Automated Analysis of Carbon in Powdered Geological and Environmental Samples by Raman Spectroscopy

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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 characterize a geological sample and its intrinsic heterogeneity, several spectra must be collected and analyzed 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-fitting procedures are defined that allow for rapid processing of large datasets. For very disordered CM, Lorentzian profiles are fitted to five characteristic peaks, for highly graphitized material, three Voigt profiles are fitted. Peak area ratios and peak width measurements are used to classify each spectrum and allow easy comparison between samples. By applying this technique to samples collected in Taiwan after Typhoon Morakot, sources of carbon to offshore sediments have been identified. Carbon eroded from different areas of Taiwan can be seen mixed and deposited in the offshore flood sediments, and both graphite and amorphous-like carbon have been recycled from terrestrial to marine deposits. The practicality of this application illustrates the potential for this technique to be deployed to sediment-sourcing problems in a wide range of geological settings.

Index Headings: Taiwan; Raman spectroscopy; Sediment; Graphite; Typhoon Morakot; Grinding; Organic carbon; Kerogen.

INTRODUCTION

Raman spectroscopy is a precise tool for analyzing the structure of carbonaceous material in geological, biogeochemical, and environmental samples. The method targets individual carbon particles that can be finely dispersed, with variable structural ordering, making the measurement of a large number of spectra for a given sample a prerequisite for robust interpretation. Established methods acquire Raman spectra from thin sections by passing the incident light through an overlying transparent mineral onto a carefully aligned graphite crystal or directly from raw sediment grains or powders. This is followed by manual peak fitting of the collected data, which is time-consuming and limits the rate of work. This is not a problem for metamorphic studies, where only a few spectra are required, but hundreds or thousands of different spectra can be collected when analyzing sedimentary rocks. Here, we describe methods of sample preparation and peak fitting that facilitate rapid acquisition of Raman spectra and analysis of carbon structure for the benefit of geological and environmental applications. This involves short-period ball-mill grinding of solid rock or sediments, which releases carbonaceous material without introducing structural changes, and automated peak fitting, permitting objective analysis and comparison of many spectra without requiring manual intervention while allowing for the checking of individual fitting results.

While crystalline graphite is the thermodynamically stable form of carbon in the Earth’s lithosphere, its formation is kinetically hindered by Earth surface conditions. Sedimentary organic matter transforms progressively to graphite through the loss of oxygenated functional groups, followed by aliphatic groups and subsequent structural reorganization, with the application of heat and pressure at depth within the Earth. However, once formed, graphite does not revert easily to a disordered state. Beyssac et al. showed that heat is the main driving force for the crystallization of graphite below Earth’s surface. As burial depth increases, heat diffused from Earth’s deep interior and from radioactive decay in the surrounding rocks provides the energy required to form graphite crystals. This is a gradual process, which is only completed when the temperature approaches 650 °C; at lower temperatures carbon remains partially disordered, although a couple exceptions have been reported. First, CO₂-rich fluid can deposit graphite during hydrothermal alteration at temperatures as low as 500 °C. Second, thin films of graphite can form on mineral faces at moderate metamorphic temperatures, leading to structural heterogeneity within a sample. Crystallinity of graphite can be measured with Raman spectroscopy; spectra from disordered carbon exhibit multiple broad peaks, especially at 1350 and 1600 cm⁻¹. With increasing crystallinity, these peaks are replaced by a single, sharp peak (full width half-maximum [FWHM] as little as 15 cm⁻¹) at 1580 cm⁻¹. The degree of crystallinity, determined by comparing peak areas, has been correlated to the maximum temperatures experienced by the carbon-containing rock, as quantified by mineral assemblages. Complex geological settings such as mountain belts contain rocks that have experienced a wide range of peak temperatures. On erosion, these rocks yield carbon with a commensurate range of structures. Together with sediment, eroded carbon is conveyed by rivers from erosional source areas into depositional basins. During transport, river load is thoroughly mixed, so that analysis of the full range of carbon structures present in a sediment sample allows the input of each carbon type to be investigated, and insight to be gained into the geological processes to which the source rocks and their erosional products have been subjected. Eroded, highly graphitized...
carbonaceous material can survive fluvial and submarine transport unaltered over thousands of kilometers, and be re-deposited in new sedimentary formations,\textsuperscript{10} while disordered and semi-graphitized material is more prone to oxidation en route.\textsuperscript{11,12} In smaller systems where the transport distance is an order of magnitude shorter, loss of fossil organic carbon is less pronounced,\textsuperscript{13} so that the carbon inventory of basin deposits can be representative of the pattern of erosion in the sediment source area. The mountain island of Taiwan is an example of such a small system.

Taiwan is situated at 22–23° N, within the Intertropical Convergence Zone, at the convergent boundary between the Asian continent and the Philippine Sea Plate. In 2009, Typhoon Morakot stalled over southern Taiwan, precipitating up to 3600 mm of monsoon-supplied water in four days and causing extensive flooding and the mobilization and export of large quantities of sediment.\textsuperscript{14} The deposits of this exceptionally large event are rich in carbonaceous material, spanning the full compositional breadth, from terrestrial plant biomass to fully graphitized carbon. In order to systematically and efficiently determine the source of carbonaceous material in a large number of samples collected from Morakot’s deposits and the geological formations from which these deposits were sourced, several methodological requirements must be met. The sample preparation method must ready different precursors such as bedrock, coarse-grained fluvial sediment, and fine-grained offshore sediment for analysis in a uniform fashion. The heterogeneous carbon species present in these samples must all be probed, with enough data collected to represent the population of carbon compounds within a single sample. Some of these carbon types can be present encased within rock fragments. Finally, having collected a large dataset, there must be an automated processing system in place to analyze the spectra and report the results. In this paper, we present a new method for automated analysis of carbon in powdered geological materials by Raman spectroscopy and review its use in an assessment of the sourcing of carbon during Typhoon Morakot.

**MATERIAL AND METHODS**

**Sample Acquisition.** After Typhoon Morakot, we collected samples of flood deposits in the floodplain of the Gaoping River in southwestern Taiwan and from the shelf and submarine canyon offshore where the river had delivered material to the sea (Fig. 1). These samples represent the wide range of metamorphic grades and lithologies exposed in the Gaoping catchment and allow investigation of metamorphic carbon from source to sink in a tectonically active setting after an extreme climatic event. They also contain a full range of particulate organic carbon in a diverse range of geological materials, offering a suitable opportunity to test the versatility and practicality of the new approach. Offshore core samples were collected by the Taiwan research vessel *Ocean Researcher I* during sampling cruise number 915 by using a box-coring process, in which a container of sediment is collected from the seafloor and separately cored after recovery. The exception is core K1, which was collected by driving a weighted tube directly into the sea floor. Cores were cut longitudinally and subsampled at centimeter resolution, and each subsample individually freeze-dried. Of this, a representative 5 g aliquot was collected at selected locations within the core. Meanwhile, samples of river sediments were taken beside the Gaoping main channel at the Pingtung Line railway bridge, and from two tributaries in Ligang Township. The western tributary drains mostly lowland areas and foothills underlain by sedimentary rocks of the Cholan and Tuokoshan Formations. The eastern tributary drains mostly highland rock units exposed in the central mountain belt, although the location of sampling is within the lowland units.

The central mountain belt has been sampled extensively,\textsuperscript{15} finding a range of graphite-bearing rock units. These units contain autochthonous partially graphitized material, with detrital highly graphitized crystals reported in the Hsuehshan Range and Backbone slates.

The Cholan and Tuokoshan Formations in Western Taiwan comprise marine to terrestrial sediments of Late Pliocene–Early Pleistocene age. Hand-specimen samples were collected from outcrops exposed in a riverbed to the east of Taichung City, along strike from the Gaoping river basin. In each case, 50–300 g of solid rock was collected.

Bedrock and fluvial sediment samples were dried overnight at 80 °C after collection, to prevent microbial decay. Rock samples contrast with the individual sediment grains of the river and fine mud of the offshore samples, providing a processing challenge in which each type of sample must be prepared equivalently to facilitate rapid acquisition of multiple Raman spectra of carbonaceous materials. This involves size reduction of coarser materials. Investigations of the introduction of disorder to graphite crystals by grinding in air with an agate mortar found that grinding for many hours can introduce disorder peaks at 1350 and 1620 cm\textsuperscript{-1}.\textsuperscript{11,16} However, grinding periods of less than 1 h did not significantly alter the Raman spectra of the graphite samples. Similar work\textsuperscript{17} corroborated this finding by using Raman spectroscopy, X-ray diffraction, and high-resolution transmission electron microscopy to show that the crystallinity of high-grade graphite was unchanged after up to 120 min of grinding. Although neither of these papers considered changes in semi-graphitized or disordered precursor material, we adopted a grinding approach to sample preparation in this study and tested its effect on carbon structure. We ground dry sediment and rock samples in a PM-400 agate ball-mill grinder (Retsch) for 12 min at 250 rpm (sun wheel speed), the standard procedure for preparation for geochemical analysis. Stainless steel claddings on the grinding pots served to keep the material cool. After grinding the volume weighted mean particle diameter was 20 μm, with median diameter of 9.2 μm, as measured by a Mastersizer 2000 laser grain sizer (Malvern Instruments). The effect of this homogenization procedure on semi-graphitized material was assessed by comparison with un-ground equivalents, where dry sediments were placed directly onto glass slides.

**Raman Spectroscopy Techniques and Methods.** Graphitic carbon has been investigated with Raman spectroscopy for over 40 years. Semi-graphitized materials produce a Raman peak at 1350 cm\textsuperscript{-1}, the D1 peak, which decreases in amplitude and width with increasing order.\textsuperscript{18} This peak is sensitive to excitation frequency, lowering its Raman shift with increasing incoming wavelength.\textsuperscript{19} To maintain comparability with previous studies on geological carbonaceous material,\textsuperscript{20} we also used a 514 nm Ar-ion laser to collect spectra. A further three disorder peaks—D2, D3, and D4—appear in increasingly disordered carbonaceous materials.\textsuperscript{21,22} The 1620 cm\textsuperscript{-1} D2 peak combines with and dominates the crystalline-graphite G peak (1580 cm\textsuperscript{-1}) in highly disordered material, forming a
single G band, while the D3 and D4 peaks are minor components that appear at 1500 cm$^{-1}$ and 1150–1250 cm$^{-1}$, respectively, in the most disordered material.

Raman spectra from sediment cores were collected with Ramascope-1000 and InVia Raman spectrometers (Renishaw). One spatula (approximately 0.25 g) of material was pressed between glass slides to produce a flattened sample area with 2 cm diameter. This removed the depth-of-field effect of the high-magnification lens, reducing the requirement to refocus the microscope, which occurs when sampling sediment directly. Within this sample area, ten to 20 flakes of carbonaceous material were usually visible with a 50× magnification objective lens. Measurements were taken from each carbonaceous grain by using a 514 nm Ar-ion laser, set to 0.75–1.8 mW for 30 s to avoid damaging the target. The open-air exposure of the graphite grains and surrounding sediments minimizes thermal damage to the samples; no such damage was seen during the work. Raman shift was measured from 800–3200 cm$^{-1}$ by using the “Synchroscan” function.

Peak Fitting. Spectroscopic peaks are often fitted best by using Voigt profiles, which are a combination of Lorentzian and Gaussian broadening behaviors. Gaussian profiles alone do not accommodate sufficient peak broadening, while Lorentzian profiles can be excessively broad. A published peak-fitting method for semi- and highly graphitized material fits Voigt profiles to three peaks: G, D1, and D2.7 A linear baseline is removed from each sample, as background intensity tends to increase with Raman shift. This technique was calibrated for

Fig. 1. A map of Taiwan and the surrounding bathymetry, showing the location of samples used in this study. Black circles are offshore cores, white triangles are rock samples from the Cholan and Tuokoshan formations, inverted white triangles are sediments from the Gaoping River. The Gaoping catchment is shown in white, with the Plio-Pleistocene sedimentary formations cross-hatched. Main tributaries of the Gaoping River are shown with black lines. Note that some river samples are from tributaries that mostly drain the mountains of the Central Range.
CM submitted to metamorphic burial temperatures above 360 °C.

Another published fitting procedure, designed for fitting of spectra from more disordered materials, fits Lorentzian profiles to five Raman peaks, covering typical ranges for G, D1, D2, D3, and D4. In this procedure, Lorentzian profiles were chosen rather than Voigt profiles to reduce the degrees of freedom available when fitting, as the multiparameter approach of Voigt fitting produced unstable fits for complex spectra. Increasingly disordered material has larger peak widths, for which the broad Lorentzian profile is a good match.

For this study, two automatic fitting routines were created with the software Gnuplot. The first routine is based on the Voigt fitting procedure. Three Voigt profiles are fitted with a linear baseline. If required, nonlinear equations for the baseline could be incorporated, although tuning the baseline for every individual spectrum removes some objectivity. Initial conditions are provided by sampling relevant parts of the input spectra, namely, the amplitudes and locations of the G and D1 peaks. Initial D2 amplitude is also measured from the input spectra. The width and location parameters are then allowed to vary within certain ranges, defined in Table I, while amplitude is allowed to vary without limit. The Voigt profile is defined as:

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

(1)

where $G(x)$ is a Gaussian function and $L(x)$ is a Lorentzian function, $\sigma$ is the standard deviation of the Gaussian function, and $\gamma$ is the half-width at half-maximum of the Lorentzian function. The Voigt function is computationally complicated, and Gnuplot uses a rapid approximation of the Voigt profile, accurate to one part in $10^4$. Thus, the function fitted is

$$ f(x) = \sum \text{area}_i \times \text{Voigt}(x - \text{location}_i, \text{width}_i), i = \text{peaks G, D1–D4} + mx + c. $$

(2)

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

$$ f(x) = \sum \text{area}_i \times \text{Lorentzian}(x - \text{location}_i, \text{width}_i^2), i = \text{peaks G, D1–D4} $$

(3)

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

Carbon Classification. To resolve differences within populations of graphite and disordered carbon, samples can be characterized with a variety of parameters. The R1 and R2 measurements, applied to Voigt-fitted spectra, characterize intermediate- and high-grade graphite very successfully, and have been calibrated for peak temperature by using metamorphic petrology, making the carbonaceous-material geothermometer a useful tool:

$$ R1 = \frac{D1_{\text{height}}}{G_{\text{height}}} $$

(4)

$$ R2 = \frac{D1_{\text{area}}}{G_{\text{area}} + D1_{\text{area}} + D2_{\text{area}}} $$

(5)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Initial height</th>
<th>Constraints when choosing (cm⁻¹)</th>
<th>Initial location (cm⁻¹)</th>
<th>Constraints when fitting (cm⁻¹)</th>
<th>Initial width (cm⁻¹)</th>
<th>Constraints when fitting (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>From data</td>
<td>1580–1600</td>
<td>From initial height</td>
<td>1550–1630</td>
<td>17</td>
<td>&lt;80</td>
</tr>
<tr>
<td>D1</td>
<td>From data</td>
<td>1200–1450</td>
<td>From initial height</td>
<td>1300–1400</td>
<td>72</td>
<td>&lt;200</td>
</tr>
<tr>
<td>D2</td>
<td>From data</td>
<td>1610–1640</td>
<td>1601</td>
<td>1630–1640</td>
<td>17</td>
<td>&lt;80</td>
</tr>
<tr>
<td>D3</td>
<td>From data</td>
<td>1490–1510</td>
<td>1500</td>
<td>1475–1525</td>
<td>100</td>
<td>&lt;200</td>
</tr>
<tr>
<td>D4</td>
<td>From data</td>
<td>1140–1150</td>
<td>1250</td>
<td>1200–1250</td>
<td>150</td>
<td>&lt;200</td>
</tr>
</tbody>
</table>

* FWHM = full width half-maximum.
While both ratios have been calibrated for temperature, R2 is the preferred metric. In samples where D1 is wide but has low intensity, the R1 parameter can show a reversed trend, and it is also more sensitive to the accuracy of baseline corrections and D2 fitting. R2 is particularly effective at characterizing highly crystalline material, up to perfectly graphitized crystals, with \( T = 645 \degree \text{C} \). However, R2 measurements saturate above \( 0.7 \) (metamorphic temperatures below approximately 330 \( \degree \text{C} \)). The RA2 measurement is applied to disordered materials with Lorentzian fits, but the temperature correlations are less certain:\(^{22}\)

\[
\text{temperature} = -441 \times R2 + 645
\]

The fitting procedures were calibrated by comparison with a collection of spectra with known metamorphic temperatures, fitted manually by using the program PeakFit,\(^{7,22}\) covering a wide range of carbon structures. Figure 3 shows cross-plotted results for R1, R2, RA1, and RA2, with very good agreement between the manual and automatic fits. For RA1 and RA2, automated fitting results are related to manual fits with a linear 0.95:1 relationship and \( R^2 \) values in excess of 0.925. For the Voigt procedure, R1 values correlate with a linear 1.004:1 relationship and \( R^2 = 0.999 \), while R2 values have a 0.91:1 relationship and an \( R^2 \) value of 0.991.

It is important that spectra are fitted with the appropriate procedure. Applying the Voigt fit to disordered material, or the Lorentzian fit to highly graphitized material, leads to poor fits and incorrect parameterizations. In order to choose the correct procedure automatically, the following workflow was implemented: In the first instance, spectra were fitted with the Voigt procedure, as this is computationally more efficient and can fit graphitized carbon as well as low-temperature material, albeit with less precision. The results of this fit were analyzed, and if the R2 value was below 0.6 and either the D1 peak width below 120 cm\(^{-1}\) or the R1 value was less than 0.5, then the Voigt fit was accepted. If the fit had R2 > 0.6, or D1 width >
120 cm$^{-1}$ and $R_1 > 0.5$ (values chosen by inspection of a range of spectra), then a Lorentzian fit was applied. While $R_2$ values of 0.65 or 0.7 can be collected from reasonably graphitized material, and thus, the Lorentzian fit is applied. If the $R_A2$ value calculated from this fit was $>2$ (the maximum value measured in previous studies), then the procedure reverted back to the Voigt fit. Finally, each spectrum was characterized with two parameters, the estimated metamorphic temperature as calculated from the $R_2$ or $R_A2$ value (as applicable) and total width (the sum of the G, D1 and D2 peak widths).

This workflow leads to the identification of three groups of spectra. Spectra from highly graphitized material have a high $R_2$ temperature, above 360 °C. Partially graphitized and disordered materials both have low estimated temperatures, but the former has intermediate and the latter, high total peak widths. Spectra fitted with the Voigt procedure have a temperature of more than 360 °C, and corresponding samples have experienced significant metamorphic conditions. Values of the total width parameter ($G_1 + D_1 + D_2$ widths) vary, reaching up to 250 cm$^{-1}$ in these spectra. Those fitted with the Lorentzian procedure are less metamorphosed—published $R_A2$ values cover temperatures as low as 200 °C$^{22}$—and in some cases, are little more than charcoal or lignite grade. The total width distinguishes between these two groups. By inspection of fitting results, low-grade metamorphic material has a total width less than 290 cm$^{-1}$, while spectra collected from lignite clasts in the Plio-Pleistocene of Taiwan have total widths up to 350 cm$^{-1}$. By plotting measured total width against temperature, spectra from each sample fit into one of three carbon classes. Figure 4 shows a collection of spectra from sample K1-19, just offshore Taiwan, plotted in this fashion.

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

**RESULTS AND DISCUSSION**

**Effects of Grinding and the Utility of Sample Homogenization.** While pure graphite has previously been shown to be robust in grinding and lengthy fluvial transport, the disordered and partially graphitized nature of the material found in the river sediment could have made it prone to damage during grinding. To assess the effect of grinding on the structure and relative abundance of different types of carbonaceous material in our samples, we compared results for ground and unground aliquots of samples KP2A and KP3B from the Gaoping River. Figure 5 shows a comparison of Lorentzian fitting results, plotted as $R_A2$ temperature against
total width. Eight data points collected from powdered sediment have average temperature and total-width values that lie within one standard deviation of the equivalent averages for five data points collected from the un-ground aliquot. Similarly, the results from sample KP3B show a matching clustering of spectrum properties for both raw and powdered materials. Both sets of spectra show a slight and statistically insignificant increase in total width after grinding, with little or no impact on the estimated temperatures. These results demonstrate that grinding has not introduced significant disorder into the samples, and we proceed assuming that this holds for all other samples in our study. Although we have not considered variable grinding times and methods, we anticipate that any grinding procedure that reduces grain sizes to the \(10\mu m\) range can be applied without significant effect on the structure of carbonaceous material in geological and environmental samples.

**Application: Morokot Flood, Taiwan.** To test the practicality of our method, we investigated the sourcing and distribution of carbonaceous material in sediments from the Gaoping Canyon. We collected 201 spectra from 19 samples of sediment deposited during Typhoon Morokot and rocks exposed in its source area. In general, at least ten spectra with a signal-to-noise ratio greater than three were acquired. Particles with a graphitic appearance under the microscope and a graphitic spectrum were found in five of eight samples from the Cholan and Tuokoshan Formations, one of three samples from the Gaoping River, and in all eight samples from the Gaoping submarine canyon, although the proportion of this material to other types of carbonaceous material varied greatly. Some form of disordered carbon or semi-graphitized material was found in all samples, but its shape varied considerably.

Most of the Plio-Pleistocene Cholan Formation samples contained highly disordered carbonaceous material (Fig. 6a). Sample 17 was a 10 \(\times\) 10 cm piece of lignite, which still had the physical characteristics of a small log; hence, we are confident that it was a piece of woody biomass that had been incorporated directly into the sediments. All spectra from this specimen had a high total width and low RA2 temperature. Six out of seven other samples from the Cholan Formation contained similarly disordered carbon, creating a cluster of disordered carbon spectra at the top of Fig. 6a. This is interpreted as woody material of millimeter to centimeter size, incorporated into the Plio-Pleistocene sediments during deposition and subsequently transformed to lignite, indicating that the burial depths experienced by the Cholan and Tuokoshan Formations were insufficient to induce metamorphism. Carbon with a higher degree of order in these formations is likely to have a bedrock source, eroded from rocks exposed in the emerging Taiwan Mountain Belt at the time of deposition of the Cholan and Tuokoshan sediments. There is highly graphitized material present in six out of seven Cholan and Tuokoshan sedimentary samples and semi-graphitized material in five out of seven. Disordered carbon
is much more common than semi-graphitized material; samples 2, 3, 6, and 8 tend toward a bimodal distribution of highly graphitized and disordered material. This could reflect the lesser outcrop of metamorphic rocks containing semi-graphitized carbon in the Central Range during Plio-Pleistocene times, or the loss of this carbon during exhumation and erosion of the Taiwan Mountains at this time.

Figure 6b shows the range of spectra collected from Gaoping River sediments, the majority of which was semi-ordered material derived from a branch draining the Central Mountain Range. This material has experienced moderate metamorphism\textsuperscript{15} but did not approach conditions where crystalline graphite is usually achieved. The only graphite grains found in the Gaoping River are from the branch draining the western plains, in which the graphite-rich Cholan and Tuokoshan Formations crop out.

Offshore sediments show a range of material that is a combination of both the Central Range semi-graphitized carbon and the fully graphitized and disordered carbon of the Plio-Pleistocene rocks. Semi-graphitized and highly graphitized materials were contained in all samples, including samples collected on the continental shelf and the Gaoping Canyon (Figs. 6c and 6d, respectively), but the shelf cores contained less disordered carbon. The abundance of disordered material in canyon cores compared with shelf cores hints at variations in the hydrodynamic processes depositing material in these locations. The sedimentation rate on the shelf is less than 1 cm year\textsuperscript{-1}, while the canyon deposits were sourced in a single flood event, transported by sediment gravity currents.

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**Fig. 5.** A comparison of spectral properties (total width vs. RA2 temperatures) from two river sediment samples (a) before and (b) after 12 min of ball-mill grinding. The large symbols show the average value along with one σ error bars. In each case, the average results are within error of each other, suggesting that no significant change in structure is introduced through grinding.
along the seafloor. This rapid transport and deposition process could entrain and bury buoyant disordered material more efficiently than the gradual raining down of material onto the shelf from the sea surface. This indicates that the transport distance along the Gaoping Canyon system (20–200 km) is too short for comprehensive loss of semi-graphitized carbon by oxidation during sediment transport, in contrast to the Bengal Fan system, wherein offshore transport pathways are an order of magnitude longer (2000 km).

CONCLUSION

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

Automatic focusing onto the sample surface, combined with

Fig. 6. Results from four locations in Taiwan and the Gaoping Canyon showing the range of carbon morphologies present in these locations. The Plio-Pleistocene formations (a) supply large amounts of highly graphitized and disordered material to the Gaoping. The highland branch of the Gaoping River (b) drains the Central Range of Taiwan and is dominated by semi-graphitized material. Highly graphitized sample comes from the western branch, draining graphite bearing Plio-Pleistocene units. All three types of carbon are seen offshore, although varying distributions of disordered material are seen in the Gaoping Canyon (c) and continental shelf (d).
a fast mapping procedure, will make spectral acquisition more efficient. The automatic processing technique is even more important in this situation, to filter out non-carbonaceous spectra. These techniques are now becoming available on spectroscopic equipment.

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SUPPLEMENTAL MATERIAL

All supplemental material mentioned in the text, including a shell script written for Linux that implements the fitting procedure described here, can be found in the online version of the journal at http://www.s-a-s.org.