study. Although we have not considered variable  
371 grinding times and methods we anticipate that any grinding procedure which  
372 reduces grain sizes to the ( $\sim 10 \mu\text{m}$ ) range can be applied without significant  
373 effect on the structure of carbonaceous material in geological and environmental  
374 samples.

### 375 **Application: Morakot flood, Taiwan**

376 To test the practicality of our method, we investigated the sourcing and  
377 distribution of carbonaceous material in sediments from the Gaoping canyon. We  
378 collected 201 spectra from 19 samples of sediment deposited during typhoon  
379 Morakot and rocks exposed in its source area. In general, at least ten spectra  
380 with a signal-to-noise ratio greater than three were acquired. Particles with a  
381 graphitic appearance under the microscope and a graphitic spectrum were found  
382 in five of eight samples from the Cholan and Tuokoshan formations, one of three  
383 samples from the Gaoping River and in all eight samples from the Gaoping

384 submarine canyon, although the proportion of this material to other types of  
385 carbonaceous material varied greatly. Some form of disordered carbon or semi-  
386 graphitized material was found in all samples, but its shape varied considerably.

387 Most of the Plio-Pleistocene Cholan formation samples contained highly  
388 disordered carbonaceous material (Figure 6a). Sample 17 was a 10 x 10 cm piece  
389 of lignite, which still had the physical characteristics of a small log, hence we are  
390 confident that it was a piece of woody biomass that had been incorporated  
391 directly into the sediments; all spectra from this specimen had a high total width  
392 and low RA2 temperature. Six out of seven other samples from the Cholan  
393 formation contained similarly disordered carbon, creating a cluster of disordered  
394 carbon spectra at the top of Figure 6a. This is interpreted as woody material of  
395 mm to cm size incorporated into the Plio-Pleistocene sediments during  
396 deposition and subsequently transformed to lignite, indicating that the burial  
397 depths experienced by the Cholan and Tuokoshan formations were insufficient to  
398 induce metamorphism. Carbon with a higher degree of order in these formations  
399 is likely to have a bedrock source, eroded from rocks exposed in the emerging  
400 Taiwan mountain belt at the time of deposition of the Cholan and Tuokoshan  
401 sediments. There is highly-graphitized material present in six out of seven  
402 Cholan and Tuokoshan sedimentary samples and semi-graphitized material in  
403 five out of seven. Disordered carbon is much more common than semi-  
404 graphitized material; samples 2, 3, 6 and 8 tend towards a bimodal distribution  
405 of highly-graphitized and disordered material. This may reflect the lesser outcrop  
406 of metamorphic rocks containing semi-graphitized carbon in the Central Range  
407 during Plio-Pleistocene times, or the loss of this carbon during exhumation and  
408 erosion of the Taiwan Mountains at this time.



409 Figure 6b shows the range of spectra collected from Gaoping River sediments,  
410 the majority of which was semi-ordered material derived from a branch draining  
411 the Central Mountain Range. This material has experienced moderate  
412 metamorphism<sup>15</sup> but did not approach conditions where crystalline graphite is  
413 usually achieved. The only graphite grains found in the Gaoping River are from  
414 the branch draining the western plains, in which the graphite-rich Cholan and  
415 Tuokoshan formations crop out.

416 Offshore sediments show a range of material that is a combination of both the  
417 Central Range semi-graphitized carbon and the fully-graphitized and disordered  
418 carbon of the Plio-Pleistocene rocks. Semi-graphitized and highly-graphitized  
419 materials were contained in all samples, including samples collected on the  
420 continental shelf and the Gaoping canyon (Fig. 6c and 6d respectively) but the  
421 shelf cores contained less disordered carbon. The abundance of disordered  
422 material in canyon cores compared to shelf cores hints at variations in the  
423 hydrodynamic processes depositing material in these locations. The  
424 sedimentation rate on the shelf is less than 1 cm yr<sup>-1</sup>, whilst the canyon deposits  
425 were sourced in a single flood event, transported by sediment gravity currents  
426 along the seafloor. This rapid transport and deposition process could entrain and  
427 bury buoyant disordered material more efficiently than the gradual raining-down  
428 of material onto the shelf from the sea surface. This indicates that the transport  
429 distance along the Gaoping Canyon system (20-200 km) is too short for  
430 comprehensive loss of semi-graphitized carbon by oxidation during sediment  
431 transport, in contrast to the Bengal Fan system where offshore transport  
432 pathways are an order of magnitude longer (2000 km).

## 433 **Conclusions**

434 Grinding of sediments into a fine powder has allowed efficient collection of many  
435 hundreds of Raman spectra from a range of samples from Taiwan. This process  
436 did not introduce significant disorder into individual grains of carbon within a  
437 sample. Thus short-period grinding and spectra-collection from powder is a  
438 suitable method for quickly sampling a population of samples in a fair and  
439 thorough manner. Collected Raman spectra were analysed automatically using  
440 peak-fitting techniques based on two published procedures - five characteristic  
441 Lorentzian peaks or three Voigt peaks. Automated analysis significantly reduced  
442 the processing time and removed the possibility of human variation or bias, thus  
443 allowing easy and fair comparison of the spectra, whilst output results figures  
444 allow inspection of spectral quality and fitting accuracy. A combination of these  
445 methods allowed identification of the sources of graphite and disordered material  
446 from Taiwan to the South China Sea following typhoon Morakot.

447 Automatic focussing onto the sample surface, combined with a fast mapping  
448 procedure, will make spectral acquisition more efficient. The automatic  
449 processing technique is even more important in this situation, to filter out non-  
450 carbonaceous spectra. These techniques are now becoming available on  
451 spectroscopic equipment.

452 Acknowledgements: The authors would like to thank Olivier Beyssac for help,  
453 encouragement and spectrometer access. Robert Sparkes was funded by an  
454 EPSRC studentship, James T. Liu by grant number NSC 95-2745-M-110-001 for  
455 the FATES-HYPERS program which provided the cores in this study.

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531 Table I: Peak fitting constraints used in the Voigt fitting procedure

Peak	Initial Height	Constraints when choosing	Initial Location	Constraints when fitting	Initial Width (FWHM)	Constraints when fitting
G	From data	1575-1600 $\text{cm}^{-1}$	From initial height	1575-1605 $\text{cm}^{-1}$	5 $\text{cm}^{-1}$	<80 $\text{cm}^{-1}$
D1	From data	1200-1450 $\text{cm}^{-1}$	From initial height	1300-1400 $\text{cm}^{-1}$	12.7 $\text{cm}^{-1}$	<200 $\text{cm}^{-1}$
D2	From data	1605-1640 $\text{cm}^{-1}$	1620 $\text{cm}^{-1}$	1610-1625 $\text{cm}^{-1}$	2.2 $\text{cm}^{-1}$	<32 $\text{cm}^{-1}$

532

533 Table II: Peak fitting constraints used in the Lorentz fitting procedure

Peak	Initial Height	Constraints when choosing	Initial Location	Constraints when fitting	Initial Width	Constraints when fitting
G	From data	1580-1600 cm <sup>-1</sup>	From initial height	1550-1630 cm <sup>-1</sup>	17 cm <sup>-1</sup>	<80 cm <sup>-1</sup>
D1	From data	1200-1450 cm <sup>-1</sup>	From initial height	1300-1400 cm <sup>-1</sup>	72 cm <sup>-1</sup>	<200 cm <sup>-1</sup>
D2	From data	1610-1640 cm <sup>-1</sup>	1601 cm <sup>-1</sup>	1630-1640 cm <sup>-1</sup>	17 cm <sup>-1</sup>	<80 cm <sup>-1</sup>
D3	From data	1490-1510 cm <sup>-1</sup>	1500 cm <sup>-1</sup>	1475-1525 cm <sup>-1</sup>	100 cm <sup>-1</sup>	<200 cm <sup>-1</sup>
D4	From data	1140-1150 cm <sup>-1</sup>	1250 cm <sup>-1</sup>	1200-1250 cm <sup>-1</sup>	150 cm <sup>-1</sup>	<200 cm <sup>-1</sup>

534



535 Figure 1:

536 A map of Taiwan and the surrounding bathymetry, showing the location of  
537 samples used in this study. Black circles are offshore cores, white triangles are  
538 rock samples from the Cholan and Tuokoshan formations, inverted white  
539 triangles are sediments from the Gaoping River. The Gaoping catchment is  
540 shown in white, with the Plio-Pleistocene sedimentary formations cross-hatched.  
541 Main tributaries of the Gaoping River are shown with black lines. Note that some  
542 river samples are from tributaries that mostly drain the mountains of the Central  
543 Range.

544

545 Figure 2:

546 Examples of fits of four spectra collected from sample K1. These represent a  
547 range from highly-graphitized to disordered material. Upper figures (a and b)  
548 show Voigt fits, lower figures (c and d) Lorentzians. Spectra have had a linear  
549 background removed automatically during fitting. The fitted peaks are shown  
550 with dashed lines, the sum of these is a solid line that matches the spectra with  
551 minimal residual signal.

552

553 Figure 3:

554 Cross-plotting area ratio values ( $a=R1$ ,  $b=R2$ ,  $c=RA1$ ,  $d=RA2$ ) from manual and  
555 automated fits shows that the automated analysis procedure is a suitable  
556 substitute for manual curve fitting. In each graph the best fit line is almost  
557 collinear with a 1:1 relationship.

558 Figure 4:

559 Spectra collected from sample K1-19 (19 cm depth in sediment core K1,  
560 collected from the Gaoping Canyon). A linear background correction has been  
561 fitted and applied to each spectrum. There are a range of carbonaceous  
562 materials here: highly-graphitized (dark grey), semi-graphitized (mid grey) and  
563 disordered material (light grey) plotted in total width – temperature space. Using  
564 these axes to analyse large populations of spectra can easily show patterns  
565 within the degree of graphitization.

566

567 Figure 5:

568 A comparison of spectral properties (total-width vs. RA2 temperatures) from two  
569 river sediment samples, a) before and b) after 12 minutes of ball-mill grinding.

570 The large symbols show the average value along with  $1\sigma$  error bars. In each case  
571 the average results are within error of each other, suggesting that no significant  
572 change in structure is introduced through grinding.

573

574 Figure 6:

575 Results from four locations in Taiwan and the Gaoping canyon showing the range  
576 of carbon morphologies present in these locations. The Plio-Pleistocene  
577 formations (a) supply large amounts of highly-graphitized and disordered  
578 material to the Gaoping. The highland branch of the Gaoping river (b) drains the  
579 Central Range of Taiwan and is dominated by semi-graphitized material. Highly  
580 graphitized sample comes from the western branch, draining graphite bearing  
581 Plio-Pleistocene units. All three types of carbon are seen offshore, although  
582 varying distributions of disordered material are seen in the Gaoping Canyon (c)  
583 and continental shelf (d).

584