Marine Sequestration of Particulate Organic Carbon from Mountain Belts

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This dissertation is submitted for the degree of

Doctor of Philosophy

30th March 2012
This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration except where specifically indicated in the text. No part of this dissertation is substantially the same as any work that has been, or will be submitted for any other qualification at any other University. The total length does not exceed the 60,000 word limit for the Degree Committee of Materials Science and Metallurgy.

Robert Bryon Sparkes

30th March 2012
Acknowledgements

First of all I would like to thank Vasant Kumar, Niels Hovius and Albert Galy for their supervision, advice and support. Their help and guidance on this project has been essential for its success. Thanks to Vasant, Bill Clyne, Rosie Ward and Margaret Johnston for helping to set up the collaboration between the Materials Science and Earth Sciences departments, through which I have had an unique opportunity to combine the analytical techniques available in each department and enhance the project in many ways. Niels and Albert have been invaluable both in Cambridge and in the field, always willing to discuss ideas and bring their knowledge to bear on any problems.

Working in three field areas has involved several collaborations, and I am grateful to many people around the world for their help. James Liu at National Sun Yat-Sen University supplied core samples from typhoon Morakot, and provided me the opportunity to discuss my results with several researchers in Taiwan. Doug and Fanta from his office were particularly helpful during my time in Kaohsiung. Peter Talling’s expertise was invaluable when collecting samples from the Apennines, his stratigraphic precision and volumetric calculations allow this thesis to explore organic carbon sequestration to a degree unavailable elsewhere. Josep Muñoz and colleagues at the University of Barcelona provided stratigraphic advice in the Pyrenees that enabled time-equivalent lateral transects to be collected, and sedimentary facies to be compared. In Taiwan it was a pleasure to work with Josh West, whose field assistance when collecting material from the Gaoping Catchment was more productive than either of us would have predicted. Olivier Beyssac has been extremely helpful when acquiring and processing Raman spectra, and his guidance on the finer aspects has greatly improved the general applicability of my work. Xiaomei Xu at UC Irvine kindly provided $^{14}$C data on material from Typhoon Morakot.

In the lab, James Rolfe and Jason Day have given lots of their time to help me prepare and analyse samples, and thanks should also go to Martin Walker and Nigel Johnson for their assistance. Discussion in the department with Mike Bickle, Alex Piotroski, Nick Tosca, Ed Tipper, Sasha Turchyn, Peter Friend and Nick McCave have helped guide my thoughts. In the office and at group meetings, Jo Smith, Caroline Martin, In-Tian Lin, Andy Wilson, Jens Turowski, David Wilson, Carsten Schwandt and Ollie Shorttle have been supportive and insightful, while conference discussions with Bob Hilton, Sean Willett, Valier Galy, Tim Eglinton among others have helped with specific details and general ideas. Special thanks to Bob Myhill for his field assistance, computational knowledge and willingness to help in all manner of ways.

I would like to thank my parents and sister for their continued love and support through seven and a half years in Cambridge. Lastly, and mostly, I thank Sonya. Thank you for your belief in me from the start, for your support throughout the project, even in the field, for the insightful questions you have asked, for the advice and guidance, and for the love you have always given me. I love you with all my heart.
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Robert Bryon Sparkes

The harvesting from mountain belts and subsequent delivery to the oceans of particulate organic carbon (POC) is a significant part of the global carbon cycle. The volume of carbon dioxide (CO$_2$) removed from the atmosphere as plant growth (POC$_{biomass}$) and subsequently exported from an active mountain belt by erosion can surpass the amount of CO$_2$ consumed by silicate weathering in the same area. However, to effectively sequester CO$_2$ by POC$_{biomass}$ erosion two conditions must be fulfilled. Firstly, the eroded material must be transported to a location where it can be buried and stored on geological timescales, without being oxidised (and releasing CO$_2$ to the atmosphere). Secondly, the amount of CO$_2$ released by the mobilisation and oxidation of ancient “fossil” carbon previously contained in the rocks of the mountain belt must be lower than the volume sequestered by POC$_{biomass}$ burial. The volumes and nature of organic carbon exported from active mountain belts has been studied in detail, but the preservation potential of this material once deposited offshore is poorly constrained.

This thesis investigates the marine sequestration of POC exported from modern and ancient mountain belts, considering the types of POC preserved in a range of sedimentary environments. Three submarine sedimentary basins were studied, each fed by clastic sediments sourced from rapidly-exhumed mountain belts: the Central Range of Taiwan, the Spanish Pyrenees and the Italian Apennines. Distribution and preservation patterns of modern and ancient organic carbon within sedimentary transects from fluvial to marine facies were investigated, and calculations made of the volume of carbon sequestered in offshore sediments.

Using a coupled approach of Raman spectroscopy and isotope geochemistry, the type of organic material present in sediments was characterised. An automated implementation and extension of published spectroscopic methods for quantifying the crystalline state of organic material was developed and applied to samples collected in order to investigate sediment sourcing and burial. In addition, both elemental concentrations of organic carbon and nitrogen, their stable isotope compositions and radiocarbon concentration were analysed and procedures for determining inputs of different organic carbon species developed. Combining these two methods provided more information than could be acquired from either technique individually.

In Taiwan the material delivered to the South China Sea by a major storm, Typhoon Morakot, was collected from the Gaoping submarine canyon and surrounding shelves. The contribution of a wide range of organic carbon types to the offshore sediments was then quantified. These
types include POC_{biomass}, fossil carbon from metamorphic rocks of the Central Range, aged lignite-grade material recycled from Plio-Pleistocene sediments, and marine organic matter from ocean productivity. Terrestrial material dominates sedimentation in the Gaoping canyon, and contributes significantly to deposition on the shelf. Radiocarbon analysis highlights the importance of recycling during erosion and burial, less than one third of the organic carbon present in the offshore sediments was sourced from the modern biosphere, whilst Raman spectroscopy identifies crystals of graphite that have undergone at least three orogenic cycles.

In the Pyrenees, fluvial-marine transects from two different time horizons were studied to investigate the burial potential of organic carbon over geological timescales. A wide range of sedimentary facies were sampled, from river deposits to distal basin turbidites. In each location the proportion of each organic carbon input species was quantified using isotope geochemistry, and Raman spectroscopy was used to investigate the changes in carbon input as the orogeny progressed. Delta front localities contained 0.4 ±0.15 wt% POC_{biomass} whilst the turbidites deposited further offshore also contained 0.4 ±0.25 wt% C, half of which was POC_{biomass}, and were volumetrically important facies for carbon sequestration.

Turbidites of the Marnoso Arenacea formation in the Apennines were sampled due to the exceptional constraints available on their sediment volume. These sediments were sourced by erosion in the Alps during the Miocene. Combining elemental / isotopic and Raman spectroscopic results showed that sandy parts of the turbidites contain little POC whilst the majority of the total carbon preserved was concentrated into the silty and muddy parts of the turbidite and mostly consists of POC_{biomass}, either directly harvested from soils and plant material or recycled from earlier sedimentary systems on the southern flank of the Alps. Graphitic fossil carbon concentrations were uniformly low throughout. By collecting detailed sedimentary profiles through a single turbidite bed in multiple localities the volume of organic carbon stored in the turbidite was quantified, some 57.4 million tonnes, of which 11.7 Mt is fossil carbon and 45.7 Mt is non-fossil. This exceeds estimates for contemporary global annual organic carbon burial.

Combining multiple analytical techniques and field areas has shown that terrestrial POC is effectively sequestered in a range of marine environments. Nearshore deposition in deltas and submarine canyons is dominated by POC_{biomass}, whilst further offshore there are large volumes of POC_{biomass} and marine carbon preserved in turbidite deposits for millions of years. Fossil POC is stabilised by metamorphism to graphite and recycled along with more disordered sedimentary POC through multiple erosion and deposition cycles, minimising oxidative release of CO_2. Thus erosional transfer of POC from mountain belts to marine sediments efficiently sequesters significant volumes of CO_2.
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<td>POC</td>
<td>Particulate Organic Carbon</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>TN</td>
<td>Total Nitrogen</td>
</tr>
<tr>
<td>$\delta^{13}$C</td>
<td>Stable carbon isotopic ratio</td>
</tr>
<tr>
<td>$\delta^{15}$N</td>
<td>Stable nitrogen isotopic ratio</td>
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<tr>
<td>OM</td>
<td>Organic Matter</td>
</tr>
<tr>
<td>OC</td>
<td>Organic Carbon</td>
</tr>
<tr>
<td>CM</td>
<td>Carbonaceous Material</td>
</tr>
<tr>
<td>CWD</td>
<td>Coarse Woody Debris</td>
</tr>
<tr>
<td>POC$_{terrbio}$</td>
<td>Organic carbon from terrestrial plant matter, including soils</td>
</tr>
<tr>
<td>POC$_{fossil}$</td>
<td>Organic carbon from bedrock sources</td>
</tr>
<tr>
<td>Gt</td>
<td>Giga-tonne ($10^{15}$ g)</td>
</tr>
<tr>
<td>Mt</td>
<td>Mega-tonne ($10^{12}$ g)</td>
</tr>
<tr>
<td>Myr</td>
<td>Million years</td>
</tr>
<tr>
<td>Ma</td>
<td>Million years ago</td>
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<tr>
<td>HWHM</td>
<td>Half-Width at Half Maximum</td>
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Chapter 1

Introduction

1.1 Motivation

Erosion of terrestrial particulate organic carbon (POC) is a large component of the global carbon cycle. CO$_2$ is removed from the atmosphere by biological productivity, and the removal of this as POC$_{terrbio}$ from active mountain belts can account for a larger carbon flux than is consumed by silicate weathering. However organic carbon erosion is only able to draw-down CO$_2$ if the POC is buried in sediments on geological timescales. POC is transported by rivers to floodplains, deltas, continental shelves and ultimately the ocean floor, and can be stored in any or all of these locations transiently or long-term. Quantification of this burial, and investigation of the most efficient burial locations, is an important corollary to terrestrial POC erosion studies.

As well as CO$_2$ draw-down by modern (“fresh” or “non-fossil”) POC growth and erosion, mountain belts are sources of “fossil” organic carbon. This is material that has been previously buried and stored for long periods as organic-rich material, ranging from lignite and coal to graphite, and can be sourced from the weathering of sedimentary and metamorphic rocks. Prior to erosion, fossil POC has been stored in the earth for geological periods, locked away from the short-term carbon cycle. Weathering and erosion exposes this material to oxygen, and can lead to degradation, producing CO$_2$, but re-burial in new sedimentary rocks produces a closed loop with no CO$_2$ release. Thus an active mountain belt can be both a source and sink of CO$_2$, with the balance between the two depending on the volume of each carbon species eroded, the efficiencies of the fluvial transport and
burial process and the possibility for long-term geological storage.

This thesis aims to characterise and quantify submarine POC storage. This will involve developing methods to identify the fossil and non-fossil carbon in fluvial and marine sediment, identifying and exploring the locations at which the POC burial is most effective, and calculating the volume of POC sequestered offshore.

1.2 Global Carbon Cycles

Carbon cycling on Earth involves a large number of interconnected processes. These can be broadly split into the Long-term and Short-term carbon cycles (Berner, 1999). The Long-term carbon cycle considers exchange of carbon between stable reservoirs, the crust and mantle, including fossil fuel deposits, and the ocean-atmosphere-biosphere-soil system (see Figure 1.1). Carbon would be expected to remain in these reservoirs for thousands to millions of years. The Short-term cycle involves rapid exchange within this surface system, on timescales ranging from days to decades.

The Long-term carbon cycle can be split into two processes, silicate weathering and organic carbon burial (see Figure 1.2). Silicate weathering involves mildly acidic rainwater dissolving silicate rocks, transporting the resulting carbonate ions through the fluvial
system and depositing calcium carbonate in the oceans. This process consumes twice as much CO$_2$ as it releases.

$$2CO_2 + H_2O + CaSiO_3 \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2$$ \hspace{1cm} (1.2.1)

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$$ \hspace{1cm} (1.2.2)

thus overall

$$CO_2 + CaSiO_3 \rightarrow CaCO_3 + SiO_2$$ \hspace{1cm} (1.2.3)

Weathering of carbonate also removes CO$_2$ from the atmosphere, but it is released again upon carbonate deposition and so the process acts as a time-delayed closed loop.

The other half of the Long-term cycle consists of the burial and erosion of organic carbon. Photosynthesis draws CO$_2$ from the atmosphere to produce glucose, which can be stabilised in plant matter. Upon erosion this material can be transported to sedimentary sinks and buried, whereupon continuing biogenic productivity can draw further CO$_2$ from
the atmosphere. However, erosion of organic carbon rich sediments can expose this stored carbon, leading to oxidation and CO$_2$ release.

$$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{O} + \text{O}_2 \quad (1.2.4)$$

Metamorphic reactions and volcanic processes can lead to the breakdown of carbonate or organic rich sediments, leading to CO$_2$. Increased temperature leads to the breakdown of carbonate minerals:

$$\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CO}_2 + \text{CaSiO}_3 \quad (1.2.5)$$

Metamorphic and volcanic processes can also cause temperature-induced decomposition of organic matter:

$$2\text{CH}_2\text{O} \rightarrow \text{CH}_4 + \text{CO}_2 \quad (1.2.6)$$

$$\text{CH}_4 + \text{CO}_2 + 2\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \quad (1.2.7)$$

These long-term processes all move carbon into or out of the Short-term carbon cycle, which involves the movement of carbon in various states between the atmosphere, biosphere, soils and ocean on much shorter time scales (see Figure 1.3).

Fluvial transport carries terrestrial POC to the ocean. Other methods of land-ocean transport include direct coastal erosion and aeolian transport - whose magnitude will vary with location and climate. Coastal erosion and aeolian transport have previously been described as negligible (Hedges and Keil [1995]), although recent studies in the Arctic Ocean have shown that coastal erosion of permafrost can introduce large amounts of ancient carbon to the marine system (Vonk et al. [2012]). Aeolian material may represent 5 - 10% of the fluvial transport of POC (Gebhardt et al. [2005]). Short-term processes sequester CO$_2$ from the atmosphere but the amount removed is limited by the magnitude of the biosphere and soil reservoirs. Geological storage is required in order to remove larger amounts of CO$_2$ from the atmosphere. Ocean burial transfers carbon to the Long-term cycle, however the majority of carbon exported by rivers does not receive this fate; at all stages along the
Figure 1.3: Movement of carbon through the Short-term carbon cycles. Figure taken from Berner (1999).

transport route carbon is returned to the atmosphere by decomposition and degassing - processes known as remineralisation.

1.2.1 Magnitude of organic carbon reservoirs and fluxes

When considering the carbon cycle, it should be noted that the various stores and processes involved do not necessarily involve similar quantities of carbon. For example, Hedges et al. (1997) estimate that there are 570 Gt of organic carbon existing in terrestrial biota, 70 Gt in plant litter, yet only only 3 Gt present in marine matter. Similarly there are 700 Gt OC dissolved in the ocean, 700 Gt C in upper 1 m of global marine sediment, yet 1600 Gt in the top 1 m of soils. The long-term carbon reservoirs are much larger than this, 75 million Gt C are stored in sedimentary rocks, with one fifth being organic carbon, the rest carbonates (Hedges and Keil 1995).

The magnitudes of carbon transfer between reservoirs also varies greatly. For example, the production of marine organic matter is approximately 50 Gt C yr\(^{-1}\); the amount of POC delivered by rivers is a fraction of that, 0.15 Gt C yr\(^{-1}\) (Hedges et al. 1997). However, sedimentary burial of TOC is also in the range 0.1 - 0.2 Gt C yr\(^{-1}\) (Ittekkot 1988).
meaning that more than 50% of the riverine POC and 99.5% of the marine productivity must be remineralised in the water column and not sequestered. These numbers are global estimates though, and different burial settings and sedimentation rates lead to more than two orders of magnitude difference between organic carbon burial efficiencies (see Figure 1.4). These global averages are often poorly constrained. The Bengal Fan system is the largest sedimentary deposit in the world yet estimates of carbon burial are based on a small number of cores. Detailed studies have led to large changes in organic carbon burial volume calculations (Galy et al., 2007b). Burdige (2005) cite high sedimentation rates as efficient sites for organic carbon burial, a high-resolution study of the sediment exported from an active mountain belt will allow study of many sedimentary facies with high deposition rates.
1.2. GLOBAL CARBON CYCLES

1.2.2 Tracing organic carbon

Figure 1.5: Fluvial and marine organic matter compositions as measured offshore Washington State (Prahl et al., 1994), plotted as $\delta^{13}C$ vs N/C. Suggested compositions for woody debris, soil organic matter and marine POC are also plotted (Prahl et al., 1994; Benner et al., 1997; Hedges et al., 1997; Hilton et al., 2010; Kao et al., 2003, 2006). In this erosional system, POC compositions seem to trend between soil and woody debris values onshore to marine values deep offshore. Higher N/C values seen in fossil carbon by Hilton et al. (2010) are not reported in this catchment. Circle diameters scale with TOC measured in the sample.

Isotopic methods, especially the ratio of $^{13}C$ to $^{12}C$, have been used to identify the presence of terrestrial plant matter in marine sediments for over thirty years (Spiker, 1981; Showers and Angle, 1986). Isotopic ratios are reported using "delta notation":

$$\delta^{13}C = 1000 \left[ \frac{(^{12}C)_{sample} - (^{12}C)_{standard}}{(^{12}C)_{standard}} \right],$$

(1.2.8)
where the standard for carbon isotope values is PDB. Nitrogen isotopic measurements can also be recorded, and have been used to differentiate between terrestrial and marine organic matter (Spiker, 1981). Plants produce organic matter via photosynthesis along one of two chemical pathways, which each introduce an isotopic fractionation. The C3 pathway introduces a 20‰ fractionation, leading to terrestrial OM with $\delta^{13}C$ of -27‰ and marine OM with values of -18 to -25‰ (Popp et al., 1989, 1998; Meyers, 1994; Hayes et al., 1999). These differences arise because the different locations draw their carbon from the atmospheric and oceanic inorganic carbon pools, with present day values of 0 and -7‰ respectively. Fractionation factors depend on phytoplankton shape and local pCO$_2$, [CO$_2$aq] variations, and have changed by up to 7‰ over geological time (Popp et al., 1989; Francois et al., 1993; Popp et al., 1998).

The alternate photosynthetic pathway, C4, introduces only -7‰ fractionation (Smith and Epstein, 1971), hence terrestrial plant matter created this way has $\delta^{13}C$ of -14‰. Fluvial output contains a mixture of the terrestrial material, hence a variety of carbon isotopic values in the range -25 to -30‰ (Showers and Angle, 1986).

A third method for differentiating terrestrial and marine carbon has been the C/N elemental ratio. Carbon-rich cellulose in vascular plants leads to high C/N ratios, greater than 20, whilst its absence in marine algae means that values here range from four to ten. Upon decomposition and algal consumption in soils, the C/N ratio of vascular material can be reduced from a maximum of 30 or 40 down to around 15 (Redfield, 1958; Hedges et al., 1986; Meyers, 1994). In this thesis, the inverse ratio will be presented, N/C, as it allows linear mixing calculations to be carried out when $\delta^{13}C$ is plotted against N/C. Figure 1.5 shows a selection of sediment samples from a fluvial-marine transect (Prahl et al., 1994) plotted in this space, along with a collection of typical compositions of marine, soil and vascular plant organic matter (Prahl et al., 1994; Benner et al., 1997; Hedges et al., 1997; Hilton et al., 2010; Kao et al., 2003, 2006).

1.3 Transport and burial of Organic Carbon

1.3.1 Global organic carbon export observations

Despite the large remineralisation estimates, organic-rich sediments exist in the geological record. POC has been observed being transported in large quantities from active mountain
belts and being buried in submarine deposits.

Hilton et al. (2008b) made measurements of fossil and non-fossil carbon export from the LiWu river, Taiwan, during regular and typhoon conditions. Organic carbon concentration ranged from 0.16 % to 0.42 %, with a POC$_{terr,bio}$ component up to 0.43 coinciding with highest carbon concentrations. Thus rivers are able to transport POC from hillslopes to the floodplain.

Showers and Angle (1986) showed that fluvial transport carries organic matter to the continental shelf, by studying TOC and $\delta^{13}$C from the Amazon river. They estimate that 4.5 MtC yr$^{-1}$ are deposited on the shelf, of which 69 % are from terrestrial sources. This is a significant volume of carbon, some 9 % of the global organic carbon burial flux (France-Lanord and Derry 1997).

In a similar study, Galy et al. (2007b) show that organic carbon export from the Himalaya to the Bengal Fan can account for 7.2 MtC yr$^{-1}$, 10 to 20 % of the global burial flux. A combination of high sedimentation rate in the Ganges-Brahmaputra system and low oxygen availability in the Bengal basin mean that an estimated 3.7 MtC yr$^{-1}$ of recent organic matter is delivered to the Bay of Bengal, and deposited up to 2000 km offshore. These large-scale sedimentary systems contain significant amounts of organic carbon, but are fed by some of the world’s longest river systems.

Masson et al. (2010) studied organic deposition offshore a much smaller system, the Nazaré canyon off Portugal. 12.5 KtC yr$^{-1}$ (just 0.03 % of global OC burial) are deposited in the canyon, with TOC values up to 2 %. OC burial rates in the canyon are 30 times higher than the neighbouring continental slope, showing that OC may be concentrating into particular submarine sedimentary facies. OC deposition in the Nazaré canyon is two orders of magnitude higher than the global average.

Offshore study of marine sediments can be difficult if the source of the material is not from a flood or submarine collapse. Deposition rates can vary greatly, such that an organic carbon-rich sample may have deposited over weeks or centuries, and precise dating of cores can be difficult. Widely-spaced cores can make lateral facies correlation difficult, and the cores may not be representative of the sample as a whole.
An important feature of all these studies has been burial efficiency. At each stage along the sediment routing system, a proportion of the POC is degraded and lost to the atmosphere (see Figure 1.2).

Galy et al. (2008) estimate that only 30 - 50% of the organic material eroded from the Himalaya is preserved through to burial in the Bengal Fan, and this is from a sedimentary system described as highly effective for OC burial. Showers and Angle (1986) calculate that despite significant carbon burial, only 6% of the terrestrial organic carbon exported from the Amazon is successfully buried on the shelf. Clearly there are inefficiencies within the system.

Ittekkot (1988) analysed organic matter in suspended sediment and found that 35% was labile, and prone to oxidation in estuaries and oceans, whilst the remainder, up to 150 MtC yr$^{-1}$ (a value higher than France-Lanord and Derry (1997) estimated), has degraded already and is now in a refractory state that should minimise further loss.

When considering marine organic matter, remineralisation effects are even more pronounced. Up to 99% of marine primary productivity can be degraded in the water column and at the seafloor (Hedges and Keil, 1995). Longer exposure to seawater reduces survivability further, such that only 0.25% of marine organic matter in the open ocean is buried, compared to 1.3% or less on the continental shelves. As marine organic matter is so labile, up to one third of organic carbon deposited offshore has a terrestrial source (Burdige, 2005).

Grainsize and oxygenation effects are also important. Kennedy and Wagner (2011) showed that a combination of anoxic conditions and fine-grained high-surface-area clay mineral deposition in the Cretaceous Atlantic Ocean led to TOC measurements of 18%, compared to 3 - 5% when only one of these factors was present. Organic material appeared to be deposited on the surface of the clay minerals themselves and in interlayer sites. Kennedy and Wagner (2011) speculated that when deposited in oxic environments, only the inter-layer organic matter was preserved.
1.3. TRANSPORT AND BURIAL OF ORGANIC CARBON

1.3.3 Processes that are particularly effective at OC transfer

So it is seen that a large volume of organic material is exported from the continents and can produce carbon-rich sedimentary deposits, yet it is also prone to significant amounts of remineralisation during transport. To resolve this dichotomy, it has been noticed that certain tectonic, climatic, biological and sedimentological processes can enhance the transport and burial efficiency of organic matter.

Hilton et al. (2008a) show that landsliding in tectonically active settings harvests both POC\(_{\text{terrbio}}\) and POC\(_{\text{fossil}}\) from hillslopes and transports it to river channels. The large sediment volumes released by landsliding are homogenised into a mixture of fresh and fossil carbon, which is available for subsequent erosion. It was estimated that POC\(_{\text{terrbio}}\) removal from the Southern Alps of New Zealand averages 39 \(\times 10^6\) gC km\(^{-2}\) a\(^{-1}\). If only 10\% of this material can be transported to the deep ocean and stored in marine sediments then the removal of POC from these mountains will contribute more to CO\(_2\) draw-down than silicate weathering.

Hilton et al. (2008b) show that typhoons and other extreme climatic events transport disproportionate amounts of POC\(_{\text{terrbio}}\) through the fluvial system. During a Taiwanese typhoon the proportion of non-fossil POC (F\(_{\text{mod}}\)) in the LiWu river, usually less than 0.05, increased to 0.43 (see Figure 1.6). The majority of non-fossil POC is transported during these rare events, and simultaneous increases in suspended sediment load mean that the POC is harvested at a time when the rivers are rapidly delivering both water and sediment to the ocean. This can improve the transport efficiency of the POC, reducing transport time and forming hyperpycnal density currents when the river meets the ocean.

Figure 1.6: POC transport during Taiwanese typhoons, from Hilton et al. (2008b). Note how non-fossil POC export is greatly biased towards events with very long return times.
CHAPTER 1. INTRODUCTION

Hyperpycnal flows have often been discussed as efficient methods of sediment transfer to the deep ocean (Goldsmith et al., 2008; Dadson et al., 2003, 2005). Fresh river water with a high suspended sediment concentration can be denser than seawater, despite its salt content. This leads to the river water flowing underneath the seawater, along the sea floor. This transports sediment, including POC, to the seafloor much faster than would be achieved during settling from a surficial sediment plume, meaning that the material spends less time exposed to the oxidising seawater. Thus organic matter preservation is more likely in these conditions. Hyperpycnal delivery of river water can lead to submarine turbidity currents, which can transport material rapidly and for great distances, both across shelves and through submarine canyons (Talling et al., 2007a; Masson et al., 2010; Huh et al., 2009). In contrast, flood sediment delivered hypopycnally by the Eel river in 1995 formed a thin layer spread across the continental shelf (Wheatcroft et al., 1997), ideal conditions for carbon remineralisation. In this setting, the Eel Canyon is disconnected from the Eel River, and turbidity currents flowing down the canyon are the result of resuspension of previously deposited marine sediments rather than a direct inflow of terrestrial sediment. In these conditions, terrestrial POC must survive deposition on the shallow shelf prior to mobilisation into the submarine canyon if it is to be sequestered.

1.3.4 Sub-aqueous sediment density flows

Large submarine mass-transfer events are critical to the movement of sediment in the oceans. A single submarine sediment density flow can transport 100 km$^3$ of sediment, ten times the annual global fluvial sediment output (Milliman and Syvitski, 1992; Talling et al., 2012). Submarine sediment flows can transport material for thousands of kilometres, travelling at up to 19 ms$^{-1}$ along surfaces of minimal gradient, as low as 0.2° (Bagnold, 1962; Middleton, 1993; Talling et al., 2007b). These flows can be both erosive and depositional, feeding on sediment as they pass by yet leaving behind a settling plume of sediment. Differences in water content, grain size and sediment concentration can lead to a wide range of flow styles, ranging from very dense debris flows to turbulent water-sediment mixtures known as turbidity currents to suspended nepheloid layers. A single flow event may contain all three of these flow behaviours; variations in the angle of slope beneath the flow can lead to transformations between them, and from depositional to bypassing or to erosive interactions with the seafloor. Low-concentration mud clouds above such flows can extend hundreds of metres above the seafloor, collecting into topographic lows and depositing up to 20 m of fine sediment onto the top surface of the coarser-grained deposits.
1.3. TRANSPORT AND BURIAL OF ORGANIC CARBON

Figure 1.7: Typical turbidite layering, as described by Bouma (1962) and Talling et al. (2012). Variations in sediment concentration, grainsize, topography and water content can lead to significant differences between these idealised turbidites and reality. This figure, taken from Talling et al. (2012), shows the classical Bouma sequence, as well as variations on bed structure and geometry seen in the field.
CHAPTER 1. INTRODUCTION

Turbidites are one of the sedimentary deposits formed by these submarine density flows, specifically turbidity currents. Turbidites are stereotypically classified into five layers based on their grainsize and bedforms, as summarised in Table 1.1 and Figure 1.7 however the wide range of conditions experienced by sediment density flows in the real world leads to a wide range of observed sedimentary deposits. For this study, samples were collected from several turbidite deposits in three different locations.

During transport within a turbidity current, material is sorted based on its hydrodynamic properties. Heavier material will be deposited first, initially as graded beds and later as rippled and laminated bedforms. Particle density as well as size are important here, with Stokes’ Law determining particle settling velocities, such that large but lightweight woody debris may settle after small, dense, mineral grains. Stokes’ Law states that

$$v_s = \frac{2(\rho_p - \rho_f)}{9\mu} g R^2,$$

where $v_s$ is the settling velocity, $g$ is the gravitation acceleration, $\rho_p$ is the particle density, $\rho_f$ is the fluid density, $\mu$ is the dynamic viscosity and $R$ is the particle radius.

Responsible for carrying large quantities of sediment rapidly to the ocean floor, turbidity currents dominate the final section of land-ocean sediment transport and can form stacked turbidite deposits several kilometres thick. They are a key sedimentary facies to be understood if the preservation of organic carbon in marine sediments is to be quantified. Quantifying POC burial in turbidites requires detailed knowledge of both the organic carbon distribution within the deposit, and the volume of sediment in each turbidite layer, which involves bed-scale correlations over large areas.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Bedforms</th>
<th>Cause</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>Fine un laminated mud</td>
<td>Hemi-pelagic settling</td>
</tr>
<tr>
<td>D</td>
<td>Laminated silt</td>
<td>Waning flow speed, lower flow regime</td>
</tr>
<tr>
<td>C</td>
<td>Cross bedded and rippled sand</td>
<td>Bedload transport in ripple stability field</td>
</tr>
<tr>
<td>B</td>
<td>Laminated sand</td>
<td>Decelerating turbulent flow, upper flow regime</td>
</tr>
<tr>
<td>A</td>
<td>Graded coarse sand</td>
<td>Heaviest material deposited first</td>
</tr>
</tbody>
</table>

Table 1.1: Characteristic sediment bedforms of the Bouma sequence (Bouma, 1962; Shanmugam, 1997).
1.4 Aims

Following the work of France-Lanord and Derry (1997), Galy et al. (2007b), Hilton et al. (2008a) and West et al. (2011), export of terrestrial POC from active mountain belts has been shown to be a significant factor in the carbon cycle. However without tracing this material to the submarine domain the fate of the POC is largely unknown and must be inferred, using isotopic means (Hedges et al., 1997) or otherwise. Thus a comprehensive study of terrestrial carbon burial in submarine sediment is required, with the following lines of investigation.

1.4.1 Characterise the types of carbon eroded from a mountain belt

In order to understand marine burial of POC, input material must be suitable characterised. Methods of carbon characterisation must be investigated and samples collected which analyse the types of POC delivered by rivers to the ocean. Both Raman spectroscopy and isotope geochemistry will be used to characterise the organic carbon sampled from three study areas, two ancient foreland basins and a modern submarine canyon and shelf system.

1.4.2 Determine the efficiency of transport through a fluvial-marine setting

A technique is required that can compare the POC transported into and buried within a submarine sedimentary system. By comparing the organic carbon composition of fluvial sediments to the carbon deposited offshore, efficiencies in the transport system can be investigated.

1.4.3 Work out the locations of burial, laterally and vertically

Field locations are required that can determine where within a submarine sedimentary system the POC is buried, and whether it is concentrated into particular sedimentary
horizons within those locations. Samples collected in lateral transects from fluvial to distal marine settings will show which areas organic carbon concentrates into, whilst high-resolution vertical profiles will show where within each facies the POC is actually stored.

1.4.4 Calculate the volume of material sequestered in such locations

To determine whether submarine organic carbon burial is an important part of the global carbon cycle, descriptions of POC burial locations must be turned into quantifications of POC storage. This will be achieved by combining the high-resolution vertical profiles with estimates of layer volumes.

1.4.5 Determine the erosional history of POC from orogeny to burial

Combining results from multiple field areas and time periods, the history of marine POC storage and sediment recycling during and after orogeny can be investigated.

1.4.6 Requirements

Thus, two sets of requirements exist. In order to characterise the carbon present in any particular sample, suitable analysis methods need to be developed. These should be implemented in a series of sample locations from modern and ancient systems that can fulfil the following specifications: a transect through a sedimentary basin, detailed vertical profiles through particular sedimentary facies and volumetric estimates of sediment deposition and hence carbon storage.

Combining these techniques and areas will allow comparisons in the style, location and volume of organic carbon burial in foreland basins and nearshore marine sediments, and to investigate burial efficiencies by comparing fluvial input to marine sediments and modern systems to ancient basins.
Chapter 2

Sample locations and Methods

These wide-ranging aims cannot be completed using a single technique or sample area.

In order to characterise the organic matter being transported through submarine systems, two techniques were employed. 1) Raman Spectroscopy, which can be used to assess the degree of graphitisation of individual carbonaceous material (CM) particles, and hence to track the various of sources of CM to a sedimentary sample. However quantification of the total volume of carbon present in a sample, or the relative importance carbon inputs from different sources, is hard to carry out with this technique. 2) Isotope Geochemistry, which quantifies the amount of carbon present in a sample and can also be used to infer its source, but is less accurate at fingerprinting than Raman spectroscopy.

Combining these two techniques in a series of sample locations allowed a comprehensive study of terrestrial POC export and submarine burial to be undertaken, investigating all sections of the covering a wide spatial and temporal range - from fluvial to basin settings. A series of bedrock, fluvial and offshore samples collected in Taiwan provide material from a wide range of sedimentary environments and produce a snap-shot of carbon export from a contemporary orogenic belt. However these samples cannot be used to estimate carbon loss over time, and thus a second sedimentary transect was collected in the Spanish Pyrenees, which provide the distribution of carbon within sediments deposited in the late Cretaceous and Eocene. For a more detailed study of a particular sedimentary facies, basin turbidites, samples from the well-studied Marnoso Arenacea Formation in the Apennines have been used to quantify carbon burial within a single event-bed. This chapter introduces both the techniques and study areas.
CHAPTER 2. SAMPLE LOCATIONS AND METHODS

2.1 Techniques

2.1.1 Raman Spectroscopy

Raman Spectroscopy is a precise tool for analysing the structure of carbonaceous material in geological (Beyssac et al., 2003b) and environmental samples (Schmidt et al., 2002). The method targets individual carbon particles that are often finely dispersed and have variable crystallography, making the acquisition of a large number of measurements for a given sample a prerequisite for robust interpretation. A new analysis procedure for preparing, measuring and interpreting Raman spectra, aiming to speed up and objectivise this method, has been developed.

Whilst crystalline graphite is the thermodynamically stable form of carbon at temperatures up to 4000 K and pressures up to 1 GPa (Bundy, 1989), its formation is kinetically hindered at Earth-surface conditions. Disordered carbon will transform progressively to graphite with the application of heat and pressure at depth within the Earth but once formed, graphite does not revert easily to a disordered state, meaning that the peak crystallisation state is preserved. Beyssac et al. (2002b) showed that the application of heat is the main driving force for the crystallisation of graphite below the Earth’s surface. As burial depth increases, pressure from material above and heat diffused from Earth’s deep interior and from radioactive decay in the surrounding rocks provide the energy required to form graphite crystals. This is a gradual process which is only completed when the temperature approaches 650 °C.

Crystallinity of graphite can be measured using Raman Spectroscopy. A monochromatic light source is analysed for a change in photon frequency following inelastic interaction with the sample. Changes in frequency are reported in wavenumber units (cm⁻¹). Raman spectra from disordered CM exhibits multiple broad peaks, especially at 1350 and 1600 cm⁻¹. With increasing crystallinity, these peaks are replaced by a single, sharp peak (half-width at half-maximum as little as 7 cm⁻¹) at 1580 cm⁻¹ (Wopenka and Pasteris, 1993). The degree of crystallinity, as defined by the area ratio of disorder to graphitic peaks, has been correlated to the maximum temperatures experienced by the C-containing rock, as recorded by changing mineral compositions (Beyssac et al., 2002b).

Complex geological settings, such as mountain belts, contain rocks that have experienced a wide range of metamorphic temperatures. Upon erosion, these rocks yield carbon
with a wide range of morphologies. Together with clastic sediments, eroded carbon is conveyed by rivers into depositional basins. In transport, river load is thoroughly mixed so that analysis of the full range of carbon morphologies 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 rocks in the source area have been subjected. However, crystalline graphite is more resistant to oxidation and bacterial decomposition than complex organic compounds. As a result, highly-graphitised carbonaceous material can survive fluvial and submarine transport unaltered over 1000s of km (Galy et al., 2008), while disordered and semi-graphitised material is oxidised en-route. In systems where the transport distance is significantly shorter, this loss is less pronounced (Hilton et al., 2011) so that the carbon inventory of basin deposits is representative of the pattern of erosion in the sediment source area. Thus a combination of short fluvial transport distance and proximal deposition should lead to a well-preserved carbon export and preservation signal.

### 2.1.2 Isotopic / Elemental Analysis

Isotopic and elemental analysis of combusted POC separates provides two useful readings, both the total proportion of carbon and nitrogen in a sample, and their isotopic compositions. Hilton et al. (2010) describe a procedure for collecting, preparing and analysing POC from bedrock and suspended sediments in Taiwan, which has been followed in this study.

Having collected TOC concentrations, the isotopic and elemental ratio results can be used to estimate the proportion of different types of carbon present in the samples. Hilton et al. (2010) describe a technique which separates the TOC into “fossil” (sourced from erosion of metamorphosed bedrock) and “non-fossil” (POC_terrBio - woody material, leaf litter and soil carbon) components without having to use expensive $^{14}$C analysis, and that is applicable to samples older than 50 kyr, beyond which radiocarbon analysis is not available.

For this study, automated routines have been developed that can differentiate between fossil carbon, marine carbon and terrestrial plant material (POC_terrBio). This is based on unmixing calculations based not only N/C and δ$^{13}$C, but also δ$^{15}$N measurements. Detailed descriptions of the sampling and analysis techniques are found in Section 2.5.
CHAPTER 2. SAMPLE LOCATIONS AND METHODS

2.2 Study Areas

A three-pronged approach was used to investigate the the position of carbon within the sedimentary system. The following subsections introduce each region briefly, a full description is included at the start of the relevant chapter.

2.2.1 Gaoping River and Canyon

Modern POC export was studied in Taiwan, a tectonically active mountain belt, which provided near-simultaneous measurement of carbon export and burial. Taiwan is situated at 22-23 degrees North at the convergent boundary between the Asian continent and the Philippine Sea plate (Figure 2.1) within the Inter-Tropical Convergence Zone. Rapid tectonic shortening (80 mm yr$^{-1}$) across Taiwan (Yu et al., 1997) gives rise to 4 km high mountains experiencing high erosion rates of 3-6 mm yr$^{-1}$; despite occupying only 0.024 % of Earth’s subaerial surface, Taiwan supplies ~2 % of the global suspended sediment discharge to the oceans (Dadson et al., 2003). Erosion is driven by extreme meteorological events. Taiwan experiences frequent typhoons, sometimes enhanced by the addition of heat and water vapour from the Asian monsoon system (Ge et al., 2010). This occurred in 2009, when Typhoon Morakot stalled over south Taiwan, precipitating up to 3600 mm of monsoon-supplied water in four days and causing extensive flooding and the mobilisation and export of large quantities of sediment (West et al., 2011).

Precipitation in south-eastern Taiwan is routed through the Gaoping River and into the South China Sea. After crossing the Gaoping Shelf via the Gaoping Canyon, final sediment deposition occurs in the Manila Trench. Landslides triggered by typhoon Morakot affected 129.8 km$^2$ of the Gaoping River basin, 3.9 % of the area (West et al., 2011), releasing 285 Mt of sediment (Liu, Pers. Comm.). Hyperpycnal flows initiated at the river mouth and flowed through the Gaoping canyon (Kao et al., 2010). Within nine hours, communication cable breaks were reported in the Gaoping canyon and Manila trench attributed to seafloor turbidity currents (Su et al., 2012). A suspended sediment plume extending 10 km along the Gaoping Canyon was observed (Kao et al., 2010). The deposits of this exceptionally large event are rich in carbonaceous material spanning the full compositional breadth from POC$_{terrbi}$ to fully graphitised carbon. Following the storm, sediment cores were collected up to 35 km offshore on the Gaoping shelf and slope, in water depths of up to 1200 m, in an attempt to understand the fate of sediment under such extreme conditions.
Figure 2.1: Topographic and bathymetric map of Taiwan showing the geographical setting offshore China, and the tectonic setting on the boundary between the Eurasian and Philippine Sea plates.
Studies in Taiwan allow investigation of carbon distribution laterally and vertically, but do not account for long-term preservation. To do this, samples must be collected from ancient sedimentary systems where the effects of diagenesis can be included. However, in such places the temporal resolution and links to source areas are inherently weaker. Thus a combined approach, comparing the modern system to carefully chosen ancient sedimentary basins, should provide a complete picture. Whilst Taiwan is exceptional in comparison to many contemporary margins, both in terms of tectonic activity and biological productivity, it is comparable to some ancient active mountain belts. During the Alpine Orogeny there were large volumes of material eroded from active mountain belts ranging from Europe to Asia. Some of these deposited material close to the source, and the increased global temperatures experienced in the past should mean that biological productivity would also have been enhanced in comparison to modern rates, making these areas comparable to modern tropical regions.

2.2.2 Spanish Pyrenees

The Pyrenees formed during the Alpine Orogeny, from the Late Cretaceous to Mid Miocene [Lopez-Blanco et al. 2003]. During this time, the continent of Iberial converged with Eurasia, forming a ~500 km mountain belt (see Figure 4.1). Sediment eroded from the newly forming Pyrenees, at exhumation rates up to 1.5 mm yr$^{-1}$ [Gibson et al. 2007], was deposited in a series of sedimentary basins in front of the mountains. In some cases, these basins were involved in subsequent mountain-building process, being uplifted, recycled and re-deposited further from the mountain front. This proximal deposition and reworking is comparable to the sedimentary processes operating offshore Taiwan. Figure 2.2 shows the current topography of the Pyrenees.

Using guidance from the Prof. J. A. Muñoz at the University of Barcelona [Lopez-Blanco et al. 2003; Falivene et al. 2010], we concentrated our studies in two basins in the South-Central Pyrenees (Figure 2.4, see Figure 4.7 for a geological map showing the metamorphic rocks in the centre of the mountain belt and the series of foreland basins in front of it). The Tremp-Graus basin was formed in the Late Cretaceous as a piggy-back basin on the Montsec thrust sheet [Lopez-Blanco et al. 2003] and contains the Aren sandstone, a predominantly deltaic sequence dated as 76 - 74 Ma [Ardevol et al. 2000]. The most shoreward outcrops of this unit occur east of the town of Tremp; turbiditic deposits can be found up to 100 km further to the west (see Figure 2.4).
Figure 2.2: Topography of the Pyrenees. The Pyrenees lie at the western end of Alpine orogenic belt, several thousand kilometres of mountains formed when Iberia, Africa and India collided with Eurasia.

The Castissent Formation, also within the Tremp-Graus basin, is younger. It forms part of the Eocene Montanyana Group (53 - 44 Ma), and is dated by biostratigraphy using the marine phytoplankton fossil *Discoaster lodoensis* as 51.5Ma [Marzo et al., 1988]. Continued uplift of the Tremp basin is believed to have caused erosion of the Aren formation, leading to recycling of material into the Castissent rocks along with basement sources from the centre of the Pyrenees. Sediment routing systems changed from orogen-parallel in the Late Cretaceous and Palaeocene to orogen-transverse in the Late Eocene [Whitchurch et al., 2011]. This situation may allow us to study multiple depositional cycles within the South Pyrenean system.

Both of these formations contain a range of depositional facies, from terrestrial and proximal marine through to distal basins, along the axis of the foreland basin. This allows extensive lateral sampling, but unlike Taiwan it is not possible to correlate samples to a particular event. Further sampling in the Apennines allows per-bed correlation between
CHAPTER 2. SAMPLE LOCATIONS AND METHODS

Figure 2.3: Sedimentary environments in the Southern Pyrenees. Figure taken from Lopez-Blanco et al. (2003), detailing the range of facies present in the Roda sandstone, a formation similar to and slightly preceding the Castissent formation.

Figure 2.4: Geological Map of the Tremp-Graus basin overlain onto the Topographical map. Sampling locations in the Aren and Castissent formations are shown by red and blue circles respectively.
distant samples.

2.2.3 Apennines

The Marnoso Arenacea formation of the Italian Apennines provides an opportunity to quantify the volume of carbon that can be stored in turbidites. The Miocene sediments of the Marnoso Arenacea range in volume from 3 to 15 km$^3$ per bed, and contain POC eroded from the Alps during the Alpine Orogeny with some recycling of emerging Apennine sediment (Talling et al., 2007a; Chiocchini and Cipriani, 1992). This material generally flowed south in sporadic large flows, constrained within an elongate basin. Occasionally, flows were sourced from a carbonate platform in the South East (Talling et al. 2007b). A particularly thick southern-sourced turbidite, known as Contessa (RicciLucchi and Valmori, 1980) from the early Serravallian (14 Ma) (Lucente, 2004), was used as an index bed in this study, such that stratigraphically identical samples could be collected across a wide field area. In each Apennine locality, samples were collected from the fifth and sixth beds above Contessa as these are very well characterised volumetrically and sedimentologically.

Volumetric calculations from the Marnoso Arenacea (Talling et al. 2007a) show that these turbidites contain large amounts of sediment. Bed 6 above the Contessa has a volume of at least 7.007 km$^3$, probably more due to post-depositional tectonic shortening and erosion in the basin.

2.3 Sample Collection and Preparation

Samples were required that represented both the local-scale heterogeneity within a sample locality, but were also able to represent the large-scale patterns within a basin. For example, field observations showed POC laminations on a mm- and cm-scale, such that particular horizons looked especially rich in organic carbon. These laminations were important to characterise for their TOC and the contributing organic carbon types, yet should not be used to represent an entire locality that might otherwise have been carbon-poor. Thus, where possible, a wide range of samples were collected at each locality, with suitable field observations recorded in each case.

General requirements of the field samples were:
Figure 2.5: Topography of Northern Italy, showing the southern part of the Alps, thought to be the source region for the Marnoso Arenacea turbidites. The field area is shown as a black outline, major sample locations are shown with yellow dots.
Large enough to represent the local sedimentology - about 100 g of material was collected from bedrock sites for later homogenisation.

Location within a sedimentary log was recorded, such that volumetric estimates and grain-size patterns could be investigated later.

Locations within a wider-scale sedimentary system were generally selected to provide the largest range of environments.

Field samples were collected from bedrock outcrops by hammering and drilling. Sample sites were preferentially restricted to sections exhibiting deep excavation for example by road cutting. Drilled samples were preferred due to the consistency of sample size collected, ability to sample from non-weathered outcrop, and lower amounts of preparation work required before further processing. Prior to drilling, rock faces were cleaned using hammers and picks such that the sample site was devoid of vegetation, modern sediment coatings and, where possible, oxidised rock. This often required several centimetres of material to be removed before fresh surfaces could be accessed - once the orange/brown oxidation band had been removed the sample was collected from the grey-coloured sediment behind. Drilled samples were collected using a Hilti TE-7A battery-powered hammer-drill equipped with a 50 mm diameter coring drill bit. The drill tips were coated with tungsten carbide cutting surfaces. The drill bit contained a central guide-bit which provided stability when initiating drilling, once the collar of coring teeth had eaten into the rock face, the guide-bit was removed so that a central hole through the core was avoided where possible. Drilling continued until the drill could no longer make progress, giving samples with a length of 5 to 10 cm. Sometimes the collected core would break-off within the drill bit. When this did not occur, samples were removed from the rock face using a hammer and chisel. The painted surfaces of hammers and chisels were abraded prior to use so that paint did not contaminate the samples.

Hammered samples were collected where it was impossible to find a suitable drilling surface. These ranged in size from a few grammes to over a kilogramme and often contained weathered surfaces which required subsequent cleaning and removal. Once samples were collected they were bagged and labelled.

Fluvial sediment samples in Taiwan were collected by hand (see Figure 2.6). Riverbank deposits of loose sediment or soft mud were picked up and placed into sample bags. Where differences in sedimentology were visible, such as colour or grain size, these were sampled individually.
CHAPTER 2. SAMPLE LOCATIONS AND METHODS

For a full description of offshore core sample methods see Section \ref{offshore_core_methods}. Core samples from typhoon Morakot were split, photographed and cut into 1 cm resolution slices, which were then freeze-dried. 5 g aliquots of selected 1 cm horizons were collected; these horizons were chosen based on variations in grain-size, colour, or by variations in visible POC content.

Once returned to Cambridge, wet samples were dried overnight at 80 °C. Aluminium trays covered by aluminium foil were placed into a fan-assisted oven. After this, weathered surfaces were removed using a water-cooled rock saw. The saw was also used to remove pervasive oxidation after cleaning, in order to check for differences between oxidised and reduced parts of the same sample. After sawing, samples were dried again either on a hot plate (below 100 °C) or in the oven as described before.

Once cleaned, samples were crushed into chips using a Sturtevant jaw-crusher. The chips of rock produced were caught in a plastic tray and transferred to a sample bag, the tray was then cleaned with compressed air. The crusher has removable cast iron.

Figure 2.6: Sampling recent fluvial sediment at location KP4 with Josh West.
crushing plates to enable a thorough clean between uses. After each use, the crushing plates were removed and washed with mains water whilst scrubbing with a paintbrush. After scrubbing, the plates were rinsed with mains water and dried using compressed air. The remainder of the jaw crusher was cleaned with a soft brush after each use, and with compressed air and a vacuum cleaner when necessary.

A Retsch PMP-400 orbital ball-mill grinder was used to homogenise the samples and increase their surface area. Around 50-80 g of crushed sample was placed into a 250 ml agate grinding vessel along with five agate balls. Four pots at a time were loaded into the grinder and milled for 12 minutes at 250 rpm (sun wheel speed). Stainless steel claddings kept the samples cool during grinding. After grinding, the agate balls were removed using a metal spatula, which was also used to scrape off any material adhered to the sides of the grinding vessel before it was emptied into a sample bag. The balls, grinding vessel and lid were then cleaned using mains water and allowed to air-dry. Periodically, and especially if any discolouration of the grinding balls or vessels was seen, clean building sand (likely quartz and feldspar) was ground instead of samples in order to clean the grinding surfaces.

The grain size and surface area of a powdered sample were checked using a Malvern Instruments Mastersizer 2000 laser grain-sizer. Small amounts of powder were suspended in water and passed in front of a laser. The particle size distribution showed a single broad peak; the volume weighted mean particle size ($D_{4,3}$) was 21.2 $\mu$m, with median diameter ($d(0.5)$) of 9.3 $\mu$m. 16 results collected from an older Malvern Mastersizer E instrument showed average values of 13.8 ± 3.62 $\mu$m and 6.49 ± 1.86 $\mu$m (1$\sigma$) respectively. The largest 90th percentile measurements ($d(0.9)$) were 60.2 $\mu$m on the Mastersizer 2000, and 60.64 $\mu$m on the Mastersizer E. These powdered, homogenised samples were then studied using Raman spectroscopy, isotope geochemistry and other techniques.

### 2.4 Spectroscopic Analysis

Several organic petrography techniques exist for studying sedimentary carbon, due to its importance in the oil industry. One of the most common techniques, vitrinite reflectance, is calibrated for low-temperature applications

In order to use Raman spectroscopy to systematically and efficiently determine the source and nature of carbonaceous material in a large number of samples collected from sedimentary deposits and the geological formations from which these deposits were sourced,
several methodological requirements must be met. The sample preparation method must prepare bedrock, coarse-grained fluvial sediment and fine-grained offshore sediment for analysis in uniform fashion. The heterogeneous carbon species present in these samples must all be probed, with enough data collected to represent the distribution of carbon species within a single sample. Some of these carbon types may be present encased within lithic grains. Finally, having collected a large dataset there must be an automated processing system in place to analyse the spectra and report the results. This section will explore previous analysis techniques, and describe a method for sample preparation and spectrum acquisition, fitting, parametrisation and analysis which leads to efficient sample investigation.

2.4.1 Literature Review

All materials with a non-zero temperature vibrate. These vibrations have particular styles and frequencies depending on the material, and are known as phonons. Phonons can exist in a discrete range of excited vibrational states. Both elemental composition and crystal structure cause variations in phonon frequency, such that knowledge of the phonons present in a material can be used for characterisation. Raman spectroscopy is a frequently used technique for doing this.

2.4.1.1 Raman Scattering

Raman spectroscopy is based on elastic and inelastic scattering of light by materials. Monochromatic light, usually sourced from a laser beam, is shone onto the surface of the sample. The majority of this light interacts with the material elastically - phonons are excited by the photons, gaining energy, then relax to their previous state and release a photon with exactly the same energy (hence frequency) as before. This is known as Rayleigh scattering and is not useful in Raman spectroscopy, hence it is filtered out.

A minority of the incoming photons, perhaps one in $10^5$, interact inelastically with the material. When the photon hits the material, the phonon gains energy as before but relaxes to a different vibrational state. Usually this state is higher than the initial state, and as such the subsequently released photon has a lower energy and frequency than the incoming radiation. This process is known as Stokes-scattering (see Figure 2.7). The frequency shifts exhibited by the scattered photons depend on the energy gaps of the phonons, and as such
2.4. SPECTROSCOPIC ANALYSIS

Figure 2.7: Rayleigh, Stokes and Anti-Stokes scattering. Stokes and Anti-Stokes scattering cause a change in the frequency of emitted photos, which can be seen using Raman Spectroscopy. The frequency change is equal and opposite for the two Raman scattering mechanisms, but as Stokes scattering is more common it is the only style that is measured. Rayleigh-scattered photons show no change in frequency and are filtered out.

the location and relative intensities of the photons is characteristic of the sample material.

Occasionally the incoming photons cause phonons to move from more excited vibrational states back to a lower state. This Anti-Stokes scattering produces photons which have more energy and higher frequencies than the incoming radiation (see Figure 2.7). The effect on photon frequencies exactly mirrors the Stokes scattering, and as fewer photons are scattered in this manner the Anti-Stokes scattering is usually ignored. The change in photon frequency is reported in wavenumber units, as these produce values of a convenient magnitude. Raman scattering is usually measured in the range 0 to 3200 cm\(^{-1}\).

\[ wavenumber(\tilde{\nu}) = 1/wavelength(\lambda) \quad (2.4.1) \]

In terms of energy, where \( h \) is the Planck constant,

\[ E[J] = h\tilde{\nu} \quad (2.4.2) \]
2.4.1.2 Raman Spectroscopy equipment

A modern Raman spectroscopy set-up as follows. An optical microscope is used to position and focus the sample. The light pathway is then altered so that laser light shines through the same optics and onto the sample. Thus the laser beam should be perfectly focussed and the target known precisely. The spot-size of the incoming laser light is dependent on the objective magnification, but is of the order 1-5 \( \mu \text{m} \) with a 50\( \times \) lens. Radiation is scattered from the sample in all directions, but that which returns through the microscope is filtered by gratings so that Rayleigh scattered photons are removed. Stokes-scattered photons are diffracted into a spectrometer and the intensities are measured.

The spectrometer measures intensities in a certain window of wavenumbers. If a larger sample range is required, the sample gratings can be dynamically altered to cover the extended range. With the addition of a motorised XY-stage, maps of Raman spectra can be collected by rastering the laser point across the surface, or defocussing the laser beam into a line and scanning this across the sample.

Raman spectroscopy has several advantages over other characterisation methods:

- It is generally non-destructive, although at high laser powers the concentrated radiation can cause sample heating.
- It is a remote technique, able to interact with the sample from working distances ranging from a few mm to a few cm, although the intensity of the radiation decreases with the square of the working distance. If the sample and receiver are separated by a larger distance then optical fibres can be used to transmit the signal.
- It is a local technique, taking measurements from a very small area, especially in comparison to conventional X-ray diffraction.
- It is cheaper than synchrotron-sourced X-ray diffraction.

2.4.1.3 Raman spectra of organic carbon

Organic carbon has been investigated using Raman spectroscopy for over 40 years. Tuinstra and Koenig [1970] produced spectra from a range of materials, including graphite, charcoal and black carbon. Pure crystalline graphite has an atomic arrangement of linked sheets of
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Figure 2.8: Atomic vibrations in graphite and carbon, giving rise to G and D peaks. The G peak is due to bond-stretching of pairs of sp² atoms, while D is a “breathing mode” as hexagonal rings expand and contract. This figure from Ferrari and Robertson (2000) shows the proposed A₁g breathing mode for the D peak, although this has since been questioned by several authors (Ferrari, 2007).

hexagonally-arranged carbon atoms. This structure can only vibrate in one way, by bond-stretching of pairs of sp² atoms (see Figure 2.8). This single vibration leads to one peak in the 800 - 2000 cm⁻¹ region, at around 1580 cm⁻¹. Further peaks appear in the range 2500 - 3000 cm⁻¹, with their nature changing as the number of graphene layers within the sample increases.

Semi-graphitised materials produce a Raman peak at 1350 cm⁻¹, the D₁ peak, which decreases in amplitude and width with increasing order. The D₁ peak is formed by the expansion and contraction of hexagonal rings of carbon atoms in a so-called “breathing” mode, which is not permitted in fully-crystalline graphite. The peak was initially attributed to the “A₁g” breathing mode (Tuinstra and Koenig, 1970), but has since been suggested to be a doubly-resonant longitudinal oscillation (Thomsen and Reich, 2000; Ferrari, 2007). This peak is sensitive to excitation frequency, lowering its wavenumber with increasing incoming wavelength (Mernagh et al., 1984; Thomsen and Reich, 2000).

A further three disorder peaks, D2, D3 and D4, appear with increasingly disordered
carbonaceous material (Beyssac et al., 2002a; Lahfid et al., 2010). The 1620 cm\(^{-1}\) D2 peak combines with and dominates the crystalline-graphite G peak (1580 cm\(^{-1}\)) in highly disordered material, forming a single “G band”, while the D3 and D4 peaks are minor components which sit at 1500 cm\(^{-1}\) and 1150-1250 cm\(^{-1}\) respectively in the most disordered material.

As well as showing qualitatively the progression of Raman spectra for carbonaceous material in a range of metamorphic rocks, Wopenka and Pasteris (1993) have discussed a range of methods for preparing such samples for Raman analysis. Producing flat specimens by polishing was shown to mechanically introduce severe defects to graphite crystals, making them appear more disordered (Beyssac et al., 2003a). Instead, the recommended procedure is to probe carbonaceous flakes within a thin section through an overlying transparent mineral, preventing abrasion during polishing. This method has been used in subsequent studies (Beyssac et al., 2002a, 2003a; Barrenechea et al., 2009; Quirico et al., 2005), despite increased labour requirements. One disadvantage is that the spectrum of a crystal can be orientation-dependent, and graphite crystals are usually sampled perpendicular to basal planes. This requires that the thin-section is rotated so that the graphite crystal is in the correct orientation.

To further characterise the Raman spectra of carbonaceous material, the area ratios of the various peaks have been used to determine the grade of crystallinity (Beyssac et al., 2002a, 2003a). For highly crystalline material, where only the G, D1 and D2 peaks are significant, the “R1” and “R2” ratios have been defined:

\[
R1 = \frac{D1_{\text{height}}}{G_{\text{height}}} \tag{2.4.3}
\]

\[
R2 = \frac{D1_{\text{area}}}{G_{\text{area}} + D1_{\text{area}} + D2_{\text{area}}} \tag{2.4.4}
\]

R2 has been calibrated for peak temperature using metamorphic minerals (Beyssac et al., 2002a). Perfectly-graphitised crystals have \(T = 645 \, ^\circ\text{C}\).

\[
T(\circ\text{C}) = -445 \times R2 + 641 \tag{2.4.5}
\]

However, R2 measurements saturate above \(~0.6\) (metamorphic temperatures below
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∼374 °C). The RA1 and RA2 measurements are applicable for more disordered material and can be applied to spectra containing G, D1, D2, D3 and D4 peaks. Temperature calibrations are still in development, but a correlation has been published along with a fitting procedure (Lahfid et al., 2010).

\[ RA1 = \frac{D_{1\text{area}} + D_{4\text{area}}}{G_{\text{area}} + D_{1\text{area}} + D_{2\text{area}} + D_{3\text{area}} + D_{4\text{area}}} \]  

(2.4.6)

\[ RA2 = \frac{D_{1\text{area}} + D_{4\text{area}}}{G_{\text{area}} + D_{2\text{area}} + D_{3\text{area}}} \]  

(2.4.7)

\[ T(°C) = \frac{RA2 - 0.27}{0.0045} \]  

(2.4.8)

![Figure 2.9: The effect of grinding on graphite crystallinity, from Nakamizo et al. (1978), plotting R1 against grinding time. For short-period grinding, as carried out in this study, there is a negligible change in disorder.](image)

Release of graphite from sediments by grinding, and subsequent analysis of the powder, has potential for rapid acquisition of spectra, when compared to the thin-section method. After grinding, a homogeneous, well-mixed sample is produced. However, the effect of grinding on the structure of graphite crystals and disordered carbon must be minimal to preclude systematic bias. Nakamizo et al. (1978) investigated the introduction of disorder to graphite crystals by grinding in air using an agate mortar. They found that grinding for many hours can introduce disorder peaks at 1350 and 1620 cm\textsuperscript{-1}. However, grinding periods of less than one hour did not significantly alter the Raman spectra of the graphite samples (Figure 2.9). Similar work by Crespo et al. (2006) corroborated this finding using Raman spectroscopy, XRD and HRTEM to show that the crystallinity of high-grade
graphite was unchanged after up to 120 minutes of grinding. Neither of these studies con-
sidered the effects of grinding on disordered or semi-graphitised material. This has been
investigated for this study, to justify the use of ground material (see Section 2.4.7).

2.4.2 Spectrum collection

Raman spectra were collected using a Renishaw Ramascope-1000 or Renishaw InVia Ra-
man spectrometer. One spatula (~0.25g) of material was pressed between glass slides to
produce a flattened sample area with 2 cm diameter. Within this sample area, 10-20 flakes
of POC were usually found using a 50 times magnification objective lens. The smallest
particle sizes analysed were approximately 2-3 µm. Sub-micron kerogen constituents, for
example mono-molecular films on clay particles, were not studied with this method. Their
presence or absence, and relative importance compared to discrete microscopic and macro-
scopic POC, cannot be estimated when using Raman spectroscopy in this manner. The
process of flattening between slides tends to align graphite flakes with the sample surface,
meaning that the laser beam is incident perpendicular to the basal planes. Measurements
were taken using a 514 nm Ar-ion laser, chosen to maintain comparability with previous
studies (Beyssac et al., 2002a) and set to 0.75 - 1.88 mW for 30 seconds to avoid dam-
aging the target. The open-air nature 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$^{-1}$. Where possible, collection of spectra
continued until at least ten spectra with a signal-to-noise ratio greater than 3 had been
found, however on some samples less than ten suitable spectra could be collected.

2.4.3 Peak Fitting

Spectroscopic peaks are often fitted best using Voigt profiles, which are a combination of
Lorentzian and Gaussian broadening behaviours. Gaussian fits alone do not accommodate
sufficient peak-broadening, while Lorentzian peaks can lead to excessively broad peaks.
Beyssac et al. (2003b) describe a peak-fitting method for semi- and highly-graphitised
material. In this procedure Voigt profiles are fitted to three peaks: G, D1 and D2. A
linear baseline is removed from each sample, as background intensity tends to increase with
wavenumber. This technique was calibrated for metamorphic burial temperatures above
360 °C. Beyssac et al. (2002a) compared Voigt-fitted spectra of a selection of rocks from
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the Schistes Lustrés in the Western Alps and the Sanbagawa metamorphic belt in Japan to
metamorphic temperatures calculated from various mineralogical constraints (rock facies,
Fe-Mg partition coefficients).

Increasingly disordered material has larger peak widths, for which the broad Lorentzian
profile is a good match. A second fitting procedure, designed for fitting spectra from more
disordered material, was described by Lahfid et al. (2010). This fitting routine fits Raman
peaks with five Lorentzian distributions, covering typical ranges for G, D1, D2, D3 and D4.
In their procedure, Lorentzian distributions were chosen rather than Voigt distributions to
reduce the degrees of freedom available when fitting, as the multi-parameter approach of
Voigt fitting produced unstable fits.

Two automatic fitting routines have been created using the software “GNUPlot”. The
first routine is based on the Beyssac et al. (2002a) fitting procedure. Three Voigt peaks are
fitted, with a linear baseline. 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 2.2 whilst amplitude is
allowed to vary without limit. The Voigt profile is defined as:

\[
V(x; \sigma; \gamma) = \int_{-\infty}^{\infty} G(x'; \sigma) L(x-x'; \gamma) \, dx, \tag{2.4.9}
\]

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 (HWHM) of
the Lorentzian function. This function is computationally complicated, and GNUPlot uses
a rapid approximation of the Voigt profile, accurate to one part in 10^4 (Wells, 1999). Thus
the function fitted is:

\[
f(x) = \sum_i \text{area}_i \times \text{voigt}(x - \text{location}_i; \text{width}_i)_{i=\text{peaksG,D1,D2}} + mx + c \tag{2.4.10}
\]

Where \text{width} is the half-width at half-maximum of the peak and \text{voigt}(x; \text{width}) is
the inbuilt Voigt profile function. \(m\) and \(c\) refer to the gradient and intercept of a linear
background signal fitted concurrently. Peak height is calculated as the value of this function
when \((x - \text{location}) = 0\).
The second routine is based on the Lahfid et al. (2010) method, and fits five Lorentzian peaks. 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 (see Figure 2.10). The peak amplitudes are again free to vary unrestricted, while peak widths and locations are fixed within certain ranges, as defined in Table 2.1. The equation for fitting Lorentzian profiles is:
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\[ f(x) = \sum \text{height}_i \left( \frac{\text{width}_i^2}{(x - \text{location}_i)^2 + \text{width}_i^2} \right) + mx + c \quad (2.4.11) \]

The area below a Lorentzian profile is:

\[ \text{area} = \text{height} \times \pi \times \text{width} \quad (2.4.12) \]

Where \text{width} is HWHM, \text{height} and \text{location} refer to the peak maximum, \pi is the ratio of the circumference to the diameter of a circle. Fitting results are reported in terms of full-width at half maximum (FWHM).

Both of these procedures are able to fit spectra rapidly with minimal residual intensity (the difference between the input spectra and the fit). The fitting procedure was iterated until the change in residual from one iteration to the next was less than \(10^{-9}\) of the total residual.

2.4.4 Peak Fit Parameters

To resolve differences within populations of graphite and disordered carbon, samples were characterised using a variety of parameters. The R1 and R2 measurements, applied to Voigt-fitted spectra, characterise intermediate- and high-grade graphite (Beyssac et al., 2002a). The RA1 and RA2 measurements are being developed for low-grade carbonaceous material (Lahfid et al., 2010) and have been supplemented with another parameter, the sum of peak widths, in order to differentiate between alternate forms of disordered carbon.

Peak fitting procedures have been calibrated using a selection of hand-fitted spectra (Beyssac Pers.Comm.) covering a wide range of carbon morphologies. For these spectra, peak locations were picked manually before PeakFit® software fitted curves to these peaks. A linear background correction was also chosen by the operator. Figure 2.11 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 0.95:1 relationship and R2 values in excess of 0.925. For the Voigt procedure, R1 values correlate with a 1.004:1 relationship and R2 = 0.999, while R2 values have a
Table 2.1: Input and fitting constraints when fitting Raman spectra with Lorentzian profiles.

<table>
<thead>
<tr>
<th>Peak Height</th>
<th>Initial Height Range</th>
<th>Initial Location Range</th>
<th>FWHM Constraints</th>
<th>Constraints when fitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>1200-1450</td>
<td>1300-1400</td>
<td>72</td>
<td>From data</td>
</tr>
<tr>
<td>D2</td>
<td>1500</td>
<td>1475-1525</td>
<td>100</td>
<td>From data</td>
</tr>
<tr>
<td>D3</td>
<td>1250</td>
<td>1200-1250</td>
<td>150</td>
<td>From data</td>
</tr>
</tbody>
</table>

Table 2.2: Input and fitting constraints when fitting Raman spectra with Voigt profiles.

<table>
<thead>
<tr>
<th>Peak Height</th>
<th>Initial Height Range</th>
<th>Initial Location Range</th>
<th>FWHM Constraints</th>
<th>Constraints when fitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>1200-1450</td>
<td>1300-1400</td>
<td>12.7</td>
<td>From data</td>
</tr>
<tr>
<td>D2</td>
<td>1605-1640</td>
<td>1610-1625</td>
<td>2.2</td>
<td>From data</td>
</tr>
<tr>
<td>D3</td>
<td>1610-1640</td>
<td>1605-1640</td>
<td>17</td>
<td>From data</td>
</tr>
</tbody>
</table>
2.4. SPECTROSCOPIC ANALYSIS

Figure 2.11: Comparing manual and automated fitting procedures on a collection of reference spectra from New Zealand and the Alps. These were supplied and manually peak-fitted by Beyssac, and the automated fitting procedure tuned such that the difference between results was minimised, producing the parameters shown in Tables 2.2 and 2.1. A 0.91:1 relationship and R² value of 0.991. The advantage of using an automated procedure for this type of analysis is twofold. Firstly, the analysis requires only computation time. Spectra and analysis graphs can be produced automatically as new data is collected, or if it is decided to perform the peak analysis differently, without requiring large amounts of time spent re-fitting peaks by hand. Secondly, there is no bias introduced through “looking” for peaks, each spectrum has been treated in exactly the same manner. This eliminates differences in operator skill or technique and removes subjectivity. Reproducibility of results should be enhanced by this method, even if fitting precision is slightly worse than manually-fitted peaks. This allows for consistent comparison between sample sets.

Variations in peak widths were also used to parameterise the spectra. For each fitted spectrum, the sum of G, D1 and D2 widths was recorded. Although spectroscopically this is an unusual parameter to measure, it is useful for determining the amount of disorder in a sample. Graphitic spectra have very narrow G bands, and minimal D bands, low-grade metamorphic carbon has moderately wide G and D bands, whilst lignite and other
very disordered material has extremely wide D bands, leading to a large “Total Width”
measurement.

It is important to select the correct fitting procedure. Applying the Voigt fit to disor-
dered material, or the Lorentzian fit to highly-graphitised material, leads to a poor fit and
an incorrect parameterisation. In order to choose the correct procedure automatically, the
following workflow was followed. In the first instance, spectra were fitted with the Voigt
procedure, as this is computationally more efficient and can fit low-temperature material
as well as graphitised carbon, albeit with less precision. The results of this fit were anal-
ysed and if the R2 value was below 0.6, and the D1 peak width was 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 R1 > 0.5 then the Lorentzian fit was applied. The RA2
value was then calculated from this fit. If RA2 was greater than 2, the maximum value
measured by Lahfid et al. (2010), then the degree of order was reasonably high and the
procedure reverted back to the Voigt fit. Each spectrum was then characterised using two
parameters, the estimated peak metamorphic temperature as calculated from the R2 or
RA2 value (as applicable) and the sum of the peak widths for G, D1 and D2.

2.4.5 Carbon Classification

![Graphitic reference samples](image)

Figure 2.12: Parameters from graphitic spectra supplied for reference by Beyssac. The
raw spectra were analysed using the peak fitting procedure and plotted in Total Width vs.
Temperature space.
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Figure 2.13: Parameters from low-grade metamorphic spectra supplied for reference by Beyssac. The raw spectra were analysed using the peak fitting procedure and plotted in Total Width vs. Temperature space.

Figure 2.14: Raman spectra from sample 17 in the Plio-Pleistocene formations of Taiwan (see Section 3.5), plotted in Total-width vs. Temperature space. These spectra were collected from a large piece of lignite and are representative of woody material that has not undergone any significant metamorphism. Temperature estimates in the upper grey box are meaningless as they are outside the published range of spectral properties.
This workflow leads to three groups of spectra when plotted as temperature (from R2 or RA2) vs. Total Width. Highly-graphitised material has a low total width and high temperature. Semi-graphitised and disordered materials have low temperatures, but the former have intermediate and the latter high total widths. Those which were fitted with the Voigt procedure and have a temperature of more than 360 °C have experienced significant metamorphic conditions. The total peak width parameter (G1 + D1 + D2 widths) varies, reaching up to 250 cm$^{-1}$ in the graphitic spectra (see Figure 2.12). Those fitted with the Lorentzian procedure are less metamorphosed - the RA2 values published by Lahfid et al. (2010) cover temperatures as low as 160 °C - and in some cases are little more than charcoal or lignite-grade material which has not experienced any real metamorphism. The total peak width distinguishes between these two groups - total widths are lower in low-grade metamorphic samples than lignite and other extremely disordered material. Temperature estimates for these extremely disordered samples are meaningless, the method simply distinguishes these from semi-ordered material. See Figure 2.13 for examples of low-grade metamorphic material, and Figure 2.14 for examples of very disordered material.

By inspection of the fitting results, low-grade metamorphic material has a total peak 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 total width against temperature, spectra from each sample fit into one of three regions. Figure 2.15 shows a collection of spectra from a sample collected just offshore Taiwan, plotted in this fashion.

### 2.4.6 Geological vs. atmospheric samples

The presence of fine graphitic particles within sediments need not be due to erosional processes. Forest fires and anthropogenic combustion can produce soots and other fine carbonaceous particles which could be incorporated into sediments, especially offshore. To investigate this, a published spectrum of atmospheric carbon (Mertes et al., 2004) was analysed using both Voigt and Lorentzian fitting routines (Figure 2.16). The atmospheric carbon is clearly different to both disordered and graphitic material found in sedimentary rocks, giving an RA2 value greater than 6 having a D band taller than the G band, unlike the geological samples (Figure 2.17).

![Raman spectra](image)

Figure 2.16: Raman spectra collected by Mertes et al. (2004) from atmospheric carbon, black carbon (labelled as Monarch 71) and graphite. Note that the horizontal axis is reversed compared to those plots in the rest of this thesis.
2.4.7 Effects of grinding and the utility of sample homogenization

To assess the effect of grinding on the structure and relative abundance of different types of carbonaceous material in the samples, results for ground and un-ground aliquots of samples KP2A and KP3B from the Gaoping River, Taiwan, were compared (see Figure 3.1 for locality information). Figure 2.18 shows a comparison of Lorentzian fitting results plotted as RA2 temperature against total width. 8 data points collected from powdered sediment have average temperature and total width values that lie within one standard deviation of the equivalent average for 5 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 material. Both sets of spectra show a slight but statistically insignificant increase in total width after grinding. In sample KP3B there was no effect on the estimated temperatures at all, in sample KP2A the average peak temperature estimate was reduced by 25 ‰ but the ground and un-ground samples are still within one standard deviation. These results demonstrate that grinding has not introduced significant disorder into the samples. Although multiple grinding times and methods were not tested, it is anticipated that any grinding procedure which reduces grain sizes to the 10 µm range can be applied without significant effect on the structure of carbonaceous material in geological
2.4. SPECTROSCOPIC ANALYSIS

Figure 2.18: Comparing the Raman spectra of ground and un-ground sediment. In each sample, a collection of grains were measured for their RA2 temperature and Total Width. Averages were calculated, with one-sigma error bars. There does not seem to be a significant deviation when samples are ground for 12 minutes in an agate mortar.
and environmental samples.

Grinding the samples had significant methodological benefits. Collection of spectra from powder was much easier, as the sample could be flattened before examining for carbon particles. This removed the depth-of-field effect of the high-magnification lens, whereas sampling sediment directly required constant manual refocusing of the microscope. Moreover, grinding can break up larger sedimentary grains, also known as lithic fragments, releasing encased graphite grains that would otherwise have remained invisible, but this has not been directly observed.

2.5 Elemental / Isotopic Analysis

2.5.1 Introduction

Section 1.2.2 describes the isotopic composition of organic material relevant to this study. Hilton et al. (2010) describe a method of sample preparation and analysis when studying POC. With a few alterations, this was the procedure used in this study. The method consists removal of carbonate from the samples and analysis via isotope-ratio mass spectrometry, followed by endmember unmixing calculations to separate the various types of carbon present in the samples.

2.5.2 Data collection

Samples were prepared for isotopic / elemental analysis using the method of Hilton (2008) and Hilton et al. (2010). Carbonate removal is required because combustion within the elemental analyser would decompose carbonate minerals and release inorganic CO$_2$. The possible presence of dolomite in the sediment samples means that leaching with hot acid is required (Galy et al., 2007a). This process will remove a portion of the organic carbon, some 14 to 19% in river sediments, yet is unavoidable. Powdered samples were decarbonated with hydrochloric acid. 0.9-1.1 g of sample was weighed into a glass beaker. 21.3 ml of de-ionised water was added to the powder, and it was ensured that the powder was well-mixed with the water. This was usually achieved during the addition of the water, but occasionally glass rods were used to stir. In a fume cupboard, 2 ml of 11.65 N HCl was added to the beaker, giving 1 N acid, and a watch-glass placed on top.
2.5. ELEMENTAL / ISOTOPIC ANALYSIS

The beaker was left on a hot plate at 80 °C for 3 hours. Elevated decarbonation temperatures should lead to complete dissolution of dolomite. After removal from the heat source the acid solution was pipetted from the beaker and replaced with 40 ml of de-ionised water to rinse. The suspension was allowed to settle at which point the liquid was removed and replaced two more times. After the third rinse with de-ionised water, the samples were dried overnight in an oven at 80 °C. The decarbonation process led to the formation of an organic-rich scum at the top of the liquid in some cases. This was also reported by Hilton et al. (2010), who found that the remaining organic carbon consists only of the more recalcitrant species. Therefore there is likely to be a disproportionate loss of marine organic matter, which tends to be more labile. To suppress this bias, the molarity of the acid used during decarbonation was kept to a minimum. The dilution gives an acid strength of 1N. Tests with various acid concentrations showed that this volume and concentration is sufficient to remove carbonate from the samples, whilst minimising the inevitable loss of some organic matter.

![Graph](image)

Figure 2.19: The effect of decarbonation on isotopic composition. Removal of carbonate minerals from samples leads to a lowering of $\delta^{13}C$ after acid leaching. No effect is seen on nitrogen isotopic composition.

Whilst acid leaching was necessary to remove inorganic carbon, its effect on isotopic values was also considered by analysing particularly carbon-rich samples with and without a leaching stage. Figure 2.19a shows that acidification was necessary even in organic rich samples, as the presence of carbonate with higher $\delta^{13}C$ is seen to be lost on leaching. When considering nitrogen isotopes, there is no systematic change after acidification (Figure 2.19b). Dried decarbonated samples were scraped from the beaker into glass vials and homogenised by grinding with a glass rod. Approximately 20 mg of decarbonated powder was weighed into a tin capsule. This was reduced for POC-rich samples.
Weight percent organic carbon (TOC; %) and nitrogen (TN; %) and stable carbon isotopes ($\delta^{13}$C; ‰) and stable nitrogen isotopes ($\delta^{15}$N; ‰) were determined by EA-IRMS following Hilton (2008) and Hilton et al. (2010).

A single sample was combusted in oxygen using a Costech CHN elemental analyser (EA) to produce both CO$_2$, NO$_x$ and N$_2$ gases. The volume of gas produced was compared to that produced by four standard samples of Acenanilide (containing 71.90 % C and 10.36 % N), which when combined with the sample mass allows TOC and TN to be calculated. The four standard runs allowed for internal calibration and blank correction. Isotopic compositions were measured using a Delta V isotope ratio mass spectrometer (IRMS). Between the EA and the IRMS, a gas chromatography column (GC) separated the CO$_2$ and N$_2$ into separate pulses and a CONFLO-III interface introduced two pulses of references gases of known isotopic composition. Before each run, two standards were used to calibrate the isotopic measurements and calculate an internal blank. These were caffeine and USGS40, and the results of the standard runs were used to calibrate each subsequent sample measurement. The instrumental precision was below 0.1 ‰ for both isotope ratios.

![Histogram of nitrogen amplitudes](image)

Figure 2.20: A histogram of measured nitrogen amplitudes, showing that several samples produced small peaks of less than 600 mV.

The measured peak height for these samples was less than ideal, but limited by the low TOC and TN of the samples in question. 1000mV or higher is ideal for accurately
2.5. ELEMENTAL / ISOTOPIC ANALYSIS

Figure 2.21: A plot of nitrogen isotopic composition against peak area and 1/peak area showing no systematic trend in isotopic composition with very low nitrogen concentrations.

calculating isotopic ratios, however whilst average measurement peaks were 5000mV for carbon, they were only 500mV for nitrogen. The amount of material that could be loaded into the EA was limited by the amount able to undergo complete flash combustion, about 20 mg. In OM-poor samples this led to small measurements of less than 100mV for nitrogen concentration. These measurements are less reliable since the height of the measured peak is very dissimilar to the reference gas peak. Approximately two thirds of samples produced peaks lower than 500mV for nitrogen (see Figure 2.20). However, given the restrictions on sample volume, this problem is unavoidable with this experimental set-up. Hilton (2008)
investigated the effect of peak size on reported nitrogen isotopic composition and found that small peaks (greater than 20 Vs) did not adversely affect the measurements significantly, this corresponds to 500 - 600 mV amplitude, so the nitrogen isotopic composition of several samples requires careful consideration. Plotting isotopic composition against peak area (Figure 2.21) shows that there is no trend in isotopic composition with low-volume samples, which suggests that there is no systematic effect affecting small samples.

Radiocarbon measurements of selected aliquots of modern sediment samples from Taiwan were made by Dr Xiaomei Xu at the University of California, Irvine, by Accelerator Mass Spectrometry on prepared graphite samples.

2.5.3 Carbon Concentration Correction

When reporting POC concentrations the measured carbon concentration can be affected by dissolution of carbonate during sample preparation, and ignoring this event can lead to systematically biased POC concentration measurements. Whether this is taken into account depends on the type of carbonate present in the samples, specifically whether it is due to carbonate grains or a diagenetic cement. A carbonate rich sample will report higher POC concentrations than a carbonate poor sample with the same initial wt % POC, as the POC will be a proportionally larger part of the remaining material. If the carbonate content is due to sedimentary grains, then the lost material should be considered as part of the sediment in the sample and corrected for. If not, and it is simply a cement that formed diagenetically, then in some situations this correction is not necessary, such as if comparing like-for-like with a modern, non-cemented sample. If the correction is required, the equation required is:

\[
[TOC]_{Corrected} = [TOC]_{Measured} \times (1 - \text{ProportionDissolved})
\]  

2.5.4 Data analysis

The potential contributors to TOC in offshore sediment samples are marine carbon, contemporary terrestrial organic matter (a mixture of woody debris, vegetation and soils, which can be grouped together as POC_{terrbio}), low-grade sedimentary carbon and highly metamorphosed fossil carbon. It is useful to be able to quantify the proportions of these
carbon types within each sample. Hilton et al. (2010) described a method of discriminating between “fresh” (POC\textsubscript{terrbio}) and “fossil” carbon based on N/C and $\delta^{13}$C measurements. A linear range of fossil carbon compositions can be dealt with. Coupled carbon and nitrogen measurements give four readings for each sample, TOC, TN, $\delta^{13}$C and $\delta^{15}$N, which allows for multiple endmembers to be differentiated.

Figure 2.22: Hilton et al. (2010) method for unmixing organic carbon into fresh and fossil components. The “three endmember mixing” technique deconvolves a sample with composition X into a non-fossil (nf) component and a range of fossil components lying along a mixing line. The proportion of fossil and non-fossil carbon is calculated using the lever rule, based on the location relative to the non-fossil point and the mixing line.

In terrestrial rivers draining high-grade metamorphic lithologies, a binary mixing calculation can be constructed based on mixing between POC\textsubscript{terrbio} and fossil carbon (Hilton et al., 2010). Given a mixing line of fossil carbon compositions, generally with higher N/C ratios and/or $\delta^{13}$C isotopic compositions than POC\textsubscript{terrbio}, a measured sample composition can be placed on a mixing line constructed between a defined POC\textsubscript{terrbio} composition and the measured range of fossil compositions. Extrapolation from POC\textsubscript{terrbio} through the sample composition to the fossil mixing line creates a “dynamic” fossil endmember. Linear mixing calculations in $\delta^{13}$C - N/C space can then be carried out (see Figure 2.22).
CHAPTER 2. SAMPLE LOCATIONS AND METHODS

For this study, an automated script for carrying out this analysis was developed (see Appendix A.2), which was used in the Pyrenees and Apennines with POC$_{terrbio}$ and fossil compositions chosen based on the collected data. Endmember choices for this analysis are very important, as discussed in Section 6.1.5.1 Hilton et al. (2010) used the trend of results from bedload combined with $^{14}$C data to define endmembers. In this study, endmember values were chosen from POC-rich samples, published fossil carbon compositions and the full range of analysed sample compositions.

Marine material is a potentially important component in foreland basin sediments. Whilst nitrogen isotope measurements did not produce any remarkable results, there was no trend observed between or within the study areas, the variation of nitrogen isotopic values allowed an additional term to be considered when estimating the contributions to marine sediments (see Appendix A for $\delta^{15}$N values). To perform this analysis quickly and automatically, multi-component unmixing calculations were carried out, where marine carbon could be deconvolved from POC$_{terrbio}$ and POC$_{fossil}$. $^{14}$C measurements in some Taiwanese samples enhanced this process and allowed further deconvolution of POC$_{terrbio}$ into younger and older material. When considering three variables a maximum of four endmembers can be separated. Two fossil compositions are required, to cover a range of TOC concentrations and nitrogen isotopic values, and marine carbon must be considered as well, thus some potential inputs must be joined together. The composition of endmembers for deconvolution were determined in many ways.

Analysis of lignite-grade clasts from the Plio-Pleistocene Cholan formation in western Taiwan gives $\delta^{13}$C = -27.2 ‰, $\delta^{15}$N around 3.5 ‰ and N/C ratio = 0.011, analysis of fresh vegetation from floodplain deposits gives $\delta^{13}$C = -26.84 ‰, $\delta^{15}$N = -3 ‰ and N/C = 0.013. Fresh woody material can show a wide range of $\delta^{13}$C values (Hilton et al., 2008b), the defined value is based on a mixture of woody debris, leaf litter and soil carbon. As such inputs of modern POC$_{terrbio}$, representing CWD, leaf tissue, roots soil carbon, were amalgamated with sedimentary lignite-grade material to make a representative of modern or recently buried biomass. When using $^{14}$C measurements, five endmembers can be considered and therefore modern POC$_{terrbio}$ was differentiated from Plio-Pleistocene age sedimentary carbon by the $^{14}$C composition, 0 ‰ and -1000 ‰ respectively, and varying nitrogen isotope ratios.
Fossil carbon can show a range of compositions in rivers (Hilton et al., 2008b) but for a given catchment mixing during transport to the sea seems to result in a constant $\delta^{13}C$ and N/C ratio. However a range of $\delta^{15}N$ values were required in order to balance the mixing calculations, these ranged from 2.5 to 5 based on readings taken by Hilton et al. (2010) on bedrock samples. Bedrock $\delta^{13}C$ and N/C values from Taiwan are variable (Hilton et al., 2010) but the homogenising action of the Gaoping River means that a single composition can be used. Inspection of core material found some samples with a coarse grained, slaty appearance and no visible POC clasts. One particular sample, K12-17, with the largest N/C value, was used as the fossil carbon endmember as it seems to have negligible POC$_{terr.bio}$ and marine carbon.

Marine carbon around Taiwan has been investigated by Kao et al. (2003), who found that the N/C ratio in mid to outer shelf settings approached the the Redfield ratio of 15 atom% (17.6 wt%) (Redfield, 1958), whilst coastal sites contained some terrestrial POC with lower N/C values. $\delta^{13}C$ values of -18 \permil were used to define marine carbon isotopic compositions, as it is the upper bound measured by Hofmann et al. (2000). Shelf sediment offshore Taiwan has carbon isotopic values as high as -19.6 \permil (Kao et al., 2003) and this will likely contain some fine-grained terrestrial material. Fluvial or lacustrine production of marine-style POC should be a minor component of flood-sourced POC, and the limited number of available endmembers means that it cannot be individually quantified. Zigah et al. (2012) measured isotopic values of POC filtered from a lacustrine water column and found very depleted $\delta^{13}C$ values, comparable to terrestrial biomass or resuspended sedimentary organic matter. They concluded that autochthonous production within the lake was not the major source of POC, and therefore any terrestrial aquatic productivity in this study is likely to be small in comparison to other POC sources.

Exact compositions of each endmember were tuned manually until no component produced negative inputs to the dataset, and until fluvial material contained no marine carbon. The method is not overly sensitive to endmember compositions. Changes of more than 1 \permil in $\delta^{13}C$ and 5 \permil in $\delta^{15}N$ produced results within 0.05 \permil TOC for each component. Automated iterative sensitivity analysis was not carried out. Each endmember was assumed to remain constant during erosion, transport and burial, since adjusting endmember compositions based on the location within a sedimentary system and inferred diagenetic history would have added significant complexity to the calculations.

The four (five when $\Delta^{14}C$ can be used to differentiate between modern and ancient vegetation) endmembers were differentiated using simultaneous mixing equations:
CHAPTER 2. SAMPLE LOCATIONS AND METHODS

<table>
<thead>
<tr>
<th>End member</th>
<th>C (wt%)</th>
<th>N (wt%)</th>
<th>$\delta^{13}C$ (%o)</th>
<th>$\delta^{15}N$ (%o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil 1</td>
<td>0.466</td>
<td>0.133</td>
<td>-23.63</td>
<td>5</td>
</tr>
<tr>
<td>Fossil 2</td>
<td>0.117</td>
<td>0.033</td>
<td>-23.63</td>
<td>2.46</td>
</tr>
<tr>
<td>Woody Debris</td>
<td>60</td>
<td>0.9</td>
<td>-27</td>
<td>1</td>
</tr>
<tr>
<td>Modern marine matter</td>
<td>40</td>
<td>6.68</td>
<td>-18</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2.3: Endmembers used when un-mixing carbon species using stable isotopes and elemental concentrations.

\[
TOC_{sample} = \sum f_i \times TOC_i \quad (2.5.2)
\]

\[
TN_{sample} = \sum f_i \times TN_i \quad (2.5.3)
\]

\[
\delta^{13}C_{sample} \times TOC_{sample} = \sum f_i \times \delta^{13}C_i \times TOC_i \quad (2.5.4)
\]

\[
\Delta^{14}C_{sample} \times TOC_{sample} = \sum f_i \times \Delta^{14}C_i \times TOC_i \quad (2.5.5)
\]

\[
\delta^{15}N_{sample} \times TN_{sample} = \sum f_i \times \delta^{15}N_i \times TN_i, \quad (2.5.6)
\]

where \( i \) represents each endmember being considered. Multiplying \( f_i \), the fraction of each component in the sample, with \( TOC_i \), the carbon content of that sample, gives the carbon contribution of each endmember to the sample. The endmember compositions were tuned to the dataset such that no component was calculated as having a negative input to a sample. The uncertainty associated with each result is approximately 0.1 wt % carbon, such that a component contributing less than this may not be present at all (see Section 3.4.1.1).

Consideration of the applicability of these two methods to different sedimentary settings is discussed in Section 6.1.5.
Chapter 3

Modern system - Gaoping River and Canyon

3.1 Introduction

Before considering the fate of organic carbon over long periods, it is necessary to build an understanding of the harvesting, routing and deposition of organic carbon in a contemporary fluvial-marine sedimentary system. This chapter will characterise a series of organic carbon types present in eroded orogenic material, and identify their contributions to a range of sedimentary facies during normal and extreme conditions. The Gaoping River and Canyon in south-western Taiwan is used as a case study in order to assess the nature of the organic matter eroded from a mountain belt, and its burial locations offshore. An extreme meteorological event, Typhoon Morakot in 2009, provided an opportunity to study the carbon export of a system undergoing intense erosional flux, conditions that can later be applied to ancient sedimentary systems.

A combination of fast tectonic shortening (80 mm yr$^{-1}$, (Yu et al., 1997)) and frequent typhoons means that Taiwan exports a large amount of terrestrial sediment into the ocean. As the island is situated within the biologically productive tropical belt, within the sediment are large amounts of organic carbon in various forms. These include “fresh” POC$_{terrbio}$, harvested from soils and standing biomass on hillslopes and floodplains, and several types of POC$_{fossil}$, eroded from exposed bedrock on the island. Work on the LiWu River in NE Taiwan by Hilton et al. (2008b) showed that mobilisation of POC$_{fossil}$ from
Figure 3.1: A topographic and bathymetric map of Taiwan, showing the catchment and tributaries of the Gaoping River, the location of samples and the exposure of the Plio-Pleistocene Cholan and Tuokoshan formations.
landslide deposits occurs throughout the year, and that large rainfall/flood events add POC$_{\text{terrbio}}$ to the suspended load. Clastic sediment concentration in rivers increases by two orders of magnitude during storms, leading to an increase in fluid density and the formation of hyperpycnal flows and turbidity currents, which can quickly and efficiently transport river suspended material into marine basins. The combination of high carbon concentrations and high deposition rates means that relatively rare flood events and ensuing turbidity currents can lead to large amounts of carbon storage, leading to offsetting (partial, complete or excessive) of the oxidation of POC$_{\text{fossil}}$ during erosion and transport. In order to fully understand these processes, identification and quantification of the various carbon species eroded and transported by the fluvial system needs to be matched with quantifications of the burial and long-term storage potential of carbon in offshore sediments.

Within Taiwan, lithologies containing ancient POC fall into two broad categories, metamorphic carbon and sedimentary carbon. Metamorphic carbon is sourced from erosion of the Central Range (Beyssac et al., 2007), the Gaoping catchment drains both the Pilushan (Eocene) and Lushan (Miocene) Formations. Within these formations, the Gaoping mostly samples rocks which have experienced metamorphic temperatures below 330 °C, but may include some which have been metamorphosed to 450 °C. Carbon experiencing these temperatures will be in the form of semi-crystalline graphite (Beyssac et al., 2002a).

Sedimentary carbon comes from Plio-Pleistocene deposits on the western coastal plain and foothills of the island. These are foreland deposits, which are shallow-marine and terrestrial in origin, collecting material eroded from the emerging island of Taiwan and subsequently uplifted and exhumed during continued orogenesis. Examples of these deposits are the Cholan and Tuokoshan Formations, a series of shallow-marine and terrestrial clastic sediments containing POC clasts, up to 10 cm in diameter. These are the remains of previously eroded POC$_{\text{terrbio}}$, now transformed to low-grade coal with a chemical composition very similar to modern POC$_{\text{terrbio}}$. Also present in these formations are grains of allochthonous highly-crystalline graphite. The source and distribution of these crystals will be considered later in this chapter.

The Gaoping river catchment is the second largest in Taiwan, draining an area of 3257 km$^2$ with a mean annual discharge of $8.5 \times 10^9$ m$^3$ (Huh et al., 2009) and an average erosion rate of 49 mm yr$^{-1}$ (Dadson et al., 2003). It is set in mostly Miocene-age material in the mountains of the Central Range, with older material to the East and younger rocks to the West, and crosses the recent sediments of the Pingtung plain before entering the

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CHAPTER 3. MODERN SYSTEM - GAOPING RIVER AND CANYON

South China Sea at Kaohsiung (see Figure 3.1). Here, material can enter the Gaoping Canyon or spread across the Gaoping Shelf. The canyon is a sinuous erosional feature incised through the shelf and slope and reaches up into the Manila Trench, 260 km away.

Sedimentation in the canyon is dominated by the tropical storms (Liu et al., 2012). Typhoon Morakot in 2009 delivered exceptional amounts of rainfall to south-western Taiwan due to monsoon-feeding of the cyclone system (Ge et al., 2010), leading to 3600 mm of rainfall in four days, delivering $\sim$700 MT of sediment (Lee et al., 2011) and 3.8-8.4 MT of CWD (West et al., 2011).

During storm conditions the sediment concentration of the Gaoping River can be high enough that the river water density exceeds that of the seawater, leading to a plunging sediment plume and hyperpycnal transport of material along the sea floor (Kao et al., 2010). This transport will localise to the Gaoping Canyon, and can be depositional, by-passing or highly erosive (Liu et al., 2012). In the seas off Taiwan, sediment concentrations in excess of 40 g m$^{-1}$ can lead to hyperpycnal behaviour (Dadson et al., 2005; Goldsmith et al., 2008). This type of flow can lead to deposition of turbidite sequences. Using moored sediment traps, temperature sensors and flow measurements, Liu et al. (2012) demonstrated that turbidity currents in the Gaoping Canyon consisted of a single plume rising up to 150 m above the seabed, rather than stratified nepheloid layers, and linked an observed turbidity current in the canyon thalweg to collected sediments. If the sediment concentration is lower than the hyperpycnal threshold, hypopycnal transport will occur. The Gaoping River is not hyperpycnal during regular discharge conditions, nor for substantial episodes within a storm flood. In hypopycnal conditions, sediment spreads out over the surface of the ocean and material will fall out of suspension and deposit over a wide seabed area. Photographs after the typhoon confirm a large amount of sediment in the upper ocean following the storm. This process can lead to deposition on the shelf as well as the canyon.

Being a marine sedimentary system, the Gaoping canyon and shelf is likely to contain some marine carbon. This is usually very labile in nature, being re-mineralised easily within the water column. Preservation ratios for marine carbon are of the order of 0.5 % (Hedges et al., 1997) yet marine carbon dominates marine sediment in areas where more refractory carbon is not added to the system. Autotrophic marine carbon is produced by photosynthesis in the upper part of the ocean, and falls to the floor when the producing organisms die. Oxygenated waters are responsible for extensive remineralisation of marine carbon (Hedges and Keil, 1995). Mechanisms suggested for enhancing preservation including attachment to coprolites and mineral grains. Even at the ocean floor, bio-activity or
3.2. SAMPLE LOCATIONS AND DESCRIPTIONS

oxidation can lead to carbon being used up rapidly, so deposition in anoxic conditions enhances preservation potential [Kennedy and Wagner 2011].

This chapter will begin by describing a series of samples which represent sedimentary material from a range of sources and burial locations. Raman spectroscopy and isotope geochemistry results will be used to characterise the carbon sources and identify their depositional locations. This will allow the consequences for erosion and burial of organic carbon of extreme meteorological events to be considered.

3.2 Sample Locations and Descriptions

Three groups of samples were collected for this study. These are: bedrock samples from young sediments in western Taiwan, which provide type-specimens for “sedimentary carbon”; river sediment samples from the post-Morakot Gaoping River, representing the distribution of material eroded from the catchment during and after the storm; and sediment cores collected offshore in the Gaoping Canyon and on the Gaoping Shelf both in 2001 and following typhoon Morakot in 2009.

Bedrock samples were collected from the Pliocene Cholan and Pleistocene Tuokoshan formations, from the Tsaolhuchi section of Chen et al. (2001) (see Figure 3.3). Sedimentary facies ranging from shallow marine to terrestrial environments are represented in this section. Samples were collected by hammering along a 5 km riverbed transect. Although the sample transect is outside the Gaoping catchment, these two formations are represented in the western part of the catchment (see Figure 3.3).

River samples were collected beside the Gaoping River in November 2009. Three subdivisions can be made. Site KP1 is in the main channel, at the Pingtung line railway bridge. Samples from this site represent the entire Gaoping catchment. Samples KP2 and KP3 were collected from a tributary of the Gaoping draining mostly rocks of the Central Range, although the sample sites themselves were still within the river plain. Site KP4 is located on a tributary draining mostly material from the coastal plain, which exposes mostly young sedimentary rocks including the Plio-Pleistocene formations sampled as bedrock.
Figure 3.2: Coarse woody debris in floodplain deposits at site KP1, beside the main channel of the Gaoping River.

Figure 3.3: A topographic and bathymetric map of the Gaoping River and Canyon, showing the tributaries of the Gaoping River, the location of samples and the exposure of the Plio-Pleistocene Cholan and Toukoshan formations in this region.
3.2. SAMPLE LOCATIONS AND DESCRIPTIONS

3.2.1 Core Locations

Cores collected in 2001 were arranged in a fan shape with an internal grid pattern, providing regular samples of an area extending 35 km offshore, extending 9 - 14 km either side of the Gaoping canyon (see Figure 3.4). There were 29 localities; each consists of a core-top sample which has been studied for TOC and $\delta^{13}C$ values by In-Tian Lin who has kindly
CHAPTER 3. MODERN SYSTEM - GAOPING RIVER AND CANYON

provided the results so that a comparison can be made between background conditions and an extreme event. These cores were analysed in a different laboratory, for which blank corrections and estimates of systematic bias are not available here, but comparison with samples from 2009 showed similar patterns of TOC and δ13C values.

Eight cores were collected offshore Kaohsiung soon after typhoon Morakot by ship Ocean Research 1, cruise 915 between 28 Sept. and 4 Oct., 2009, using a variety of methods including box, gravity and piston coring (see Table 3.1). Whilst the material was not collected during the storm, and therefore cannot be explicitly linked to sediment released during typhoon Morakot, in turbiditic environments the latest depositional event will likely erode into previous sediments and turbidity currents are known to have traversed this area following the storm. Thus it is most likely that the core tops consist of sediments from typhoon Morakot.

Entire tree trunks are rarely found in submarine sediments, but have been found in the Marnoso Arenacea turbidites of the Apennines. When sampling using cores, tree trunk material will not be collected because the size of the trunks is larger than the bore of the coring device which will bounce off the trunk and coring will fail. Tree debris is reported in unsuccessful coring attempts in the Gaoping canyon.

<table>
<thead>
<tr>
<th>Core</th>
<th>Lat.</th>
<th>Long.</th>
<th>Water Depth</th>
<th>Type</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>22.4577</td>
<td>120.4142</td>
<td>160</td>
<td>Box Core</td>
<td>Nearest river mouth</td>
</tr>
<tr>
<td>K12A</td>
<td>22.4055</td>
<td>120.4085</td>
<td>350</td>
<td>Box Core</td>
<td></td>
</tr>
<tr>
<td>K25B</td>
<td>22.4003</td>
<td>120.3437</td>
<td>436</td>
<td>Box Core</td>
<td></td>
</tr>
<tr>
<td>K8</td>
<td>22.3325</td>
<td>120.2543</td>
<td>711</td>
<td>Gravity Core</td>
<td></td>
</tr>
<tr>
<td>K8X</td>
<td>22.2951</td>
<td>120.2857</td>
<td>749</td>
<td>Box Core</td>
<td></td>
</tr>
<tr>
<td>K15</td>
<td>22.3137</td>
<td>120.2257</td>
<td>976</td>
<td>Box Core</td>
<td></td>
</tr>
<tr>
<td>K11A</td>
<td>22.2532</td>
<td>120.1763</td>
<td>957</td>
<td>Box Core</td>
<td>Beside canyon</td>
</tr>
<tr>
<td>L9</td>
<td>22.1840</td>
<td>120.3613</td>
<td>495</td>
<td>Box Core</td>
<td>On Gaoping Shelf</td>
</tr>
</tbody>
</table>

Table 3.1: Cores used in this study, from cruise Ocean Research 1-915.

Within the sandy material, POC_{terrbio} was present on a range of sizes, from mm-scale elongate flecks to cm-scale twigs. Above the sand was a mud cap, within which no visible particulate carbon was observed. Cores K1, K12, K25, K8, K8X and K15 were collected from the Gaoping canyon. Core K11 was collected from the canyon side, whilst core L9 was collected from the shelf, 20 km from the canyon. Both of these cores consisted of laminated mud. Given the annual deposition rate of 0.6 g cm\(^{-2}\) yr\(^{-1}\) (Huh et al. 2009) in these locations is substantially lower than the core depth of 30 - 45 cm, these cores are
3.2. SAMPLE LOCATIONS AND DESCRIPTIONS

likely to represent more than the sediment deposited as a result of Typhoon Morakot. \[3.3\] shows the location of these cores.

Core-top samples collected in 2001 during more normal sedimentary conditions cover the same area as the Morakot cores and provide a contrasting dataset, as POC export during low-flow periods can be very different to peak flow conditions (Hilton et al., 2008b).

### 3.2.2 Core Descriptions

Core K1 was located 2.5 km from the mouth of the Gaoping River and was the most proximal core in this study. Despite being close to the shore, there is a canyon with 80 m relief, this sample was collected from the thalweg. The lower 11 cm of the core are sandy material. There was a 10 cm fining-up sequence of coarse to fine sand, containing POC\textsubscript{terrebio} up to 40 mm in length and muddy rip-up clasts, especially at the base of the sequence. This is interpreted as a turbidite deposit. Below the coarse sand, the lowest cm contained fine sand and mud without visible POC. This is likely the highest preserved part of the layer below the turbidite. The top 37 cm were homogeneous clay-rich mud, with some air bubbles and very rare carbonate grains. No POC was visible to the naked eye within the mud. However microscopic analysis showed that graphite and POC\textsubscript{terrebio} were both present in the sample.

10 km from the Gaoping river mouth, box core K12A was the second closest to the shore, near to the thalweg on the outside of a canyon meander. The base of the core consisted of coarse, slaty sand grains with some carbonates, up to 6 mm in size. The grains were angular and fined-upwards to a sharp transition into a 3 cm mud cap, inter-bedded with some fine sand layers. Visible POC\textsubscript{terrebio} was present as rare elongate woody particles, up to $10 \times 3 \times 1$ mm in size, present in half of the samples. Microscopic analysis determined that amorphous carbon is present, along with graphite. This core showed the largest grain sizes of all collected material, suggestive of a decelerating sediment density flow producing “Bouma A” bedforms.

16 km along the Gaoping canyon, and again from the centre of the channel, core K25B showed a finer grain size than those higher up the canyon. At the base were 12 cm of fine sand with fine POC\textsubscript{terrebio} clasts, smaller than in the more proximal cores but still elongate, with typical dimensions $5 \times 0.5 \times 0.5$ mm. The upper five cm contained mud and fine sand with multiple small POC grains. Unlike most cores, this mud-bound POC was large.
enough to be seen by the naked eye.

Cores K8 and K8X were equidistant along the Gaoping canyon, either side of a bifurcation. Core K8 contained 6 cm of fine sand at the base, POC was present in fibrous clasts up to $50 \times 2 \times 2$ mm in size. Clasts of this size were not seen anywhere else in the offshore samples, but were comparable to material left on the Gaoping River floodplain after typhoon Morakot (sampled at locality KP1). Above the sand were 4 cm of mud. POC$_{terrbio}$ was present as elongate fibrous strands of woody material, with typical dimensions $15 \times 1 \times 1$ mm. POC$_{terrbio}$ appeared more abundant than in any of the other studied cores. Core K8X contained 15 cm of fine to medium sand below 4 cm of mud and fine sand. There was no internal bedding or apparent coarsening in clastic grains with depth. POC$_{terrbio}$ clasts increased in size down-core, up to $25 \times 10 \times 10$ mm at the base of the core, although $10 \times 1 \times 1$ mm was a more representative size for the sandy part of the core.

Core K15 is the furthest offshore core collected from the Gaoping canyon, 25 - 30 km from the Gaoping River mouth. It is located at the point where the bifurcating channels rejoin and is collected from the thalweg. It is also the smallest core in this study, with only 2 cm of mud and 3 cm of fine sand collected by box coring. Visible POC was absent in the mud and seen as occasional fibrous strands of $10 \times 1 \times 1$ mm in two of the three sand samples.

Core K11A was collected by box coring from a site near to the Gaoping canyon, in a water depth of 957 m. The canyon floor in this area is 1134 m deep; therefore the sample was taken on the slope beside the main canyon rather than the thalweg. There was no sandy material collected in this core. The 31 cm of mud samples were very clay rich, showing mm-scale lamination. No POC clasts were macroscopically visible in the samples.

Core L9 was located on the shelf, ~20 km east of the Gaoping canyon. As with core K11A, L9 contained no sandy material, but 41 cm of clay-rich mud were recovered. There are no obvious grain-size variations through the core, but there were cm-scale colour changes clearly visible suggesting that the material was not deposited simultaneously. No POC clasts were visible to the naked eye anywhere in the core, but microscopic analysis showed that both graphite and aged woody material were present.

In summary, cores K11 and L9 were from a slope setting, with much of the material unrelated to Typhoon Morakot. Cores K1 - K15 were from the Gaoping Canyon thalweg and mainly or exclusively sampled sediment deposited by turbidites caused by the typhoon.
3.3 Elemental / Isotopic Results

Figure 3.5: Isotopic / elemental results from 2001 and 2009 cruises, reported as TOC and δ^{13}C. 2001 samples are interpolated using a spline function. 2009 samples are split into sandy and muddy parts of the turbidites.

The 29 core-top samples from 2001 (analysed by In-Tian Lin) had TOC values ranging from 0.22 to 0.78 % and δ^{13}C values ranging from -22.5 to -24.7 ‰ (see Figure 3.5). TOC readings were higher on the shelf and lower in the canyon. The highest δ^{13}C values were on the offshore part of the shelf, furthest from the Gaoping river mouth, whilst lowest δ^{13}C values were midway down the Gaoping canyon at around 600 m water depth. In general the shelf material had a higher δ^{13}C than the canyon.

The post-Morakot core samples produced a range of isotopic / elemental values (see Figure 3.6). TOC ranged from 0.21 to 0.36 wt%, N/C from 0.05 to 0.3, δ^{13}C from -26.0 to -22.5 ‰ and δ^{15}N from 1.29 to 3.30 ‰. Δ^{14}C values ranged from -794 to -544 ‰, indicating a fraction-modern of 0.21 to 0.45.

3.3.1 Core-specific results

In core K1 the majority of both sandy and muddy samples had similar δ^{13}C and N/C properties, -24.01 to -25.04 ‰ and 0.153 to 0.209 respectively. TOC concentration (corrected for carbonate dissolution) was fairly constant in the mud (average 0.42 %) but enriched at the core top, 0.59 %. Within the sand, the coarse nature of the POC led to very vari-
able measurements. Where a coarse POC particle was included in the 5 g aliquot (sample K1-41), TOC content rose to 1.12 %, with low $\delta^{13}$C (-25.86 ‰) and N/C (0.071). These values were similar to modern woody POC$_{terrestrial}$ collected beside the Gaoping River, and indicated the presence of large woody debris. $^{14}$C analysis of sample K1-41 shows an $F_{mod}$ of 0.36. This means that it contained mostly old, previously buried material despite a large piece of modern CWD being seen. This means that there must also have been significant amounts of POC$_{fossil}$ with a low $\delta^{13}$C and N/C ratio present in the sample, likely CWD recycled from earlier sedimentary units.

The muddy section of K12 had an average TOC of 0.36 wt%, whilst the eight samples from the sandy part of this core had a very constant TOC of 0.22 ± 0.036 (2σ) wt %. The sandy samples without visible POC had the highest N/C ratio in this study, around 0.29, with $\delta^{13}$C of -23.4 ‰ (see Figure 3.7). Whilst total organic carbon in this sample was low, the relative proportion of graphite particles was high. With $\delta^{13}$C of -23.63 ‰ and N/C of 0.287, sample K12-17 was very similar to the bedrock units Ep and EO1 (Hilton et al., 2010).

Within core K25 the lower five samples had very similar $\delta^{13}$C and N/C results, with -25.0 ±0.37 ‰ (2σ) and 0.18 ± 0.03 (2σ) respectively. The core-top sample, K25-0, had the highest TOC at 0.48 %. The remainder of the core averaged 0.39 %.

Core K8 had a variable TOC content, ranging from 0.26 to 1.36 %. Samples K8-2 and K8-4 had the lowest TOC and plotted in a similar region to cores K1, K12 and K25.
3.3. ELEMENTAL / ISOTOPIC RESULTS

Figure 3.7: Isotopic / elemental results from core K12, plotted as $\delta^{13}$C vs. N/C. Sample K1-41 contains a large piece of woody debris. Woody POC$_{terrbio}$ samples were collected beside the Gaoping River at site KP1. Hilton (2008) report woody debris $\delta^{13}$C values of $-28.1 \pm 2.5 \, \%$ and N/C 0.005 $\pm$0.002 for terrestrial Pinus morrisonicola stems. Data from core K12 are the least like POC$_{terrbio}$, which matches the sedimentary observations of coarse slaty grains with few or no woody fragments visible.

The other samples all had TOC higher than 0.8 %, which is significantly higher than the average of the rest of the material in this study. This enrichment was due to the presence of coarse POC in the samples, and gave rise to a low N/C ratio (average 0.086). $\delta^{13}$C measurements were more varied; sample K8-8 had $\delta^{13}$C $= -22.9 \, \%$ whilst the other three high-TOC samples in this core averaged -25.35 $\, \%$. The large amounts of coarse woody material seen in the samples were likely responsible for these variations in $\delta^{13}$C.

Core K8X was unlike core K8 and much more like the other proximal canyon cores. The lowest sample, K8X-18, was POC$_{terrbio}$ rich and had the highest TOC (0.55 %) and lowest $\delta^{13}$C ($-25.00 \, \%$) of this core. The higher samples had a very uniform N/C (0.20 $\pm$ 0.06) and $\delta^{13}$C ($-24.48 \pm 0.53 \, \%$). TOC in these samples was quite uniform at 0.24-0.33 %, but rose to 0.44 % at the core top.

Core K15 had very uniform $\delta^{13}$C and N/C measurements, -24.45 $\pm 0.12 \, \%$ and 0.20 $\pm 0.01$, respectively, including samples from both mud and fine sand. TOC decreases with depth, from 0.53 % at the core top to 0.31 % at the base of the core, 5 cm below.

In core K11, $\delta^{13}$C values were heavier than in the canyon cores (Figure 3.8), ranging from -22.5 $\, \%$ to -23.3 $\, \%$. N/C ranged from 0.17 to 0.19, and TOC was also relatively
CHAPTER 3. MODERN SYSTEM - GAOPING RIVER AND CANYON

Figure 3.8: Isotopic / elemental results from core K11, plotted as $\delta^{13}$C vs. N/C. “Woody debris” samples were collected beside the Gaoping River at site KP1. Data from the canyon cores is also included to show the clear offset between shelf and canyon material. Both datasets show a linear trend towards the input of woody material.

high, with an average of 0.52 %. Three $^{14}$C results gave an $F_{mod}$ of 29 % to 37 %.

In core L9, $\delta^{13}$C measurements varied between -25.0 ‰ and -23.0 ‰ with N/C ratios between 0.15 and 0.20. This was a similar range to sample K11, which also had similar sedimentology and TOC values. Radiocarbon measurements showed this core to be enriched in $^{14}$C, the youngest samples had $F_{mod} = 0.46$. The top few cm of this core were different to the rest of the core, both in appearance and carbon isotope composition. Samples below the core top were significantly less depleted in $^{13}$C than the core top itself (-25 ‰ at the core top compared to -23.45 ± 0.61‰ elsewhere in the core).

3.3.2 River samples

Riverbank sediments contained a variety of grain sizes. Sample sites KP1 and KP3 consisted of very fine grained floodplain sediment deposited beside the river at the peak of the flow. Sample site KP2 was a re-worked sand bar containing coarse slaty grains, similar in size and appearance to core K12. Site KP4 consisted of layered mud and fine sand from a mud flat (this site is Figure 2.6). The samples (Figure 3.9) had a high N/C ratio (0.20 - 0.27) and low to moderate TOC (0.16 - 0.37 % with an average of 0.25 %). They
generally sat within the range of suspended sediment data collected from gauging stations on the Gaoping River (Hilton et al., 2010), although the highest N/C values recorded here were greater than seen before. $\delta^{13}$C values of -23 to -25‰ sit within the range of both the previous river samples and offshore material discussed in Section 3.3.1 (see also Figure 3.10).

### 3.4 Elemental / Isotopic Interpretation

The results from both terrestrial and offshore material collected post-Morakot contained a range of isotopic / elemental values, which are likely due to input of carbon from a range of sources. Endmember unmixing allows estimation of the relative importance of each carbon source throughout the cores, such that the burial locations of different types of organic carbon can be deduced. First this analysis will be carried out in the Gaoping River, where marine carbon influence should be minimal and therefore the composition of other endmembers can be calibrated, before considering the distribution of carbon throughout
Figure 3.10: Isotopic / elemental results from the Gaoping River, collected for this study, plotted as δ¹³C vs. N/C. Data from the Gaoping Canyon and shelf (grey dots) shows that the river follows a similar trend to the canyon material.

3.4.1 4-component endmember mixing

3.4.1.1 Gaoping River

Four-component endmember analysis was applied to fluvial and offshore samples. The four components chosen are defined in Table[2.3] and comprise marine material, $POC_{terrbio}$, both modern and recycled, and two fossil carbon compositions which are summed to give the total fossil carbon contribution.

A lateral transect from the Gaoping River to offshore cores (Figure[3.11]) shows that the fluvial samples from tributaries draining the Central Range were dominated by $POC_{fossil}$. Marine carbon was barely present in the rivers, as expected for fluvial samples. $POC_{terrbio}$ was also rare in the Gaoping River, yet present offshore in much higher concentrations. It is likely that $POC_{terrbio}$ was added to the fluvial system as coarse woody debris which was not seen in the coarse sediments collected from the river itself after the storm, but
Figure 3.11: Downslope profile of carbon inputs. For each offshore core, weighted averages were calculated to correct for the irregular sample spacing. The “River” composition were calculated as a simple mean of all river samples.

was very obvious in floodplain deposits (see Figure 3.2). The large size of the fluvial POC clasts prevented representative sampling of this material. Comparing the river samples to the offshore cores shows that POC_fossil was high in all cores, that POC_terrbio was high in all cores apart from K12, and that marine carbon was greatly enriched in the shelf and slope cores (K11 and L9) compared to the canyon cores. A detailed profile of each core will now be discussed.

A breakdown of the Gaoping River results is shown in Figure 3.12, where the amount of carbon from each species is plotted for each sample. “Marine” carbon contributed 0.1 wt% TOC or less to each sample. POC_terrbio was almost always present in higher concentrations than “marine” carbon, except for sample KP2 which consisted of coarse slaty grains without visible organic matter. Fossil carbon generally made the greatest single contribution to the total carbon concentration in the river samples.

The inclusion of “marine” carbon within the terrestrial river sediment is likely due to uncertainties within the unmixing method. The two defined fossil compositions have identical δ^{13}C and N/C values, with different TOC and δ^{15}N. This means that in δ^{13}C vs. N/C
CHAPTER 3. MODERN SYSTEM - GAOPING RIVER AND CANYON

Figure 3.12: Endmember mixing results from the Gaoping River, showing the contribution from marine carbon, woody material (both modern and recycled) and fossil carbon. Samples KP1 are from the main channel, KP2 and KP3 from a tributary draining mostly mountainous regions, and KP4 from a tributary draining mostly lowland regions.

space, mixing between $\text{POC}_{\text{terrbio}}$ and $\text{POC}_{\text{fossil}}$ is defined as a single mixing line. Deviation from this line will lead to marine carbon being included in the mixing calculations, as happens in some of the Gaoping River samples. Changing the fossil composition slightly would alter the mixing line position, changing the supposed marine carbon content of the samples, yet with the observed spread recorded in the river sediment it is impossible to remove the marine component completely. Fossil carbon compositions cannot be determined precisely either before or after the storm. Due to the stochastic nature of erosion during such a flood, the composition will not be a simple homogenisation of all exposed bedrock. The importance of endmember compositions is discussed in Section 6.1.5.1.

As the river sediments collected by Hilton et al. (2010) show, material eroded from the Gaoping catchment did not have a single fossil carbon composition anyway (see Figure 3.9). The river samples record some of this variability, although less so than in Hilton’s samples from individual gauging stations, and therefore produce a slight marine carbon signal. In view of this an uncertainty to the amount of each carbon species identified by the endmember unmixing procedure, perhaps up to 0.1 wt% C, is attributed to the unmixing process. Thus attention can now turn to the offshore cores. In each case the results are presented as a combined figure showing the grain size distribution and dissolved
3.4. ELEMENTAL / ISOTOPIC INTERPRETATION

3.4.1.2 Core K1

4-component endmember analysis shows that the concentration of marine-sourced carbon was low in all sections of core K1, below the uncertainty of 0.1 wt% (Figure 3.13). Fossil carbon input was fairly constant at 0.15 to 0.25 wt%. There was a peak in POC\textsubscript{terrbio} matching that seen in the $^{14}$C and hand specimen analysis, at K1-41. The lower parts of this core were all rich in coarse woody debris, the addition of up to 1 % TOC from this debris could apply to the lower section of this core in its entirety. This lower, sandier section of this core was dominated by the input of coarse POC\textsubscript{terrbio}, which was not present in the mud above. Fine POC\textsubscript{terrbio}, either in the form of Plio-Pleistocene POC grains or very fine modern woody debris, added about 0.2 wt%C to the muddy sections of the core, with the core top richest in this material at 0.35 wt%.

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Figure 3.13: Downcore-profile (in cm) of grainsize, TOC and unmixed carbon components for core K1. Note the coarse turbiditic layer at the bottom of the core. This is assumed to be from Morakot, with the mud cap above settling within the two-month period between the storm and sampling cruise. The peak in woody debris coincides with the particularly sandy layer.
Figure 3.14: Downcore-profile (in cm) of grain size, TOC and unmixed carbon components for core K12.

Figure 3.15: Downcore-profile (in cm) of grain size, TOC and unmixed carbon components for core K25.
3.4. ELEMENTAL / ISOTOPIC INTERPRETATION

Figure 3.16: Downcore-profile (in cm) of grainsize, TOC and unmixed carbon components for core K8.

Figure 3.17: Downcore-profile (in cm) of grainsize, TOC and unmixed carbon components for core K8X.
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Figure 3.18: Downcore-profile (in cm) of grainsize, TOC and unmixed carbon components for core K1.

Figure 3.19: Downcore-profile (in cm) of grainsize, TOC and unmixed carbon components for core L9.
3.4. ELEMENTAL / ISOTOPIC INTERPRETATION

3.4.1.3 Core K12

When plotted as δ^{13}C vs. N/C, core K12 samples plotted along a well-defined, positively-correlated trend with r^2 of 0.78. The wood-dominated sample - K1-41 - fits this trend line, suggesting that the trend was caused by mixing of varying amounts of POC_{terrbio} and bedrock-derived POC_{fossil} (Figure 3.7). These samples were most susceptible to changes in the composition of the fossil endmember. According to 4-component endmember mixing, the core was dominated by fossil carbon, with a slight increase in POC_{terrbio} at the core top (Figure 3.14). Marine carbon concentrations are estimated at less than 0.1 wt%C in all samples, and given the linear trend in δ^{13}C vs. N/C space (Figure 3.7) are likely negligible. POC_{terrbio} was only significant at the core top, contributing 0.15 wt%C. It was rare but present in lower parts of the core, with 0.05 wt%C suggested by the endmember mixing calculations which is within uncertainty.

3.4.1.4 Core K25

The five samples from core K25 also plotted on a linear trend, similar to K12. Endmember unmixing showed a negligible amount of marine carbon, less than the 0.1 wt%C uncertainty in all samples (Figure 3.15). Fossil carbon is uniformly present at around 0.12 wt%C. The variance in δ^{13}C and TOC seen in the isotope geochemistry is explained by variation in the amount of POC_{terrbio} in the core, up to 0.37 wt%C at the core top. In δ^{13}C vs. N/C space, the core top plotted away from the trend of the other samples.

3.4.1.5 Core K8

Endmember mixing results imply that there was to 1.2 wt%C POC_{terrbio} in samples from core K8 (Figure 3.16). The high δ^{13}C value (-22.9 ‰) of sample K8-8, and moderate to high values in K8-6 and K8-9, led to an apparent increase in marine carbon away from the <0.2 wt%C typical of the samples at the top of the core. This may be an artefact caused by the representation a wide range of vegetation compositions using a single value of δ13C, especially given the variation in δ^{13}C between C3 and C4 vegetation. Apart from the lowest three samples, the mixing results showed a near-constant amount of fossil carbon in all samples, with changes in TOC mirrored by changes in the amount of POC_{terrbio} matching visual observations multiple large fragments of woody POC.
3.4.1.6 Core K8X

In core K8X, the presence of visually detected coarse woody debris at the base of the core was confirmed in the mixing results, with 0.38 wt%C in the sample (Figure 3.17). Both POC\textsubscript{terrbio} and POC\textsubscript{fossil} were enriched in the core top; apart from the very base, woody material and fossil carbon co-vary. Marine material was negligible, less than the 0.1 wt%C uncertainty in all samples.

3.4.1.7 Core K15

Endmember mixing results from core K15 showed a doubling in woody debris and fossil carbon at the core top, both contributing about 0.27 wt%C compared to about 0.15 wt%C down-core. Marine carbon was negligible in this core, below 0.1 %, as in all canyon samples.

![Gaoping Canyon Cores](image)

Figure 3.20: Linear regression of Gaoping Canyon cores, K1, K12, K25, K8X and K15. They define a trend between woody material and fossil carbon.

Linear regression of the canyon cores other than K8 showed that they all lie along a line with \( r^2 \approx 0.70 \) (Figure 3.20). This line represents mixing between POC\textsubscript{terrbio} and POC\textsubscript{fossil}. Core K12 was richest in fossil carbon, the sandy parts of core K1 were richest in POC\textsubscript{terrbio}. Offshore transport appears to have reduced the variability in POC\textsubscript{fossil}. 

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3.4.1.8 Core K11

Samples in core K11 did not lie on the trends shown in the canyon cores. For a given N/C value, \( \delta^{13}C \) was significantly higher than for cores from the canyon (Figure 3.8). One cause of this could be the addition of marine carbon to the sediment, with its associated higher \( \delta^{13}C \) value. 4-component endmember mixing showed much more marine carbon throughout core K11 than in the canyon samples, up to 0.23 wt\% C (Figure 3.18). POC\textsubscript{terrbio} was present, especially at the core top where the concentration rises to 0.27 \%, from around 0.17 \% below this. This could be due to sediment from typhoon Morakot. POC\textsubscript{fossil} concentration was also quite high in this core, around 0.2 \text{ wt\%} throughout the core. The \( F_{mod} \) value calculated from \( \Delta^{14}C \) was 0.34, higher than for core K1 (0.27). As both marine and fossil carbon could be responsible for an increase in N/C and \( \delta^{13}C \), the increase in radiocarbon strongly implies increased marine carbon input to this core.

3.4.1.9 Core L9

Endmember mixing results from L9 showed a similar pattern to core K11. There was around 0.2 \text{ wt\%} C marine carbon in the lower part of the core. POC\textsubscript{fossil} content was fairly uniform, at around 0.27 \text{ wt\%} C. POC\textsubscript{terrbio} concentration was variable, between 0.25 and 0.4 \text{ wt\%} C. Most interesting was the core top, in which the concentration of marine carbon drops dramatically to below 0.1 \text{ wt\%} C and the sample L9-0 plotted away from the other L9 samples in N/C vs. \( \delta^{13}C \) space. This sample had a composition much more like the canyon samples, suggesting rapid fall-out of river-derived sediment, likely due to the incorporation of Morakot material.

3.4.2 Wide-area results

Overall, Total Organic Carbon concentrations were higher in shelf sediments (cores L9 and K11) than canyon samples. These shelf settings also exhibited a \( \delta^{13}C \) signal concordant with marine carbon input of a uniform 0.2 \text{ wt\%}, yet also contained comparable amounts of fossil carbon and POC\textsubscript{terrbio}. Canyon sediments contained almost exclusively terrestrial carbon, both modern and recycled POC\textsubscript{terrbio} and fossil carbon. There was little or no robustly detected marine carbon, less than the 0.1 \text{ wt\%} uncertainty present in the unmixing method. These samples could be analysed using a simpler fresh-fossil unmixing model of
The Morakot cores showed that lateral variations in carbon content and $\delta^{13}C$ can be sizeable and rapidly expressed. For example core K11 is located very close to the Gaoping canyon yet has a slope-style composition. A nearby core from 2001 showed very low $\delta^{13}C$ indicative of terrestrial material and is likely located in the thalweg.

The 2001 core tops show a low TOC on the shallow shelf and in the deep canyon, with a higher TOC on the slope away from the canyon. Low $\delta^{13}C$ values tend to be found in the canyon, much as for the Morakot cores. Higher $\delta^{13}C$ values were found away from the canyon, on the slope. Core L9, interpreted as marine-rich, matches well with the nearby high $\delta^{13}C$ samples from 2001. The pattern of low $\delta^{13}C$ in the canyon, high $\delta^{13}C$ on the shelf and slope was systematic between the two oceanographic cruises. Together with the close agreement for the absolute values of nearby cores, such as around L9, this suggests that the data sets are comparable and not overprinted by a systematic analytical bias. Without the corresponding nitrogen measurements it is difficult to confirm marine enrichment using the endmember-unmixing process used for the Morakot cores.

The 2001 measurements did not match the Morakot samples in two locations. The wood-dominated sediment of K8 has a higher TOC content than any of the 2001 samples. This concentration of carbon seems unique amongst the Morakot cores, and is likely due to the hydrodynamic processes operating during deposition, specifically hyperpycnal turbidity currents [Liu et al. 2012]. A paucity of samples from 2001 in this area means that whether this pattern was already established before Morakot cannot be checked. However the $\delta^{13}C$ isotopic composition of the region around K8 as measured in 2001 matches K8, K8X and K15, suggesting that the style of carbon present is unchanged, rich in woody debris, but that the concentration is greater in the Morakot sediments.

The core tops of each Morakot core show an enhanced contribution from fresh organic material compared to the core as a whole, and apart from L9 (where the lower samples were from pre-Morakot sediments) an increase in TOC. This could be due to a late-stage settling of material from a turbid mud plume or from a hypopycnal sediment supply event, which would be dominated by clay-grade particles, which will be discussed further in Section 6.2.5. The variation in isotopic values and thus unmixing results for samples L9-0 suggest an affinity between this sample and the mud-rich parts of the canyon cores that is not seen in the other shelf and slope samples, the fluvial signal may have reached further than usual during this extreme event.
3.4. ELEMENTAL / ISOTOPIC INTERPRETATION

3.4.3 Effects of Typhoon Morakot compared to background conditions

In core L9, the core-top signal matches that of the canyon cores, whilst the lower samples match the shelf cores at K11. L9 is taken from the slope, 20 km from the canyon. A 45 cm core was recovered, which represents 188 years of deposition at 0.24 mm yr\(^{-1}\) (Huh et al., 2009). The majority of the core is homogenous, with a similar appearance in photographs and a very constant carbon isotopic ratio throughout (Figure 3.19). The core-top however shows a very different appearance, much darker in colour, and the chemistry matches that of the upper canyon sediments. There is no evidence of these darker layers lower in the core, which means that either they have been lost since burial, or else this is a deposit unique to Morakot. The core-top may have been uncharacteristically influenced by the typhoon material. Typhoon Morakot was a particularly large storm causing significant flooding and fluvial discharge, which may have caused large amounts of terrestrial material to be delivered hypopycnally to regions tens of km away from the usual submarine distribution system, the Gaoping canyon.

3.4.4 Isotopic / elemental Summary

Combining onshore and offshore isotopic / elemental results has shown that terrestrial POC dominates carbon deposition in submarine canyons, due to rapid deposition from submarine density currents. The isotopic / elemental signature of the post-Morakot sediments allows Morakot material to be identified both in the canyon and on the shelf better than by sedimentological observations alone. POC\(_{terrbio}\) is present in both sandy and muddy sections of the cores. Coarse Woody Debris concentrates in the lower, sandy parts of the turbidites produced by these currents, yet microscopic POC\(_{terrbio}\) is seen throughout the overlying mud caps as well. On the shelf and slope, a slower deposition rate allows marine carbon to be incorporated into the sediment as well. Under extreme conditions, material that would generally concentrate in the canyon can also be spread across the shelf. Radiocarbon results show that a large proportion of the material deposited is not modern organic matter but recycled POC sourced from both metamorphic and sedimentary rocks. Raman Spectroscopy allows investigation of the nature of this recycled POC.
3.5 Raman Spectroscopy Results

Figure 3.21: Raman spectra from the Taiwan, grouped into the Plio-Pleistocene formations, the Gaoping River, Canyon (K1 to K15) and Shelf (K11 and L9).

Given that modern material represents only about 30% of the carbon found in the post-Morakot cores, the nature of the fossil carbon should be investigated. Raman Spectroscopy provides an invaluable tool for doing this. Fossil carbon in the Morakot sediments may have been harvested from a range of geological formations exposed in the Gaoping catchment, containing carbon with different crystallography. These variances in crystallinity were used to trace the input of carbon from different formations to the marine sediment.

201 spectra were collected from 19 samples of sediment deposited during typhoon Morakot and rocks exposed in its source area. Figure 3.21 shows the acquired spectra. Particles with a graphitic appearance under the microscope and a graphitic style of spectra 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-graphitised material was found in all samples, but its shape varied considerably. The distribution of these spectral types...
varied greatly between the sample groups.

### 3.5.1 Plio-Pleistocene formations

![Raman spectra from sample 17 of the Cholan Formation, a large lignite clast.](image)

Most of the Plio-Pleistocene Cholan formation samples contained highly disordered carbonaceous material. Sample 17, a pure lignite specimen, produced very broad spectra with wide G and D bands (Figure 3.22) that can be used as a reference pattern for minimally-altered woody material buried up to 3 km in these sediments. Six out of seven other samples from the Cholan formation showed similarly disordered carbon in their spectral distributions. Also present in these sediments were highly-graphitised spectra with very sharp G bands. Intermediate-grade spectra with moderate G and D bands were rare, but present. There was highly-graphitised material present in six out of seven Cholan and Tuokoshan sedimentary samples and semi-graphitised material in five out of seven.

### 3.5.2 Gaoping River

Samples from the Gaoping River produced a lot of spectra with intermediate-width D and G peaks, indicative of semi-graphitised material. They produced no spectra with very sharp G peaks indicative of pure graphite crystals. There were also no spectra matching the very disordered spectra of sample 17 from the Plio-Pleistocene formations. The very broad red spectrum seen in Figure 3.21 was collected from a piece of modern woody debris.
and has even wider peaks than the lignite-grade material.

### 3.5.3 Gaoping Canyon

The spectra from the Gaoping Canyon showed a wide range of shapes. There were very graphitised spectra with sharp G peaks, intermediate-grade spectra with moderate G and D bands, and some very disordered material with broad G and D bands.

### 3.5.4 Gaoping Shelf

Spectra from the Gaoping Shelf were similar to the canyon, with a wide range of spectral shapes, except that spectra with very broad G and D bands were rarer. There was a significant amount of material with sharp G peaks, where the D2 peak was visible as a shoulder at 1620 cm$^{-1}$. Plotting these spectra in Total-width vs. Temperature space allowed a more thorough investigation of the distribution of spectra types.

### 3.5.5 Total-width vs. Temperature Plots

Recall that in these plots of spectral properties, dark grey represents highly- and semi-graphitised material, mid grey represents low-grade metamorphic material, while light grey shows very disordered material. When plotted in Total Width - Temperature space (see Section 2.4.5) the spectra from sample 17 plotted in the upper-left corner - designated as very disordered material (see Figure 2.14). The other disordered material from the Cholan and Tuokoshan Formations was also found in this section of the plot (see Figure 3.23). This is interpreted as mm-scale POC$_{terribio}$ incorporated into the Plio-Pleistocene sediments during deposition and subsequently transformed to lignite-grade, indicating that the metamorphic conditions experienced by the Cholan and Tuokoshan formations were very low.

Carbon which is more ordered than this is likely to have a bedrock source, from erosion of rocks exposed in the emerging Taiwan mountain belt at the time of deposition of the Cholan and Tuokoshan formations. There is a large amount of highly-graphitised material in these formations. Disordered carbon is much more common than semi-graphitised material; samples 2, 3, 6 and 8 tend towards a bimodal distribution of highly-graphitised and
Figure 3.23: Raman spectra from the Cholan and Tuokoshan formations analysed in Total-width vs. Temperature space. Note the cluster of very disordered material, these spectra were collected from a large lignite clast, and from small lignite pieces distributed within the sedimentary rocks. These therefore show that the Plio-Pleistocene formations have experienced minimal metamorphism. The dashed ellipse represents where material from the Central Range may be expected to plot, as defined by published peak metamorphic temperatures for Central Range material (Beyssac et al., 2007) and analysed graphitic spectra (Figures 2.13 and 2.12).

disordered material. This may mean that metamorphic rocks containing semi-graphitised carbon outcropped less in the Central Range during Plio-Pleistocene times, or that this material is preferentially oxidised during Plio-Pleistocene exhumation and erosion of the Central Range. Due to the short transport distance for sediment delivered to the Plio-Pleistocene sediments, the first explanation is more likely.

Figure 3.24 shows the range of spectra collected from sediments in the Gaoping River. Semi-ordered material dominates, the majority of this comes from a tributary draining the Central Mountain Range (sample KP2). This material has experienced moderate metamorphism (Beyssac et al., 2007) but has not approached graphite-grade. The only graphite grains found in the Gaoping River were from the branch draining the western
Figure 3.24: Raman spectra from the Gaoping River analysed in Total-width vs Temperature space. The majority of this material probably comes from the Central Range. There is a lack of graphitised or very disordered material here, most carbon has experienced low-temperature metamorphism.

plains (sample KP4), in which the graphite-rich Cholan and Tuokoshan formations are found, although this could also have been a piece of detrital graphite from another earlier sedimentary unit. Very disordered material is absent from all Gaoping River samples. Samples from the Gaoping River plotted similarly, but not exactly overlying, the postulated Central Range location (Figure 3.23). Differences could be due to the quality of collected spectra, or an increase in disorder during fluvial transport.

Offshore sediments from the post-Morakot cores showed a similar range of spectra to a combination of the Plio-Pleistocene and Gaoping River sediments. Semi-graphitised and highly-graphitised material were contained in all samples, including samples collected on the continental shelf. Both canyon and shelf cores (Figures 3.25 and 3.26 respectively) contained similar amounts of semi-graphitised and highly-graphitised material, but the shelf cores contained less disordered carbon.
3.6 Raman Spectroscopy Discussion

The abundance of disordered material in canyon cores compared to 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 yr\(^{-1}\), whilst the canyon deposits are sourced in a single flood event, transported by sediment gravity currents 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. Under hypopycnal conditions the disordered material could be lost due to buoyancy, floating to the sea surface, or as it is more labile than graphite it could be lost to remineralisation during hemi-pelagic settling.

Intermediate grade material was found in all offshore locations. This indicates that the transport distance along the Gaoping Canyon system (~50 km) is too short for comprehensive loss of semi-graphitised carbon by oxidation during sediment transport, in contrast...
3.6.1 Recycling of graphite through Taiwan

The pure graphite crystals found in the Plio-Pleistocene sediments were not created in-situ. These formations have not experienced any significant metamorphism, as evidenced by the presence of both large and small clasts of lignite-grade material. Thus these graphite grains must have been sourced from elsewhere and incorporated into the sediments along with the woody debris.

There are no lithologies exposed in the Gaoping River catchment today that contain autochthonous graphite of this grade - metamorphic conditions in the Central Range only reach 520 °C- yet graphite grains are common in the offshore material sourced directly from the Gaoping River. Thus the source of these graphite grains is likely the younger sediments.
outcropping to the west of the Central Range, including the Cholan and Tuokoshan Formations. Thus graphite-grade material has survived at least two cycles of erosion, transport and burial. This theme will be further investigated in the other field areas, and in Section 6.3.

3.7 Conclusions

There are two sedimentation domains affecting the Gaoping canyon. During low-flow conditions, hypopycnal delivery from the river distributes fine-grained material over a wide area of the shelf and slope as hemi-pelagic sediment. Sedimentation rates here are low, but the organic carbon composition is relatively high, in part due to the admixture of up to 0.25 wt% C modern marine organic material. During storm conditions, increased sediment load in the rivers leads to hyperpycnal delivery of terrestrially-sourced material to the Gaoping canyon. The increased sediment load can lead to a dilution of TOC, making it lower in the turbidites than the nearby slope material.

Hydrodynamic sorting within the turbidity currents means that coarse woody debris is concentrated within the sandy parts of the turbidites. Microscopic POC is present in the mud cap, where the TOC is higher on average. Radiocarbon analyses suggest that up to 70 % of the carbon present is recycled fossil material. δ^{13}C isotopic measurements show that this is both metamorphic carbon from the central mountain belt and sedimentary low-grade coal from Plio-Pleistocene foreland basin deposits.

Having seen that POC with a range of forms, from disordered woody debris to highly graphitised fossil carbon, is harvested from a mountain range during orogeny and delivered to marine sediments, its survival and sequestration over geological timescales must be investigated. POC eroded from the Spanish Pyrenees was deposited into a range of facies millions of years ago, and continued presence of POC_{terribio} and POC_{fossil} over this time will help to quantify the burial efficiency of terrestrial POC offshore.
Chapter 4

Cretaceous-Eocene - Spanish Pyrenees

4.1 Introduction

Having studied the offshore distribution of terrestrial POC in the modern Gaoping system, the foreland basins of the Spanish Pyrenees were sampled in order to study the distribution of POC in a range of ancient sedimentary facies, and to investigate the preservation potential of POC over millions of years.

4.1.1 Tectonics of the Pyrenees

The Pyrenees formed by compression at the boundary between the Iberian and European plates. Puigdefabregas and Souquet (1986) describe the tectonic history of the Pyrenees as a concatenation of cycles involving rifting and orogeny, of which the Alpine Orogeny is the latest and best constrained. A summary of this history is contained in Table 4.1. During the Mesozoic and Cenozoic the Pyrenees transformed from an extensional marine setting to a transtensional and subsequently transpressive regime, before becoming fully convergent in the latest Cretaceous and early Tertiary, forming the western extreme of the Alpine Orogeny.

Using the relative motions of Africa, Europe and Iberia in relation to the opening of
Figure 4.1: Collisional history of Iberia and Europe calculated by Rosenbaum et al. (2002), from where this figure is taken.

Table 4.1: Tectonic history of the Pyrenees, summarised from Puigdefabregas and Souquet (1986). Ages are taken from Gradstein et al. (2004); Ogg et al. (2008).

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Stratigraphic Age</th>
<th>Age / Ma</th>
<th>Tectonic Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Permian</td>
<td>300-250</td>
<td>Extensioinal basin</td>
</tr>
<tr>
<td>2</td>
<td>Triassic - Jurassic</td>
<td>250-145</td>
<td>Carbonate platform</td>
</tr>
<tr>
<td>3</td>
<td>Berriasian - Barremian</td>
<td>145-125</td>
<td>Sea-level fall and extension</td>
</tr>
<tr>
<td>4</td>
<td>Aptian - Early Albian</td>
<td>125-110</td>
<td>Submarine rifting</td>
</tr>
<tr>
<td>5</td>
<td>Mid-Albian - Early Cenomanian</td>
<td>110-99</td>
<td>Transtension to transpression</td>
</tr>
<tr>
<td>6</td>
<td>Cenomanian - Santonian</td>
<td>99-84</td>
<td>Wrench basin and sea-level rise</td>
</tr>
<tr>
<td>7</td>
<td>Santonian - Maastrichian</td>
<td>83-65</td>
<td>Transpressive basin, orogeny</td>
</tr>
<tr>
<td>8</td>
<td>Palaeocene</td>
<td>65-55</td>
<td>Foreland basin, orogeny</td>
</tr>
<tr>
<td>9</td>
<td>Eocene - Early Oligocene</td>
<td>55-30</td>
<td>Piggy-back thrust sheets</td>
</tr>
</tbody>
</table>

the Atlantic Ocean. Rosenbaum et al. (2002) discuss the timing, style and magnitude of Alpine Orogeny. The relative motion of two plates to be calculated based on their individual motion with respect to a third plate. Using a reference plate, the relative motion between
converging plates can be calculated as:

\[ A ROT_B(t) = A ROT_{REF}(t) + REF ROT_B(t). \]

Rosenbaum et al. (2002) use North America as a reference plate, allowing them to identify convergence between Iberia and Europe and between Africa and Europe. In the Pyrenees, a clear picture is seen using this method (see Figure 4.1).

Rosenbaum et al. (2002) found that in the late Cretaceous there was strike-slip motion, which gradually became compressional sometime during the Cretaceous “quiet period” (120 - 83 Ma) and was fully compressional by 83 Ma. Convergence paused in the Palaeocene, resumed in the Eocene and terminated by the Oligocene. This agrees with the sedimentary history provided by Puigdefabregas and Souquet (1986).

Figure 4.2: Cross section of the Pyrenees during the Eocene from Verges et al. (1995).

Figure 4.3: Contemporary cross section of the Pyrenees from Metcalf et al. (2009), based on the ECORS profile. The Maladeta pluton within the Orri thrust sheet has been used to assess uplift rates for the mountain range.

The central part of the Pyrenees consists of a stack of three main tectonic units (Verges...
The earliest, upper unit is the Nogueres, uplifted in the Palaeocene, followed by the Ypresian Orri and Lutetian-Bartonian Rialp thrust sheets. Figures 4.2 and 4.3 show the locations of these thrust sheets pre-and post orogeny. The Maladeta pluton is contained within the Orri thrust sheet (see Figure 4.3). Data from $^{40}\text{Ar}/^{39}\text{Ar}$ and apatite fission track studies (Metcalf et al., 2009) show rapid exhumation of the Maladeta pluton in the centre of the Pyrenees beginning at 50 Ma, especially during the Oligocene from 35-30 Ma, and decreasing after 25 Ma. Gibson et al. (2007) calculated exhumation rates of up to 1.5 mm yr$^{-1}$ in this area, decreasing to 0.03 mm yr$^{-1}$ after 30 Ma.

Figure 4.4: Cross section of the southern flank of the Pyrenees, taken from Coney et al. (1996).

Figure 4.5: Basins of the southern flank of the Pyrenees, taken from Caja et al. (2010).

Sediments eroded to the south were deposited into a series of piggy-back basins formed from foreland thrust sheets located between the axial zone and the Ebro basin to the south. From north to south, the thrust sheets of the central southern Pyrenees comprise the Boixols, Montsec and Sierras Marginales (see Figure 4.4). Above these thrust sheets lie the Tremp-Graus, Ainsa and Jaca basins (see Figure 4.5). These constrained basins
were fed from the east, with more marine facies in the western basins. The Ebro basin is located to the south of these.

The later history of the southern flank of the Pyrenees consists of backfilling, uplift and erosion. According to Coney et al. (1996), the Eocene-Oligocene uplift at the Pyrenean margins led to isolation of the Ebro basin, which filled with material eroded from the Axial zone.

Mountain building in the Pyrenees started in the mid to late Miocene and led to the development of their current relief. Rifting of the Catalan Mediterranean margin, coupled with the Messinian salinity crisis (Coney et al., 1996) caused the Ebro river to cut into the basin from the east, forming the current relief. Modern drainage patterns are thus towards the east, rather than westwards as was the case during the Cretaceous and early Tertiary.

Foreland basin deposits were formed in front of the mountain belt from the Late Cretaceous, the continued orogenic activity incorporated the Tremp-Graus, Ainsa and Jaca basins into the mountain belt itself, leading to recycling of material from the initial stratigraphy into later sedimentary units. Two time slices within the foreland stratigraphy were selected as field areas, the Late Cretaceous and Eocene, sampling distinct phases of the orogeny. During this time, sediment transport changed from orogen-parallel to orogen-transverse (Whitchurch et al., 2011). Samples were collected from the Aren and Castissent formations (see Figure 4.8), along E-W transects covering proximal continental to distal marine facies.

### 4.1.2 Sedimentary basins of the Southern Pyrenees

Figure 4.8 shows the Late Cretaceous and early Tertiary stratigraphy of the Southern Pyrenees, a series of sedimentary basins containing a wide range of depositional environments and lithologies ranging from terrestrial to marine, from coarse conglomerates to fine muds, and from silicates to carbonates and evaporites. The basins are oriented ESE-WNW, parallel to the mountain belt, draining towards the west, with a total fill depth of 3.5 to 4 km (Ardevol et al., 2000; Sutcliffe and Pickering, 2009). During the Eocene, movement of the Montsec thrust sheet uplifted the Cretaceous foreland sediments and led to recycling into the foreland basin (Sutcliffe and Pickering, 2009; Puigdefabregas and Souquet, 1986). Continuing orogeny caused the foreland basin to locate further to the south with time, whilst sedimentary fill within each iteration of the foreland basin led to sedimentary facies
moving westwards. Erosion during the Oligocene and early Miocene led to the foreland being filled with up to 3 km of continental conglomerates as the mountain belt itself was uplifted \cite{Coney1996}. The coarse conglomerates deposited during this period are conspicuous in geological maps (see Figure 4.7) and in the field.

Substantial work has been carried out on these sediments, as they provide extensive sampling opportunities for a range of investigations: turbidite facies analysis \cite{Mutti1977}; hydrocarbon analysis \cite{Ardevol2000, Falivene2010}; Palaeocene-Eocene Ther-
4.1. INTRODUCTION

Figure 4.7: Geological Map of the Tremp-Graus basin, showing mature Metamorphic rocks in the centre of the mountain range (reds), and a series of sedimentary deposits in front of the mountain range (greens and oranges).

Figure 4.8: Stratigraphy of the late Cretaceous and Tertiary Pyrenees, after Puigdefabregas and Souquet (1986). Sampled stratigraphic units are coloured yellow. Sedimentary facies are: 1 - hiatus; 2 - conglomerates; 3 - fluvial deposits; 4 - nearshore sandstones; 5 - blue marls; 6 - turbidites; 7 - slope breccias and mega-turbidites; 8 - shallow-marine carbonates; 9 - non-marine carbonates; 10 - evaporites.
4.2 Sample Locations and Descriptions

Figure 4.9: Sample locations in the Spanish South-Central Pyrenees. Red circles represent samples collected in the Cretaceous “Aren” group, blue triangles the Eocene “Castissent” group.

A reconnaissance field trip was undertaken in November 2008, and further sampling took place in April 2011. Samples were collected from two approximate time-horizons, one in the late Cretaceous and one in the early Eocene (see Figure 4.9). The initial sample locations were supplied by the research group of Prof. J. A. Muñoz at the University of Barcelona, and subsequent contemporaneous localities were chosen from a geological map and from the literature, including a section known to contain woody debris (Tyson and Follows 2000) and published turbiditic sections (Caja et al. 2010).
4.2.1 Aren Formation

Figure 4.10: Sample locations from the Aren Formation, plotted on a schematic mountain to marine transect.

The first group of samples were from the Aren Formation and other late Cretaceous stratigraphic units. Located within the Montsec thrust sheet (Coney et al. 1996) (see Figure 4.3), the Aren Formation is part of sequence K$_{2-5}$ (see Figure 4.8) consisting of nearshore sandstones and offshore turbidites and shales (Salas and Bidart marls), formed during renewed tectonic activity in the Maastrichian (Puigdefabregas and Souquet 1986). A spore colour index value of 3 shows that the sequence is thermally immature (Tyson and
Follows (2000). Samples were collected from nearshore sands, deltaic deposits and shelf material within these formations, which will subsequently all be described as “Aren” (see Figure 4.10).

Ardevol et al. (2000) identified four depositional sequences within the Aren using seismic reflection profiles, three large sequences covering the majority of the basin and one (Aren 2) smaller, confined to the eastern part of the formation (see Figure 4.11). Each sequence spans 2-3 Myr.

Tyson and Follows (2000) studied a transect through the eastern and central part of the Aren formation, from Orcau to Torre la Ribera. They found organic matter within the sedimentary deposits at fifteen localities through the basin, including woody phytoclasts, and TOC ranging from 0.1 - 0.8 %. They concluded that the sandstones were deposited in oxic conditions with a significant terrestrial component to the organic carbon. Woody debris clast size reduced with distance from the palaeo-shoreline, both throughout the sequence of sample sites and within a single sedimentary log during a sequence stratigraphic cycle. The ability to track POC through a formation with a well-constrained age range is
beneficial when comparing sedimentary facies, therefore sample sites from their work were revisited for this study.

Seventy four samples were collected from 14 localities along a 65 km transect ESE-WNW transect (see Table 4.2). Facies ranged from fluvial-marine sediments (localities 8, 9 and 21) through deltaic settings (localities 10, 83 and 84) across the shelf and slope (6, 7, 11, 13, 14 and 20) to the basin (12 and 82). Nummulites fossils were seen at localities 6, 7 and 21, suggesting that these sections are in the early Palaeocene rather than Late Cretaceous, and may have been deposited when the orogeny was slower and climatic conditions slightly different. Multiple samples were collected at most sites in order to represent the entire range of grain sizes and deposits present. Often a locality contained sandy and muddy layers, as well as POC-rich beds. POC ranged in size from sub-mm to cm-sized.

4.2.2 Castissent Formation

Figure 4.12: Eocene palaeogeography of the Southern Pyrenees from Sutcliffe and Pickering (2009), overlain with sample sites from the Castissent Formation. The palaeogeographic map contains few reference points, and has been georeferenced with respect to the towns of Ainsa and Graus only, as the defined positions of Jaca and Huesca are suspect, thus the exact locations of each sample with respect to the interpreted palaeogeography is uncertain. This figure does however show that samples have been collected from a wide range of sedimentary environments, from fluvial-deltaic to distal basin settings.
<table>
<thead>
<tr>
<th>Locality Location / Exposure Facies</th>
<th>Samples</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>N42.1575 E0.9736 Open country Fluvial-marine</td>
<td>6 Estuarine mud and conglomerates</td>
<td></td>
</tr>
<tr>
<td>N42.3254 E0.5737 Roadcut Fluvial-marine</td>
<td>9 Cross-bedded sand and mud lenses</td>
<td></td>
</tr>
<tr>
<td>N42.1610 E0.9745 Open country Foreshore</td>
<td>1 Coarse sand</td>
<td></td>
</tr>
<tr>
<td>N42.1632 E0.9707 Cliff face Delta front</td>
<td>2 POC rich sands and mud</td>
<td></td>
</tr>
<tr>
<td>N42.1630 E0.9708 Cliff face Intertidal</td>
<td>4 Interbedded sand and mud</td>
<td></td>
</tr>
<tr>
<td>N42.1630 E0.9702 Cliff face Intertidal</td>
<td>2 Very weathered</td>
<td></td>
</tr>
<tr>
<td>N42.2509 E0.7334 Riverbank Intertidal</td>
<td>8 Below low tide Coarse sand</td>
<td></td>
</tr>
<tr>
<td>N42.2509 E0.6634 Open country Intertidal</td>
<td>2 Very weathered</td>
<td></td>
</tr>
<tr>
<td>N42.3309 E0.701 HILlop Base of slope</td>
<td>10 Hard mud and silt layers</td>
<td></td>
</tr>
<tr>
<td>N42.2156 E0.9783 Hilltop Foreshore</td>
<td>3 POC rich sands and mud</td>
<td></td>
</tr>
<tr>
<td>N42.1710 E0.8577 Riverbank Delta front</td>
<td>4 Interbedded sand and mud</td>
<td></td>
</tr>
<tr>
<td>N42.1749 E0.7334 Riverbank Intertidal</td>
<td>8 Very weathered</td>
<td></td>
</tr>
<tr>
<td>N42.3009 E0.6634 Open country Intertidal</td>
<td>4 Interbedded sand and mud</td>
<td></td>
</tr>
<tr>
<td>N42.1629 E0.9722 Low cliff Lower pro-delta</td>
<td>8 Thick mud with sand bodies</td>
<td></td>
</tr>
<tr>
<td>N42.1630 E0.9708 Cliff face Intertidal</td>
<td>2 POC rich sands and mud</td>
<td></td>
</tr>
<tr>
<td>N42.1630 E0.9707 Cliff face Intertidal</td>
<td>4 Interbedded sand and mud</td>
<td></td>
</tr>
<tr>
<td>N42.1630 E0.9704 Cliff face Intertidal</td>
<td>2 Very weathered</td>
<td></td>
</tr>
<tr>
<td>N42.1630 E0.9707 Cliff face Intertidal</td>
<td>8 Very weathered</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: Samples collected from the Aren formation, arranged by sedimentary facies from terrestrial to marine.
<table>
<thead>
<tr>
<th>Locality</th>
<th>Location / °</th>
<th>Exposure</th>
<th>Facies</th>
<th>Samples</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>N42.1473 E0.7317</td>
<td>Hillside</td>
<td>Fluvial-alluvial</td>
<td>4</td>
<td>Crossbedded sands</td>
</tr>
<tr>
<td>23</td>
<td>N42.1349 E0.6910</td>
<td>Cliff face</td>
<td>Fluvial channel</td>
<td>8</td>
<td>Sand bars</td>
</tr>
<tr>
<td>22</td>
<td>N42.2367 E0.5068</td>
<td>Roadcut</td>
<td>Fluvial-marine</td>
<td>11</td>
<td>Channels, woody debris</td>
</tr>
<tr>
<td>15</td>
<td>N42.3564 E0.3780</td>
<td>River cliff</td>
<td>Outer Shelf</td>
<td>4</td>
<td>Fossiliferous marls</td>
</tr>
<tr>
<td>16</td>
<td>N42.3963 E0.2608</td>
<td>Roadcut</td>
<td>Shelf break</td>
<td>5</td>
<td>Large woody clasts</td>
</tr>
<tr>
<td>17</td>
<td>N42.4059 E0.2378</td>
<td>Roadcut</td>
<td>Base of slope</td>
<td>27</td>
<td>Turbidites A-E</td>
</tr>
<tr>
<td>18</td>
<td>N42.4234 E0.2215</td>
<td>Roadcut</td>
<td>Base of slope</td>
<td>1</td>
<td>Turbidites D-E</td>
</tr>
<tr>
<td>87</td>
<td>N42.4683 E0.1047</td>
<td>Roadcut</td>
<td>Channel-lobe transition</td>
<td>5</td>
<td>Interbedded sand and silty mudstone</td>
</tr>
<tr>
<td>85</td>
<td>N42.4357 E0.1353</td>
<td>Roadcut</td>
<td>Channel overbank deposits</td>
<td>3</td>
<td>20 cm mud beds</td>
</tr>
<tr>
<td>86</td>
<td>N42.4349 E0.2134</td>
<td>Roadcut</td>
<td>Channel overbank deposits</td>
<td>5</td>
<td>10 cm mud beds</td>
</tr>
<tr>
<td>88</td>
<td>N42.4617 E0.1168</td>
<td>Roadcut</td>
<td>Mud lobe</td>
<td>5</td>
<td>Laminated mudstones</td>
</tr>
<tr>
<td>89</td>
<td>N42.6187 W0.2002</td>
<td>Riverbank</td>
<td>Distal basin or channel lobe</td>
<td>3</td>
<td>Sand and silty mud beds</td>
</tr>
<tr>
<td>19</td>
<td>N42.6143 W0.1260</td>
<td>Roadcut</td>
<td>Distal basin or channel lobe</td>
<td>22</td>
<td>Turbidites B-C</td>
</tr>
</tbody>
</table>

Table 4.3: Samples collected from the Castissent formation, arranged by sedimentary facies from terrestrial to marine.
The second group of samples are from the Castissent formation and other early Eocene deposits, sequence TE4. They formed in the late Ypresian following eustatic sea-level fall and basin closure to the east. Turbidites sourced in the Eastern Pyrenees were deposited within the semi-enclosed basin, open to the west (Puigdefabregas and Souquet 1986). 103 samples were collected from 13 localities along an ESE-WNW transect spanning 100 km (see Table 4.3).

Sedimentological characteristics of sampled sites suggest that they encompass a wide range of facies. There were onshore samples from alluvial fans (locality 24), sand bars (23) and river channels (22). Samples from the outer shelf (15) and shelf break (16) incorporated marine fossils and coarse pieces of POC\textsubscript{terrio}. Base-of-slope localities (17 and 18) contained turbidites. A series of localities from submarine channel overbank deposits and channel lobes (85, 86, 87 and 88) contained mostly mudstone, with some sand and silt interbeds. Furthest offshore in the Ainsa basin were fine sands and silts, with fine-grained turbidites.
4.2. SAMPLE LOCATIONS AND DESCRIPTIONS

Figure 4.14: Woody debris preserved at locality Castissent 16, a shelf-break setting. This locality had several pieces of Coarse Woody Debris preserved.

Figure 4.15: Field photograph from locality 24 in the Castissent Formation, showing a concentration of POC in an otherwise carbon-poor terrestrial sand body. This could be preserved CWD.
The majority of the Castissent samples were located in the marine slope and basin, along with proximal marine muds interpreted as channel overbank deposits (Caja et al., 2010). These consisted of multiple 2-10 cm beds of muddy material, sedimentologically similar to the muddy material seen in Taiwan beside the Gaoping canyon (see Figure 4.16). Macroscopic POC in these samples was fine-grained and dispersed within the muddy sections. Up to 27 samples were collected at each site, in order to fully-represent the variety of facies exposed at each locality and in order to produce vertical profiles through
4.3. RAMAN SPECTROSCOPY RESULTS

a sedimentary section. The most samples were collected at locality 17 in order to fully characterise a complex turbiditic section (see Figure 4.13). Coarse POC$_{terrbio}$ was seen at locality Castisent sample 24 was from a terrestrial alluvial setting, with large cross-bedded sand bodies. POC here was concentrated into large deposits (10s of cm) in rare sections (see Figure 4.15).

Samples were analysed by Raman spectroscopy to constrain the range of POC inputs to the basins, and by isotope geochemistry to quantify carbon input to the various facies and to deconvolve the various carbon sources.

4.3 Raman Spectroscopy Results

4.3.1 Aren Formation

![Raman spectra](image)

Figure 4.17: Raman spectra collected from the Aren formation, scaled to fit the same y-axis, with background effects removed.

241 spectra were measured from samples collected in 2008, including 94 from nine different samples of the Aren Formation (6b, 6c, 7a, 7c, 8b4, 10a, 11a, 11b, 11d) representing
localities from the estuary to the shelf break. The most common spectral shape from the Aren formation (see Figure 4.17) showed broad D bands, with height about $\frac{3}{4}$ that of the G band, which is also broad and situated about 1600 cm$^{-1}$, and no discernible D2 peak. There are two spectra with a graphitic style, but very few with a disordered style different to the most frequent peak shape.

### 4.3.2 Castissent Formation

147 spectra were collected from 10 samples of the Castissent Formation (15a, 15c, 15cfresh, 16b, 17c, 17c2, 19b, 19c, 19e, 24b) representing facies from alluvial fans to distal basins. The Castissent samples showed more variation in spectral style. Spectra from locality 19, in the distal basin, tended to show narrower D and G bands than the Aren samples (see Figure 4.18b). Sometimes the D2 peak was visible as a shoulder to the G band, whose position varies from $\sim$1575 to $\sim$1605 cm$^{-1}$. The D4 peak was just visible as a shoulder to the D band, occurring at about 1275 cm$^{-1}$. Spectra with very broad D bands were rare in the samples from this locality. Graphitic-style spectra were also rare.

In comparison, no spectra from the turbidites at locality 17 (base of slope) matched the most common pattern from locality 19 (see Figure 4.18b). There were some spectra with very broad D bands, and several spectra with a narrow G band and minimal D band amplitude.

The remaining Castissent samples, collected from onshore, outer shelf and shelf break environments, show a range of spectra, from narrow-banded graphitic styles through to broad-banded disordered spectra (see Figure 4.19). The disordered spectra look more like those in locality 17 than locality 19.

### 4.4 Raman Spectroscopy Discussion

Comparing the results from both formations, the Aren formation contains mostly very disordered spectra with few graphitic or semi-ordered spectra, whilst the Castissent samples contain a mixture of very disordered and semi-ordered spectra, again with some graphitic spectra.
Figure 4.18: Raman spectra from locality Castissent 19, scaled to fit the same y-axis, with background effects removed.
4.4.1 Aren Formation

Plotting the Aren samples in Total-width vs. Temperature space (see Section 2.4.5) shows that most of the spectra are classified as highly disordered (see Figure 4.20). The large total-width parameter means that most carbonaceous materials present here have not experienced any significant metamorphic conditions. However, there is a smaller amount of highly graphitised material present, with temperatures estimated around 600 °C.

Localities, 8, 7, 6 and 11, the estuary, inner shelf, outer shelf and shelf break respectively, contain very disordered carbon and occasional graphitic grains. Locality 10, the lower prodelta contains mostly very disordered carbon with some semi-graphitised carbon, with temperatures below 360 °C and total peak widths below 290 cm$^{-1}$. No highly-crystalline graphite was found in this sample.
Figure 4.20: Analysed Raman spectra from the Aren Formation, plotted in Total width vs Temperature space.
Figure 4.21: Analysed Raman spectra from the Castissent Formation, plotted in Total width vs Temperature space.
4.4.2 Castissent Formation

Castissent sample 24 was the most proximal from this formation. Organic material stored here is very disordered, with a total width of $\sim 340 \text{ cm}^{-1}$ (Figure 4.21). This organic material has never been significantly metamorphosed - it was likely deposited as coarse woody debris and has experienced only minor diagenesis to lignite-grade material. In view of its large clast size it is highly unlikely that this material has been recycled through multiple orogenic cycles. Therefore it serves as an example of “one-cycle” POC$_{terrbio}$, whilst smaller grains of disordered carbon may have been deposited in the Aren and recycled into the Castissent as “two-cycle” or even “multi-cycle” POC.

Spectra from localities Castissent 15, 16 and 17, a transect across the outer shelf, shelf break and slope, contained several highly disordered carbonaceous grains with characteristics similar to locality 24. Along with this there were some very graphitised spectra in all samples and few or no spectra with a low-grade metamorphic signature.

Locality 19 in the Castissent formation is very different from the other localities, it shows no highly graphitised material and little very disordered carbon. There is a large amount of disordered material with total width about 200 cm$^{-1}$, which sits within the range of spectra collected from low-grade metamorphic material (see Figure 2.13).

4.4.3 Comparing the Aren and Castissent basins

When comparing the Aren Formation to the Castissent, the most noticeable difference is the general lack of semi-graphitised material in the Aren. Whereas locality 19 in the Castissent contain low-grade metamorphic material similar to that sourced from the Central Range of Taiwan, the Aren is dominated by very disordered carbon, similar to that seen in the Plio-Pleistocene lignite-grade deposits and in the concentrated organic matter at Castissent locality 24, along with some very graphitised grains. These detrital graphite crystals seem to be ubiquitous, appearing in a wide range of samples from multiple lithologies.

The time differences between the Aren and Castissent formations may explain this. The Aren deposits date from the Cretaceous, in the early part of the orogeny, when exhumation would have been limited. The material eroded to form the Aren was cover sediment, not significantly metamorphosed basement rock. Graphite grains could have been sourced directly from occasional deep bedrock or may have been detrital grains already present in
By the Eocene when the Castissent was formed, there had been much more exhumation in the Pyrenees, and semi-graphitised material would have been exposed. This is again very comparable to the situation in Taiwan - during the early stages of orogeny the metamorphic carbon is not exposed and so POC export is limited to modern productivity and detrital graphite. Once erosion has cut into the basement material, increasingly graphitised carbonaceous grains are harvested from the emerging hillslopes.

Lignite-grade material in the Castissent Formation could come from direct incorporation of POC\textsubscript{terrbio}, as in locality 24, or could be due to recycling of previously buried organic carbon. The offshore Castissent localities contained very disordered carbon with spectra that did not exactly match those collected from locality 24, rather they had slightly higher RA2 temperatures. This could be due to the recycling of Cretaceous foreland basin sediments into the Eocene deposits, including POC already metamorphosed to lignite grade.

Section 6.2.3 contains a comparison of the Raman spectroscopy results from the Pyrenees and Taiwan.

### 4.5 Elemental / Isotopic Results

Raman spectroscopy in the Pyrenees describes the history of the mountain belt and gives a qualitative distribution of carbon grades within it. Isotopic / elemental analysis was used to understand carbon sourcing processes and to investigate carbon storage in the different sedimentary environments. Isotopic / elemental analyses were performed on decarbonated samples from both formations, the results of which are presented in the following sections.

#### 4.5.1 Carbonate dissolution correction

Carbonate correction is an important factor when determining TOC in these sediments. Careful consideration was made whether to correct for carbonate dissolution in these samples (see Section 2.5.3). In the modern routing system of Taiwan, any carbonate present in the sediment was due to erosion of carbonate substrates, as there would not have been time for a cement to form in the few months between deposition and sampling. In ancient formations such as the Pyrenees, an initially highly porous sediment could contain 20 or
30\% cement after diagenesis. Correcting for carbonate sourced only from cement would lead to low TOC values, as the TOC at deposition would be diluted by subsequent carbonate precipitation. Thus it would be difficult to investigate the survivability of POC through time due to these artificial decreases in TOC not associated with organic carbon decomposition. However, the presence of sedimentary carbonate in the sediments means that measured TOC will be artificially high in comparison to the true proportion of organic carbon in the samples.

Sandstones of the Aren formation were described as containing predominantly quartz grains with a pervasive calcite cement (Ardevol et al., 2000). If true, this suggests that a decarbonation correction was not required for these sediments. However, the average loss on decarbonation in the Aren samples was 62\%, with a maximum of 96\%, which cannot be solely due to calcite cement. Whilst a large component of the decarbonation may well have been due to cement, there was the potential for inflated TOC measurements if the carbonate correction was not applied.

Petrographic investigations of the Eocene Hecho group (which includes the Castissent Formation) by Caja et al. (2010) showed large amounts of carbonate grains, both extrabasinal and intrabasinal. Extrabasinal carbonates (CE) comprise recycled carbonate rocks, specifically “micritic limestones, microcodium fragments, polycrystalline sparitic limestones, dolostones, bioclastic grainstones with foraminifera of Cretaceous and Palaeocene age and monocrystalline sparitic limestones”. The concentration of these carbonate grains increases through the stratigraphy and the upper, Ypresian, sections contain 20-70\% CE grains. Intrabasinal carbonates (CI), consisting of Eocene foraminifera, other shallow-water bioclasts, peloids and phosphate fragments, were present in proportions from 0 - 30\% in the same sections.

With at least 20\% of the Castissent sediment consisting of carbonate grains, and this proportion varying greatly in samples within and between localities (Caja et al., 2010), it was necessary to correct for carbonate content when reporting TOC values (see Section 2.5.3). Therefore the carbonate dissolution correction was applied to all samples from the Pyrenees, although this may have reported a conservative value of the TOC present in the sediment itself.
Figure 4.22: Isotopic / elemental results from all Aren Formation samples, displayed in $\delta^{13}C$ vs. N/C space. Samples are listed in facies order from proximal to distal.

4.5.2 Aren Formation

Samples from the Aren Formation contained a wide range of TOC values, from 0.006 to 3.2 wt%. Average TOC was 0.26 ± 0.4 (1σ) wt%. Highest TOC values were recorded in fluvial and deltaic sediments, although most settings contained a wide range of TOC concentrations. The samples as a whole occupied a wide trend in $\delta^{13}C$ - N/C space (see Figure 4.22), running from N/C of ~0.05 and $\delta^{13}C$ ~-26 ‰ to N/C ~0.5 and $\delta^{13}C$ ~-23 ‰. The most POC-rich samples plot towards the low N/C and $\delta^{13}C$ end of this trend, with carbonate-corrected values of up to 0.7 wt% C in the regular bulk-rock samples and 3.2 wt% C in especially concentrated-POC samples. Nitrogen isotopic values range from -6 to +4.3 ‰, and those samples with a higher POC tend to have values of 1 - 4 ‰. Separating the data into different facies groups, as seen in Table 4.2, allows the distribution of isotopic compositions to be explored. Figure 4.23 shows the results from each facies grouping.

Fluvial-marine and estuarine settings were sampled at locality 21 and 8 respectively. Locality 21 consisted of cross bedded sands with occasional mud lenses. TOC values were generally below 0.3 wt% with occasional POC-rich samples. POC was present in distinct layers (see Figure 4.24). A bed within the mud contained 3.2 wt% C, and had the lowest $\delta^{13}C$ and N/C values of any sampled onshore material, -25 ‰ and 0.03 respectively. Estuarine muds and conglomerates at locality 8 contained TOC ranging from 0.02 wt% to 0.06 wt%. N/C values were all above 0.1 and $\delta^{13}C$ values were between -23 ‰ and -24 ‰. Carbon isotope values from locality 21 were similar to locality 8, around -24 ‰.
4.5. ELEMENTAL / ISOTOPIC RESULTS

Nearshore samples from localities 10, 83 and 84, contained a reasonable amount of POC (mean 0.45 ± 0.22 wt% C), with low δ¹³C values (-25.47 ± 0.5 ‰) and N/C ratios (0.056 ± 0.02). Locality 10, the lower pro-delta, had slightly higher N/C ratios than the upper pro-delta samples (83 and 84), however all three localities had amongst the lowest δ¹³C and N/C values.

Material from the shelf and slope was sampled at localities 14, 13, 7, 6, 11 and 20, interpreted as the intertidal, storm wave-base, inner shelf, outer shelf, shelf break and base-of-slope respectively. These samples contained a low to moderate amount of carbon (0.16 ± 0.11 wt% C) with a wide range of isotopic values and elemental ratios. δ¹³C values range from -26.1 to -21.8 ‰, whilst N/C ranges from 0.06 to 0.25. Locality 13 was the only one in this setting that contained organic matter with low δ¹³C values (-25.87 ± 0.36 ‰) and N/C ratios (0.09 ± 0.05). Apart from this locality, there was no co-location between these samples and the pro-delta material in δ¹³C - N/C space.

Material from marine basin settings, localities 12 and 82, showed a range of isotopic / elemental values, although TOC measurements were quite consistent (0.17 ± 0.10 wt% C).
Figure 4.24: Field photograph of locality 21 showing laminated sandy grains with POC present in distinct layers.

The basin localities produced δ\textsuperscript{13}C values ranging from -25 to -23.4 ‰, overlapping with the values seen on the shelf. The same is true for the N/C range.

4.5.3 Castissent Formation

Figure 4.25: Isotopic / elemental results from all Castissent Formation samples, displayed in δ\textsuperscript{13}C vs. N/C space. Samples are listed in facies order from proximal to distal.

Samples from the Castissent Formation contained TOC ranging from 0.03 to 0.98 wt%
4.5. ELEMENTAL / ISOTOPIC RESULTS

C, along with five samples of POC clasts, with TOC measurements up to 9.8 wt%. N/C ranged from 0.01 (in a piece of coarse POC from locality 24) to 0.84 (a sand-rich sample with very little POC, also from locality 24). $\delta^{13}C$ values ranged from -25.6 to greater than -15 ‰ (see Figure 4.25). The ensemble did not describe a clear trend as in the Aren, instead it fanned out in $\delta^{13}C$ vs. N/C space from low $\delta^{13}C$ and N/C values (-25.5 ‰ and 0.39) towards higher values. Patterns were identified when the formation was separated into different sedimentary facies (see Figure 4.26).

![Figure 4.26: Isotopic / elemental results from all Castissent Formation samples, separated by facies group, displayed in $\delta^{13}C$ vs. N/C space.](image)

Onshore material, from localities 22, 23 and 24, had the widest range of isotopic values...
and elemental ratios. Samples tended to have low TOC values (0.14 ± 0.1 wt% C), but occasional layers of terrestrial POC with high TOC measurements had low δ\textsubscript{13}C and N/C values. Locality 24 in particular had very little TOC in most samples (average 0.087 wt%) with occasional layers of lignite-grade black organic material (see Figure 4.15).

Material from shelf localities 15 and 16 had a moderate TOC concentration (0.20 ± 0.09 wt% C) with a range of N/C values (0.06 to 0.22) and similar δ\textsubscript{13}C values (-24.1 ± 0.5 ‰). There were no bulk-rock samples with very low δ\textsubscript{13}C and N/C values, however four samples of coarse POC were collected (see Figure 4.14). These had high TOC measurements, up to 9 wt% C, low δ\textsubscript{13}C values (-24.9 ± 1.0 ‰) and low N/C ratios (0.015 to 0.035).

Localities 17 and 18 were interpreted as base-of-slope turbidites. Locality 17 provided excellent exposure of layers A to E from the Bouma sequence. At these sites there was a wide range of δ\textsubscript{13}C (-18.8 to -25.6 ‰) and N/C values (0.04 to 0.24), constrained within a triangular zone pointing towards the lowest values in each parameter. Lowest values were found in sample 17C.2 which was a POC-rich layer at the top of a laminated sand section, containing mm-scale POC. Within the laminated sands TOC concentrations were not necessarily high. POC-rich samples had δ\textsubscript{13}C values as high as -21 ‰. The mean TOC measurement from these sections was 0.37 ± 0.26 wt% C. TOC was low to moderate in thick sandy sections, and relatively high in the muddy section above and in a thin sand layer.

Further offshore, the Eocene formations were described as having a submarine channel and lobe architecture (Caja et al., 2010) (see Figure 4.12). Samples 85 - 88 were collected from localities containing varying proportions of sand, silt and mud, all more fine-grained than the turbiditic and basin sections, interpreted to be from outside a submarine canyon. TOC concentrations were quite high, with little variance (0.37 ± 0.11 wt% C), whilst δ\textsubscript{13}C and N/C values were comparable to the shelf samples (see Figure 4.26). Where grain size profiles existed, such as at locality 87, the sand-grade material contained less POC than either silty or muddy layers. Locality 86 showed little difference in TOC between the silty and muddy samples, both had around 0.4 wt% C.

Basin material from the Castissent Formation, sampled at localities 19 and 89, contained moderate TOC concentrations (0.25 ± 0.13 wt% C). δ\textsubscript{13}C were quite low (-24.0 ± 0.92 ‰ with a minimum of -25.2 ‰) but N/C values were relatively high (0.11 to 0.38). The distribution of isotopic / elemental parameters was different to the turbiditic samples. Sedimentologically these were finer grained than the turbidites, interbedded sandy and muddy or silty layers interpreted as part of the Bouma sequence (see field photograph in
4.6 Elemental / Isotopic Interpretation

Having collected TOC, isotopic and elemental measurements, it was possible to investigate the different types of carbon present in the Pyrenean samples, attempting to quantify the input of terrestrial biomass into the sediment.

Figure 4.27: All Aren and Castisset samples, as analysed by 2-component endmember mixing (Hilton et al., 2010). The black line represents a mixing line between endmembers defined to be “non-terrestrial”, that is POC other than woody debris, vegetation and soils. The samples to the right of the non-terrestrial mixing line contained anomalously high N/C ratios or carbon isotope measurements, and should be ignored when looking at 2-component mixing. These samples are usually less-concentrated in POC.

Given that the source rocks of the Aren and Castissent formations were submarine sediments themselves, recycling of carbon is a distinct possibility. POC with a marine carbon signature may be from intrabasinal productivity or extrabasinal erosional material. With the complexity of the source areas, and the observation that fluvial samples from both the Aren (Figure 4.23) and Castissent (Figure 4.26) contain material with a relatively high $\delta^{13}C$ value, which could be due to recycled marine carbon, full deconvolution
using multiple-endmember unmixing was unsuccessful. This issue is discussed further in Section 6.1.5.1. Rather, samples were unmixed to show the influence of terrestrial biomass addition to the sediment. The Hilton method (see Section 2.5.4) of dynamic endmember mixing was used to separate the POC signature into a terrestrial biomass endmember (POC\textsubscript{terrbio}), and a “POC\textsubscript{other}” endmember that covers fossil carbon and marine POC both from recycled marine sediments and primary productivity (see Figure 4.27). Higher δ\textsuperscript{13}C values in POC\textsubscript{other}-rich samples implies the presence of marine carbon, Raman spectroscopy evidence and field observations can support this interpretation.

Sample 16-5, a woody debris sample from the Castissent (see Figure 4.14) was used to provide the POC\textsubscript{terrbio} endmember, whilst a POC\textsubscript{other} mixing line was defined similar to that of Hilton et al. (2010), extending from (0.056,-16.37) to (0.348,-24.07). The POC\textsubscript{other} mixing line marked the boundary between a high density of POC-rich and a series of anomalous samples. These samples had low TOC concentrations and high N/C ratios compared to the remainder of the Pyrenean material. This could be due to a non-organic source of nitrogen to the samples.

By carrying out this unmixing, sample profiles could be constructed with TOC values deconvolved into two components, to show the distribution of different carbon types with distance along the basin transect or height through the locality. First the distribution of POC types within the basins will be considered, before specific vertical profiles are investigated.

4.6.1 Lateral profiles

The Aren Formation was categorised into Fluvial, Pro-Delta, Shelf Transect and Distal Basin groups. It showed a consistently low input of POC\textsubscript{other}, less than 0.1 wt% C in all categories. The POC\textsubscript{terrbio} input was within one standard deviation of the POC\textsubscript{other} for the Fluvial, Shelf and Basin groups, with between 0.08 and 0.11 wt% C. The POC\textsubscript{terrbio} signature in the Shelf group, which contained a lot of localities ranging from nearshore to base-of-slope, was mostly due to terrestrial material present at locality 13. This was the only locality in this group where samples with an isotopic and elemental concentration similar to POC\textsubscript{terrbio} (see Figure 4.23) were collected. However the pro-delta samples (localities 10, 83 and 84) were significantly different. Here the POC\textsubscript{terrbio} POC value was five times greater than the POC\textsubscript{other} contribution, and despite a large standard deviation there was a significant difference between the two.
POC<sub>other</sub> contents were uniform through all four facies groups. Given that the Aren formation tended to have lower $\delta^{13}$C values than would be expected for marine organic matter, this is likely due to fossil carbon. The fluvial input of fossil POC appears to have been preserved unchanged along the transport pathway to the basin, with minimal selective deposition or oxidation. Comparing this to the increased POC<sub>terrbio</sub> concentration in the deltaic sediments suggests either a selective deposition or preservation of POC<sub>terrbio</sub> in these settings, or in-situ production of POC<sub>terrbio</sub> on the delta.

This analysis suggests that POC<sub>terrbio</sub> delivered into the basin during the late Cretaceous was concentrated in the pro-delta rather than being delivered further into the basin. If terrestrial biomass was transported further into the basin then it has not survived long-term burial to the same extent as the pro-delta samples.

The Castissent Formation was categorised into Onshore, Shelf, Turbidites, Submarine Channel-Lobe and Distal Basin groups. POC<sub>other</sub> concentrations were similar or higher than in the Aren Formation, with between 0.10 and 0.22 wt% C. POC<sub>terrbio</sub> concentrations were usually lower than POC<sub>other</sub>, apart from in the shelf and turbidites where the concentrations were similar. Peak POC<sub>terrbio</sub> concentrations were in the turbiditic samples, whilst peak POC<sub>other</sub> concentrations were in the submarine channel overbank deposits and lobes. Unfortunately the lack of pro-delta samples from the Castissent meant that comparisons with the most POC-rich Aren samples were unavailable. If the Aren pro-delta was rich in POC<sub>terrbio</sub> due to local productivity then Castissent pro-delta deposits may also be POC-rich.
There is a large variance in the carbon concentrations within the turbiditic samples, especially in the POC\textsubscript{terrbio} content, which is due to the very localised deposition of POC within these sections. POC\textsubscript{terrbio} was seen concentrated into fine layers within the sandy parts of the turbidites (see Figure 4.13). The small variance and high POC\textsubscript{other} content of the submarine channel and lobe localities is likely due to the uniformity and small grain size of the deposits.

Overall it can be seen that POC\textsubscript{terrbio} and POC\textsubscript{other} distributions differed both within and between the two studied formations in the Pyrenees. The Aren Formation contained a large amount of POC\textsubscript{terrbio} in the deltaic sediments, whilst the Castissent Formation contained larger amounts of both POC\textsubscript{terrbio} and POC\textsubscript{other} further offshore, in turbiditic and channel-lobe settings. Looking closer at particular stratigraphic sections within these formations allows the vertical distribution of POC to be investigated further.

### 4.6.2 Vertical profiles

Localities 83 and 10 in the Aren formation were in the POC rich pro-delta group. A profile was collected across a mud-sand-mud transition at locality 83 (see Figure 4.30). All
samples contained less POC\textsubscript{other} than POC\textsubscript{terrbio}, but the 0.1 wt% POC\textsubscript{other} was similar to other facies groups. Samples from the upper and lower mud layers contained more POC than the sandy layers, over 0.5 wt% C.

The profile at locality 10 comprised five silt and mud samples, four below and one above a sandy layer (see Figure 4.31). Again all samples contained a uniform $\sim$0.1 wt% POC\textsubscript{other}. The lowest sample was from a pyritised silt deposit, and contained significantly less carbon than the other sections. The pyritisation could be due to local redox reactions, restricted to certain areas by fluid flow paths, which would consume organic material. All other samples contained more than 0.5 wt% carbon. These two low-resolution profiles suggest that muddy pro-delta material is reasonably homogeneous and carbon rich, as long as the sediment has not been oxidised. Sandy material appears to be less enriched in carbon.
In contrast to the simple distribution in the Aren Formation (see Figure 4.23), the Castissent turbidites showed a large spread of data in N/C - $\delta^{13}$C space (see Figure 4.26), which was interpreted as a wide range of concentrations for both POC$_{terrbio}$ and POC$_{other}$. A high-resolution profile through locality 17 in a Castissent turbidite sequence (Figure 4.32) showed a complex series of sand and mud beds (lower samples were seen in Figure 4.13). In the lower, thicker, sand layer the POC$_{other}$ concentration was very uniform, but one sample from the middle of the sand contained much more POC$_{terrbio}$. Moving into the mud layer above, POC$_{terrbio}$ POC was low but TOC was high (between 0.35 and 0.52 wt% C). This variability was generally accommodated by changes in the POC$_{other}$ input, which varied from 0.27 to 0.42 wt% in this layer. The thin sand layer above this contained the highest TOC concentration in the profile, 0.71 wt% C, and was rich in POC$_{terrbio}$. This profile shows that turbidity currents have the ability to sort material hydrodynamically over long transport distances, separating different classes of POC into heterogeneous layers.
“Channel-lobe transition” samples from this group of sections contained only silty and muddy material, their profiles are much more uniform with POC$_{other}$ contents between 0.2 and 0.3 wt% C and POC$_{terrbio}$ concentrations between 0.15 and 0.21 wt% C. The only sandy material present in this group was profile collected at locality 87. This showed a POC-poor (0.0 - 0.21 wt% C) sand layer sandwiched between mud layers containing moderate to high POC concentrations (Figure 4.33). POC$_{terrbio}$ was concentrated in the lower part of a silty layer above the sand, whilst POC$_{other}$ concentrations were highest in the muddy sections. In these fine-grained distal conditions, POC$_{other}$ seems to be the dominant form of carbon preserved.

The most distal profile collected was from the Castissent basin at locality 19. The facies here are fine-grained turbidites, similar to locality 17, with interbedded sand, silt and mud layers (see Figure 4.34). The TOC measurements are again quite variable, however in this
Figure 4.33: Isotopic / elemental profile through locality Castissent 87, showing corrected TOC and interpreted POC$_{terrbio}$ and POC$_{other}$ components.

section the POC$_{terrbio}$ and POC$_{other}$ values are both very similar and co-varying. Muddy sections are the richest in carbon, followed by silt, then fine and coarse sand layers.

Overall, these vertical profiles showed that POC can be highly stratified, with TOC concentrations varying greatly within a few cm. In general, finer-grained sediment was richer in POC than coarser, sandy layers, although samples of laminated sand within the turbidite deposits were rich in POC$_{terrbio}$. Silty and muddy sediments appear better at preserving POC, especially POC$_{terrbio}$. POC$_{other}$, especially that attributed to fossil carbon, seems ubiquitous and its concentration varied much less than POC$_{terrbio}$.
4.6. ELEMENTAL / ISOTOPOIC INTERPRETATION

![Castissent19 Profile](image)

Figure 4.34: Isotopic / elemental profile through locality Castissent 19, showing corrected TOC and interpreted POC\textsubscript{terrbio} and POC\textsubscript{other} components.

4.6.3 Coupling Raman Spectroscopy and Isotopic / Elemental Results

Coupling these concordant results, the isotopic / elemental unmixing process can be used to quantify the relative importance of terrestrial biological material, whilst the Raman spectra document the nature of the fossil carbon.

Raman Spectroscopy results showed that the Aren Formation was dominated by very disordered lignite-grade material, with some highly-graphitised fossil carbon present. Isotopic / elemental results confirmed this - pro-delta localities contained isotopic and elemental values suggesting almost exclusively terrestrial POC\textsubscript{terrbio}. POC\textsubscript{other} was present in the shelf transect and basin settings, Raman spectroscopy showed that it was highly-graphitised fossil material, likely detrital graphite grains.

The Castissent formation was more complex, with wider ranges of results from both the Raman and isotopic / elemental analysis. Isotopic / elemental results from shelf samples (localities 15 and 16) suggested a mixture of POC\textsubscript{terrbio} and POC\textsubscript{other} with low $\delta^{13}$C and...
high N/C, much like the Aren. Raman spectra confirmed this, there was little low-grade metamorphic material seen in these sediments, the POC$_{other}$ was likely to be graphite.

Turbidites from the Castissent show a broad range of isotopic values, which could suggest a variation in the fossil carbon input. However, Raman spectroscopy results show a distribution again dominated by very disordered material with some highly-graphitised carbon, thus it is likely that the increase in $\delta^{13}$C is due to addition of marine carbon, which would have little or no Raman signature, rather than a change in the style of the fossil carbon.

Samples from the Castissent basin showed a different result. Whilst Isotopic / elemental values were comparable to the shelf material, albeit with a slightly lower $\delta^{13}$C isotopic ratio, Raman results have shown the fossil carbon to be dominated by low-grade metamorphic material.

These comparisons show that in some cases it is Raman spectroscopy that can spot differences between isotopic / elementally similar samples, whilst sometimes the opposite is the case. Applying both techniques to the Pyrenean samples allows a fuller interpretation of the processes acting during orogeny and sediment transport.

### 4.7 Conclusions

#### 4.7.1 Insights into orogenic processes

The greatest difference between the two Pyrenean formations was the appearance of significant amounts of low-grade metamorphic material offshore in the Castissent Formation. Whilst the Cretaceous Aren formation consisted mostly of contemporaneous terrestrial biological productivity, by the Eocene there were significant amounts of POC$_{other}$, in the form of both marine carbon (autochthonous or recycled from exposed marine sediments) and fossil POC. The lack of marine carbon in the Aren suggests that a volumetrically significant amount of terrestrial sediment was exported to the foreland basin early in the orogeny, enough to dilute any marine organic matter deposited in the basin.

Raman results suggest that the Castissent low-grade fossil carbon experienced metamorphic temperatures up to 300 °C, a value that agrees with $^{40}$Ar/$^{39}$Ar results.
et al., 2009). This is suggestive of burial of up to 20 km (England, 1981), meaning that there was significant exhumation of the mountain range by the Eocene, even though the greatest uplift occurred just after this period.

Thus a model can be described in which the source material for the Aren was low-grade cover rocks, which have experienced little metamorphism. These were prone to rapid erosion and transported significant amounts of terrestrial POC\textsubscript{terrbio} into the basin. Subsequent exposure of increasingly-metamorphosed metasediments below this cover led to erosion of larger amounts of fossil carbon. Continued convergence incorporated the foreland stratigraphy into the mountain belt, allowing for recycling of sediment. This concept is discussed further in Section 6.3. Where this material ends up is a question of sedimentary processes.

### 4.7.2 Insights into sedimentary processes

The formations have non-uniform distributions of carbon types along the basin profile (see Figures 4.28 and 4.29).

In the Aren pro-delta there is a lot more terrestrial POC\textsubscript{terrbio} preserved than elsewhere in the system, mostly within fine-grained sediments. Rapid transport down the delta front has likely buried material quickly, preventing oxidation. POC\textsubscript{other} content was very similar to other Aren samples. If all facies in the Aren were given the same initial concentration of each carbon type, this section is significantly better at preserving the POC\textsubscript{terrbio}. Alternatively, in-situ productivity on the delta top may add POC\textsubscript{terrbio} to the fluvial input.

Shelf locations contain low amounts of TOC. Terrestrial POC\textsubscript{terrbio} is sparse in both formations, about 0.1 wt% C, and the shelf settings also contained the lowest amount of POC\textsubscript{other}. At localities 6 and 7, Aren inner and outer shelf samples, POC\textsubscript{terrbio} contributions average 0.05 wt% C, effectively zero in all but one sample. These localities also contained glauconite which forms in slightly reducing shallow marine conditions with slow accumulation rates. Slow delivery of POC-poor material would also lead to poor protection from oxidation, as POC grains would not be quickly covered by later material. Assuming that the graphitic material is mostly stable, the low concentration suggests that carbonaceous material is being delivered to other parts of the sedimentary system, bypassing the shelf. Such processes would include hyperpycnal delivery of fluvial material along a submarine canyon and channel system to the deep basin. Thus a combination of oxidation
and sedimentary bypassing might have caused the lack of POC on the shelf.

Sorting processes seem to be particularly important in the Castissent turbidites. There were variations in TOC, POC$_\text{terrbio}$ and POC$_\text{other}$ both within and between the sand, silt and mud layers. In the field, POC seemed to have concentrated into particular horizons within the sandy parts of the turbidites, especially the upper sections of the Bouma “B” layer.

Further offshore, in the submarine channel lobes and basin, POC$_\text{other}$ outweighed POC$_\text{terrbio}$. Assuming similar inputs to other facies, preservation rates were good in the channel-lobe section and poorer in the basin. Selective deposition of the POC during transport could be preventing some carbon species reaching the basin, especially coarser POC$_\text{terrbio}$ which is rare in the Raman Spectroscopy results, whilst there may also be slower deposition rates in the basin which would lead to a lower preservation potential for material that has been delivered.

The low-grade metamorphic material in the Castissent is concentrated into just one section, the distal basin, which has little terrestrial woody debris. Shelf material contained plentiful highly-crystalline graphite, whilst the turbidites contained marine carbon, with POC$_\text{terrbio}$ concentrated into particular horizons. These discrepancies could be due to hydrodynamic sorting during transport, or oxidative loss. Marine carbon is the most labile and fossil carbon the most stable (Galy et al., 2008). In sub-optimal preservation locations fossil carbon should outlive the other types of organic matter and dominate oxidised or semi-oxidised sediments.

Thus it appears that the depositional environment plays an important role in determining the distribution and preservation of POC in a submarine basin. There are sorting processes acting both laterally and vertically, leading to concentration of POC into certain facies, and into particular layers within those. Fast deposition nearer to the shore is the most effective at burying and preserving organic carbon, whilst slow deposition rates are associated with a lack of carbon delivery and poor preservation. The most complex depositional system are the turbidites, having a highly stratified POC distribution. They are also volumetrically significant facies, storing a significant amount of sediment and hence POC for millions of years. Both of these features will be investigated in more detail in the next chapter.
4.7.3 Overall Findings

The Pyrenean system allows investigation of a series of sedimentary facies, from fluvial to deep marine, from two time periods during an orogeny. This allows differences in the type of carbon eroded, its sorting between and within facies, and its preservation potential over millions of years.

In the Cretaceous sediments of the Aren Formation, POC\textsubscript{terrbio} is concentrated into the pro-delta muds. Fossil carbon is rare, existing as occasional detrital graphite grains. The consistent concentration of POC\textsubscript{other} from fluvial input to distal basin is suggestive of effective preservation of fossil carbon in all facies.

In the Eocene Castissent Formation, POC\textsubscript{other}, consisting of fossil or marine carbon, is much more prevalent due to continued exhumation of the mountain belt. It concentrates into turbidites, submarine channel overbank deposits and distal basins. As in the Aren the fluvial input concentration of fossil carbon is preserved throughout the formation. There is a significant amount of POC\textsubscript{terrbio} stored within particular laminae within the turbiditic sections, implying that hydrodynamic sorting processes are particularly important in this facies. Further high-resolution investigation is required. In addition, volumetric quantifications, determining how much POC has been sequestered in these sediments, are not possible in these formations. The Miocene turbidites of the Apennines provide opportunities to address both of these questions.
Chapter 5

Miocene system - Apennines

5.1 Introduction

Having found significant amounts of carbon stored in turbiditic sequences in the Pyrenees, samples were collected from the Apennines in order to constrain both the fine-scale vertical distribution of material and the volume of carbon sequestered in such deposits. The turbidites exposed in the Apennines have been extensively studied so that there are exceptionally good stratigraphic constraints available, individual turbidites can be identified across a 2600 km$^2$ field area. This has led to very accurate geometric constraints which in turn provide volumetric estimates which can be combined with elemental / isotopic observations to calculate carbon sequestration budgets.

5.1.1 Geomorphology of the Alpine and Apennine Orogeny

Like the Pyrenees, the Alps were created between the Cretaceous and present by the Alpine Orogeny. They were formed by subduction of the Eurasian plate beneath the Adriatic plate. Rosenbaum and Lister (2005) describe the plate motions from the Mesozoic to mid-Cenozoic. During the Jurassic and early Cretaceous the Piemonte and Valais oceans opened between Europe and Africa. Orogenic processes started in the Eastern Alps during the late Cretaceous, yet were quiet during the Palaeocene and it wasn’t until the Eocene that rapid orogeny is reported. High- and Ultra-High-Pressure metamorphic rocks with the Piemonte ophiolite dated at 45 Ma associated with the Piemonte Ocean closure could
CHAPTER 5. MIOCENE SYSTEM - APENNINES

represent either the initiation of subduction or a collision event. Further HP and UHP rocks from Internal Crystalline Massifs, dated at 35 Ma, are likely due to the closure of the Valais ocean and the collision between Europe and the Briançonnais terrane, which was sheared off from Iberia.

Figure 5.1: Erosion rates and sediment fluxes from the Alps, taken from Bernet et al. (2009). The de-coupling between erosion rate and flux is thought to be due to variations in the exposed lithologies.

It was from this point onwards that continental collision and rapid exhumation occurred, the rate of which can be calculated from zircon fission-track studies (Bernet et al., 2009). Erosion rates, and thus exhumation rates since there was minimal normal faulting, in the hinterland were highest during the late Eocene and early Oligocene, whilst in the foreland regions there were peaks at 35 and 8 Ma (see Figure 5.1). Erosional fluxes were more variable than erosion rates, with rapid erosion rates in the last 5 Ma linked to climatic change rather than tectonics (Kuhlemann et al., 2002), although these are not reflected
5.1. INTRODUCTION

starting with the Eastern Alps in the Cretaceous, material has been eroded from the Alps and deposited offshore northern Italy (Garzanti et al., 2006; Kuhlemann et al., 2002). Since the Eocene, the Central and Western Alps have also been exposed sub-aerially (Bernet et al., 2001). As well as petrographic provenance studies (Gandolfi et al., 1983; Valloni and Zuffa, 1984; Zattin and Zuffa, 2004), zircon fission track data can be used to investigate the source regions of the Apennine sediments (see Figure 5.2). Bernet et al. (2009) suggest that FT ages of 8 - 30 Ma represent deep metamorphic material from the Central and Western Alps, 40 - 50 Ma material from the Central and Eastern Alps, and 60 - 140 Ma material from less-buried rocks, including the possibility of recycled material from earlier orogenic events.

This Alpine material was deposited into a fore-arc basin that was subsequently involved in the Apennine orogeny due to counter-clockwise rotation of Apulia and subduction beneath the western alpine chain (Chiocchini and Cipriani, 1992).
5.1.2 Turbidite beds of the Apennines

Figure 5.3: Stacked turbidites in the Apennines. Note how the layers are sub-horizontal and show no folding or faulting, demonstrating the simpler structural history of the Marnoso Arenacea compared to the Pyrenean basins.

The Apennines are a young topographic feature (see Figure 2.5) which formed from a series of sub-parallel thrust faults which can be seen in the field, and which are currently active in the Adriatic Sea to the east. Sedimentation in front of the Apennine thrust belt during the Miocene, depositing the Marnoso Arenacea Formation, was due mostly to erosion from the Southern Alps to the north (see Figure 5.4), whilst the Western Alps drained through the Rhone (Glotzbach et al., 2011) into the western Mediterranean.

The sedimentation of the Marnoso Arenacea formation was mostly due to density-driven flow along the length of fore-arc and piggy-back basins within the evolving Apennic structure (Lucente, 2004), depositing a repeating series of turbidites and debrites. Material was also sourced from the palaeo-Apennines to the west of the Marnoso Arenacea (Conti et al., 2008). Interspersed between these siliciclastic sediments are occasional carbonate-rich deposits thought to have originated from the collapse of a carbonate shelf to the south, for example the distinctive “Contessa” carbonate bed. This interpretation is supported by petrology (Gandolfi et al., 1983) and palaeoflow measurements. Contessa has an Early Serravalian age of around 13.6 Ma (Conti et al., 2008). Further carbonate-rich marker beds are present above Contessa, known as “Columbine”. The section between Contessa...
5.1. INTRODUCTION

and Columbine 1 has been extensively studied (Talling et al., 2007a). The southerly-sourced beds are easy to identify and have been used to locate specific turbidites in over 100 localities, covering an area of $150 \times 30$ km. Amy and Talling (2006) have made stratigraphic logs of several beds above and below, following on from correlation work carried out in the 1970s (Riccilucchi and Valmori, 1980). This has allowed the volume of each component bed to be calculated. The largest turbidite in this section is the sixth above Contessa, with a minimum volume of $7 \text{ km}^3$.

Figure 5.4: Interpretation of the sediment addition to the Marnoso Arenacea. Note the majority of the turbidites are sourced from the Alps or northern Apennines, with occasional input from the southern carbonate platform. Figure taken from Amy and Talling (2006)

5.1.3 Bed 6 in the Marnoso Arenacea

The sequence of turbiditic beds just above Contessa (Riccilucchi and Valmori, 1980) has been targeted by a variety of sedimentological studies (Riccilucchi and Valmori, 1980; Amy et al., 2005; Amy and Talling, 2006; Talling, 2001; Talling et al., 2004, 2007a) and consists of a range of bed styles and thicknesses. Some beds have a clear distinction between sandy and muddy parts, while others contain a hybridised layer of mud-rich sandstone, potentially mixed with muddy clasts (see Figure 5.5). This feature is thought to be a function of mud content and flow speed (Sumner et al., 2009). Clean transitions between muddy and sandy sections were most common in turbidites from other sample areas. The sixth major turbidite above Contessa (indexed as Bed 6) is both the largest and most representative of the beds in this section. It measures $120 \times 30$ km, with a minimum volume of $7 \text{ km}^3$. It contains a thick layer of clean sand, overlain by a transition through silty material to a thick mud cap. The grainsize distribution changes from sand-dominated in the north to
The sequence of beds above Contessa (Riccilucchi and Valmori, 1980) contains a range of turbidites, of which Bed 6 is the thickest and contains clean sand rather than a hybrid grainsize structure. Bed 6 is similar to the turbidites seen in other field areas.

This unit is easily identifiable in the field.

5.2 Sample Locations and Descriptions

5.2.1 Apennine samples

The sample localities used in this chapter were chosen for their exposure quality. Many of the sites described in Amy and Talling (2006) have an excellent stratigraphic exposure, with each bed clearly visible, but are geochemically less useful due to significant weathering. The sites used here are mostly exposed by human actions, producing fresh surfaces in quarries or road cuts. When describing the sample height within the section, the base of Bed 6 was given a value of 0 cm and all samples are located relative to that. Samples in
Figure 5.6: Profiles from Talling et al. (2007a) showing the amount of sand and mud present throughout Bed 6. As expected, amount of sand decreases along palaeoflow path, whilst amount of mud increases.

Bed 5 have a negative height, Bed 6 is positive. The four localities described below (31, 34, 29 and 97) are described in order from proximal to distal. Stratigraphic logs based on field observations are shown in Figures 5.21, 5.22, 5.23 and 5.25.

5.2.2 Locality 34

Locality 34 (N43.95386°E11.74739°) was a hillside exposure 20 m above the road south west of Premilcuore (See Figure 5.8 for a view across the valley to the opposite hillside). The rocks here have been exposed by natural processes, and therefore are relatively highly weathered. The muddy sections are set back from the harder, sandy bodies. They require further removal of material in order to reach competent, fresh rock (see Figure 5.7). Sandy samples required a long core to be drilled before oxide discolouration stopped.

Bed 6 contains 140 cm of sand outcropping below 150 cm of mud, of which the lower 75 cm were available for sampling. Seven samples were collected from the sand layer of Bed 6, one from silty material between sand and mud, and seven from the mud cap. Two
Figure 5.7: Field photograph of locality 34. This photograph shows the samples collected through the Bed 6 sand body, with the mud cap above. The upper sections of Bed 5 mud are also visible beside the backpack. Note the weathered nature of both sand and mud outcrops, meaning that lots of oxidised material had to be removed prior to sampling.

samples from the top of Bed 5, at -10 and -46 cm were also collected.

5.2.3 Locality 31

Locality 31 (N44.00455°E11.93925°) was a road cutting above the village of Civatella. The section from Contessa to Columbine marker beds is exposed. Bed 6 consists of 90 cm of sandy material with 110 cm of mud exposed above. The lower sandy material is very homogeneous with no internal structure, while at 90 cm there is transition through silt into the mud cap. Isolated mm-scale POC was visible within the mud cap. Four samples were collected from Bed 6 sand, one from the silt and one from the mud. Bed 5 consists of 185 cm of mud above 40 cm of exposed sandy material (see Figure 5.11). In this bed, three samples were collected from the sand layer and nine samples were collected from the mud. Within the mud cap, at -120 cm, a sandy burrow lined with black POC was sampled (see Figure 5.10).
5.2. SAMPLE LOCATIONS AND DESCRIPTIONS

Figure 5.8: Looking across the valley from locality 34, the Contessa bed is clearly visible on the hillside, the thick bed toward the base of the section.

5.2.4 Locality 29

Locality 29 (N43.62816°E12.24578°) was a disused quarry north west of the town of Lamoli. The Contessa bed was clearly identifiable, and a section from Contessa to Columbine 1 was exposed with an accessible, vertical surface. Figure 5.12 shows this locality.

Bed 6 consists of 110 cm of clean sand which grades into 10 cm of fine sandy material with layering visible. Above this is 40 cm of silty material with coarse POC visible in well-defined layers. This grades into a 1 metre mud cap, giving a total thickness of 281 cm. Five samples were collected from Bed 6 sand, eight from the fine sand and silty material, and eight from the mud cap. In Bed 5 a 330 cm thick mud cap was exposed, containing three sub-beds, two marginally coarser sections at -40 and -200 cm and a burrowed fine sandy layer at -130 cm. Eleven samples were taken from this bed.

Within muddy sections, the weathered surfaces produce a globular surface of fissile mud, with more competent material behind. When sampling, this material was removed with a hammer until a hard flat surface could be produced that would sustain drilling. Within

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Figure 5.9: Field photograph of locality 31. The drill holes are through Bed 6, with the upper mud of Bed 5 visible below.

Figure 5.10: Field photograph of a sandy, POC rich burrow at locality 31.
Figure 5.11: Field photograph of Bed 5 at locality 31, showing the large amount of material that had to be removed in order to access non-weathered samples. Heights within the bed are labelled, from -70 cm at the top to -230 cm.
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Figure 5.12: Field photograph of locality 29, showing Bed 6 in its entirety, and the mud cap of Bed 5. Within the Bed 5 mud there are thin sandy and silty layers, leading to a more resilient rock face. Note also how much muddy material had to be removed from Bed 6 mud in order to get a clean, fresh sample. Due to the dipping beds, vertical profiles through the beds had to be collected in sections with repeated transitions along strike.

Figure 5.13: Sample profile from locality 29 showing all sample locations and highlighting POC-rich samples. Figure created by A. Galy.
5.2. SAMPLE LOCATIONS AND DESCRIPTIONS

Figure 5.14: Oxidation rim at locality 29, extending 5 cm away from those surfaces exposed to the environment. These discoloured rims were not normally present in muddy samples. To avoid collecting oxidised material in the samples, where possible these rims were removed. If this was not an option, drill cores were cut through the oxidised portion, and samples were taken from the fresh material behind.

Figure 5.15: Layers of POC within the upper fine sand and silt of location 29. The POC is very heterogeneous, present as a series of thin layers within otherwise carbon-free laminated sandy material.
sandy sections there is an oxidation front extending 5 cm from the exposed surface. When sampling, this oxidation front was drilled out along with the targeted material behind, the weathered material was removed with a rock saw. Figure 5.14 shows a weathering rim.

Visible POC was present as well-defined layers of mm-scale debris in the upper sand and silty parts of Bed 6 (see Figure 5.15), and as suspended particles within the mud caps (Figure 5.16).

5.2.5 Locality 97

Locality 97 (N43.372456°E12.458923°) is exposed at the roadside between Umbertide and Gubbio. This is the most distal of the sample sites, and Bed 6 comprises just 50 cm of sand below a thick mud cap, of which the lower 90 cm were available for sampling. One sample was collected from the sand, and five from the mud. The top 45 cm of Bed 5 were also exposed, three samples were collected.
5.2. SAMPLE LOCATIONS AND DESCRIPTIONS

Figure 5.17: Field photograph of locality 97, showing Bed 5 mud and Bed 6 sand after sampling. Being the most distal section, the sand thickness here is greatly reduced in comparison to the more proximal samples. The sand bed has been sampled 10 cm above the base, but extensive weathering made further sampling unfeasible.

5.2.6 Overall descriptions and discussion

The turbidites follow an expected grainsize evolution, with thicker sand beds at the proximal end of the section (locations 31 and 34), and more mud at the distal end (locations 29 and 97, as reported by Talling et al. [2007a]). Within the sandy sections, no POC was visible until the upper reaches of the bed, where fine layers of POC were sat within laminated sand. Within the muddy sections, large clasts of POC were visible suspended within the sediment, with no apparent layering. The lower sandy units contain no visible POC.
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Figure 5.18: Generalised structure of large-volume turbidity currents, from Talling et al. (2007a). Samples collected in this study have been added to the lower topographic profile. Locality 31 is on a different structural element, and so its location is approximate.

This could be due to mechanical sorting during transport, or post-depositional oxidation.

5.3 Elemental / Isotopic Results

All samples were analysed for TOC, TON, $\delta^{13}$C and $\delta^{15}$N. This allows investigation of the following questions:

- Where within a turbidite bed is carbon preserved?
- What types of carbon are preserved
- How much carbon is stored in the bed as a whole

The elemental / isotopic parameters were analysed with the endmember unmixing procedure to split the signal into POC$_{terrbio}$, marine and fossil carbon components. The endmembers chosen for this deconvolution are defined in Table 5.1. The POC$_{terrbio}$ endmember should account for all types of biological material, including soils and leaf litter. The fossil carbon compositions have been set to represent values at the other extreme of the
5.3. ELEMENTAL / ISOTOPIC RESULTS

dataset - $\delta^{13}C$ of -22‰ and N/C of 0.25. Two fossil compositions are required to account for variations in sample TOC, as there is no POC-free endmember and the modelled TOC and TN concentrations must match the measured values. As the samples were collected from a single event bed, a single set of endmembers should account for all variability within the turbidite.

<table>
<thead>
<tr>
<th>End member</th>
<th>[C] (wt%)</th>
<th>[N] (wt%)</th>
<th>$\delta^{13}C$ (‰)</th>
<th>$\delta^{15}N$ (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil 1</td>
<td>1</td>
<td>0.4</td>
<td>-22</td>
<td>2</td>
</tr>
<tr>
<td>Fossil 2</td>
<td>0.1</td>
<td>0.04</td>
<td>-22</td>
<td>1.5</td>
</tr>
<tr>
<td>Terrestrial POC$_{terrbio}$</td>
<td>33</td>
<td>0.99</td>
<td>-26</td>
<td>1</td>
</tr>
<tr>
<td>Marine carbon</td>
<td>40</td>
<td>6.68</td>
<td>-18</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 5.1: Endmembers used when un-mixing carbon species in the Apennines using stable isotopes and elemental concentrations.

When dealing with ancient sediments, in which radiocarbon will not be present, it is impossible to determine isotopically whether POC$_{terrbio}$ has been simply buried or recycled multiple times. Thus in this field area “non fossil” carbon represents the total biomass input, and is the sum of the POC$_{terrbio}$ and marine carbon results from the endmember unmixing as a proportion of total carbon. Burial of non-fossil carbon, of terrestrial or marine source, is a direct sequestration of atmospheric CO$_2$. Non-fossil carbon may be overestimated if orogenic recycling has eroded low-grade sediment from the mountain belt. This could take the form of POC with a biomass or marine composition.

$$F_{nf} = \frac{POC_{biomass} + marine}{POC_{biomass} + marine + total_{fossil}}$$

By plotting the results from each locality as a vector in $\delta^{13}C$ - N/C space, the variations with height through the unit are highlighted (see Figure 5.20). Logs from each locality are plotted three ways. Firstly, field observations of sediment grain size show the proportion of sand, silt and mud seen at each sample height. Overlain on this is the percentage dissolved during decarbonation. The second log shows the TOC measurement and fraction non-fossil. TOC concentrations have been corrected for dissolution of carbonate (see Section 2.5.3). The third log separates the TOC into the contribution from fossil carbon, POC$_{terrbio}$ material and marine carbon.
5.3.1 All results

Samples from the Marnoso Arenacea show a wide range of N/C values, but a relatively restricted range of $\delta^{13}C$ (see Figure 5.19). The most carbon rich of the samples are from mud layers, and have N/C values around 0.1 and $\delta^{13}C$ ranging from -23.5 ‰ to -22 ‰. Those samples lowest in TOC are from sandy parts of the turbidite and have very high N/C ratios, above 0.6. By comparison, the highest N/C ratios reported by Hilton et al. (2010) are 0.3 (see Figure 3.9). Hilton (2008) reported N/C up to 1 for soil samples in Taiwan, but the associated $\delta^{15}N$ values are much higher than these samples. Given the very low TOC values in the Italian samples, their N/C ratio could be due to a nitrogen blank from ammonium, but $\delta^{15}N$ values of -1 to 1 ‰ does not support this either. These samples are so poor in TOC that the contribution of any organic material in them to the turbidite as a whole is negligible.

Figure 5.19: All results from the four Italian localities, separated by colour. Data point size scales with carbon content; the richest in TOC have a lower N/C ratio and are lighter in $^{13}C$.

5.3.2 Locality 34

The sandy samples from locality 34 formed a cluster of points with N/C of 0.25 to 0.34, $\delta^{13}C$ of -21.8 to -22.6 ‰. There was no overlap between this cluster and the profiles collected
Figure 5.20: Results from localities 34, 31 and 29. Each line represents one bed, either mud or sand, with the arrow pointing up-section. The red line represents Bed 5 mud, purple line Bed 6 sand and blue line Bed 6 mud. Plotting as a line shows the trending nature of the results - mud samples move away from POC\textsubscript{terrbio} values (∼0.5, 0-26 ‰) and towards a more marine (0.17, -18 ‰) or fossil-dominated (high N/C, variable δ\textsuperscript{13}C) composition.
Figure 5.21: Results from locality 34 plotted as three logs, grainsize and carbonate content, TOC (corrected for carbonate dissolution), fraction non-fossil and endmember components. The wide variability in fraction non-fossil throughout the sandy samples is due to the very low carbon content.

in the mud below and above, which all had N/C below 0.21.

There was a trend within the mud layers, from N/C around 0.1 at the base to 0.2 at the top, and a concurrent trend in δ¹³C from -23 ‰ to -22.6 ‰. This trend was seen in both the eight samples of silt and mud from Bed 6, and the two samples of mud from Bed 5. The lowest δ¹³C value (-23.0) was recorded in the silt at the interface between mud and sand in Bed 6, where there was also one of the lowest N/C values for this locality, 0.11.

TOC concentrations were an order of magnitude higher in Bed 5 mud and Bed 6 mud than in Bed 6 sand (Figure 5.21). Muddy sections contained a uniform 0.5 wt% C, apart from at the top of the muddy sections where the TOC was reduced in both cases. Non-fossil fraction was very high in the mud cap, around 0.8, but very variable in the sand layer due to the large variability in δ¹³C values (see Figure 5.20).

There was an increase in all carbon types at the transition from sandy to muddy material. This increase was much more pronounced in the marine carbon (15 times) and
POC\textsubscript{terrbio} species (18 times) than the fossil carbon (five times). For most of the mud cap, terrestrial POC\textsubscript{terrbio} was the largest contributor, followed by marine carbon, but at the very top of the mud this changes and the fossil contribution overtakes the other two (see section 5.5 for more discussion of this). This pattern was seen at the top of both Bed 5 and Bed 6, and was seen in the elemental / isotopic data as a shift towards higher N/C ratio at the top of each mud bed (Figure 5.20).

### 5.3.3 Locality 31

![Figure 5.22: Results from locality 31 plotted as three logs: grain size and carbonate content, TOC and fraction non-fossil and endmember components.](image)

The sandy parts of Bed 5 and Bed 6 at locality 31 trended towards N/C ratios of about 0.1, from greater than 0.4 lower in the layer (Figure 5.20). $\delta^{13}$C values in the lower parts of the sand layers differed, with Bed 5 having a more negative value of -23.7 ‰ and Bed 6 being more positive at -21.6 ‰. These values converged towards -23 ‰ at the top of the sandy layers.

Within the Bed 5 mud layer there was a clear trend in $\delta^{13}$C from -23.3 ‰ to -22.3 ‰ and
in N/C from 0.09 to 0.15 with increasing height. The Bed 5 sand samples trended towards the base of the Bed 5 mud results. Only one measurement was collected from the Bed 6 mud, with N/C of 0.08 and $\delta^{13}C$ of -22.8 ‰ it matches the Bed 5 mud results.

Carbonate concentration was high in the mud caps and lower in the sandy layers, especially in Bed 6 sand. TOC concentrations were highest in the lowest part of Bed 5 mud (0.6 wt%), and decreased through the Bed 5 mud cap to 0.25 wt% C. $F_{nf}$ was high in all samples apart from the lowest sandy samples, where there was very little non-fossil carbon.

All three endmembers were very low in the sandy parts due to the low TOC, and increased within the mud such that the greatest contribution comes from POC$_{terrbio}$, then marine carbon, then fossil carbon. The TOC decreased through Bed 5 mud, this was mostly accounted for by a drop in the amount of POC$_{terrbio}$ - marine and fossil carbon remained stable through the mud cap. Bed 6 mud had a measurement at the very bottom and one more significantly higher, but appeared to mimic the pattern in Bed 5, with all carbon species rising at the boundary and the distribution of endmembers mid-way through the mud bed was very similar.

### 5.3.4 Locality 29

Locality 29 had the largest number of samples, showing a similar if complex pattern to the other sample sites. Bed 6 sand samples trended from high N/C ratios of up to 0.40 and $\delta^{13}C$ up to -21.6 towards a value very similar to the lower silty and muddy samples from both beds 5 and 6 mud, 0.1 and -23.3 for N/C and $\delta^{13}C$ respectively. This trend was not a simple one though, at 100 cm the values are 0.10 and -23.2, only to return to the higher values for 20 cm, and then lower again from 120 cm to the top of the silt. This reduction in N/C and $\delta^{13}C$ was concurrent with an increase in TOC, from less than 0.1 wt% to 0.5 wt%.

Within Bed 5 mud, the base of the mud, -330 cm, had a low N/C ratio of 0.10, and $\delta^{13}C$ of -23.3. The $\delta^{13}C$ value rose to -22.0 by -200 cm, then remained between this value and -22.3 for the remainder of the mud cap. Within this region, N/C varied between 0.11 and 0.20. In the Bed 6 mud a similar pattern was seen, N/C was consistently around 0.1, but $\delta^{13}C$ increased from -23.0 in the silt to around -22.5 in the upper muddy samples. The variation in N/C ratio was not seen.
Carbonate content was variable in these sections, but tended to be highest in the muddy sections and lower in the sandy parts. The sedimentary log of Bed 5 mud was more complex than in other localities. TOC concentrations were high in the lower parts of Bed 5 and Bed 6 mud caps, and concentrations reduced by half in the upper parts of Bed 5 mud.

Within Bed 6 sand the TOC was generally low, and entirely composed of fossil carbon. Unlike previous sections, there was a clear distinction between the fossil carbon input and the other species. While still low, the fossil contribution of 0.08 wt% C was an order of magnitude higher than the calculated input of the other two (which were negligible).

Higher up in the sand however, layered sedimentary structures contained a high concentration of visible POC flakes (Figure 5.16), which was illustrated by the rise in POC at 102 cm. This was accompanied by a rise in POC\textsubscript{terrbio} input of more than two orders of magnitude, a signal that decreased just as rapidly and was then repeated again from 119 - 120 cm to the top of the section.

Moving up into the silt and mud of Bed 6, the TOC increased to a maximum of nearly...
1 wt%, accounted for once again by a large increase in POC$_{\text{terrbio}}$, a moderate increase in marine carbon and a slight increase in fossil carbon. This pattern continued to the top of the Bed 6 mud samples, which did not quite cover the entire mud bed due to severe weathering in the upper section.

In the Bed 5 mud, a similar pattern was seen. Starting in silty material at -330 cm, the high TOC measurement was mostly due to POC$_{\text{terrbio}}$. Moving up, the decreasing TOC was accompanied by a decrease in POC$_{\text{terrbio}}$, yet the marine and fossil carbon contributions remained constant. At -200 to -165 cm the pattern reversed, the marine and POC$_{\text{terrbio}}$ components were lower and stable, whilst the fossil carbon concentration was higher and variable. This upper mud pattern was also seen at the top of Bed 6 at locality 34.
5.3.5 Locality 97

![Graph showing grain sizes, sample TOC wt%, and components](image)

Figure 5.25: Results from locality 97 plotted as three logs, grainsize and carbonate content, TOC and fraction non-fossil and endmember components.

Both Bed 5 and Bed 6 mud from locality 97 plotted in the same region, with $\delta^{13}C$ of -23.45 to -23.69 and N/C of 0.10 to 0.11 (see orange dots on Figure 5.19). The single sand sample from this locality had N/C of 0.25 and $\delta^{13}C$ of -23.23, so was significantly different from the muddy samples. There was no trend within the mud layers, they all had $\delta^{13}C$ compositions lower than the other localities.

Locality 97 showed a relatively homogeneous pattern, with the concentration of each carbon species remaining fairly constant through the muddy layers and the majority of the organic carbon being composed of POC$_{terrbio}$. The heterogeneity seen elsewhere was not observed, either due to homogenisation by long-distance transport or a paucity of samples. The upper sand section was laminated as at locality 29, but weathering prevented sampling at this locality (see Figure 5.17). TOC concentration was highest in this laminated section at locality 29, thus the average TOC in locality 97 may be underestimated. Figure 5.18 (Talling et al., 2007b) shows that this locality was at the distal end of the turbidite, where a lot of sandy material would already have been sorted and deposited and muddy material...
was ponding, meaning that deposition conditions could have been different here compared to the rest of the bed.

5.3.6 Overall patterns

![Figure 5.26: Breakdown of carbon types in each Apennine locality, ordered from proximal to distal with sandy and muddy layers separated.](image)

The overall pattern in these cores is that the sandy parts of the turbidites are low in carbon, with endmember unmixing calculations implying that fossil carbon concentration is reduced less than other carbon types (Figure 5.26). Marine carbon and POC$_{terrbio}$ are distributed throughout the silty and muddy sections, and their concentration here is an order of magnitude higher than in the sandy sections. The large variability in TOC and carbon species input over a distance of just a few cm within the turbidite shows that vertical heterogeneity is an important consideration in these sediments. Whilst the coarse, massive sand bodies at the base of the turbidites seem to contained little organic carbon, whilst the upper sand contained substantial amounts. This could be due to sedimentary sorting or variations in burial efficiency (see Section 5.5).

These results can be investigated further using Raman Spectroscopy, which was used in these samples to test the distribution patterns for fossil carbon and POC$_{terrbio}$.
5.4 Raman Spectroscopy Results

Raman spectra profiles were collected from localities 31 and 34, with a few additional spectra collected from locality 29. When collecting the profiles, it was noticeable that sand-dominated samples had very low carbon concentrations - organic material was very hard to find under the microscope and it was mostly present as shiny graphite grains. Mud-dominated samples contained shiny graphite crystals as well as dark grains of disordered POC (see Figure 5.27). Semi-graphitised material is rare in all samples.

This observation is reflected in the spectral results. At locality 31, highly-graphitic spectra (minimal D peaks, sharp G peak) were found in both mud and sand layers. Little to no disordered spectra were collected from the sand layers (see Figure 5.28), whereas...
Figure 5.28: Spectra from the sand at locality 31, after analysis by the peak fitting method, including removal of any linear background.

Figure 5.29: Spectra from the mud at locality 31, after analysis by the peak fitting method, including removal of any linear background.
there many disordered spectra were acquired within the mud cap (Figure 5.29). Plotted in profile along with endmember unmixing results (Figure 5.30), the disordered material coincides with an increase in $\text{POC}_\text{terrbio}$.

![Graph showing vertical profile of Raman spectra from locality 31, showing the changing spectral properties (peak temperature and total width) with height through the deposit.](image)

Figure 5.30: Vertical profile of Raman spectra from locality 31, showing the changing spectral properties (peak temperature and total width) with height through the deposit.

At locality 34 the sand layers contain mostly very graphitic spectra, sharp G peaks where D2 peaks at 1620 cm$^{-1}$ are rare and D bands are very small. Unlike locality 31 there are also occasional semi-graphitised spectra, with G and D bands of equal height, and disordered spectra with broad G and D bands. A profile through the turbidite at this...
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Figure 5.31: Spectra from the sand at locality 34, after analysis by the peak fitting method, including removal of any linear background.

Figure 5.32: Spectra from the mud at locality 34, after analysis by the peak fitting method, including removal of any linear background.
5.4. RAMAN SPECTROSCOPY RESULTS

locality, plotted in Total-width vs. Temperature space (Figure 5.33), shows that the non-graphitic spectra from the sand are contained in the sample from 100 cm, the remainder of the sand contains only graphitic material. There is no semi-graphitised material in the mud cap.

Figure 5.33: Vertical profile of Raman spectra from locality 34, showing the changing spectral properties (peak temperature and total width) with height through the deposit.

5.4.1 Comparing Sand and Mud results

Grouping the collected spectra from sandy and silty/muddy layers separately, spectra were plotted in Total-width vs. Peak Temperature space (Figure 5.34). Once again the lack of disordered material in the sand layers is clearly shown. Whilst there are not enough spectra for a fully-statistical study, disordered carbon represents only 15 % of spectra from the sand, but 47 % of spectra from the silt and mud. Neither groups contain much semi-graphitised material. This could be due to sourcing constraints, if little low-grade carbon was exposed it could not be harvested, if the grain size was too small it may be
missed by the spectrometry method, or it could be due to selective oxidation of semi-graphitised material during riverine transport, shelf deposition, collapse, remobilisation and basin transport (Galy et al., 2008).

Figure 5.34: Raman spectra from sandy and silty/muddy layers compared in Peak Temperature vs Total Width space. Note how the sandy layers are virtually devoid of non-graphitic carbonaceous material. High-width samples in the graphitic domain are likely due to low-intensity spectra producing high HWHM measurements.

5.5 Discussion

Both elemental / isotopic analysis and Raman spectroscopy have shown that the sandy layers of the Marnoso Arenacea contain little organic carbon, with much less POC$_{terrbio}$ than elsewhere in the turbidites and many samples comprised mostly of graphite, whilst in the silty and muddy layers there is POC$_{terrbio}$ preserved in concentrations up to 0.5 wt% C. Elemental / isotopic analysis also suggests the presence of marine carbon in these upper beds. Careful examination of the two datasets allows more questions to be addressed: how much sediment is present in each turbidite of the Marnoso Arenacea, and what sourcing mechanisms can supply that volume; what are the relationships between the different carbon species being stored, which sedimentary processes are affecting the distribution of carbon, how much carbon has been stored in these turbidites, and what are the implications for global carbon cycling?
5.5. DISCUSSION

5.5.1 Sediment volume in the Marnoso Arenacea

The volume of sediment contained in individual Marnoso Arenacea beds (up to 7 km$^3$, $1.5 \times 10^{13}$ kg (Talling et al., 2007a)) is comparable to the present annual sediment supply to the ocean (Milliman and Syvitski, 1992), and at least 350 times more than the annual sediment yield of the Gaoping River (Dadson et al., 2003; Huh et al., 2009). As such these turbidites cannot be sourced hyperpycnally from a single storm event. This is in direct contrast to the Taiwanese samples, which are believed to be sourced from a known single event.

Talling et al. (2007a) propose that submarine slope collapse would be able to supply a suitable amount of material (an average of 7 m erosion from an area 100 km $\times$ 10 km). The observation of plentiful organic carbon was used as evidence for the incorporation of deltaic sediments. They believed that the organic material had been stored in the delta for a limited time period before remobilisation. Deltaic sediment in the Aren formation was rich in POC$_{terrbio}$ (see Section 4.6).

5.5.2 The volume of carbon exported and stored

5.5.2.1 Carbon storage in Bed 6

Using volumetric estimates from Talling et al. (2007a), the mass of carbon sequestered in a single turbidite, Bed 6, was calculated. This bed has a total volume of 7 km$^3$ with 50% muddy and 50% sandy material. Within each of the four measured sections, average carbon composition (corrected for carbonate dissolution) within the mud and sand beds was calculated using an “area under the curve” approach, with a linear interpolation between measured beds, such that the irregular spacing of sample heights could be taken into account.

$$[TOC]_{\text{locality average}} = \frac{\sum \text{spacing between samples} \times \frac{[TOC]_1 + [TOC]_2}{2}}{\text{locality thickness}}$$

At locality 29 there is a significant carbon contribution at the interface between sand and mud. This section appears to be a mixed layer, containing both sand and mud rather
than having a silty grainsize. TOC concentrations from mud and sand are shown in Table 5.2.

The four localities were then placed along a line representing the flow direction of the current, in their relative positions within the turbidite, and the total carbon content was calculated taking into account the distances along the turbidite transect.

\[
[TOC]_{\text{total average}} = \frac{\sum \text{section width} \times \frac{\text{height}_1 \times [TOC]_1 + \text{height}_2 \times [TOC]_2}{2}}{\sum \text{section width} \times \frac{\text{height}_1 + \text{height}_2}{2}}
\]

<table>
<thead>
<tr>
<th>Locality</th>
<th>Position along turbidite (km)</th>
<th>Sand thickness (cm)</th>
<th>Mud thickness (cm)</th>
<th>Sand [TOC]$_{av}$</th>
<th>Mud [TOC]$_{av}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>30</td>
<td>140</td>
<td>150</td>
<td>0.058</td>
<td>0.526</td>
</tr>
<tr>
<td>31</td>
<td>40</td>
<td>90</td>
<td>110</td>
<td>0.056</td>
<td>0.542</td>
</tr>
<tr>
<td>29</td>
<td>85</td>
<td>120</td>
<td>160</td>
<td>0.132</td>
<td>0.650</td>
</tr>
<tr>
<td>97</td>
<td>110</td>
<td>50</td>
<td>200?</td>
<td>0.078</td>
<td>0.530</td>
</tr>
</tbody>
</table>

Table 5.2: Height-weighted TOC concentrations in Bed 6 as measured in the four profiles. Note that the upper height of Bed 6 mud at locality 97 is unknown, as samples were only collectable from the bottom 90 cm of mud - the upper reaches were heavily weathered - but there was at least two metres of mud present. Positions within the 120 km turbidite are used to calculate weighted [TOC] for the entirety of the sand and mud layers.

[TOC]$_{\text{average}}$ in Bed 6 sand is 0.110 wt%, Bed 6 mud contains 0.746 wt%. By mass, there is 6.8 times more carbon stored in the mud layer than the sand layer. Combining this with the along-transect grainsize distribution (see Figure 5.18), the more distal parts of the turbidite will store more carbon than the proximal sections.

Knowing the volume of Bed 6, total carbon storage can be quantified using the following equation:

\[
C_{\text{turbidite}} = \text{volume} \times \text{density} \times [TOC]_{\text{layer average}}
\]

With layer volume $= 3.5 \times 10^9$ m$^3$ each for the sandy and muddy parts of Bed 6, and sedimentary rock density $= 2500$ kg m$^{-3}$, the amount of carbon stored in the beds is on the order of mega-tonnes (Mt). The sand layer contains 7.4 Mt C, the mud layer 50.0 Mt
5.5. DISCUSSION

C, totalling 57.4 Mt C stored in Bed 6. Using endmember unmixing estimates of fossil and non-fossil (POC\textsubscript{terrbio} plus marine carbon) contributions, the sand layer contains 3.2 Mt of fossil carbon and 4.2 Mt non-fossil carbon. The mud layer contains 8.5 Mt fossil carbon and 41.5 Mt non-fossil carbon, giving Bed 6 a total fossil content of 11.6 Mt C and 45.7 Mt non-fossil carbon. Of the non-fossil carbon, the sand layer contains 2.6 Mt POC\textsubscript{terrbio} and 1.6 Mt marine carbon, the mud layer contains 27.0 Mt POC\textsubscript{terrbio} and 14.5 Mt marine carbon. These results are shown in Table 5.3.

<table>
<thead>
<tr>
<th>Layer</th>
<th>TOC (Mt)</th>
<th>Fossil C (Mt)</th>
<th>Non-fossil C (Mt)</th>
<th>POC\textsubscript{terrbio} (Mt)</th>
<th>Marine C (Mt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>7.4</td>
<td>3.2</td>
<td>4.2</td>
<td>2.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Mud</td>
<td>50.0</td>
<td>8.5</td>
<td>41.5</td>
<td>27.0</td>
<td>14.5</td>
</tr>
<tr>
<td>Total</td>
<td>57.4</td>
<td>11.7</td>
<td>45.7</td>
<td>29.6</td>
<td>16.1</td>
</tr>
</tbody>
</table>

Table 5.3: Carbon contents of Bed 6 in the Marnoso Arenacea, calculated from height-and position-weighted averages of four geochemical profiles.

Figure 5.35: Volumetric calculations of the Bed 6 carbon content show that 57.4 Mt of carbon is stored in the sediment, with 50 Mt in the mud layer and just 7.4 Mt in the sand, despite each having a volume of 3.5 km\textsuperscript{3} (Talling et al., 2007a).
5.5.2.2 The plausibility of large-volume carbon storage

For comparison, current global organic carbon burial is estimated at 13.2 (France-Lanord and Derry, 1997) to 48 Mt C yr\(^{-1}\) (Galy et al., 2007b). If the mobilisation, transport and burial of organic carbon in single sedimentary deposits can outstrip annual global fluxes, there must be a more complex procedure than single storms in mountainous regions (c.f. Morakot. Hilton et al. (2008b). Hilton et al. (2008a) calculate a supply of POC\(_{\text{terrbio}}\) from the Southern Alps of New Zealand of 39 TC km\(^{-2}\) yr\(^{-1}\). Estimates of POC\(_{\text{fossil}}\) supply from Taiwan are 12 - 246 TC km\(^{-2}\) yr\(^{-1}\), with an average of 82 TC km\(^{-2}\) yr\(^{-1}\) (Hilton et al., 2011), but these are extreme values and are unlikely to be representative in this case. Assuming an outcrop area of 500 × 50 km for the European Southern Alps (25,000 km\(^2\)) the carbon contribution to Bed 6 is 1184 TC km\(^{-2}\). With POC\(_{\text{terrbio}}\) export rates of the New Zealand Southern Alps this is 30 years worth of POC export from the mountain belt.

Based on sediment volume, Talling et al. (2007a) suggested that the Marnoso Arenacea turbidites were sourced from delta collapses, and this hypothesis is supported by the carbon content and isotope data. \(\delta^{13}\)C data from the turbidites shows a trend towards a much higher carbon isotope value than was seen in Taiwan, where terrestrial material dominates. The endmember unmixing results suggest that there is a significant amount of marine carbon in the Marnoso sediments, which could either be sourced from suspension of marine sediment during the turbidite flow, or could have been present in a deltaic setting whilst the sediment ponded offshore.

Bernet et al. (2009) estimate that 15 000 km\(^3\) Ma\(^{-1}\) of sediment was eroded from the Swiss and Western Alps during the Miocene (see Figure 5.1). If all of this material was delivered to the Marnoso Arenacea it would take 466 years to deliver 7 km\(^3\). Using maximum exhumation values of 0.7 mm yr\(^{-1}\) (Bernet et al., 2001) across an area of 500 × 50 km it would take 400 years to remove 7 km\(^3\) of sediment. Based on Miocene exhumation rates of 0.25 - 0.3 mm yr\(^{-1}\) (Bernet et al., 2009) the time required increases to ~1000 years. Using estimates of sediment supply to the Apennines of 1600 km\(^3\) Ma\(^{-1}\) (Kuhlemann et al., 2002) it would take 4300 years. Estimates of the return time of hyperpycnal events from an active mountain belt (Dadson et al., 2005) range from 1 to 30 years, which is much less than the time required to source the volume of sediment present in each of the Marnoso Arenacea beds. If each storm-sourced hyperpycnal flow were to reach the Marnoso Arenacea then the stratigraphy would consist of deposits 10 to 100 times thinner than is observed. Thus the material eroded from the Alps must have ponded near to the mountain belt and been
remobilised in a catastrophic event.

Turbidites in the Marnoso Arenacea number in the thousands, the 3500 m thick formation was deposited over about 10 Ma (Amy and Talling 2006), and so a return time of 5000 years per large event, or 100 - 1000 years for smaller turbidites, is not unreasonable. 61 Mt POC could be supplied in 63 years if the POC export is comparable to the Southern Alps of New Zealand (Hilton et al. 2008a). Then the delta would have to preserve between 1.5 and 15 % (depending on turbidite return times) of the POC exported from the Southern and Western Alps and remobilise it into the Marnoso Arenacea turbidites. These estimates are entirely reasonable.

5.5.2.3 Deltaic productivity and recycling

As seen in the Pyrenees, deltaic and shallow marine settings can store terrestrial carbon. Medium-term carbon storage in deltas, estuaries and shelves has been widely reported, the collapse of these structures would deliver this carbon to the deep sea. The Canadian Mackenzie delta traps riverine POC subaerially (Emmerton et al. 2008) and also hosts in-situ terrestrial organic carbon productivity, while shallow shelves can store both marine and terrestrial carbon. Showers and Angle (1986) calculated that 6 % of the organic carbon exported by the Amazon is accumulating in shelf sediments, but Aller et al. (1996) revised this up to 35 %. Applying this preservation ratio to the European Southern Alps, enough carbon would be present on the shelves to supply the Marnoso Arenacea. The presence of significant amounts of marine carbon in the turbidites suggests that submarine storage of the source material before flow initiation may be more likely, although large turbidity currents would have a high erosive power and could mobilise marine mud during the flow, incorporating marine organic carbon and detrital carbonate during transit.

5.5.2.4 Deltas and shelves as a source of massive sediment flows

The largest of the Marnoso Arenacea flows contain so much sediment that even a single delta collapse might be unrealistic. Deltas can be very large, but in the Southern Alps the current day spacing of rivers draining into the Po basin is of the order 10 - 50 km. Assuming a semicircular delta of radius \( r \), the depth \( d \) of material that needs to be mobilised for a turbidity current of volume \( v \) in the collapse is denoted by:
Mobilising a delta with radius 10 km, the average landslide depth would be 44 m, reducing to 7 m with radius 25 km. Sultan et al. (2010) described a submarine landslide with a depth of up to 28 m offshore Southern France, however this event was much smaller than the collapses discussed here, liberating 1000 times less material than is stored in Bed 6. Also, relying on a single delta collapse for sediment sourcing would increase the sediment build-up time since the source would be a single river rather than the entire mountain belt.

Shelf collapse, where the submarine landslide can harvest the combined output of multiple river sources, can liberate up to 1000 times more material than is present in Bed 6. Such submarine slides in the North Sea (Storegga and similar) are believed to have return times of 100 000 years (only 100 times longer than the Marnoso) and are sourced from a 200 km length of the continental slope (Solheim et al., 2005). Assuming that the Southern Alps export similar or greater volumes of sediment than Norway, the sediment supplied into and transported out of a submarine shelf would be sufficient to feed the Apennine turbidites.

The trigger mechanism for the Storegga Slide is hypothesised as an earthquake (Solheim et al., 2005). As the Alps were very tectonically active during the Miocene this is a plausible reason for sediment supply into the Apennines being massive and sporadic. A large-magnitude earthquake could destabilise shelf sediments through liquefaction, releasing material from a wide area. These have been cited as the cause of slope failures producing up to 100 km$^3$ of sediment offshore New Zealand (Lamarche et al., 2008).

5.5.3 Elemental / Isotopic Relationships

5.5.3.1 Relationships between carbon species

Further analysis of the endmember unmixing method results allows the relationship between TOC and carbon components to be investigated. The fossil and non-fossil (POC$_{\text{terrbio}}$ plus marine carbon) contributions to each sample were plotted against the measured TOC as corrected for carbonate dissolution (Figure 5.36). This showed that with increasing TOC, the input of fossil carbon does not increase substantially, from around 0.1 wt% in the low-TOC samples to around 0.15 wt% in high-TOC samples, with a maximum of
Figure 5.36: Fossil and non-fossil carbon amounts, and fraction non-fossil, plotted against TOC for samples from Italy. Carbon loading in high TOC samples is almost entirely due to addition of non-fossil TOC.

\[
F_{nf} = 0.88C_{TOC} - 0.05,
\]

with \( r^2 \) of 0.95. Thus the incorporation of non-fossil carbon is almost entirely responsible for the changing TOC in the turbidites, apart from the varying fossil inputs in the upper mud caps. In samples with a very low TOC, there is little or no non-fossil carbon present, all measured TOC is supplied by the fossil carbon, as seen by the non-zero intercept of the fossil carbon regression line. These low-TOC samples represent the sandy units of the
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turbidites.

Breaking the non-fossil carbon into marine and POC\textsubscript{terrbio} components (Figure 5.37) shows that both marine and POC\textsubscript{terrbio} have linear relationships with total carbon, but that terrestrial POC\textsubscript{terrbio} accounts for more of the TOC than marine carbon. Regression lines through both carbon species converge close to zero wt\% TOC, with an offset of -0.01 wt\% for marine carbon and -0.04 wt\% for POC\textsubscript{terrbio}, which are likely within error of the endmember unmixing method. Regression of POC\textsubscript{terrbio} gives a relationship of 0.58:1 with $r^2$ of 0.94, marine carbon gives 0.30:1 with $r^2$ 0.86. Breakdowns for each locality individually show a similar pattern for localities 34, 31 and 29, but at locality 97 the marine and fossil carbon components lie parallel, all converging on the origin.

Figure 5.38 shows that at low carbon concentrations, marine carbon and POC\textsubscript{terrbio} preservation rates have a 1:1 relationship, but that as the amount of carbon present in the sample increases there is increased scatter and the contribution from POC\textsubscript{terrbio} exceeds the marine carbon input. Again this pattern could be due to a greater initial contribution from POC\textsubscript{terrbio}, but with a similar tendency for loss in oxidising environments such as the sandy parts of the turbidite, or sorting during transport.

Plotting the contributions from POC\textsubscript{terrbio} and marine carbon against fossil carbon input (Figure 5.39) shows that the ubiquitous low concentrations of fossil carbon are not related to the concentrations of the other carbon types. Overall these breakdowns show that burial of terrestrial POC\textsubscript{terrbio} is more important than marine carbon burial in the turbidite as a whole, but that both are much more liable to oxidation than fossil carbon.

5.5.3.2 Relationships between stratigraphy, proportion dissolved and carbon species

Using the endmember unmixing results, the organic carbon types present in the samples was compared to the proportion lost during decarbonation (Figure 5.40). Sandy sections contain little organic carbon and little carbonate, less than 25 % was lost during decarbonation. Fossil carbon concentration tends to increase with carbonate proportion, although the correlation is weak ($r^2 = 0.32$). Marine carbon and POC\textsubscript{terrbio} show maxima between 35 and 50 % dissolution. This corresponds to samples collected in the lower parts of the mud layers (Figures 5.21, 5.22 and 5.23). The upper mud caps at localities 34 and 29 contain more carbonate, 55 to 65 % dissolution, and contain on average more fossil car-
Figure 5.37: Fossil C, marine C and POC_{terrbio} carbon amounts plotted against TOC for samples from Italy.
Figure 5.38: Marine carbon vs. POC\textsubscript{terrbio} in Italy, showing that preservation of these two carbon types appears to be coupled, especially at low carbon concentrations. A 1:1 relationship line is also plotted.

Figure 5.39: POC\textsubscript{terrbio} and marine carbon vs. fossil carbon in Italy, showing that fossil POC contents are decoupled from the other inputs.
5.5. DISCUSSION

![Graph showing carbon content vs proportion dissolved for All Italian Samples]

Figure 5.40: Relationship between proportion dissolved and carbon components in the Italian samples, separated into fossil, POC$_{terrbio}$ and marine carbon.

Bon than non-fossil species. Thus it is not just organic carbon that is stratified within turbidites, but carbonate content too. Potential effects of changing carbonate content on elemental / isotopic results will be discussed in Section 6.1.1. As the carbonate is likely detrital, sourced from marine sediment, a lack of strong correlation with terrestrial carbon species is not surprising. Dissociation between marine POC and marine carbonate in the upper mud caps could be due to poor preservation between turbidites or hemi-pelagic sedimentation, and will be discussed next.

5.5.3.3 Changing carbon concentrations at the top of mud layers

Noticeable at the top of Bed 6 mud in locality 34, and in the top 150 cm of Bed 5 mud in locality 29, is the increase in fossil carbon and decrease in non-fossil species, accompanied by a decrease in TOC. At localities 31 and 97 the POC$_{terrbio}$ and marine carbon contributions decrease towards the top of Bed 5 mud without an increase in fossil carbon. The change in TOC could be due to a different sedimentary history within the mud layers - either sorting of material or variations in supply, or sub-optimal preservation of organic carbon in the upper mud layers.
Turbiditic mud clouds will settle slowly after the coarse material has already been deposited. Hemi-pelagic fall-out of mud-grade material will continue to build a mud cap (Bouma E layer) until the next turbidite comes along. Some of this mud may be removed by scouring of the coarse material travelling past, the intensity of which may vary between sites. There are multiple sources of hemi-pelagic material, including fluvial transport during low-flow conditions and coastal suspension. Assuming that some of the hemi-pelagic material had a fluvial source, and has been preserved, it would be transported into the Adriatic Sea without the need for hyperpycnal delivery or shelf collapse. Hilton et al. (2008b) show that background flow conditions in Taiwan are dominated by fossil carbon eroded from fluvial bedload and bedrock, with $F_{n, f}$ as low as 0.04. Thus although in terms of carbon volume the low-flow fossil carbon contribution is small, at a time of low sediment transport there could be a build-up of fossil carbon at the top of these turbidites. Fossil carbon contributions in the upper part of the Gaoping shelf cores, deposited slowly over several years are higher than in the rapidly deposited canyon cores (see Figures 3.13 and 3.19).

The second sedimentary process that could be causing this pattern is sorting of material within the turbidite mud cloud, such that marine and $\text{POC}_{\text{terrbio}}$ deposit before the fossil material. This process would depend on Stokes’ Law:

$$w_s = \frac{\rho_s - \rho_w gd^2}{18 \mu},$$

where $w_s$ is the settling velocity, $\rho_s$ the density of the particle, $\rho_w$ the density of the fluid, $g$ is the acceleration due to gravity, $d$ the particle diameter and $\mu$ the dynamic viscosity of the fluid. Very fine tabular graphite grains will not float, but may settle very slowly, meaning that they would be present toward the top of the settling mud cloud. Observing this grain size variability directly is hampered by the difficulty of disaggregating or thin-sectioning the mud layers, and the macroscopically observed grains have been ground in the ball-mill. Smaller graphite grains were observed in the upper mud during Raman Spectroscopy, but the influence of grinding cannot be ignored. In order to explain the increase in fossil carbon concentration within the upper mud, fine graphite would have had to be significantly more abundant in the turbidity currents than coarser graphite.

$\text{POC}_{\text{terrbio}}$ settling velocities depend greatly on $\rho_s$, which in turn depends on whether the organic matter is waterlogged or not. Dry organic matter floats, and will not sink until it has become saturated. At this point, it sinks slightly faster than mud, but slower than sand. This process would explain the build-up of layered CWD at the sand-mud interface,
while slower settling of nearly-saturated material would allow some POC$_{terrbio}$, especially smaller, slower-settling particles, to be incorporated into the lower mud.

The third process that could cause a change in carbon species concentration is the degradation in the upper sections of the deposit. Diagenesis, particularly bioturbation or bacterial and biological respiration of organic matter, can remove a significant proportion of the organic carbon present in the water column and upper sediments, whilst deeper burial, preferably anoxic [Kennedy and Wagner 2011], can lead to preservation. If the upper parts of the mud cap were exposed on the sea floor for a significant time then the labile carbon species, especially marine carbon but also some terrestrial POC$_{terrbio}$, could be oxidised whilst the more refractory graphite crystals would survive. Burrows were seen up to 150 cm below the top of Bed 5 mud at locality 31, and the upper half of the Bed 5 mud cap at localities 29 and 31 contains 50 % less carbon than the lower half. Turbidite structure was not completely removed however, so extensive bioturbation cannot have taken place.

Endmember mixing calculations for the upper part of Bed 5 suggest that it is POC$_{terrbio}$ and marine carbon that are reduced (see Figures 5.22 and 5.23). Assuming that the initial mud cap contained a homogeneous carbon distribution equivalent to that at the bottom of the layer, a worst-case scenario for non-fossil oxidation can be calculated. Applying a 25 % loss to the Bed 6 carbon volume calculations from Section 5.5.2.1 means that up to 13.8 Mt non-fossil carbon could have been oxidised after burial.

If the changing carbon distribution at the top of the mud is just a matter of preservation potential, and the mud cap had started off with a homogeneous profile in each carbon species, then whilst the relative importance of fossil carbon can increase with height, the absolute amount calculated by endmember unmixing should not increase, merely decrease for the oxidised species. Thus while this process can explain the reduction in POC$_{terrbio}$ and marine carbon with height, the increase in fossil carbon cannot be explained by oxidation and must correspond to sorting and/or transport processes. This analysis depends greatly on the choice of endmember compositions (see Section 6.1.5.1).

The difference in source material between turbidites and low-flow conditions explains the observed pattern only if the hemi-pelagic deposits are preserved between flows. This is more likely in distal settings (localities 29 and 97) than the more proximal ones (34 and 31), where the ability of high bed shear stresses to re-suspend the upper parts of the mud layer is significant. The section with increased fossil input is larger in the distal localities than the single measurement of this effect at locality 34, which may support this hypothesis,
but the absence of an enriched fossil section in Bed 5 for localities 31 and 97 suggests that there is no change in sedimentary sourcing or processes here, and the variations may be a local effect instead.

Sorting processes are harder to investigate using the endmember calculations, as the grainsize data is not quantitative. The labour requirements of thin sectioning and grainsize measurements using a Scanning Electron Microscope were outside the scope of this study. However, looking at the Taiwanese turbidites (Figures 3.13 and 3.18) shows that POC\textsubscript{terrbio} is usually enriched rather than depleted at the top of the mud cap, and that fossil carbon tends not to be enriched. Obviously the scale and transport distances of the Taiwanese and Italian deposits differ greatly, but the initial observations do not support the concept of slow-settling for fossil carbon.

Overall, it might be that a combination of factors is causing this pattern. The tail-end of the turbidity current, and subsequent low-flow conditions, should contain relatively more fossil carbon (Hilton et al., 2008b), hence the enhanced fossil contribution. Coupled with this, the material deposited in these conditions would have been buried slower, allowing labile species to be oxidised whilst the refractory fossil carbon survived.

5.6 Conclusions

Having collected detailed sample profiles at four localities in the Marnoso Arenacea, clear patterns have emerged. In sandy sections of the turbidites, POC concentrations were low, and fossil carbon in the form of graphite was proportionally more important here than in other parts of the turbidites. In silty and muddy sections the carbon concentration was much higher, and whilst fossil carbon was still present in similar concentrations to the sand layers, there were also significant amounts of POC\textsubscript{terrbio} and marine carbon, leading to a large volume of carbon being sequestered in these deposits.

At the most proximal locality, 34, Bed 6 consisted of a 150 cm sand layer below 100 cm of mud, with the upper mud of Bed 5 also exposed. Elemental / isotopic results showed that the sand body was low in TOC, devoid of POC\textsubscript{terrbio} and marine carbon. Raman spectroscopy confirmed this, with only graphite and semi-ordered fossil carbon present. The mud cap contained 0.5 wt\% C, with POC\textsubscript{terrbio}, marine carbon and fossil carbon distributed in the ratio 3:2:1.
5.6. CONCLUSIONS

At the next locality along the transect, 31, Bed 6 consisted of 90 cm of sand, 10 cm of silt and 100 cm of samplable mud cap. Bed 5 was well exposed, with 50 cm of sand and 170 cm of mud samplable. TOC concentrations were low in the lower sand layers and consisted mostly of graphite. Carbon concentrations were higher in the upper parts of the sand layers and in the mud caps, again $\text{POC}_{\text{terrbio}}$ dominated the carbon distribution here.

Bed 6 at locality 29 consisted of 100 cm of sand, 100 cm of laminated fine sand and silt, and 80 cm of mud. In Bed 5, 330 cm of mud and silt were exposed. Bed 6 sand contained little carbon, mostly graphitic. The silty sections were stratified with carbon rich and poor samples collected. The Bed 6 mud cap contained more than 0.5 wt% C, mostly $\text{POC}_{\text{terrbio}}$. Carbon concentrations and type distributions in Bed 5 were varied, with TOC concentrations significantly lower in the upper parts of the mud cap.

In the most distal locality, 97, Bed 6 consisted of 50 cm of sand overlain by 100 cm of mud cap. The sand layer contained little POC, whereas the mud layer contained a near-homogeneous 0.55 wt% C, of which more than half was $\text{POC}_{\text{terrbio}}$. The upper 45 cm of Bed 5 were also sampled, and contained a similar carbon distribution to the Bed 6 mud.

Common patterns observed between all four localities include the lack of TOC in the sandy layers, a ubiquitous low concentration of graphite in all sections and a $\text{POC}_{\text{terrbio}}$-rich mud cap containing around 0.5 wt% C. Differences between localities include the degree of homogeneity within the silt and mud layers, with locality 29 showing the greatest variation within the upper parts of the turbidite whilst locality 97 is very homogeneous. Another difference between localities is the reduction in TOC in the upper parts of Bed 5 mud, from 0.5 wt% to 0.25 wt%. Localities 31 and 29 showed this for over 100 cm of mud layer, whilst in localities 34 and 97 less than 50 cm at the top of the mud cap had reduced TOC.

Using endmember unmixing results from each locality, and published sediment volumes, the mass of carbon sequestered in Bed 6 was calculated. The bed contained a total of 57.4 Mt of POC, 87 % of which was within the mud and silt layers. 11.7 Mt of fossil carbon was stored and 45.7 Mt non-fossil carbon, of which 29.6 Mt was $\text{POC}_{\text{terrbio}}$ and 16.1 Mt marine carbon. The large volumes of both sediment and POC present mean that single hyperpycnal flows following storm events cannot be the source of these mega-turbidites. Various sourcing mechanisms were considered, of which the collapse of multiple deltas or the continental shelf due to shaking by large or great earthquakes is the most plausible. These rare catastrophic events are compatible with the volumes of carbon and sediment present in the turbidites, and the frequency of their deposition. The mass of carbon contained in a single turbidite exceeds estimates of global annual terrestrial organic carbon.
export, meaning that the Marnoso Arenacea turbidites are important POC sequestration locations.
Chapter 6

Synthesis and Conclusions

By comparing results from all three field areas, covering a range of lateral scales, time periods and sediment volumes, investigations into global processes can be made. This chapter deals with data from multiple sample areas, and considers the following questions:

- Does the liquid HCl leaching system remove all carbonate from the samples?
- What are the sources of nitrogen in organic-rich sediments?
- Does the combination of Raman spectroscopy with elemental / isotopic geochemistry enhance the study of POC?
- What are the differences between the dynamic fresh-fossil unmixing technique and the multi-endmember method?
- What are the interbasinal trends in offshore POC deposition?
- Do variations in the amount of carbon delivered to the ocean in a single event lead to changes in deposition?
- How well can POC survive over geological time?
- Is marine carbon sequestered in terrestrially-derived sediment?
- How resilient is graphite and intermediate-grade fossil carbon to oxidation during transport?
- How do these three case studies compare to other regions?
CHAPTER 6. SYNTHESIS AND CONCLUSIONS

- How important is recycling of POC during orogeny?
- What are the optimum burial conditions for efficient carbon sequestration?

6.1 Methodology

6.1.1 Investigating the presence of un-dissolved carbonate

The presence of carbonate grains and cement in the fluvial and marine sediments used in this study meant that samples had to be decarbonated before analysis for TOC and carbon isotope values. Ideally this decarbonation would involve complete removal of carbonates, both calcite and dolomite, without any loss of organic carbon. The proportion of carbonate lost during decomposition could then be corrected for to produce the as-sampled TOC concentration (cTOC). However, widely varying carbonate contents and mineralogies in the samples could have led to incomplete decarbonation, especially if dolomite concentrations were high. The possibility of residual carbonate being present, affecting both TOC and $\delta^{13}C$ measurements and therefore influencing endmember unmixing results, is investigated here.

![Theoretical relationships between non-dissolved carbonate and TOC measurements](image)

**Figure 6.1:** Theoretical relationships between non-dissolved carbonate and TOC measurements. Corrected TOC = Measured TOC \times (1 - Proportion Dissolved)
The acid strength and volume used during decarbonation was kept low in order to avoid POC degradation, which has been reported in previous studies (Galy et al., 2007a; Hilton et al., 2010). This introduces the possibility that some material (most likely dolomite, as this is harder to dissolve) survived the decarbonation process. Two behaviours were modelled and tested for.

In the first scenario, a constant amount of dolomite (1 wt%) survives decarbonation. As proportion carbonate increases the measured TOC increases exponentially, whilst the corrected TOC shows the constant surviving dolomite (Figure 6.1 a). When plotting corrected TOC against measured TOC, the relationship is a line of zero gradient (Figure 6.1 b).

In the second scenario a constant proportion (1 %) of the carbonate present in the sample survives decarbonation. Measured TOC again increases exponentially with increasing proportion carbonate (Figure 6.1 c). Corrected TOC shows a linear increase with increasing carbonate concentration. The relationship between corrected and measured TOC is parabolic (Figure 6.1 d).

Figure 6.2 plots measured and corrected TOC values against proportion dissolved for four sample subsets. In Taiwan there is very little carbonate present, and the measured and corrected TOC values are very similar. It is unlikely that dolomite has survived in these samples. In the Pyrenees the measured TOC values show no trend with increased proportion carbonate, meaning that corrected TOC values are lower when the dissolved proportion is high. This also indicates an absence of residual dolomite in these samples. The Apennines data do not show either of the modelled patterns. Low-TOC samples follow an apparently increasing pattern, but TOC values peak at proportion dissolved = 0.35-0.45 and decrease once the proportion dissolved exceeds 0.5. This pattern does not suggest the presence of residual dolomite either, rather that organic material is best preserved in sections that incidentally also contain moderate amounts of carbonate, namely the marly silts and muds above the turbidite sand layers.

When plotted as corrected TOC vs. measured TOC, the Italian samples lie on a linear trend (Figure 6.3). This trend is best explained by the presence of 45 wt% carbonate in the samples, completely removed during decarbonation. This proportion carbonate could vary from sample to sample, but there is no evidence of a residual proportion. Attempts to explain this trend using the constant residual amount scenario are completely unsuccessful. A model using a constant proportion of residual carbonate fits best with 1.5% of the initial carbonate remaining, but the fit is less successful than with a complete decarbonation of
Figure 6.2: The relationship between TOC, cTOC and proportion dissolved. The decreased carbon concentrations at high dissolution proportions suggests that it is not dolomite that is causing the increased TOC measurements.

Overall these tests suggest that the decarbonation process is complete for the volume (23 ml) and strength (1 N) of acid used in this study. Results in this study are not affected by the presence of residual carbonate.
Figure 6.3: The relationship between TOC and cTOC in samples from the Italian Apenines. The “1:1 relationship” line represents the scenario with no carbonate dissolution. The “45% carbonate” line represents the trend if every sample contained 45% carbonates, which were all fully removed during decarbonation. The “Model” line represents the best match between the constant proportion scenario and the data, in which 1.5% of the initial carbonate is not removed by the leach. The data does not fit the model trend well, suggesting that the measured carbon signal is derived from organic matter.

Figure 6.4: Plots of TN vs. TOC from all study areas. These plots show a slight positive intercept, indicative of a minor amount of inorganic nitrogen. Very carbon-rich samples have been ignored when performing linear regression, since their high C/N ratios are not helpful in this analysis.
CHAPTER 6. SYNTHESIS AND CONCLUSIONS

6.1.2 Sources of nitrogen to organic-rich sediments

Whilst nitrogen is an important component of chlorophyll and amino acids, terrestrial matter tends to contain much less nitrogen than carbon, with N/C less than or equal to 0.05. This ratio can be increased during diagenesis in soils or sediment (Helie and Hillaire-Marcel, 2006) as bacteria mineralise nitrogen whilst respiring CO$_2$. Marine N/C is higher, at or around 0.16. However, ratios approaching 1.0 were seen in some carbon-poor samples, indicating that either the diagenetic effects are very large or there is an inorganic source of nitrogen to the samples. Plotting TN vs. TOC and performing linear regression (Figure 6.4) gives a slight positive intercept in all cases, possibly indicative of a minor input of inorganic nitrogen, less than 0.025 wt%. One potential cause of this is the low volume of both nitrogen and carbon in some samples. The TN-TOC relationship in Italy shows a cluster of points with 0.01 - 0.03 wt% N, which would have produced very small gas peaks during analysis, less than 500mV. This means that a small nitrogen addition from an instrumental blank or minor amounts of ammonium-containing minerals could lead to such an offset. In terms of carbon volumes, there should be no effect on the conclusions of this study, as this applies to low-TOC samples.

6.1.3 The applicability of coupled elemental / isotopic and Raman Spectroscopic analysis

This project has shown that Raman Spectroscopy can bring some clear benefits to questions of organic carbon provenance. The ability to sample individual carbon grains, and concurrently collect images of the sampled grain, means that inputs to a heterogeneous sedimentary rock can be identified and analysed individually. Analyses are fast - ten high-quality spectra can be collected from a powdered sample in about one hour on a Ramascope 1000 machine, more on more modern spectrometers with motorised stages and other automated systems (e.g. InVia Raman hardware). This compares to over one hour’s total processing time to decarbonate, weigh and analyse an elemental / isotopic sample.

The disadvantage of the Raman analysis is that quantitative interpretation of carbon sources is limited. Careful examination of the material present on the slide and collection of a limited number of spectra will give a representation of the types of carbon present in the sample, but quantifying the relative abundance of each isn’t possible. For example, analysis of a 300 × 300 µm micrograph from samples 11A suggested that 1 % of the image was
black or silver in colour, and could be POC. Some of this material was not organic carbon, but other opaque minerals. Other particles present in the micrograph were less than 3 \(\mu m\), below the resolution of the spectrometer. The estimated TOC of non-decarbonated powder in this sample was 0.2 wt\%, reinforcing the idea that not everything that appears to be POC under the microscope is carbon. However, with the micrograph analysis overestimating the carbon content of the sample, it is plausible that the majority of the POC is present as discrete particles rather than sub-micron kerogen. Full quantification with the Raman spectrometer would require collection of a much larger number of spectra. This is possible, especially on newer equipment, but time requirements are increased accordingly. The automated processing method eliminates time constraints when peak fitting - a quick check that each spectrum has analysed properly requires only a few seconds.

Conversely, elemental / isotopic analysis provides a quantitative result, but interpreting isotopic and elemental ratio values when there are multiple endmembers requires careful consideration of endmember compositions and is not a direct measurement in the same way that the Raman spectra are (see Section 6.1.5.1).

Coupling Raman spectroscopy with isotope geochemistry brings the advantages of both methods. Elemental / isotopic studies give quantitative measurements of TOC, and estimates of the relative amounts of each carbon type present in the samples, which can then be confirmed by the Raman method. Additionally, chemically similar material, such as semi- and fully-graphitised fossil carbon, can be distinguished and the presence of recycled low-grade carbon with a chemical signature similar to fresh POC\textsubscript{terrbio} can be identified. This significantly enhances the ability to investigate the resilience of POC over orogenic cycles.

With increasing numbers of carbon types, the coupling of Raman spectroscopy and isotope geochemistry allows finer insights to be seen than would be found from each method individually.

6.1.4 Applicability of the new Raman spectroscopy techniques to sedimentary and environmental samples

Using carbon classification based on Raman spectroscopy can complement or replace stable isotope geochemistry as a method of quantifying the input of different carbon sources to a sedimentary deposit. In order to do this, a fully-representative dataset should be collected
from each sample. On modern hardware, collecting 100 or more spectra from each sample is quicker and cheaper than the elemental / isotopic alternative. Automatic focussing onto the sample surface, combined with 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 samples. These techniques are now becoming available on modern spectroscopic equipment, although were not usable in this study.

The Raman spectroscopy techniques developed in this study have advantages over other organic petrographic techniques, such as vitrinite reflectance. Firstly the range of meta-morphic conditions identifiable by the fitting method is very large, characterising both thermally immature and fully-graphitised organic matter. Secondly, the rapid and automatic application means that questions of sedimentary source and process can be concurrently investigated.

### 6.1.5 Comparing endmember mixing models

Two mixing models for determining the contribution of varying carbon species to TOC were used in this study. One is the Hilton et al. (2010) model, which mixes a fixed POC\(_{\text{terrbio}}\) endmember and a dynamically-generated POC\(_{\text{fossil}}\) endmember. This sets the POC\(_{\text{fossil}}\) composition along a pre-determined mixing line, defined from experimental results. This procedure works when marine carbon input is insignificant, but the addition of a second non-fossil composition introduces complexity beyond the scope of this model. To fully deconvolve multiple fossil and non-fossil carbon inputs in a marine setting, a second, multi-endmember unmixing procedure was developed. This worked by solving simultaneous equations based on the TOC, TN, \(\delta^{13}\)C and \(\delta^{15}\)N content of each sample. In these endmember mixing model results POC\(_{\text{terrbio}}\) represents the sum of POC\(_{\text{terrbio}}\) and marine carbon endmembers, as these are both inputs of freshly-produced organic matter and can be deconvolved from the fossil carbon input. The comparison between these two methods is shown in Figure 6.5.

In a terrestrially dominated system with little marine carbon input, such as the Gaoping Canyon, results from the two methods are reasonably comparable. Both non-fossil and fossil carbon plot parallel to a 1:1 relationship in this location. The offset from the 1:1 line depends on the choice of non-fossil and fossil endmembers.

On the Gaoping Shelf, marine carbon input is significant (Figures 3.18 and 3.19). When
6.1. METHODOLOGY

Figure 6.5: Comparison between dynamic-fossil and multi-endmember mixing models in the Gaoping Canyon. Core K8 has been ignored since it has very different $\delta^{13}$C and N/C values from the other cores. Hilton method follows Hilton et al. (2010). Linear regression lines through POC$_{terrbio}$ and POC$_{other}$ are plotted for comparison with a 1:1 relationship.

Comparing the two methods there, they are greatly offset from the 1:1 relationship, and neither fossil nor non-fossil material trends with that line. Thus the “Hilton” method is unsuitable for describing systems with a large input of marine carbon to the sediment.

In the Italian Apennines, the disparity between the two methods is less severe, and simpler, than in Taiwan. The addition of marine carbon (see Figures 5.21, 5.22, 5.23, and 5.25) means that the “Hilton” method with a single fresh component underestimates the
non-fossil contribution to the sediments in comparison to the multi-endmember method, and hence overestimates the fossil contribution.

\[\delta^{13}C\]

Figure 6.6: Mechanics of two endmember unmixing methods, the dynamic fossil and multi-endmember unmixing models. The grey data shows the Apennine samples. The red data point shows how a single sample is interpreted by the two methods.

Samples from the Apennines lie along a trend with a restricted range of $\delta^{13}C$ (see Figure 5.19). The low N/C extreme of this distribution, representing the non-fossil dominated samples, has a $\delta^{13}C$ value around -23 ‰, intermediate between marine and terrestrial biomass. Thus when considering the fossil and non-fossil contributions, the two models
will assess each data point along differing mixing lines, as illustrated in Figure 6.6.

Given the location of marine carbon in $\delta^{13}$C - N/C space, and the range of $\text{POC}_\text{fossil}$ compositions considered by the “Hilton” dynamic fossil mixing method, it is not surprising that incorporation of marine carbon into sediment leads to a mis-calculation of non-fossil input. However, if the composition of $\text{POC}_\text{fossil}$ is similar to that of marine carbon then the endmember unmixing model is not applicable. Mixing model choices and endmember compositions must be considered carefully.

6.1.5.1 Importance of the choice of models and endmembers

Figure 6.7: Endmember unmixing results for marine carbon in the Pyrenees. Marine carbon should not be present in fluvial samples, demonstrating the problems caused by poorly-constrained endmember compositions.

The choice of endmember locations becomes increasingly important as the complexity of the mixing method increases. In the simple biomass-fossil system described by Hilton et al. (2010) a change in endmember location will change the relative proportions of $\text{POC}_{\text{terrbio}}$ and $\text{POC}_\text{fossil}$. In the multi-endmember method the proportions of each are more sensitive to changes - if estimation of marine carbon input depends on the deviation from a mixing line between a single $\text{POC}_\text{fossil}$ endmember and $\text{POC}_{\text{terrbio}}$, then the position of this line is very important. In the case-studies presented in this thesis, the $\text{POC}_\text{fossil}$ composition was tuned by iterating the endmember unmixing procedure with changing values until no component produced negative contributions. This procedure was successful in Taiwan and Italy, but the Pyrenean samples contained $\text{POC}_\text{fossil}$ with a composition similar to that of marine carbon. Figures 4.23 and 4.26 show samples from onshore facies with $\delta^{13}$C compositions heavier than the offshore samples. This means that the endmember unmixing model attributes large amounts of marine carbon ($\delta^{13}$C = -18‰) to these samples, when that cannot be the case (see Figure 6.7). Marine carbon should only be present in fluvial
samples via recycling of marine sediment.

The endmember unmixing model is an appropriate tool only in situations where the endmembers are distinct and well-constrained.

6.2 Interbasin trends in offshore POC burial

6.2.1 Distribution of POC\textsubscript{terrbio}

Burial of POC\textsubscript{terrbio} is an important natural method of CO\textsubscript{2} sequestration. Figure 6.8 shows the geographic distribution of POC\textsubscript{terrbio} in each sample area. Fluvial samples from Taiwan were artificially low in POC\textsubscript{terrbio} because of the presence of unsamplable coarse woody debris in the riverside flood deposits. Offshore Taiwan the concentration of POC\textsubscript{terrbio} varied from less than 0.1 wt% near to the shore up to nearly 0.3 wt% on the shelf. The lower, coarse sand, parts of the turbidites from the Gaoping Canyon contain lots of POC\textsubscript{terrbio}, including both twigs up to 5 cm in length and fibrous tree-trunk material. In the Marnoso Arenacea formation, both elemental / isotopic and Raman data suggest that the lower sandy parts of the turbidites contain little or no POC\textsubscript{terrbio}, but concentrations are high in the muddy parts of the turbidite. POC\textsubscript{terrbio} exists at the top of the sandy
layers, in regions of fine sand and silt just below the mud cap. Shelf material in the Pyrenees contained less POC\textsubscript{terrbio} than the Gaoping Shelf, but the degree of loss is lower. Other facies within the Pyrenean basins contained more POC\textsubscript{terrbio} than the shelves - the Aren pro-delta and Castissent turbidites had the highest concentrations.

### 6.2.2 Terrestrial POC deposited offshore

![Average carbon contributions](image)

Figure 6.9: Distribution of carbon types offshore Taiwan, from canyon and shelf/slope settings. Endmember-unmixing calculations were performed and the resulting carbon component contributions turned into height-weighted averages to compensate for sample distribution within the cores.

All three sample locations have shown that terrestrially sourced POC can be found in offshore sedimentary settings, both in the form of disordered woody debris and lignite-grade sedimentary POC, and as crystalline graphite. 4-endmember unmixing calculations carried out on samples from Taiwan showed that fluvial samples contained lots of POC\textsubscript{fossil}, riverbanks were also rich in POC\textsubscript{terrbio}. The fluvial input of POC\textsubscript{fossil} is consistent along the Gaoping Canyon and across the shelf. Terrestrial POC dominates submarine canyon settings, with marine POC contributing only 17 \% of the carbon in the Gaoping Canyon but 30 \% of shelf and slope material (see Figure 6.9, and also Figure 3.11).

Dynamic endmember mixing calculations from the Pyrenees grouped samples into terrestrial POC\textsubscript{terrbio} and other carbon types, as marine and fossil carbon could not be distinguished effectively here. POC\textsubscript{terrbio} contributions to each sedimentary facies were generally
similar to those from POC\textsubscript{other}. The pro-delta in the Aren formation was dominated by POC\textsubscript{terrbio}, potentially local productivity. Delta or shelf collapse is suggested as the source of the Apennines turbidites, which are also dominated by POC\textsubscript{terrbio} over other carbon species. Channel-lobe overbank deposits in the Castissent formation contained more POC\textsubscript{other} than POC\textsubscript{terrbio} (see Figures 4.28 and 4.29). Turbidites were the Castissent facies richest in POC\textsubscript{terrbio}, and the Apennines turbidites were also very rich in terrestrial POC. Marine carbon represented only 28% of the 57.4 Mt C stored in Bed 6 despite being deposited far offshore, the remaining 72% had a terrestrial source, 52% was POC\textsubscript{terrbio}, 20% fossil carbon (see Table 5.3). Sediment in the turbidites was potentially delivered through erosive submarine canyons systems similar to the Gaoping system. Canyons are efficient conduits for the transport of terrestrial POC, as sediment-laden hyperpycnal flows and turbidity currents can bypass the marine carbon-rich shelf environment, and even in the Apennines when delta or shelf collapse could have been the sediment source, the flow of sediment may have localised into channels between the mountain belt and the depocentre. Rapid channelised flow would limit the potential for marine carbon erosion, especially if submarine canyons experience frequent turbidites which would prevent the build up of large amounts of hemi-pelagic marine POC. Overflow of material from the submarine canyon to the surrounding shelves would allow marine carbon deposits from the basin floor to be incorporated into the sediment.

In conclusion there is clear evidence of terrestrial POC, both POC\textsubscript{terrbio} and fossil carbon, being exported to and sequestered within marine sediments, from nearshore to distal facies. Rapid sediment transport, as hyperpycnal flows and turbidity currents, leads to dominance of terrestrial POC over marine carbon in some facies.

6.2.3 Raman insights into offshore POC deposition

Samples from the Aren Formation contained mostly very disordered spectra with occasional highly graphitised material and rare semi-ordered carbon (see Figure 4.20). This pattern is similar to that seen in the Plio-Pleistocene deposits in Taiwan (Figure 3.23). Looking within lateral profiles of spectra collected in the Castissent Formation (Figure 4.21), the distribution of the three carbon types matched well with the pattern seen in the Gaoping
Canyon and Shelf. Disordered woody material was concentrated closer to the shore, whilst semi-graphitised material was preserved further offshore (see also Figures 3.25 and 3.26). Fully graphitised material was more ubiquitous, although rarer in the offshore samples here than in the Gaoping Shelf samples. The distribution in samples forming a shelf transect, Castissent 15, 16 and 17, appeared similar to the canyon cores from typhoon Morakot and uplifted marine sequences (see Figures 3.23 and 3.25). The distribution of spectra from locality 19 was similar to the Gaoping River and shelf samples from Taiwan (see Figures 3.24 and 3.26).

Coarse Woody Debris and recycled POC_{terrbio} were found in cores from within the Gaoping Canyon, where high-energy turbidity currents had passed through and deposited material rapidly. In the Pyrenees, POC_{terrbio} was more prevalent in the shelf and slope than the distal basin. In Taiwan the fossil carbon sourced from the Central Range was transported into the low-energy shelf and slope facies, and material of a similar metamorphic grade was seen in the fine-grained distal turbidites of the Castissent and not in the nearshore higher energy sediments.

Thus Raman spectroscopy shows that distributions of fossil carbon in Taiwan match depositional patterns observed in similar ancient sedimentary basins, with POC_{terrbio} concentrated into high-energy deposits and fossil carbon in lower-energy environments.

6.2.4 Distribution of POC in turbidites of different volume and length

All three field areas contained turbidite deposits, but the volume of these varied by orders of magnitude. Bed 6 in the Apennines has a volume of 7 km$^3$ (Talling et al., 2007b), which at a density of 2500 kg m$^{-3}$ equates to 17500 Mt sediment, whilst total sediment export during Typhoon Morakot was estimated at 700 Mt (Lee et al., 2011), which was much smaller than the Bed 6 volume yet, 20-times higher than mean annual output of the Gaoping River and around 50% of the annual sediment supply to the Bengal Fan (France-Lanord and Derry, 1994). The upper reaches of the Gaoping Canyon trapped only a limited amount of sediment, most of it continued through the canyon to the South China Sea and Manila Trench (Su et al., 2012), so the Morakot cores low-volume nearshore turbidites. The Marnoso Arenacea turbidites represent the final depositional location for the turbidity current, hundreds of km offshore. Turbidites were also found in the Aren and
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Castissent formations. Although bed volumes were not available, based on their thicknesses the turbidites likely represent volumes intermediate between the other two field areas.

Despite these differences in bed volume, turbidites show similar structures with a sand layer topped by a mud cap (see Figures 3.13, 4.32 and 5.29). In the Apennines, POC\textsubscript{terrbio} was located in laminated fine sand and silt at the top of the sandy layer, and throughout the mud cap. Lower sandy sections were virtually devoid of POC\textsubscript{terrbio}. In the Pyrenees, sandy layers contained some POC\textsubscript{terrbio} concentrated into particular laminae, with a homogeneous, high-concentration of POC\textsubscript{terrbio} in muddy layers. In the Gaoping Canyon POC\textsubscript{terrbio} was spread throughout both sand and mud layers, with the highest amounts within the sand layer when fragments of CWD were present. When allowed to settle naturally from a well-mixed suspension, unsaturated POC\textsubscript{terrbio} tends to locate at the top of the sediment, whilst saturated POC\textsubscript{terrbio} deposits between sand and mud-sized particles. This study has not considered whether there is a separation of lignin-rich, cellulose-rich and leaf-matter-rich material within turbidity currents and hence turbidites, however future plans for analysis by Gas Chromatography - Mass Spectrometry should allow this to be investigated. The survivability of POC\textsubscript{terrbio} in different layers is discussed next (Section 6.2.5).

A possible explanation for these differences is the variation in transport history of the POC\textsubscript{terrbio} observed in the sediments. The Gaoping material was harvested from unsaturated standing biomass and from saturated soil carbon, both of which would tend to deposit above the sand layer. Sumner et al. (2009) determined the grainsize distribution of flows with varying amounts of sand and mud decelerating for different times, and showed that slow deceleration of low-concentration flows led to clean sand with a mud cap, whilst rapid deceleration led to rippled and laminated bedforms and that high solids concentrations led to mixed muddy sand layers. Deposition in the Gaoping Canyon was reasonably rapid, within days of the storm, and sediment concentrations in the upper canyon were likely very high. The total offshore transport distance was less than 30 km to core K15. High turbidity in the hyperpycnal flows may have prevented effective sorting (Amy et al., 2006).

In the Apennines, material was likely sourced from shelf or delta collapse, meaning that the POC\textsubscript{terrbio} would have been saturated and should have located at the sand-mud interface, where large quantities were indeed measured. Transport distances of 300 km or more may have given the material time to reach its equilibrium location within the flow and for flow densities to decrease, with POC\textsubscript{terrbio} rising above the coarse sand grains. Talling...
et al. (2007b) report mud ponding at the distal end of the turbidites (see Figure 5.18), the slow deposition of which would allow saturated POC\textsubscript{terrbio} to locate at the sand-mud boundary.

Sourcing mechanisms for the Pyrenean turbidites are not known, but the transport distance from the fluvial sections to the turbidites was longer than the nearshore Gaoping cores. Profiles through the turbidites show some POC-rich layers within the sand, but generally the mud layers are richer in POC. These intermediate transport distances could have allowed incomplete sorting of POC\textsubscript{terrbio} to the upper sand and mud layers.

A further consideration when dealing with these three sample areas is that the Gaoping Canyon deposits are modern sediments and have not had the chance to lose carbon during diagenesis. This issue will be discussed next.

### 6.2.5 Survivability of POC\textsubscript{terrbio} material over geological time

Raman spectroscopy results have shown that graphite survives in all sedimentary environments, but the potential for other carbon types to survive millions of years of burial can be tested by comparing samples from Taiwan with those from the Apennines and Pyrenees. POC\textsubscript{terrbio} concentrations offshore are almost always higher than the interpreted POC\textsubscript{terrbio} concentration in fluvial samples. If the fluvial signal has been efficiently preserved, this means that many facies are effective at sequestering POC\textsubscript{terrbio}.

Turbidites contain large volumes of sediment and POC\textsubscript{terrbio}. Turbidite samples from the Gaoping Canyon contain POC\textsubscript{terrbio} throughout, but the larger turbidites of the Marnoso Arenacea do not contain much POC\textsubscript{terrbio} in the sand-rich layers. The apparent loss of POC\textsubscript{terrbio} from sandy parts of the turbidites after deposition could be due to three processes. Firstly, the Apennines turbidites could have originated with a similar POC\textsubscript{terrbio} distribution to the Taiwanese samples, but the permeability of the lower sand units could have led to oxidation over time. Oxidation fronts were often seen in the field reaching back from an exposed surface, but these merely represent iron oxidation. It could be that organic matter oxidised at a different rate to iron. The second possibility is that the longer transport distances of the Apennines compared to the Gaoping Canyon (hundreds of km vs. less than 30 km) meant that the POC\textsubscript{terrbio} did not have a chance to be successfully sorted into its optimal height within the turbidites (see Section 6.2.4). Thirdly, the initial POC\textsubscript{terrbio} content of the sediments could be different due to variations in source material.
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For shelf sediments, post-depositional loss was less prevalent, probably due to the higher mud content. Kennedy and Wagner (2011) discussed the ability of mud-grade sediment to preserve large amounts of organic matter, both as films of organic matter covering clay particles, and as organic compounds within the tabular crystal structure of the clay minerals themselves. Anoxic burial conditions greatly enhance the ability of the marine muds to preserve organic carbon. $\text{POC}_{\text{terrbio}}$ was present as mm-scale clasts of organic matter as well as microscopic grains and possibly as mineral coatings. The presence of mud itself, regardless of coatings, could be preserving $\text{POC}_{\text{terrbio}}$ by reducing sediment permeability, thus preventing oxygen reaching the organic matter.

Deconvolving the effects of transport distance and mud content on $\text{POC}_{\text{terrbio}}$ preservation would require directly equivalent modern and ancient systems, or cores from Typhoon Morakot sediments much further offshore. However from the available samples, conclusions can be implied.

Sandy submarine sediments are poor at sequestering carbon over long time-scales. Muddy sections in turbidites, pro-deltas and shelves contain similar concentrations of $\text{POC}_{\text{terrbio}}$ as the fluvial input, and are likely locations of efficient $\text{POC}_{\text{terrbio}}$ storage.

6.2.6 Incorporation of marine material

![Graph showing marine carbon concentration](image)

Figure 6.10: Profiles of marine carbon concentration from multiple sample areas.

Marine material is more labile than other carbon species, and can be remineralised in the water column, consumed by oxidation or bioturbation in the sediment, or dissolved during decarbonation. Despite all these potential losses, it is still present in significant volumes in some offshore sediments. Using estimates of marine carbon input to the Gaoping and Marnoso Arenacea sediments, nearshore, terrestrially-sourced, and distal, submarine
sourced, turbidites can be compared (Figure 6.10). The samples from the Gaoping Canyon are low in marine carbon, less than 0.1 wt%, but the shelf samples contain about 0.2 wt%. Delta or shelf collapse was the likely source of the Marnoso Arenacea turbidites, and the muddy sections of localities 34, 31 and 29 contained just less than 0.2 wt% marine carbon. Locality 97 contained less marine carbon, just over 0.1 wt%. The sandy layers of these turbidites contained much less marine carbon, less than 0.025 wt%. Sandy parts of the Gaoping Canyon turbidites contained up to three times more carbon than this, despite the canyon cores being terrestrially dominated.

Preservation of marine carbon in the turbidite sands was poor, which is not surprising given the higher permeability of the sandy layers and the absence of fine particles upon and within which marine organic carbon could be preserved (Kennedy and Wagner, 2011). Note that the uncertainty in the endmember unmixing procedure of 0.1 wt% means that this analysis is under-constrained but patterns are consistent.

6.2.7 The survivability of fossil carbon

Galy et al. (2008) demonstrated that over transport distances up to 2000 km, intermediate-grade fossil carbon within a terrestrial sediment flow was oxidised, leaving only highly-crystalline material. Transport distances in the Pyrenees and Gaoping Canyon are much lower than this, allowing for the possibility of more efficient preservation of the large amounts of fossil carbon delivered from active mountain belts to the ocean (Hilton et al., 2011).

Figure 6.11 shows geographic profiles of fossil carbon content, as estimated by the endmember unmixing procedure and dynamic endmember unmixing methods. In the Aren and Castissent formations, an average fossil concentration with one-sigma error bars was plotted, based on the “terrestrial” and “non-terrestrial” distributions calculated using the dynamic endmember method. In the Gaoping Canyon and Marnoso Arenacea Bed 6, high-resolution vertical profiles were collected and thus a weighted average fossil composition was plotted based on data from the endmember unmixing procedure.

In the Gaoping Canyon, transport distance to core K15 is only 25 - 30 km, and the fossil carbon concentration is 0.2 wt%. Fossil carbon concentrations in the Gaoping Canyon as a whole ranged from 0.13 to 0.22 wt% with an average of 0.18 wt%, and were noticeably
similar to the fluvial fossil carbon concentration with no downslope reduction in POC\textsubscript{fossil}. In the Pyrenees, transport distances to the basins were around 50 km in the Aren Formation and varied in the Castissent Formation due to orogen-transverse transport. In each case, POC\textsubscript{fossil} concentrations were generally greater than the fluvial facies concentration. Basin fossil carbon concentrations were 0.09 wt% in the Aren and 0.04 in the Castissent. In the Marnoso Arenacea, transport distance to locality 34 was approximately 300 km, with another 120 km to locality 97. Fossil carbon concentrations in the muddy part of the turbidites were around 0.1 wt% here, apart from locality 31 which contained less fossil carbon. In the sandy layers there was less fossil carbon than in the mud. At locality 97 there was very little fossil carbon, but this was likely due to the single sample collected being from the lower part of the sand layer. Locality 29, also distal, contained the most sandy fossil carbon.

Fluvial concentrations of fossil carbon appear to have been preserved in nearshore marine stratigraphy. None of these field areas showed a systematic reduction in fossil carbon concentration with increasing distance offshore, in fact, contrary to the pattern seen in the Bengal Fan, in the Pyrenees there was more fossil carbon in the Aren basin samples than in nearshore sediments. Thus over short transport distances, fossil carbon appears to be preserved efficiently.
6.2.8 Comparison to other sedimentary systems

Source-to-sink investigations have been carried out in other areas. Wheatcroft et al. (2010) devised rating curves of POC and sediment discharge based on the output of material from various small, mountainous rivers around the world, highlighting the importance of high discharge events in comparison to larger river systems. For example, despite not producing turbidity currents directly, high-concentration outflows from the Eel River in California will be concentrated by wave action until a gravity current is formed, whilst low-concentration flows do not concentrate further and the POC is distributed across the shelf, prone to repeated erosion and deposition cycles, and prone to remineralisation. They produced an analytical model predicting the relationships between water, sediment and POC discharge, and estimated the behaviour of different carbon species within the system. In contrast, the Kaoping River and Canyon produced turbidity currents immediately, without a concentration phase, and the Apennine turbidites were likely sourced from submarine sediments and triggered by tectonic rather than climatic events.

In terms of POC transport, the carbon present in a single event bed in the Apennines (57 Mt C) is three orders of magnitude higher than the 20 Kt C transported from the LiWu river during Typhoon Mindulle (Hilton et al., 2008b), which is in itself an extreme event when compared to many rivers around the world. In terms of spatial POC yield, landsliding in the Kaoping catchment during Morakot transferred 360 - 740 tC km$^{-2}$ CWD to the oceans, whilst the LiWu river transports 16 - 202 tC km$^{-2}$ yr$^{-1}$ and mountainous catchments outside ITCZ are smaller still, 5 - 8 tC km$^{-2}$ yr$^{-1}$. Also, catchments away from the ITCZ produce less sediment (Leithold et al., 2006). The Siuslaw catchment in Oregon, USA contains 5 % TOC, yet yields 100 times less sediment (100 t km$^{-2}$ yr$^{-1}$) than New Zealand (10000 t km$^{-2}$ yr$^{-1}$) and Taiwan (15000 t km$^{-2}$ yr$^{-1}$ (Liu et al., 2009)). In the absence of high sediment concentrations, preservation of labile POC may be restricted in oxic water, whilst the concurrent delivery of POC and sediment during large events can lead to long-term preservation as shown in the Pyrenees and Apennines. Pacific ocean islands are ideal settings for both biomass production and sediment erosion (Milliman and Syvitski, 1992) and deliver 50 - 90 Mt C km$^{-2}$ yr$^{-1}$ (Hilton et al., 2008b), hence there is likely to be significant sequestration through the pathway investigated in this study. However the CO$_2$ sequestration facilitated by extreme amounts of sediment and POC export in these settings may not be replicated outside of the tropics, due to a lack of either sediment delivery or terrestrial biological productivity. POC export and sequestration in temperate or polar settings will likely vary in both amount and process compared to tropical POC export.
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6.3 Recycling of organic material during orogeny

In an ongoing orogeny, recycling of ancient material into new sedimentary units is unsurprising. This project has been able to investigate recycling, and found it to be a pervasive and important feature of nearshore sedimentary rocks.

6.3.1 Recycling from earlier to later sedimentary units

Remobilisation of sediment means that a few considerations are required. Firstly, it should not be assumed that material transported out to sea and successfully buried has been sequestered forever. Whilst geological processes are slow, and it takes time to exhume marine material to the point of recycling, the carbon stored within Taiwan’s Cholan and Tuokoshan formations was only removed from the short-term carbon cycle for 1-3 million years. Whilst some of the Cretaceous Aren material has clearly survived until now, another part is likely to have been recycled and the carbon re-worked within this time span. Quantifying this loss is not possible without greatly improved constraints on sediment volume and TOC concentrations at deposition. Each re-working introduces the potential for oxidative loss during the erosion, transport, burial and lithification processes. Ittekkot (1988) talked of the survivability of non-labile terrestrial POC, such as this recycled carbon, and thus loss during transport should be smaller than if it were fresh, labile material. Galy et al. (2008) showed that even reasonably graphitised carbon can be lost during transport if the transport distances were particularly long. Over the shorter distances in the studied basins, longitudinal profiles of carbon content are reasonably consistent and do not show a reduction in TOC concentration further offshore, suggesting that losses within these sedimentary systems were limited.

$^{14}$C data from Taiwan has shown that aged woody debris, likely sourced from Plio-Pleistocene age fluvial-marine sediments, was recycled into the Morakot sediment. This material was of lignite grade and had limited resilience within the erosional system, consisting of very fine grains in the Morakot cores. This recycling is corroborated by $^{13}$C and Raman spectroscopy data. Looking to the Pyrenees, it is more difficult to trace recycling from the Aren to the Castissent without the facility of $^{14}$C data, but comparisons between them using both Raman and elemental / isotopic data show distinct similarities between the Aren and the near-shore Castissent.
6.3.2 Recycling from low-grade metamorphic rock

Harvesting of carbon-bearing metasedimentary rocks exposes carbon previously stored in the long-term, introducing the possibility of oxidation and CO$_2$ release from deep geological storage. Both the Taiwanese and Pyrenean samples show a progressive exhumation of metamorphic carbon, with the initial sediments largely devoid of intermediate-grade carbonaceous material when analysed with Raman spectroscopy but later formations showing metamorphic temperatures compatible with metamorphism within the mountain belt. This fossil carbon is sourced from the metamorphic units of the mountain belt itself, not from detrital graphite in cover sediments.

In Taiwan this low-grade fossil carbon is seen in the Gaoping River, Canyon and Shelf, being the major form of organic carbon analysed in the river and shelf sediments. In the Pyrenees, Raman spectroscopy results showed that it dominates in the distal Castissent basin (see Figure 4.18). Elemental / isotopic results from the Castissent show that the submarine channel overbank deposits have a similar geochemistry to the distal basin (see Figure 4.26), and may well also contain low-grade metamorphic carbon. Other Castissent Formation localities do not share this elemental / isotopic distribution. One explanation of this would be that the moderately-metamorphosed POC$_{fossil}$ is stable enough to survive transport distances up to 100 km, and is transported as fine, lightweight particles that are preferentially deposited far offshore or in calmer environments beside the submarine canyons. Preservation as far as the basin suggests that loss during transport is minimised and there may be a semi-closed loop between source and sink for this type of material when transport distances are short. Galy et al. (2008) show however that this type of material is lost over longer transport distances, over 1000 km. Steep mountains delivering material into a foreland basin are likely much more efficient than the Bengal Fan system.

6.3.3 Recycling of very graphitised material

Very crystalline allochthonous graphite was found in all three sample regions (see Figures 3.23, 3.26, 4.17, 4.18 and 5.29.) This material has Raman spectra indicative of near-perfect crystallinity, something that is not formed in orogenic belts until metamorphic temperatures have approached 650 °C. The metamorphic grade of rocks currently exposed in Taiwan and in the Pyrenees during the Cretaceous and Eocene do not approach this condition, with a range of <300-475 °C in the Hsuehshan range of Taiwan (Beyssac et al. 2007), and peak temperatures of ~300 °C recorded in plutons of the central Pyrenees.
Thus this graphitic material must have been sourced outside the mountain range.

In Taiwan, significant amounts of highly-crystalline graphite were seen in the Gaoping Canyon and Shelf, as well as in the Plio-Pleistocene sedimentary units. The Gaoping river did not appear to contain much pure graphite, especially samples from the tributaries draining the highlands of the Central Range. Thus the source of graphite to the Gaoping Canyon and Shelf was unlikely to be the currently-exposed metamorphic units. The Cholan and Tuokoshan formations contained a bimodal distribution of disordered and graphitic carbon (see Figure 3.23). Raman spectra from Gaoping River tributaries draining the coastal plain and western foothills showed some graphitic material. What then was the source of graphite to the Plio-Pleistocene formations? The lower Cholan formation had a marine setting (Chen et al., 2001), and thus could potentially have been fed graphite directly from China, meaning that the graphite seen in the Morakot cores experienced at least one previous erosional cycle. However, graphite crystals were also present in the upper Cholan and Tuokoshan formation, which had an intertidal or fluvial setting and must have been fed directly from Taiwanese erosion. Thus graphite sourced from these sections to the Gaoping experienced a further erosional cycle. Beyssac et al. (2007) mentioned detrital graphite within the Eocene Tachien Sandstone of the Hsuehshan Range and the Miocene Lushan Formation. This graphite must have been sourced from outside Taiwan, as the island did not exist when the sediments were deposited. Graphite is exposed terrestrially in Southern China (Orberger et al., 2007) (although it is not suggested that the Taiwanese graphite was sourced from this exact location), and could have been exported from mainland protoliths into the South China Sea to provide the detrital graphite.

The inferred history of the Taiwanese graphite is as follows: after erosion from China it would have been deposited in the South China Sea margin, being incorporated into marine sediments. As these were uplifted and Taiwan emerged from the ocean, the detrital graphite was remobilised and transported offshore into what became the Cholan and Tuokoshan formations, along with woody material removed from the early forests. The graphite remained in the Plio-Pleistocene formations until they themselves were incorporated into the growing Taiwan orogen, uplifted and exposed, eroding rapidly into the rivers of western Taiwan and connected offshore canyons. The graphite has thus experienced three cycles of erosion and deposition since exhumation of its continental source. Quantification of oxidation along this complex transport route is impossible, but the survival through three orogenic cycles demonstrates the resilience of pure graphite and its potential importance for long-term carbon sequestration.
6.3. RECYCLING OF ORGANIC MATERIAL DURING OROGENY

The findings from Taiwan are corroborated in Spain. The source material of the late Cretaceous formations is described as “heterogeneous materials from Cretaceous carbonates and sandstones to Triassic shales and various basement rocks” (Puigdefabregas and Souquet, 1986), following a period of renewed compression in the Pyrenees. This does not suggest that highly-metamorphosed material was exposed at this time - Metcalf et al. (2009) suggested that the Maladeta pluton in the centre of the Orri thrust sheet only exhumed in the Oligocene. Large et al. (1994) described graphite from the Trois Seigneurs Massif, a low-pressure, high-temperature regional metamorphic massif in southern France, yet it would not have been exposed until much later than the Aren and Castissent rocks were sourced. Thus the likelihood is that the graphite in the Aren was sourced from cover material, much like Taiwan, with the source to that cover being much older continental lithologies. However with a more complex orogenic history and less isolated setting, tracing graphite through multiple erosional cycles is more difficult in the Pyrenees. What is certain is that graphite appears ubiquitous.

Pervasive graphite is also seen in the Apennines samples. Graphite is present in all samples, be they oxidised sands or well-preserved muds (see Figure 5.33). Any hydrodynamic sorting of POC*terr bio* into upper silt and mud layers does not seem to have affected the distribution of graphite. A source of this graphite isn’t precisely constrained. The source area for these sediments is large and a sampling transect across the Alps proved inconclusive. However it has not been formed in-situ in the Marnoso Arenacea formation, the metamorphic grade of the formation is too low, and has thus survived erosion from the Alps, transport across the Po basin in large, violent turbidity currents and burial for millions of years.

6.3.4 History of POC erosion from a mountain belt

The Cretaceous Aren formation from Spain and the Plio-Pleistocene Cholan and Tuokoshan formations of Taiwan represent the earliest part of the orogeny. As the mountain belt forms and becomes vegetated, its continued uplift causes terrestrial erosion and deposition into the neighbouring seas. These early sediments contain plentiful terrestrial POC*terr bio*, in sizes ranging from millimetre to metre scale, which transforms via diagenesis into lignite and coal. Absent from these sections are significant amounts of metamorphic carbon, as the deeply-buried rocks that contain this material are not yet exhumed (see Figures 4.28, 3.23 and 4.20), unless it is contained in sedimentary cover as detrital grains.
Progressive orogeny leads to the exhumation of both the deeper metamorphic rocks and the earlier sediments, which are mixed together in the river network and delivered into the evolving foreland basin. The material currently carried by the Gaoping River into the Gaoping Canyon is comparable to the source of the Castissent formation during the Eocene. Upon reaching the sea, rivers can deposit material in submarine canyons and onto the shelf and slope. Both of these facies have been sampled in this study - canyon samples K1, K12, K25, K8, K8X and K15 from Taiwan contain turbidite layers consisting of graded sand and mud. Turbidites are also found in the Castissent formation, especially at locality Cast17 (see Figure 4.13). These contain POC that has been sorted during transport into well-defined layers, with coarse POC$_{terrbio}$ concentrated in the layered fine sand and silt just below the mud cap, and significant amounts of fine POC distributed throughout the upper muddy layers. Away from the submarine canyon, fine-grained overbank deposits form beside the channel and across the shelf and slope, containing both terrestrial and marine carbon (samples K11, L9 and Cast85-88).

In turn, these rocks too may be engaged in orogeny, allowing for further recycling of the marine sediments along with primary erosion from the centre of the mountain range until orogeny ceases and the foreland basin is filled.

6.3.5 Optimal burial conditions for carbon sequestration

If organic carbon burial is to be an effective sink of CO$_2$, it must be remove significant volumes of carbon from the short-term cycle, for as long as possible. Given that nearshore sediments on active margins are prone to uplift and recycling (e.g. the Cholan and Tuokoshan formations recycling into the Gaoping Canyon), transport further into the deep basin would be preferable. The sediment would avoid recycling for millions of years. However, transport to distal basins can lead to a loss of POC$_{terrbio}$ and partially ordered fossil carbon, via oxidation during transport or after deposition.

The presence of mud appears to greatly enhance the preservation potential of POC offshore. Deltaic settings, such as the nearshore Aren formation, contain significant amounts of fresh terrestrial woody material within thick muddy layers, but their overall volume is low in comparison to distal facies. Shelf sediments offshore south-western Taiwan also contain large amounts of both POC$_{terrbio}$ and marine carbon, yet deposition rates can be quite slow and carbon preservation over long timescales in the Aren Formation is lower here than in pro-delta settings (see Figure 6.8). Turbidites, such as those found in the
southern flank of the Pyrenees and especially in the Apennines, can contain much larger volumes of sediment than nearshore facies. The muddy parts of these formations can sequester millions of tonnes of POC in a single event bed, equivalent to contemporary annual organic carbon transport to the oceans. Transport of sediment to smaller turbidites can be via hyperpycnal fluvial export, whereupon $\text{POC}_{\text{terrbio}}$ may locate in sand layers which may not survive long-term burial. Mega-turbidites require the collapse of deltas or shelves to source the required sediment volumes, hence effective temporary storage in these facies is important for long-term turbiditic sequestration, while also introducing the possibility of additional \textit{in-situ} productivity of $\text{POC}_{\text{terrbio}}$ on the delta top.

Optimum conditions therefore appear to be the build-up of organic material nearshore, in mud-rich deltas and continental shelves and slopes, the collapse of which causes turbidity currents that transport material rapidly to distal basins, whereupon $\text{POC}_{\text{terrbio}}$ is buried along with marine and fossil organic carbon in turbidite mud caps.

Successful long-term burial of $\text{POC}_{\text{terrbio}}$ is an effective natural form of CO$_2$ sequestration, as further plant growth will replace the eroded carbon, drawing CO$_2$ out of the atmosphere. Continued orogenic uplift, harvesting POC and providing sediment in which to bury it, coupled with efficient delivery to offshore facies rich in mud, can lead to episodic sequestration of globally significant volumes of POC.
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Appendix A

Computer Scripts

A.1 Raman Spectrum processing script

#!/bin/bash

# This script analyses Raman spectra of Carbonaceous Material, by fitting Lorentzian distributions
# to the G, D1, D2, D3 and D4 peaks, as well as correcting for a linear background.
# The input is taken from a series of text files as produced by a Renishaw Raman spectrometer using
# Wire software. Proprietary .wxd files can be converted into two–column space–separated text files
# (wavenumber intensity) using the "Wire Batch Convert" program. The text files should be contained
# within one single folder, or grouped into sub–folders.
# The script outputs three graphs, containing the raw spectra with linear background identified,
# raw spectra with overall fit superimposed and a residual shown, and the spectra following the fitting,
# showing the fitted peaks after the background has been removed. The

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fitting parameters (peak locations, # amplitudes, widths and areas, as well as characteristic area ratios) are outputted to a summary file

# for further analysis
#
# The script requires the following software to run:
# − A Unix / Linux environment (tested with Ubuntu)
# − Bash terminal program
# − Dos2unix text file conversion software
# − Gnuplot graphing software.
# − Version 4.5 is required, which is still only available as source code
# − I have compiled this into an installable .deb file
# − Ghostscript PostScript and PDF manipulation software
# − The script ”prepraman.sh” should be run before the first files in a given folder are analysed.
# This script creates folders and initiates some datafiles for the subsequent fits
# − Both this fitting script and ”prepraman.sh” require permission to execute as programs
#
# The script executes from the command line, in the form
#$ sparkesfitraman.sh [options] [input files]
#
# The options are
# −q Quiet mode – graphs appear on screen but immediately disappear
# −d Delete – removes previous files from ”acombinedresults.txt”
# −t[value] Threshold – the signal–to–noise ratio below which a peak is too noisy to process
#
# Input files can be listed individually, or selected all at once using a wildcard (e.g. *.txt)
# After analysis the results are written to a file entitled ”acombinedresults.txt”. Any filename # already in this file will be ignored and not re–fitted, hence the delete option.
#
# Example code to prepare for and then analyse all samples with ”taiwan” in the file name:
A.1. RAMAN SPECTRUM PROCESSING SCRIPT

# $ prepraman.sh
# $ sparkesfitraman.sh -d -q -t 5 taiwan*.txt
#
# Note: The included script "cropraman.sh" will take a file and crop
to certain wavenumbers. The
# fitting procedure is less accurate if files extend too far beyond
1900 cm⁻¹ as the assumption
# of a linear background is no longer valid.
#
# Firs the options are collected

quiet=false
persist=persist
delete=false
delans=n
threshold=2
silthreshold=2

# r2 limit should be 100 times greater (and an integer)
 r2limit=60

while getopt 'dqt:' option
do
case $option in
  d) delete=true;;
  q) quiet=true;;
  t) threshold=$OPTARG;;
esac
done
shift $((OPTIND - 1))

if [ "$delete" = "true" ] ; then
  echo "Really delete all records? (y/n)"
  read delans

if [ "$delans" = "y" ]; then
  echo "name\_g\_height\_g\_location\_g\_width\_g\_area\_d1\_height\_d1\_location\_d1\_width\_d1\_area\_d2\_height\_d2\_location\_d2\_width\_d2\_area\_r1\_ratio\_r2\_ratio\_r2\_temp\_ra1\_ratio\_ra1\_temp\_ra2\_ratio\_ra2\_temp\_r2\_voigt\_plottemp\_totalwidth\_totalwidth\_voigt" > acombinedresults.txt
  echo "Records deleted!"
else
  echo "Records saved!"
fi

if [ "$quiet" = "true" ]; then
  persist=""
fi

echo "$#"  
echo "$@

function processesample {
  #Prepare input file
  filename=$1
dos2unix $filename
  nicename=${filename%\.*}
  echo $nicename
  shortname='echo $nicename | awk 'BEGIN { FS = " " } { print $2 }''
  echo $shortname

  outputresult='awk 'match($1, '/$nicename/')' acombinedresults.txt
  if [ "$outputresult" = "" ]; then
    rm fit.log
  fi

  #-------------------------------------------------  GNUPLOT Voigt Curve Fitting
A.1. RAMAN SPECTRUM PROCESSING SCRIPT

```bash
# Initialize awk scripts
awk 'END { print $2 }' $1

grad='echo "scale=2;($yend-$yinit2)/($xend-$xinit)" | bc'

yinit='echo "scale=2; $yinit2-($grad*$xinit)" | bc'

echo background = $grad x + $yinit

# Calculate SNR, exit if too noisy

snrmax='awk 'BEGIN { max = 1 } (( $1 > 1790 ) && ( $1 < 1830 )) { if ( max < $2 ) max = $2 } END { print max }' $1

snrmin='awk 'BEGIN { min = $snrmax } (( $1 > 1790 ) && ( $1 < 1830 )) { if ( min > $2 ) min = $2 } END { print min - 0.1 }' $1

signalmax='awk 'BEGIN { max = 0 } ( $1 > 1200 ) && ( $1 < 1790 ) { if ( max < $2 ) max = $2 } END { print max - ( 1600 * $grad + $yinit ) }' $1

snr='echo "scale=0;($signalmax-$snrmin)/($snrmax-$snrmin)" | bc'

echo snrmax = $snrmax

echo snrmin = $snrmin

echo signalmax = $signalmax

echo snr = $snr

if (( "$snr" < "$threshold" ))
then

echo "Noisy/No signal"

gnuplot <<EOF

set term post landscape color solid 8
set output 'combined.ps'
set title "$nicename=Noisy"

EOF
```

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APPENDIX A. COMPUTER SCRIPTS

plot '$1' with lines title "'$nicename'_Noisy"
EOF

ps2pdf combined.ps ${nicename}combined.pdf
rm combined.ps

echo $nicename Noisy >> acombinedresults.txt
return

# Sets up initial values of fitting parameters by looking at the spectrum

d1height='awk 'BEGIN { max = -100000000000 } (($1 > 1200) && ($1 < 1450)) { if ( max < $2 ) max = $2 } END { print 10 * ( max - ( '$yinit' + 1350 * '$grad' ) ) }' '$1'
d1heightb='awk 'BEGIN { max = -100000000000 } (($1 > 1200) && ($1 < 1450)) { if ( max < $2 ) max = $2 } END { print 15 * max }' '$1'
d1loc='awk '/$d1heightb/ && ($1 > 1200) && ($1 < 1450) { print $1 }' '$1'
d2height='awk 'BEGIN { max = -100000000000 } (($1 > 1605) && ($1 < 1640)) { if ( max < $2 ) max = $2 } END { print 10 * ( max - ( '$yinit' + 1600 * '$grad' ) ) }' '$1'
d3height='awk 'BEGIN { max = -100000000000 } (($1 > 1490) && ($1 < 1510)) { if ( max < $2 ) max = $2 } END { print 10 * ( max - ( '$yinit' + 1500 * '$grad' ) ) }' '$1'
gheight='awk 'BEGIN { max = -100000000000 } (($1 > 1575) && ($1 < 1600)) { if ( max < $2 ) max = $2 } END { print max - ( '$yinit' + 1600 * '$grad' ) }' '$1'
gheightb='awk 'BEGIN { max = -100000000000 } (($1 > 1575) && ($1 < 1600)) { if ( max < $2 ) max = $2 } END { print 10 * max }' '$1'
gloc='awk '/$gheightb/ && ($1 > 1550) && ($1 < 1650) { print $1 }' '$1'

# Remember to change these lines if d1 fitting restrictions change

sindloc='echo s(3.14159*($d1loc−1300)/100)/100−1') be −1'
cosdloc='echo c(3.14159*($d1loc−1300)/100)/100−1') be −1'
A.1. RAMAN SPECTRUM PROCESSING SCRIPT

\[ 3.14159/2 \cos(\omega) \] | bc 
\[ \tan\text{d1loc} = \text{echo} \text{ scale=5; }\sin\text{d1loc}/\cos\text{d1loc} \] | bc 

# Remember to change these lines if fitting restrictions change
\[ \sin\text{gloc} = \text{echo} \text{ scale=5; }\sin\text{gloc}/\cos\text{gloc} \] | bc 
\[ \cos\text{gloc} = \text{echo} \text{ scale=5; }\sin\text{gloc}/\cos\text{gloc} \] | bc 
\[ \tan\text{gloc} = \text{echo} \text{ scale=5; }\sin\text{gloc}/\cos\text{gloc} \] | bc 

\[ \text{echo d1height = } \$\text{d1height} \] 
\[ \text{echo d1loc = } \$\text{d1loc = } \$\text{tand1loc} \] 
\[ \text{echo d2height = } \$\text{d2height} \] 
\[ \text{echo gheight = } \$\text{gheight} \] 
\[ \text{echo gloc = } \$\text{gloc} \] 

\[ \text{echo grad = } \$\text{grad} >> \text{param.txt} \] 
\[ \text{echo int = } \$\text{yinit} >> \text{param.txt} \] 

\[ \text{echo gheight = } \$\text{gheightb} >> \text{param.txt} \] 
\[ \text{echo gwidth = } -5 >> \text{param.txt} \] 
\[ \text{echo gloc = } \$\text{tangloc} >> \text{param.txt} \] 

\[ \text{echo d1height = } \$\text{d1height} >> \text{param.txt} \] 
\[ \text{echo d1width = } -5 >> \text{param.txt} \] 
\[ \text{echo d1loc = 0.1 >> param.txt} \] 

\[ \text{echo d2height = } \$\text{d2height} >> \text{param.txt} \] 
\[ \text{echo d2width = } -5 >> \text{param.txt} \] 
\[ \text{echo d2loc = 0.6 >> param.txt} \] 

\[ \text{echo d3loc = 0.1 >> param.txt} \] 
\[ \text{echo d3height = } \$\text{d3height} >> \text{param.txt} \] 
\[ \text{echo d3width = } -5 >> \text{param.txt} \] 

# Send spectrum and fitting parameters to GNUPL

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APPENDIX A. COMPUTER SCRIPTS

gnuplot $persist <<EOF

# Restrict gloc to the range of [1563:1605] and amplitude positive
# with width up to 80 cm
g(x) = (1605-1563)/pi*(atan(x)+pi/2)+1563
gh(x) = sqrt(x**2)
gw(x) = 40/pi*(atan(x)+pi/2)+0.1

pr g($tangloc)

# Restrict d2 to the range of [1605:1625] and width to range 1–36cm
d2(x) = (1625-1605)/pi*(atan(x)+pi/2)+1605
d2h(x) = sqrt(x**2)
d2w(x) = 16/pi*(atan(x)+pi/2)+0.1

# Restrict d1 to the range of [1300:1400] and width to range 1–200cm
d1(x) = (1400-1300)/pi*(atan(x)+pi/2)+1300
d1h(x) = sqrt(x**2)
d1w(x) = 100/pi*(atan(x)+pi/2)+0.1

# Restrict d3 to the range of [1475:1525] and width to range 1–200cm
d3(x) = (1525-1475)/pi*(atan(x)+pi/2)+1475
d3h(x) = sqrt(x**2)
d3w(x) = 100/pi*(atan(x)+pi/2)+1

bg(x) = int + grad * x

gpeak(x) = gh(gheight) * voigt(x - g(gloc) , gw(gwidth))
d1peak(x) = d1h(d1height) * voigt(x - d1(d1loc) , d1w(d1width))
d2peak(x) = d2h(d2height) * voigt(x - d2(d2loc) , d2w(d2width))
#d3peak(x) = d3h(d3height) * voigt(x - d3(d3loc) , d3w(d3width))
d3peak(x) = 0 * x
d4peak(x) = 0 * x

# f(x) = gpeak(x) + d1peak(x) + d2peak(x) + d3peak(x) + bg(x)

EOF
A.1. RAMAN SPECTRUM PROCESSING SCRIPT

\[ f(x) = g\text{peak}(x) + d1\text{peak}(x) + d2\text{peak}(x) + bg(x) \]

\[ p(x) = g\text{peak}(x) + d1\text{peak}(x) + d2\text{peak}(x) \]

\#plot \{x=1000:1900\} '1' using 1:($2 - bg(\$1))', p(x)

FIT\_LIMIT = 1e-9
FIT\_MAXITER = 1000
fit f(x) '1' using 1:2:(1) via 'param.txt'

set table "residual.xy"
plot [x=1000:1900] '1' using 1:($2 - f(\$1))

set table "lorentzians.xy"
plot [x=1000:1900] p(x)

set table "bgremoved.xy"
plot [x=1000:1900] '1' using 1:($2 - bg(\$1))

set table "d1peak.xy"
plot [x=1000:1900] d1peak(x)

set table "d2peak.xy"
plot [x=1000:1900] d2peak(x)

set table "gpeak.xy"
plot [x=1000:1900] gpeak(x)

set table "bgremoved.xy"
plot [x=1000:1900] '1' using 1:($2 - bg(\$1))

pr "gloc", g(gloc)
pr "garea", gh(gheight)
pr "gwidth", gw(gwidth)
pr "gheight", gh(gheight)*voigt(0,gw(gwidth))

pr "d1loc", d1(d1loc)
pr "d1area", d1h(d1height)
pr "d1width", d1w(d1width)
APPENDIX A. COMPUTER SCRIPTS

pr "d1height", d1h(d1height)*voigt(0,d1w(d1width))

pr "d2loc", d2(d2loc)
pr "d2area", d2h(d2height)
pr "d2width", d2w(d2width)
pr "d2height", d2h(d2height)*voigt(0,d2w(d2width))

pr "d3loc", d3(d3loc)
pr "d3area", d3h(d3height)
pr "d3width", d3w(d3width)
pr "d3height", d3h(d3height)*voigt(0,d3w(d3width))

pr "int", int
pr "grad", grad

set print 'param3a.txt'
pr "gloc", g(gloc)
pr "garea", gh(gheight)
pr "gwidth", gw(gwidth)
pr "gheight", gh(gheight)*voigt(0,gw(gwidth))

pr "d1loc", d1(d1loc)
pr "d1area", d1h(d1height)
pr "d1width", d1w(d1width)
pr "d1height", d1h(d1height)*voigt(0,d1w(d1width))

pr "d2loc", d2(d2loc)
pr "d2area", d2h(d2height)
pr "d2width", d2w(d2width)
pr "d2height", d2h(d2height)*voigt(0,d2w(d2width))

pr "d3loc", d3(d3loc)
pr "d3area", d3h(d3height)
pr "d3width", d3w(d3width)
pr "d3height", d3h(d3height)*voigt(0,d3w(d3width))

pr "int", int
pr "grad", grad
update 'param.txt' 'param2.txt'

save "savefilevoigt.plt"

EOF

# Remove scientific notation
sed 's/e−/\*10^−/' param3a.txt > param3.txt

# Find final parameters #
gloc='awk ' $1~/gloc/ { print sqrt($2^2) } ' param3.txt'
gheight='awk ' $1~/gheight/ { print $2 } ' param3.txt'
gwidth='awk ' ( NR > 4) $1~/gwidth/ { print $2 } ' param3.txt'
garea='awk ' ( NR > 4) $1~/garea/ { print $2 } ' param3.txt'
d1loc='awk ' $1~/d1loc/ { print sqrt($2^2) } ' param3.txt'
d1height='awk ' $1~/d1height/ { print $2 } ' param3.txt'
d1width='awk ' $1~/d1width/ { print $2 } ' param3.txt'
d1area='awk ' ( NR > 4) $1~/d1area/ { print $2 } ' param3.txt'
d2loc='awk ' $1~/d2loc/ { print sqrt($2^2) } ' param3.txt'
d2height='awk ' $1~/d2height/ { print $2 } ' param3.txt'
d2width='awk ' $1~/d2width/ { print $2 } ' param3.txt'
d2area='awk ' ( NR > 4) $1~/d2area/ { print $2 } ' param3.txt'
d3loc='awk ' $1~/d3loc/ { print sqrt($2^2) } ' param3.txt'
d3height='awk ' $1~/d3height/ { print $2 } ' param3.txt'
d3width='awk ' $1~/d3width/ { print $2 } ' param3.txt'
d3area='awk ' ( NR > 4) $1~/d3area/ { print $2 } ' param3.txt'
bggrad='awk ' $1~/grad/ { print $2 } ' param3.txt'
bgint='awk ' $1~/int/ { print $2 } ' param3.txt'

echo G height = $gheight
echo G location = $gloc
echo G width = $gwidth
APPENDIX A. COMPUTER SCRIPTS

```
echo G area = $garea

echo D1 height == area = $d1height
echo D1 location = $d1loc
echo D1 width = $d1width
echo D1 area = $d1area

echo D2 height == area = $d2height
echo D2 location = $d2loc
echo D2 width = $d2width
echo D2 area = $d2area

echo Lorentz solid offset = $bgint
echo Lorentz inclined offset = $bggrad

# R1 ratio
r1ratio='echo "scale=5; $d1height/$gheight" | bc'

echo R1 ratio = $r1ratio $r1ratiocheck

# R2 ratio
r2ratio='echo "scale=5; $d1area/( $d1area + $garea + $d2area)" | bc'

r2ratioa='echo "scale=2; $d1area/( $d1area + $garea + $d2area)" | bc'

bc
rc2ratiovoigt=$r2ratio

totalwidthvoigt='echo "scale=2; $gwidth + $d1width + $d2width" | bc'

echo R2 ratio = $r2ratio $r2ratiocheck

r2tempa='echo "scale=3; (-445*$r2ratio)/(641 + $r2ratio)" | bc'

echo R2 temp = $r2tempa

bdwidthcheck='echo "scale=0; $d1width/1" | bc'

# Check whether this is a successful Voigt fit
if (( "$r2ratiocheck" < "$r2limit" && "$bdwidthcheck" < "60" ))
then
fitstyle=Voigt
```
A.1. RAMAN SPECTRUM PROCESSING SCRIPT

```bash
# Standard Raman spectrum processing script

temp="Standard_R2\temp_r2tempa"
plottemp=$r2tempa

ra1ratio=na
ra2ratio=na
ra1temp=na
ra2temp=na

mv param3a.txt paramvoigt.txt

totalwidth=`echo "scale=2;\$gwidth+\$d1width+\$d2width" | bc`
savefile=savefilevoigt.plt

# Check whether this is a Voigt fit due to the RI rule
elif (( "$r2ratiocheck" < "$r2limit" && "$r1ratiocheck" < "50" ))
then

fitstyle=Voigt3

temp="Standard_R2\temp_r2tempa"
plottemp=$r2tempa

ra1ratio=na
ra2ratio=na
ra1temp=na
ra2temp=na

mv param3a.txt paramvoigt.txt

totalwidth=`echo "scale=2;\$gwidth+\$d1width+\$d2width" | bc`
savefile=savefilevoigt.plt

else

echo "R2 or D1 width too high for Voigt fit, trying Lorentzians"

mv param3a.txt paramvoigt.txt
```

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### APPENDIX A. COMPUTER SCRIPTS

```bash
# # # # # # # # # # # # # # # # # # # # # # # # #
# GNUPLOT Lorentzian Curve Fitting # # # # # # # # # # # # #
yinit2='awk 'END { print $2}' $1'
yend='awk 'NR==1 { print $2}' $1'
xinit='awk 'END { print $1}' $1'
xend='awk 'NR==1 { print $1}' $1'
grad='echo "scale=2;($yend-$yinit2)/($xend-$xinit)" | bc'
yinit='echo "scale=2;\$yinit2-($grad*\$xinit)" | bc'
d1height='awk 'BEGIN { max = -100000000000 } { if ( max < $2 ) max = $2 } END { print max - ( \$yinit + 1350 * \$grad ) }' $1'
d1heightb='awk 'BEGIN { max = -100000000000 } ( ($1 > 1200) && ( $1 < 1450) ) { if ( max < $2 ) max = $2 } END { print max }' $1'
d1loc='awk '/\$d1heightb/ && ( $1 > 1200 ) && ( $1 < 1450 ) { print $1 }' $1'
d2height='awk 'BEGIN { max = -100000000000 } ( ($1 > 1450) && ( $1 < 1640) ) { if ( max < $2 ) max = $2 } END { print max - ( \$yinit + 1600 * \$grad ) }' $1'
d3height='awk 'BEGIN { max = -100000000000 } ( ($1 > 1490) && ( $1 < 1510) ) { if ( max < $2 ) max = $2 } END { print max - ( \$yinit + 1500 * \$grad ) }' $1'
d4height='awk 'BEGIN { max = -100000000000 } ( ($1 > 1140) && ( $1 < 1150) ) { if ( max < $2 ) max = $2 } END { print max - ( \$yinit + 1500 * \$grad ) }' $1'
gheight='awk 'BEGIN { max = -100000000000 } ( ($1 > 1580) && ( $1 < 1600) ) { if ( max < $2 ) max = $2 } END { print max - ( \$yinit + 1600 * \$grad ) }' $1'
gheightb='awk 'BEGIN { max = -100000000000 } ( ($1 > 1580) && ( $1 < 1600) ) { if ( max < $2 ) max = $2 } END { print max }' $1'
gloc='awk '/\$gheightb/ && ( $1 > 1550 ) && ( $1 < 1650 ) { print $1 }' $1'
```

---

### If not a Voigt, fit using Lorentzians

rm fit.log
A.1. RAMAN SPECTRUM PROCESSING SCRIPT

# Remember to change these lines if d1 restrictions change
sind1loc="echo \"scale=5;\$(\frac{3.14159}{2}\frac{3.14159}{200}(d1loc-1300)/100-\frac{3.14159}{2})\" | bc -l"

cosd1loc="echo \"scale=5;\$(\frac{3.14159}{2}\frac{3.14159}{200}(d1loc-1300)/100+\frac{3.14159}{2})\" | bc -l"

tand1loc="echo \"scale=5;\$\sin(d1loc/\cos(d1loc))\" | bc -l"

# Remember to change these lines if g restrictions change
singloc="echo \"scale=5;\$(\frac{3.14159}{2}\frac{3.14159}{40}(gloc-1567)/40-\frac{3.14159}{2})\" | bc -l"

cosgloc="echo \"scale=5;\$(\frac{3.14159}{2}\frac{3.14159}{40}(gloc-1567)/40+\frac{3.14159}{2})\" | bc -l"

tangloc="echo \"scale=5;\$\sin(gloc)/\cos(gloc)\" | bc -l"

echo d1height = $d1height
echo d1loc = $d1loc = $tand1loc
echo d2height = $d2height
echo gheight = $gheight
echo gloc = $gloc
echo grad = $grad >> param.txt
echo int = $yinit >> param.txt
echo gheight = $gheight >> param.txt
echo gwidth = -1.5 >> param.txt
echo gloc = $tangloc >> param.txt
echo d1height = $d1height >> param.txt
echo d1width = -0.5 >> param.txt
echo d1loc = $tand1loc >> param.txt
echo d2height = $d2height >> param.txt
echo d2width = -1.5 >> param.txt
echo d2loc = -5 >> param.txt
echo d3loc = 0.1 >> param.txt
echo d3height = $d3height >> param.txt
echo d3width = 1 >> param.txt
APPENDIX A. COMPUTER SCRIPTS

```
echo d4loc = 5 >> param.txt
echo d4height = $d4height >> param.txt
echo d4width = 1 >> param.txt

# Send GNUPLOT the spectrum and fitting parameters
gnuplot $persist <EOF

# Restrict glc to the range of [1567:1605] and amplitude positive
# with width up to 80 cm
g(x) = (1605−1567)/pi*(atan(x)+pi/2)+1567
gh(x) = sqrt(x**2)
gw(x) = 40/pi*(atan(x)+pi/2)+1

pr g($tangloc)

# Restrict d2 to the range of [1600:1630] and width to range 1−80cm
d2(x) = (1630−1600)/pi*(atan(x)+pi/2)+1600
d2h(x) = sqrt(x**2)
d2w(x) = 40/pi*(atan(x)+pi/2)+1

# Restrict d1 to the range of [1300:1400] and width to range 1−200cm
d1(x) = (1400−1300)/pi*(atan(x)+pi/2)+1300
d1h(x) = sqrt(x**2)
d1w(x) = 100/pi*(atan(x)+pi/2)+1

# Restrict d3 to the range of [1475−1525] and width to range 1−200cm
d3(x) = (1525−1475)/pi*(atan(x)+pi/2)+1475
d3h(x) = sqrt(x**2)
d3w(x) = 100/pi*(atan(x)+pi/2)+1

# Restrict d4 to the range of [1200−1250] and width to range 1−200cm
d4(x) = (1250−1200)/pi*(atan(x)+pi/2)+1200
d4h(x) = sqrt(x**2)
d4w(x) = 100/pi*(atan(x)+pi/2)+1

bg(x) = int + grad * x

gpeak(x) = gh(gheight) * ((gw(gwidth))^2 / ((x − g(gloc))^2 + gw)
A.1. RAMAN SPECTRUM PROCESSING SCRIPT

\[ gwidth \]  
\[ d1peak(x) = d1h(d1height) \times (d1w(d1width))^{2} / ((x - d1(d1loc))^{2} + (d1w(d1width))^{2}) \]  
\[ d2peak(x) = d2h(d2height) \times (d2w(d2width))^{2} / ((x - d2(d2loc))^{2} + (d2w(d2width))^{2}) \]  
\[ d3peak(x) = d3h(d3height) \times (d3w(d3width))^{2} / ((x - d3(d3loc))^{2} + (d3w(d3width))^{2}) \]  
\[ d4peak(x) = d4h(d4height) \times (d4w(d4width))^{2} / ((x - d4(d4loc))^{2} + (d4w(d4width))^{2}) \]  
\[ f(x) = gpeak(x) + d1peak(x) + d2peak(x) + d3peak(x) + d4peak(x) + bg(x) \]  
\[ p(x) = gpeak(x) + d1peak(x) + d2peak(x) + d3peak(x) + d4peak(x) \]  

FIT LIMIT = 1e-9  
FIT MAXITER = 1000  
fit f(x) '$_1$' using 1:2:(1) via 'param.txt'  
set table "residual.xy"  
plot [x=800:2200] '$_1$' using 1:($2 - f(\$_1)$)  
set table "lorentzians.xy"  
plot [x=800:2200] p(x)  
set table "bgremoved.xy"  
plot [x=800:2200] '$_1$' using 1:($2 - bg(\$_1)$)  
set table "d1peak.xy"  
plot [x=800:2200] d1peak(x)  
set table "d2peak.xy"  
plot [x=800:2200] d2peak(x)  
set table "gpeak.xy"
APPENDIX A. COMPUTER SCRIPTS

plot [x=800:2200] gpeak(x)

set table "bgremoved.xy"
plot [x=800:2200] '$1' using 1:(\$2 - bg(\$1))
pr "gloc\", g(gloc)
pr "gheight\", gh(gheight)
pr "gwidth\", gw(gwidth)
pr "d1loc\", d1(d1loc)
pr "d1height\", d1h(d1height)
pr "d1width\", d1w(d1width)
pr "d2loc\", d2(d2loc)
pr "d2height\", d2h(d2height)
pr "d2width\", d2w(d2width)
pr "d3loc\", d3(d3loc)
pr "d3height\", d3h(d3height)
pr "d3width\", d3w(d3width)
pr "d4loc\", d4(d4loc)
pr "d4height\", d4h(d4height)
pr "d4width\", d4w(d4width)
pr "int", int
pr "grad", grad

set print 'param3.txt'
pr "gloc\", g(gloc)
pr "gheight\", gh(gheight)
pr "gwidth\", gw(gwidth)
pr "d1loc\", d1(d1loc)
pr "d1height\", d1h(d1height)
pr "d1width\", d1w(d1width)
pr "d2loc\", d2(d2loc)

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A.1. RAMAN SPECTRUM PROCESSING SCRIPT

pr "d2height", d2h(d2height)
pr "d2width", d2w(d2width)
pr "d3loc", d3(d3loc)
pr "d3height", d3h(d3height)
pr "d3width", d3w(d3width)
pr "d4loc", d4(d4loc)
pr "d4height", d4h(d4height)
pr "d4width", d4w(d4width)
pr "int", int
pr "grad", grad

update 'param.txt', 'param2.txt'
save "savefilelor.plt"
EOF

# Find final parameters #
gloc='awk' ' $1 ~ /gloc/ { print $2 } ' param3.txt
ghheight='awk' ' $1 ~ /gheight/ { printf "%i", $2 } ' param3.txt
gwidth='awk' ' $1 ~ /gwidth/ { print $2 } ' param3.txt
d1loc='awk' ' $1 ~ /d1loc/ { printf "%i", sqrt( $2 ^ 2 ) } ' param3.txt
d1height='awk' ' $1 ~ /d1height/ { printf "%i", $2 } ' param3.txt
d1width='awk' ' $1 ~ /d1width/ { print $2 } ' param3.txt
d2loc='awk' ' $1 ~ /d2loc/ { printf "%i", sqrt( $2 ^ 2 ) } ' param3.txt
d2height='awk' ' $1 ~ /d2height/ { printf "%i", $2 } ' param3.txt
d2width='awk' ' $1 ~ /d2width/ { print $2 } ' param3.txt
d3loc='awk' ' $1 ~ /d3loc/ { printf "%i", sqrt( $2 ^ 2 ) } ' param3.txt
d3height='awk' ' $1 ~ /d3height/ { printf "%i", $2 } ' param3.txt
APPENDIX A. COMPUTER SCRIPTS

d3width=`awk ' $1 ~ /d3width/ { print $2 } ' param3.txt`

d4loc=`awk ' $1 ~ /d4loc/ { printf "%i", sqrt( $2 ^ 2 ) } ' param3.txt`

d4height=`awk ' $1 ~ /d4height/ { print $2 } ' param3.txt`

d4width=`awk ' $1 ~ /d4width/ { print $2 } ' param3.txt`

bggrad=`awk ' $1 ~ /grad/ { print $2 } ' param3.txt`

bgint=`awk ' $1 ~ /int/ { print $2 } ' param3.txt`

```
# Calculate SNR

snrmax=`awk 'BEGIN { max = -100000000000 } (($1 > 1700) && ($1 < 1800)) { if ( max < $2 ) max = $2 } END { print max }' bgremoved.xy`

snrmin=`awk 'BEGIN { min = 100000000000 } (($1 > 1700) && ($1 < 1800)) { if ( min > $2 ) min = $2 } END { print min }' bgremoved.xy`

bgremovedmax=`awk 'BEGIN { max = -100000000000 } ($1 > 1200) { if ( max < $2 ) max = $2 } END { print max }' bgremoved.xy`

snr=`echo "$scale=0;~$bgremovedmax_~/~($snrmax_~$snrmin)" | bc`
```

echo snrmax = $snrmax

echo snrmin = $snrmin

echo bgremovedmax = $bgremovedmax

echo snr = $snr
# Calculate Areas

garea = `echo scale=5; \$gheight * 3.14159 * \$gwidth` | bc

d1area = `echo scale=5; \$d1height * 3.14159 * \$d1width` | bc

d2area = `echo scale=5; \$d2height * 3.14159 * \$d2width` | bc

d3area = `echo scale=5; \$d3height * 3.14159 * \$d3width` | bc

d4area = `echo scale=5; \$d4height * 3.14159 * \$d4width` | bc

```
echo G area = \$garea

echo D1 area = \$d1area

echo D2 area = \$d2area

echo D3 area = \$d3area

echo D4 area = \$d4area
```

```
r1ratio = `echo scale=5; \$d1height / \$gheight` | bc

d1ratio = `echo scale=5; \$d1area / (\$d1area + \$garea + \$d2area)` | bc

d2ratio = `echo scale=2; \$d1area / (\$d1area + \$garea + \$d2area)` | bc

```
echo R2 ratio = \$r2ratioa

echo R2 temp = \$r2tempa
```

```
r1ratioa = `echo scale=5; \$d1area + \$d4area / (\$d1area + \$garea + \$d2area)` | bc

r2ratioa = `echo scale=2; \$d1area / (\$d1area + \$garea + \$d2area)` | bc

```
echo RA1 ratio = \$ralratioa

echo RA1 temp = \$raltemp
```

```
r2ratioa = `echo scale=5; \$d1area + \$d4area / (\$garea + \$d2area + \$d3area)` | bc

```
echo RA2 ratio = \$ra2ratioa

echo RA2 temp = \$ra2tempa
```

```
echo G area = \$garea

echo D1 area = \$d1area

echo D2 area = \$d2area

echo D3 area = \$d3area

echo D4 area = \$d4area
```

```
r2ratioa = `echo scale=2; \$d1area / (\$d1area + \$garea + \$d2area)` | bc

```
echo R2 ratio = \$r2ratioa

echo R2 temp = \$r2tempa
```

```
r2ratioa = `echo scale=5; \$d1area + \$d4area / (\$garea + \$d2area + \$d3area)` | bc

```
echo RA1 ratio = \$ra1ratioa

echo RA1 temp = \$ra1temp
```

```
r2ratioa = `echo scale=5; \$d1area + \$d4area / (\$garea + \$d2area + \$d3area)` | bc

```
echo RA2 ratio = \$ra2ratioa

echo RA2 temp = \$ra2tempa
```
echo RA2 temp = $ra2temp
ra2ratiocheck='echo "scale=0;\$ra2ratio*100/1.\" | bc'

# Check whether it is a successful Lorentzian fit
if ("$ra2ratiocheck" > "200")
then

echo "RA2 too high, returning to Voigt"

# Find Voigt parameters #
gloc='awk '$1~/gloc/ { print sqrt( $2^2 ) }' paramvoigt.txt'
gheight='awk '$1~/gheight/ { print $2 }' paramvoigt.txt'
gwidth='awk ' ( NR > 4) $1~/gwidth/ { print $2 }' paramvoigt.txt'
garea='awk ' ( NR > 4) $1~/garea/ { print $2 }' paramvoigt.txt'
d1loc='awk ' $1~/d1loc/ { print sqrt( $2^2 ) }' paramvoigt.txt'
d1height='awk ' $1~/d1height/ { print $2 }' paramvoigt.txt'
d1width='awk ' $1~/d1width/ { print $2 }' paramvoigt.txt'
d1area='awk ' ( NR > 4) $1~/d1area/ { print $2 }' paramvoigt.txt'
d2loc='awk ' $1~/d2loc/ { print sqrt( $2^2 ) }' paramvoigt.txt'
d2height='awk ' $1~/d2height/ { print $2 }' paramvoigt.txt'
d2width='awk ' $1~/d2width/ { print $2 }' paramvoigt.txt'
d2area='awk ' ( NR > 4) $1~/d2area/ { print $2 }' paramvoigt.txt'
d3loc='awk ' $1~/d3loc/ { print sqrt( $2^2 ) }' paramvoigt.txt'
d3height='awk ' $1~/d3height/ { print $2 }' paramvoigt.txt'
d3width='awk ' $1~/d3width/ { print $2 }' paramvoigt.txt'
d3area='awk ' ( NR > 4) $1~/d3area/ { print $2 }' paramvoigt.txt'
bggrad='awk ' $1~/grad/ { print $2 }' paramvoigt.txt'
b gint='awk ' $1~/int/ { print $2 }' paramvoigt.txt'

echo G height = $gheight
echo G location = $gloc
echo G width = $gwidth
echo G area = $garea
A.1. RAMAN SPECTRUM PROCESSING SCRIPT

```bash
# D1 height == area
$\texttt{echo D1 height == area = d1height}

# D1 location
$\texttt{echo D1 location = d1loc}

# D1 width
$\texttt{echo D1 width = d1width}

# D1 area
$\texttt{echo D1 area = d1area}

# D2 height == area
$\texttt{echo D2 height == area = d2height}

# D2 location
$\texttt{echo D2 location = d2loc}

# D2 width
$\texttt{echo D2 width = d2width}

# D2 area
$\texttt{echo D2 area = d2area}

# Lorentz solid offset
$\texttt{echo Lorentz solid offset = bgint}

# Lorentz inclined offset
$\texttt{echo Lorentz inclined offset = bggrad}

# R1 ratio
$\texttt{r1ratio='echo " scale=5;\$d1height/\$gheight" | bc'}

# R2 ratio
$\texttt{r2ratio='echo " scale=5;\$d1width/\$gwidth\$d1area/\$garea/\$d2area" | bc'}

$\texttt{r2ratioa='echo " scale=2;\$d1area/\$garea/\$d1area/\$garea/\$d2area" | bc'}

$\texttt{r2ratiovoigt=$r2ratio}

$\texttt{r2ratiocheck='echo " scale=0;100*\$r2ratioa/1" | bc'}

# R2 temp
$\texttt{echo R2 temp = $r2tempa}

$\texttt{ra2temp="na"}

$\texttt{rai1temp="na"}

$\texttt{fit style=Voigt2}

$\texttt{temp="Standard\$R2\$r2temp\$r2tempa"}

$\texttt{plottemp=$r2tempa}

$\texttt{totalwidth='echo " scale=2;\$gwidth+\$d1width+\$d2area" | bc'}

$\texttt{savefile=savefilevoigt.plt}
```
APPENDIX A. COMPUTER SCRIPTS

else

    fitstyle=Lorentzians
    temp="Low temperature temp $ra2temp"
    plottemp=$ra2temp

    totalwidth='echo"scale=2;gwidth+d1width+d2width" | bc'
    savefile=savefilelor.plt

fi

fi

echo $temp
echo $fitstyle

# Find the number of iterations
iterations="too many"
iterations=`awk'/the fit converged/ { print $2 }' fit.log`

# Go back to Gnuplot to make the final graphs

gnuplot $persist <<EOF

load "$savefile"

set title "$nicename R2=r2ratio Temp=$plottemp"

# Uncomment the following to line up the axes
# set lmargin 6

set term wxt font ",6"

set size 1,1
set origin 0,0

set multiplot
A.1. RAMAN SPECTRUM PROCESSING SCRIPT

```
set title "\$nicename"
set size 0.4,0.5
set origin 0,0.5
plot [x=1000:1900] bg(x) title "Background", \$1' title "\$nicename" with lines

set title "\$nicename\_R2=$r2ratio\_Temp=$plottemp"
set size 0.6,1
set origin 0.4,0
plot [x=1000:1900] \$1' using 1:(\$2 - bg(\$1)) title "Background removed" with lines, d2peak(x), d1peak(x), gpeak(x), d3peak(x), d4peak(x), p(x) title "\$fitstyle"
#plot [x=1000:1900] \$1' using 1:(\$2 - bg(\$1)) title "Background removed" with lines, d2peak(x), d1peak(x), gpeak(x), d3peak(x), d4peak(x), p(x)

set title "\$nicename\_\_iterations\_iterations"
set size 0.4,0.5
set origin 0,0
plot [x=1000:1900] f(x) title "\$fitstyle", \$1' title "\$nicename" with lines, \$1' using 1:(\$2 - f(\$1)) title "Residual" with lines

unset multiplot
reset

set term post landscape color solid 8
set output 'combined.ps'

# Uncomment the following to line up the axes
# set lmargin 6

#set size ratio 1.5 1.5,1
set origin 0,0
set multiplot
```
set title "$nicename"

set size 0.33, 0.5
set origin 0, 0.5
plot [x=1000:1900] bg(x) title "Background", '$1' title "'$nicename'" with lines

set title "$nicename\_R2 = $r2ratio \_RA2 = $ra2ratio \_Temp = $plottemp"

set size 0.67, 1
set origin 0.33, 0
plot [x=1000:1900] '$1' using 1:(\$2 - bg(\$1)) title "Background removed" with lines, d2peak(x), d1peak(x), gpeak(x), d3peak(x), d4peak(x), p(x) title "$fitstyle"

#plot [x=1000:1900] '$1' using 1:(\$2 - bg(\$1)) title "Background removed" with lines, d2peak(x), d1peak(x), gpeak(x), p(x)

set title "$nicename\_i terations"

set size 0.33, 0.5
set origin 0.0
plot [x=1000:1900] f(x) title "Voigt", '$1' title "'$nicename'" with lines, '$1' using 1:(\$2 - f(\$1)) title "Residual" with lines

unset multiplot
reset

#set title "$nicename R2 = $r2ratioa"

set terminal png
set output 'data.png'
plot [x=1000:1900] bg(x) title "Background", '$1' title "'$nicename'" with lines

set output 'fit.png'
plot [x=1000:1900] f(x) title "$fitstyle", '$1' title "'$nicename'" with lines, '$1' using 1:(\$2 - f(\$1)) title "Residual" with lines

set output 'peaks.png'
A.1. RAMAN SPECTRUM PROCESSING SCRIPT

```
plot [x=1000:1900] '$1' using 1:($2 - bg(\$1)) title "Background removed" with lines, d2peak(x), d1peak(x), gpeak(x), d3peak(x), d4peak(x), p(x) title "$fitstyle"

# Output results to text files in case they're needed later
awk ' NR>4 && length > 3 { print $1, $2 / '$bgremovedmax' } ' lorentzians.xy > ${nicename}lorentzianschart.xy
awk ' NR>3 && length > 3 { print $1, $2 / '$bgremovedmax' } ' bgremoved.xy > ${nicename}bgremovedchart.xy

ps2pdf combined.ps ${nicename}combined.pdf
rm combined.ps

mv data.png ${nicename}data.png
mv fit.png ${nicename}fit.png
mv peaks.png ${nicename}peaks.png

# Output to a combined results file for later processing
echo ${nicename} $gheight $gloc $gwidth $garea $d1height $d1loc $d1width $d1area $d2height $d2loc $d2width $d2area $r1ratio $r2ratio $r2tempa $ra1ratio $ra1temp $ra2ratio $ra2temp $r2ratiovoigt $plottemp $totalwidth $totalwidthvoigt >> acombinedresults.txt

echo Congratulations, new sample analysed
return
else
  echo $outputresult
  echo Sample already processed
  echo
fi
```

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function tidy {

# Tidy up
#rm *.xy
mv *.png jpg
mv *combined.pdf pdf

# Make combined output
gs -dBATCH -dNOPAUSE -q -sDEVICE=pdfwrite -sOutputFile=
   allanalysedraman.pdf pdf/ *.pdf
}

while :
do
echo $# to go
if [[ $# > 0 ]]
then
echo $# files left to process
processsample $1
shift

else
tidy
exit
fi
done
A.2 Dynamic endmember mixing script

#!/bin/bash

# This code will analyse a single text-file database of geochemical results using the dynamic endmember-mixing model of Hilton et al. 2010. A user-defined subset of the input file is plotted in d13C – N/C space. Using Fresh and Fossil carbon compositions defined in the script or called as external files, the proportion of each endmember is then calculated.
# These results, along with the other parameters held in the file, can then be plotted as horizontal profiles or as vertical logs, or as crossplots with user-defined axes.

# The code runs from the following command:
# $ profile.sh [options]
# where the available options are:
# -a creates crossplot rather than profile
# -s plots points rather than lines
# -o the calculations should be carried out on the measured TOC rather than corrected TOC
# -d plots the proportion dissolved
# -c plots the measured TOC
# -b plots the corrected TOC
# -n plots the nitrogen concentration
# -r plots the N/C ratio
# -t plots the d13C
# -f plots the d15N
# -v plots the fraction of non-fossil carbon
# -q plots the amount of non-fossil carbon
# -w plots the amount of fossil carbon
# -e [ARGUMENT] defines X-axis title
# -x [ARGUMENT] defines X-axis variable
# -l [ARGUMENT] search string that defines the samples required from the input file
# This function helps collect and format data from the input file
function collectnumbers {
    echo collectnumbers $@
    awk ' $1 ~ '/location'/ { print $1 }' $inputfile > positions.txt
    collectpositions 'awk ' { print $1 }' positions.txt'

    # Find fixed-axis range
    min='awk '{ if(min="") {min=$1}; if($1<min) {min=$1}} END{ print min * 0.9 }' dissolved.xy'
    max='awk '{ if(max="") {max=$1}; if($1>max) {max=$1}} END{ print max * 1.1 }' dissolved.xy'
    echo "min=\$min max=\$max"
    return
}

# This function helps collect and format data from the input file
function collectpositions {
    echo collectposition $@
    rm input1.txt
    rm input2.txt
    rm input2b.txt
    rm input3.txt
    while [[ "$#" > "0" ]]: do

    # -i [ARGUMENT] location of input file
    # -p [ARGUMENT] name of output file
    # -k [ARGUMENT] name of appropriate figure legend file
    # -g [ARGUMENT] location of fossil carbon definition file
    # -h [ARGUMENT] location of fresh carbon definition file
# Check whether scaling to TOC or CorrTOC

```
awk '/$1/' { print $1, $2, $3, $4, $5, $6, $7, $8, $9, $10, $11, $12, $13, $14, $15, $15 * $11, (1 - $15) * $11 }' inputfile >> input1.txt
awk '/$1/' { print $1, $6 }' ${pdfname}results.txt >> input2.txt
paste -d"" input1.txt input2.txt > input2b.txt
```

if [[ "$corrtoc" = "true" ]]; then
  awk '{ print $1, $2, $3, $4, $5, $6, $7, $8, $9, $10, $11, $12, $13, $14, $15, $15 * $11, $11 - $16 }' input2b.txt > input3.txt
else
  awk '{ print $1, $2, $3, $4, $5, $6, $7, $8, $9, $10, $11, $12, $13, $14, $15, $15 * $8, (1 - $15) * $8 }' input2b.txt > input3.txt
fi

echo "collectdata`awk`'/$1/`{print $1,$'xaxis'}`input3.txt`"

collectdata `awk`'/$1/` { print $1, $'xaxis' }` input3.txt`

shift
done
return
```

# This function reads the formatted input data

```
function collectdata {

  echo collectdata $@

  # collect data for profile lines

  if [[ "$xaxis" = "13" ]]; then
    awk '/$1/' &$13 < 999 { printf "%s\n", $5, $'2' }' input3.txt >> dissolved.xy
  ```
APPENDIX A. COMPUTER SCRIPTS

awk ' /$1/' && $13 < 999 { printf "%s %s\n", $6, '$2' } ' input3.txt
>> d13c.xy
awk ' /$1/' && $13 < 999 { printf "%s %s\n", $7, '$2' } ' input3.txt
>> d15n.xy
awk ' /$1/' && $13 < 999 { printf "%s %s\n", $8, '$2' } ' input3.txt
>> totn.xy
awk ' /$1/' && $13 < 999 { printf "%s %s\n", $9, '$2' } ' input3.txt
>> totc.xy
awk ' /$1/' && $13 < 999 { printf "%s %s\n", $10, '$2' } ' input3.txt
>> ncratio.xy
awk ' /$1/' && $13 < 999 { printf "%s %s\n", $11, '$2' } ' input3.txt
>> corrcarb.xy
awk ' /$1/' && $13 < 999 { printf "%s %s\n", $15, '$2' } ' input3.txt
>> nonfossil.xy
awk ' /$1/' && $13 < 999 { printf "%s %s\n", $16, '$2' } ' input3.txt
>> amtfresh.xy
awk ' /$1/' && $13 < 999 { printf "%s %s\n", $17, '$2' } ' input3.txt
>> amtfossil.xy

# Find fixed-axis range

min2='awk 'min==""' || $2 < min {min=$2} END{ print min - 1}' dissolved.xy'
max2='awk 'max==""' || $2 > max && $2 < 999 {max=$2} END{ print max + 1}' dissolved.xy'

echo Min = $min2
echo Max = $max2

else

awk ' /$1/' { printf "%s %s\n", '$2', $5 } ' input3.txt >> dissolved.xy
awk ' /$1/' { printf "%s %s\n", '$2', $6 } ' input3.txt >> d13c.xy
awk ' /$1/' { printf "%s %s\n", '$2', $7 } ' input3.txt >> d15n.xy
awk ' /$1/' { printf "%s %s\n", '$2', $8 } ' input3.txt >> totc.xy
awk ' /$1/' { printf "%s %s\n", '$2', $9 } ' input3.txt >> totn.xy
awk ' /$1/' { printf "%s %s\n", '$2', $10 } ' input3.txt >> ncratio.xy
awk ' /$1/' { printf "%s %s\n", '$2', $11 } ' input3.txt >> corrcarb.xy

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A.2. DYNAMIC ENDMEMBER MIXING SCRIPT

awk '/$1/ {printf "%s
", $2, $15 }' input3.txt >> nonfossil.
awk '/$1/ {printf "%s
", $2, $16 }' input3.txt >> amtfresh.
awk '/$1/ {printf "%s
", $2, $17 }' input3.txt >> amtfossil.

function draw {

echo draw $@

if [[ "$dissolved" = "false" ]] ; then
rm dissolved.xy
fi

if [[ "$deltac" = "false" ]] ; then
rm d13c.xy
fi

if [[ "$deltan" = "false" ]] ; then
rm d15n.xy
fi

if [[ "$carbon" = "false" ]] ; then
rm totc.xy
fi

if [[ "$nitrogen" = "false" ]] ; then
rm totn.xy
fi

if [[ "$ncratio" = "false" ]] ; then
rm ncratio.xy

return
}

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APPENDIX A. COMPUTER SCRIPTS

```bash
fi

if [[ "ncratio" = "false" ]] ; then
    rm ncratio.xy
fi

if [[ "corrcarb" = "false" ]] ; then
    rm corrcarb.xy
fi

if [[ "nonfossil" = "false" ]] ; then
    rm nonfossil.xy
fi

if [[ "amtfresh" = "false" ]] ; then
    rm amtfresh.xy
fi

if [[ "amtfossil" = "false" ]] ; then
    rm amtfossil.xy
fi

if [[ "xaxis" = "12" ]] ; then
    area=`R${min}$/R${max}`

    echo $area
    proj=JX6i/6i

    echo psbasemap "$area"/0/1 $proj $X1i -K > ${pname}profile.ps
    psbasemap "$area"/0/1 $proj -B1:"Position within Basin"/1:::

    $pname_Profile:WS$K > ${pname}profile.ps
    psbasemap "$area"/0/1.5 $proj -B1:"Position within Basin"/0.25::
    CarbonContentK >> ${pname}Profile:WS$K > ${pname}profile.ps

    if [[ "deltac" = "true" ]] ; then
        psbasemap "$area"/−27/−20 $proj $X1i -B1:"Position within Basin"/1::
        d13C E K O >> ${pname}profile.ps
```
A.2. DYNAMIC ENDMEMBER MIXING SCRIPT

#Add data

echo "psxy dissolved.xy "$area"/0/1$proj -Sc0.2 -Wthin,orange-Gorange-O-K layui {pdfname} profile.ps"

if [[ "$deltac" = "true" ]]; then
    psxy dissolved.xy "$area"/0/1 $proj -X-1i -Sc0.2 -Wthin,orange -Gorange-O-K layui {pdfname} profile.ps
else
    psxy dissolved.xy "$area"/0/1 $proj -Sc0.2 -Wthin,orange-Gorange-O-K layui {pdfname} profile.ps
fi

psxy d13c.xy "$area"/−30/−16 $proj -Sc0.2 -Wthin,darkgreen -Gdarkgreen -O-K layui {pdfname} profile.ps

psxy d15n.xy "$area"/−5/5 $proj -Sc0.2 -Wthin,green -Ggreen -O-K layui {pdfname} profile.ps

psxy totc.xy "$area"/0/1.5 $proj -Sc0.2 -Wthin,blue -Gblue -O-K layui {pdfname} profile.ps

psxy totn.xy "$area"/0/1.5 $proj -Sc0.2 -Wthin,red -Gred -O-K layui {pdfname} profile.ps

psxy ncratio.xy "$area"/0/1 $proj -St0.2 -Wthin,brown -Gbrown -O-K layui {pdfname} profile.ps

psxy amtfresh.xy "$area"/0/1.5 $proj -Sc0.2 -Wthin,purple -Gpurple -O-K layui {pdfname} profile.ps

psxy amtfossil.xy "$area"/0/1.5 $proj -St0.2 -Wthin,darkslategray -Gdarkslategray -O-K layui {pdfname} profile.ps

if [[ "$line" = "true" ]]; then
    psxy dissolved.xy "$area"/0/1 $proj -Wthin,orange -O-K layui {pdfname} profile.ps
    psxy d13c.xy "$area"/−30/−16 $proj -Wthin,darkgreen -O-K layui {pdfname} profile.ps
    psxy d15n.xy "$area"/−5/5 $proj -Wthin,green -O-K layui {pdfname} profile.ps
fi
APPENDIX A. COMPUTER SCRIPTS

```
psxy totc.xy "$area"/0/1.5 $proj -Wthin,blue -O -K >> ${pdfname} profile.ps
psxy totn.xy "$area"/0/1.5 $proj -Wthin,red -O -K >> ${pdfname} profile.ps
psxy ncratio.xy "$area"/0/1 $proj -Wthin,blue -O -K >> ${pdfname} profile.ps
psxy corrcarb.xy "$area"/0/1.5 $proj -Wthin,purple -O -K >> ${pdfname} profile.ps
psxy nonfossil.xy "$area"/0/1 $proj -Wthin,black -O -K >> ${pdfname} profile.ps
psxy amtfresh.xy "$area"/0/1.5 $proj -Wthin,darkbrown -O -K >> ${pdfname} profile.ps
psxy amtfossil.xy "$area"/0/1.5 $proj -Wthin, darkslategray -O -K >> ${pdfname} profile.ps
```

```
if [[[ "$xaxis" = "13" ]]]; then
```

```
area=${{min2}}/{{max2}}
scale=50
```

```
if [[ "$deltac" = "true" ]] ; then
```

```
if [[[ "$deltac" = "true" ]]]; then
```

```
if[[ "$deltac" = "true" ]] ; then
```

```
# Add data
```

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247
A.2. DYNAMIC ENDMEMBER MIXING SCRIPT

if [[ "$deltac" = "true" ]] ; then
  psxy dissolved.xy -R0/1/"$area" $proj -Y1i -Sc0.2 -Wthin,
  orange -Gorange -N -O -K >> ${pdfname} profile.ps
else
  psxy dissolved.xy -R0/1/"$area" $proj -Sc0.2 -Wthin,orange -
  Gorange -N -O -K >> ${pdfname} profile.ps
fi

psxy d13c.xy -R−29/−16/"$area" $proj -Sc0.2 -Wthin,darkgreen -
  Gdarkgreen -N -O -K >> ${pdfname} profile.ps
psxy d15n.xy -R−5/5/"$area" $proj -Sc0.2 -Wthin,green -Ggreen
  -N -O -K >> ${pdfname} profile.ps
psxy totc.xy -R0/1.5/"$area" $proj -Sc0.2 -Wthin,blue -Gblue -
  -N -O -K >> ${pdfname} profile.ps
psxy totn.xy -R0/1.5/"$area" $proj -Sc0.2 -Wthin,red -Gred -N
  -O -K >> ${pdfname} profile.ps
psxy ncratio.xy -R0/1/"$area" $proj -St0.2 -Wthin,brown -
  Gbrown -N -O -K >> ${pdfname} profile.ps
psxy corrcarb.xy -R0/1.5/"$area" $proj -Sc0.2 -Wthin,purple -
  Gpurple -N -O -K >> ${pdfname} profile.ps
psxy nonfossil.xy -R0/1/"$area" $proj -Ss0.2 -Wthin,black -
  Gblack -N -O -K >> ${pdfname} profile.ps
psxy amtfresh.xy -R0/1.5/"$area" $proj -Sc0.2 -Wthin,darkbrown
  -Gdarkbrown -N -O -K >> ${pdfname} profile.ps
psxy amtfossil.xy -R0/1.5/"$area" $proj -St0.2 -Wthin,
  darkslategray -Gdarkslategray -N -O -K >> ${pdfname} profile
  .ps

if [[ "$line" = "true" ]]; then
  psxy dissolved.xy -R0/1/"$area" $proj -Wthin,orange -O -K >>
  ${pdfname} profile.ps
  psxy d13c.xy -R−29/−16/"$area" $proj -Wthin,darkgreen -O -K
  >> ${pdfname} profile.ps
  psxy d15n.xy -R−5/5/"$area" $proj -Wthin,green -O -K >> ${
  pdfname} profile.ps
  psxy totc.xy -R0/1.5/"$area" $proj -Wthin,blue -O -K >> ${
  pdfname} profile.ps
  psxy totn.xy -R0/1.5/"$area" $proj -Wthin,red -O -K >> ${
  pdfname} profile.ps
fi
APPENDIX A. COMPUTER SCRIPTS

```
psxy ncratio.xy -R0/1"$area" $proj -Wthin,brown -O -K >> ${pdfname} profile.ps
psxy corrcarb.xy -R0/1.5"$area" $proj -Wthin,purple -O -K >> ${pdfname} profile.ps
psxy nonfossil.xy -R0/1"$area" $proj -Wthin,black -O -K >> ${pdfname} profile.ps
psxy amtfresh.xy -R0/1.5"$area" $proj -Wthin,darkbrown -O -K >> ${pdfname} profile.ps
psxy amtfossil.xy -R0/1.5"$area" $proj -Wthin,darkslategray -O -K >> ${pdfname} profile.ps

fi

pslegend $legend -D0/−29/10/10/BL -R−10/10/−10/10 −JX6i/6i −O −K >> ${pdfname} profile.ps

fi

############################################################################### Crossplot Code
###############################################################################

if [[ "$crossplot" = "true" ]]; then

#Collect data for crossplot
awk −v xaxis="$xaxis" ' /'$1'/ && $13 < 999 { printf "%%s,%%s\n", $xaxis, 87
    $5 } ' input3.txt > dissolved.xy
awk −v xaxis="$xaxis" ' /'$1'/ && $13 < 999 { printf "%%s,%%s\n", $xaxis, 88
    $6 } ' input3.txt > d13c.xy
awk −v xaxis="$xaxis" ' /'$1'/ && $13 < 999 { printf "%%s,%%s\n", $xaxis, 89
    $7 } ' input3.txt > d15n.xy
awk −v xaxis="$xaxis" ' /'$1'/ && $13 < 999 { printf "%%s,%%s\n", $xaxis, 90
    $8 } ' input3.txt > totc.xy
awk −v xaxis="$xaxis" ' /'$1'/ && $13 < 999 { printf "%%s,%%s\n", $xaxis, 91
    $9 } ' input3.txt > totn.xy
awk −v xaxis="$xaxis" ' /'$1'/ && $13 < 999 { printf "%%s,%%s\n", $xaxis, 92
    $10 } ' input3.txt > ncratio.xy
awk −v xaxis="$xaxis" ' /'$1'/ && $13 < 999 { printf "%%s,%%s\n", $xaxis, 93
    $11 } ' input3.txt > corrcarb.xy
awk −v xaxis="$xaxis" ' /'$1'/ && $13 < 999 { printf "%%s,%%s\n", $xaxis, 94
```
A.2. DYNAMIC ENDMEMBER MIXING SCRIPT

```bash
$15 } ' input3.txt > nonfossil.xy
awk -v xaxis=""xaxis"" /'1'/ && $13 < 999 { printf "%s
", xaxis, $16 } ' input3.txt > amtfresh.xy
awk -v xaxis=""xaxis"" /'1'/ && $13 < 999 { printf "%s
", xaxis, $17 } ' input3.txt > amtfossil.xy

if [[ "$dissolved" = "false" ]]; then
  rm dissolved.xy
fi

if [[ "$deltac" = "false" ]]; then
  rm d13c.xy
fi

if [[ "$deltan" = "false" ]]; then
  rm d15n.xy
fi

if [[ "$carbon" = "false" ]]; then
  rm totc.xy
fi

if [[ "$nitrogen" = "false" ]]; then
  rm totn.xy
fi

if [[ "$ncratio" = "false" ]]; then
  rm ncratio.xy
fi

if [[ "$ncratio" = "false" ]]; then
  rm ncratio.xy
fi

if [[ "$corrcarb" = "false" ]]; then
  rm corrcarb.xy
fi
```
APPENDIX A. COMPUTER SCRIPTS

```bash
if [[ "$nonfossil" = "false" ]]; then
    rm nonfossil.xy
fi

if [[ "$amtfresh" = "false" ]]; then
    rm amtfresh.xy
fi

if [[ "$amtfossil" = "false" ]]; then
    rm amtfossil.xy
fi

# Draw crossplot

area=−$R{\text{min}}$/{$\text{max}$}
div="echo " scale=2;\$($max−$min)/4" | bc"

```

```bash
if [[ "$deltac" = "true" ]]; then
    psbasemap "$area"/−27/−20 $proj −X1i −B1::/1:"d13C":::E −K −O >> ${pdfname}xplot.ps
else
    psbasemap "$area"/0/3 $proj −X1i −B1::/1:"Carbon\_Content\_\%":::E −K −O >> ${pdfname}xplot.ps
fi
```

```
# Add data

```
```bash
if [[ "$deltac" = "true" ]]; then
    echo "psxy dissolved.xy "$area"/0/1 $proj −Sc0.2 −Wthin, orange −
          Gorange −O −K >> ${pdfname}xplot.ps"
else
    echo "psxy dissolved.xy "$area"/0/1 $proj −X−1i −Sc0.2 −Wthin, orange −
          Gorange −O −K >> ${pdfname}xplot.ps
fi
```
A.2. DYNAMIC ENDMEMBER MIXING SCRIPT

```plaintext
psxy d13c.xy "$area"/−30/16 $proj −Sc0.2 −Wthin, darkgreen −Gdarkgreen
−O −K >> ${pdfname}xplot.ps
psxy d15n.xy "$area"/−5/5 $proj −Sc0.2 −Wthin, green −Ggreen −O −K >> $
{pdfname}xplot.ps
psxy totc.xy "$area"/0/3 $proj −Sc0.2 −Wthin, blue −Gblue −O −K >> $
{pdfname}xplot.ps
psxy totn.xy "$area"/0/3 $proj −Sc0.2 −Wthin, purple −Gpurple −O −K >> $
{pdfname}xplot.ps
psxy ncratio.xy "$area"/0/1 $proj −St0.2 −Wthin, brown −Gbrown −O −K >> $
{pdfname}xplot.ps
psxy corrcarb.xy "$area"/0/3 $proj −Sc0.2 −Wthin, red −Gred −O −K >> $
{pdfname}xplot.ps
psxy nonfossil.xy "$area"/0/1 $proj −St0.2 −Wthin, black −Gbblack −O −K >> $
{pdfname}xplot.ps
psxy amtfresh.xy "$area"/0/3 $proj −Sc0.2 −Wthin, darkbrown −Gdarkbrown −O −K >> $
{pdfname}xplot.ps
psxy amtfossil.xy "$area"/0/3 $proj −St0.2 −Wthin, darkslategray −Gdarkslategray −O −K >> $
{pdfname}xplot.ps

if [[ "$line" = "true" ]] ; then

trend1d −Fxm −N2r dissolved.xy > dissolvedreg.xy

trend1d −Fxm −N2r d13c.xy > d13creg.xy

trend1d −Fxm −N2r d15n.xy > d15nreg.xy

trend1d −Fxm −N2r totc.xy > totcreg.xy

trend1d −Fxm −N2r totn.xy > totnreg.xy

trend1d −Fxm −N2r ncratio.xy > ncratioreg.xy

trend1d −Fxm −N2r corrcarb.xy > corrcarbreg.xy

trend1d −Fxm −N2r nonfossil.xy > nonfossilreg.xy

trend1d −Fxm −N2r amtfresh.xy > amtfreshreg.xy

trend1d −Fxm −N2r amtfossil.xy > amtfossilreg.xy

#Add data
echo "psxy dissolved.xy "$area"/0/1 $proj −Sc0.2 −Wthin, orange −Gorange −O −K >> $
{pdfname}xplot.ps"
psxy dissolvedreg.xy "$area"/0/1 $proj −Wthin, orange −Gorange −O −K >> $
{pdfname}xplot.ps
psxy d13creg.xy "$area"/−30/16 $proj −Wthin, darkgreen −Gdarkgreen −O −K
```
Gdarkgreen –O –K >> ${pname}xplot.ps
psxy d15nreg.xy "$area"/−5/5 $proj –Wthin,green –Ggreen –O –K 392
>> ${pname}xplot.ps
psxy totcreg.xy "$area"/0/3 $proj –Wthin,blue –Gblue –O –K >> ${pname}xplot.ps
psxy totnreg.xy "$area"/0/3 $proj –Wthin,red –Gred –O –K >> ${pname}xplot.ps
psxy ncratioreg.xy "$area"/0/1 $proj –Wthin,brown –Gbrown –O –K >> ${pname}xplot.ps
psxy corrcarbreg.xy "$area"/0/3 $proj –Wthin,purple –Gpurple –O –K >> ${pname}xplot.ps
psxy nonfossilreg.xy "$area"/0/1 $proj –Wthin,black –Gblack –O –K >> ${pname}xplot.ps
psxy amtfreshreg.xy "$area"/0/3 $proj –Wthin,darkbrown –Gdarkbrown –O –K >> ${pname}xplot.ps
psxy amtfossilreg.xy "$area"/0/3 $proj –Wthin,darkslategray –Gdarkslategray –O –K >> ${pname}xplot.ps
fi

pslegend $legend −D16/−10/10/10/BL −R−10/10/−10/10 −JX6i/6i −O –K >> ${pname}xplot.ps
fi

return
}

# Output pdf
function output {
  if [[ "$xaxis" = "13" ]]; then
    ps2raster ${pname}profile.ps −A −Te
    ps2pdf ${pname}profile.ps
    pdfcrop ${pname}profile.pdf
    gs −dBATCH −dNOPAUSE −q −r300 −sDEVICE=jpeg −sOutputFile=${pname}profile.jpg
    graphspdf ${pname}profile.pdf
    gs −dBATCH −dNOPAUSE −q −sDEVICE=pdfwrite −sOutputFile=${pname}graphs.pdf
    gs −dBATCH −dNOPAUSE −q −sDEVICE=pdfwrite −sOutputFile=${pname}hiltonmix.pdf
    gs −dBATCH −dNOPAUSE −q −sDEVICE=pdfwrite −sOutputFile=${pname}nitrogen.pdf
  fi
}
elif [[ "$xaxis" = "12" ]]; then
ps2raster ${pdfname} profile.ps -A -T e
ps2pdf ${pdfname} profile.ps
pdfcrop ${pdfname}profile.pdf
gs -dBATCH -dNOPAUSE -q -r300 -sDEVICE=jpeg -sOutputFile=${pdfname} profile.jpg ${pdfname}profile.pdf
gs -dBATCH -dNOPAUSE -q -sDEVICE=pdfwrite -sOutputFile=${pdfname} graphs.pdf ${pdfname}profile.pdf ${pdfname}hiltonmix.pdf ${pdfname}nitrogen.pdf

else
ps2raster ${pdfname}xplot.ps -A -T e
ps2pdf ${pdfname}xplot.ps
pdfcrop ${pdfname}xplot.pdf
gs -dBATCH -dNOPAUSE -q -r300 -sDEVICE=jpeg -sOutputFile=${pdfname} xplot.jpg ${pdfname}xplot.pdf
gs -dBATCH -dNOPAUSE -q -sDEVICE=pdfwrite -sOutputFile=${pdfname} graphs.pdf ${pdfname}xplot.pdf ${pdfname}hiltonmix.pdf ${pdfname}nitrogen.pdf

fi

# Calculate regression line of designated fossil carbon
function fossilreg {
  echo "Using fossil file $fossiltext"
  awk '{ print $2, $3 }' $fossiltext > fossil.xy

trend1d -Fx $fossil.xy > fossilreg.xy
x1f='awk ' NR=1 { print $1 } ' fossilreg.xy'
y1f='awk ' NR=1 { print $2 } ' fossilreg.xy'
x2f='awk ' { xx = $1 } END { print xx } ' fossilreg.xy'

}
APPENDIX A. COMPUTER SCRIPTS

y2f='awk' { yy = $2 } END { print yy }' fossilreg.xy'
gradientf='echo "scale=3;($y2f-$y1f)/($x2f-$x1f)" | bc'

awk
BEGIN
{ yy = $2 }
END
{ print yy }

fossilreg

echo Fossil Gradient = $gradientf

y0f='echo "scale=2;($y2f-$y1f)/($x2f-$x1f)" | bc'

echo Fossil Intercept = $y0f

# Calculate regression line between fresh and datapoint
function datareg {

awk ' NR==1 { print $2, $3 }' hdatastream2.txt > data.xy
awk ' NR>1 { print $1, $2, $3 }' hdatastream2.txt > hdatastream3.txt
awk '{ print $1, $2, $3 }' hdatastream3.txt > hdatastream2.txt

echo $freshx $freshy >> data.xy

trend1d -Fxm -N2 data.xy > datareg.xy

x1='awk' NR==1 { print $1 }' datareg.xy'
y1='awk' NR==1 { print $2 }' datareg.xy'
x2='awk' { xx = $1 } END { print xx }' datareg.xy'
y2='awk' { yy = $2 } END { print yy }' datareg.xy'

gradient='echo "scale=3;($y2-$y1)/($x2-$x1)" | bc'

echo Data Gradient = $gradient

y0='echo "scale=2;($y2-$y1)/($x2*$gradient)" | bc'

echo Data Intercept = $y0
}

function process {

echo process $@

# Do this while unprocessed data still exists
while [[ "$#" > "0" ]]: do

echo $#

# Calculate fossil regression line
fossilreg

# Calculate data regression line
datareg

# Print sample number
echo $1

dynx='echo "scale=4;\(\$y0 - \$y0f\)/\(\$gradientf - \$gradient\)" | bc'
dyny1='echo "scale=4;\(\$gradientf*\$dynx+\$y0f\)" | bc'
dyny2='echo "scale=4;\(\$gradient*\$dynx+\$y0\)" | bc'
echo Dynamic x = $dynx
echo Dynamic y test1 = $dyny1
echo Dynamic y test2 = $dyny2
dynyy='echo "scale=4;\($dyny1/\$dyny2\)" | bc'
echo Comparison of y values $dynyy
dyny='echo "scale=4;\(\$dyny1+\$dyny2\)/2" | bc'

dynf='echo "scale=3;\(\$2 - \$dynx\)/\(\$freshx - \$dynx\)" | bc'
fnfx='echo "scale=3;\(\$2 - \$dyny\)/\(\$freshy - \$dyny\)" | bc'
fnf='echo "scale=3;\(\$fnfx + \$fnfy\)/2" | bc'

# Check that Nitrogen has been found
if [[ $2 == "0" ]]; then
    fnf=-999
fi

echo FNF = $fnf

echo $1 $2 $3 $dynx $dyny $fnf $4 $5 >> results.txt

# Move on to next set of data
shift
shift
shift
shift
shift
echo $#
APPENDIX A. COMPUTER SCRIPTS

done
}

# This function prints the d13C − N/C plots
function print {

# Consolidate N/C and 4d13C into an simple file
awk '{ print $2, $3, ($4^(1/3))/2 }' hdatastream.txt > plotdata.xy

# Consolidate data point attributes into a displayable text file
awk '{ if (NR>1) print $2, $3, "$O_{0.0}.TR", $1 }' $pdfname{results}.txt > plottext.txt

# Create display file for fresh carbon
echo $freshx $freshy > plotfresh.xy
awk '{ print $2, $3 }' fresh.txt > plotfresh2.xy

# Plot data, text labels and fresh carbon on same axes
area=R0/0.6/-28/-16
proj=JX8i/6i
psbasemap $area $proj $Xc -B0.1:"N/C_Ratio":1:"d13C":/"$pdfname. Hilton_Mixing_Model":WS -K > $pdfname{hiltonmix.ps}
psxy plotdata.xy $area $proj $Sc -Gblack -N -K -O >> $pdfname{hiltonmix.ps}
psxy plotfresh2.xy $area $proj $Sc0.2 -Glightgreen -N -K -O >> $pdfname{hiltonmix.ps}
psxy plotfresh.xy $area $proj $Sc0.3 -Ggreen -N -K -O >> $pdfname{hiltonmix.ps}
pstext plottext.txt $area $proj -N -Dj0.2 -K -N -O >> $pdfname{hiltonmix.ps}
p Fay fossil.xy $area $proj -Wthin -K -N -O >> $pdfname{hiltonmix.ps}

if [[ $bedrock = "true" ]] ; then
    awk ' NR>1 { print $2, $4, $3, $5 }' taiwanbedrockc.xy
    psxy taiwanbedrockc.xy -Ss0.4 -Exy -Gdarkred $proj $area -K -O >> $pdfname{hiltonmix.ps}
pstext taiwanbedrockt.xy $proj $area -Dj0.2 -K -O >> $pdfname{hiltonmix.ps}

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A.2. DYNAMIC ENDMEMBER MIXING SCRIPT

```plaintext
fi

ps2pdf ${pdfname}hiltonmix.ps
pdfcrop ${pdfname}hiltonmix.pdf
gs -dBATCH -dNOPAUSE -q -r300 -sDEVICE=jpeg -sOutputFile=${pdfname}
hiltonmix.jpg ${pdfname}hiltonmix.pdf
}
}

function printnitrogen {

# Consolidate N/C and d13C into an simple file
awk '{ print $2, $3, ($4^((1/3))/2) }' hndatastream.txt > plotdatan.xy

# Consolidate data point attributes into a displayable text file
awk '{ print $2, $3 }' hndatastream.txt > plotdatanb.xy
awk '{ if (NR>1) print "8.0,0.0,TR", $1 }' ${pdfname}results.txt > plottextna.txt
paste -d" ", plotdatanb.xy plottextna.txt > plottextn.txt

# Create display file for fresh carbon
#echo $freshx $freshy > plotfresh.xy

# Plot data, text labels and fresh carbon on same axes
area=−R0/30/−8/5
proj=−JX8i/6i
psbasemap $area $proj −Xc −B5:"C/N_Ratio":/1:"d15N"/:."$pdfname−Nitrogen Isotopes":WS −K > ${pdfname}nitrogen.ps
psxy plotdatan.xy $area $proj −Sc −Gblack −N −K −O >> ${pdfname}nitrogen.ps
#psxy plotfresh.xy $area $proj −Sc0.3 −Ggreen −N −K −O >> ${pdfname}nitrogen.ps
pstext plottextn.txt $area $proj −N −Dj0.2 −K −N −O >> ${pdfname}nitrogen.ps
#psxy fossil.xy $area $proj −Within −K −N −O >> ${pdfname}nitrogen.ps
ps2pdf ${pdfname}nitrogen.ps
pdfcrop ${pdfname}nitrogen.pdf
gs -dBATCH -dNOPAUSE -q -r300 -sDEVICE=jpeg -sOutputFile=${pdfname}nitrogen.jpg
nitrogen.jpg ${pdfname}nitrogen.pdf
```

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} #Main Program#
# This section reads the input arguments and passes the right commands to the functions defined above

rm hdatastream.txt
rm hndatastream.txt
crossplot=false
line=true
dissolved=false
carbon=false
nitrogen=false
ncratio=false
deltac=false
deltan=false
corr carb=false
xaxis=12
freshx=0.06001
freshy=-26.001
fresh file=false
nonfossil=false
amtfresh=false
amtfossil=false
legend=profilelegend.txt
fossil text=fossil.txt
bedrock=false
corrtoc=true

while getopts 'aze:sdcbnrtvqwx:l:i:p:k:g:h:jo' option
    do
case $option in
        a) crossplot=true;;
        s) line=false;;
        d) dissolved=true;;
        c) carbon=true;;

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A.2. DYNAMIC ENDMEMBER MIXING SCRIPT

b) corrcarb=true;;
n) nitrogen=true;;
r) ncratio=true;;
t) deltac=true;;
f) deltan=true;;
v) nonfossil=true;;
e) xtitle=OPTARG;;
x) xaxis=OPTARG;;
l) location=OPTARG;;
i) inputfile=OPTARG;;
p) pdfname=OPTARG;;
k) legend=OPTARG;;
q) amtfresh=true;;
w) amtfossil=true;;
g) fossiltext=OPTARG;;
h) freshfile=OPTARG;;
j) bedrock=true;;
o) corrtoc=false;;
esac
done

shift $((OPTIND - 1))

if [[ "$freshfile" != "false" ]] ; then
  echo Using an alternate fresh file
  freshx=`awk ' /'$freshfile'/ { print $2 } ' fresh.txt`
  freshy=`awk ' /'$freshfile'/ { print $3 } ' fresh.txt`
  echo $freshx
  echo $freshy
fi

### Run Hilton Mixing Model ###

awk ' $1 ~/'$location'/ { print $1, $10, $6, $11, $8 }' $inputfile > hdatastream.txt

awk ' $1 ~/'$location'/ { print $1, $10, $7, $11 }' $inputfile > hndatastream2.txt

awk '{ if ( $2 > 0 ) print $1, 1/$2, $3, $4; else print $1, "1000", $3, $4 }' hndatastream2.txt > hndatastream.txt
APPENDIX A. COMPUTER SCRIPTS

awk ' { print $1, $2, $3 } ' hdatastream.txt > hdatastream2.txt

echo Sample NC d13C dynamicX dynamicY FNF CorrCarbon RawTOC > results.txt

process 'awk ' { print $1, $2, $3, $4, $5 } ' hdatastream.txt'

mv results.txt ${pdfname}results.txt

undertake

print

printf

### Run Basin/Turbidite Profile ###

rm dissolved.xy
rm d13c.xy
rm d15n.xy
rm totc.xy
rm totn.xy
rm ncratio.xy
rm corrcarb.xy
rm nonfossil.xy
rm amtfresh.xy
rm amtfossil.xy

collectnumbers
draw
output

mv ${pdfname}graphs.pdf graphs
mv *.pdf pdf
mv *.ps ps
mv *.eps eps
mv *.jpg jpg
mv ${pdfname}results.txt resultsfiles

exit
A.3  4-COMPONENT ENDMEMBER UNMIXING SCRIPT

A.3  4-component endmember unmixing script

# Mixing 4 endmembers using amount of material x carbon concentration

# Input files required:
# endmembers.txt contains as many endmembers as might be called upon,
# in the format
# name tocc ton 13c 14c 15n
# Leave 14c as 0 if only mixing 4 endmembers
# input file is called "13cdata.txt" and contains data formatted as
# space-separated text
# Name TOC TON 13C 15N

# To run the script, give five arguments, four endmembers and the name
# of the plot (used for results file and graphs)
# Best to give two fossil endmembers first, then whatever is left

rm analysedoctavesamples*.txt

name1=$1
name2=$2
name3=$3
name4=$4
plotname=$5

# Read endmembers file

foss1c=`awk '/$1/' { print $2 }' endmembers.txt`
foss1n=`awk '/$1/' { print $3 }' endmembers.txt`
foss113c=`awk '/$1/' { print $4 }' endmembers.txt`
foss115n=`awk '/$1/' { print $6 }' endmembers.txt`
foss2c=`awk '/$2/' { print $2 }' endmembers.txt`
foss2n=`awk '/$2/' { print $3 }' endmembers.txt`
foss213c=`awk '/$2/' { print $4 }' endmembers.txt`
foss215n=`awk '/$2/' { print $6 }' endmembers.txt`
APPENDIX A. COMPUTER SCRIPTS

```
marinec='awk '/$3'/ { print $2 }' endmembers.txt'
marinen='awk '/$3'/ { print $3 }' endmembers.txt'
marine13c='awk '/$3'/ { print $4 }' endmembers.txt'
marine15n='awk '/$3'/ { print $6 }' endmembers.txt'
oldtreeec='awk '/$4'/ { print $2 }' endmembers.txt'
oldtreen='awk '/$4'/ { print $3 }' endmembers.txt'
oldtree13c='awk '/$4'/ { print $4 }' endmembers.txt'
oldtree15n='awk '/$4'/ { print $6 }' endmembers.txt'

# Read one line from a data file, process it

function process {

while:
do
echo $# to go
if [[ "$#" > "0" ]]
then

echo @

# Read data
datac=$2
datan=$3
data13c=$4
data15n=$5

octave3.2<<EOF
foss1c=$foss1c
foss1n=$foss1n
foss113c=$foss113c
foss115n=$foss115n
foss2c=$foss2c
foss2n=$foss2n
foss213c=$foss213c
foss215n=$foss215n
```

A.3. 4-COMPONENT ENDMEMBER UNMIXING SCRIPT

marinec = marinec
marinen = marinen
marine13c = marine13c
marine15n = marine15n

oldtreec = oldtreec
oldtreen = oldtreen
oldtree13c = oldtree13c
oldtree15n = oldtree15n

datac = datac
datan = datan
data13c = data13c
data15n = data15n

# Set up simultaneous equations to solve as two matrices

X = [ foss1n foss2n marinen oldtreen;
foss1c foss2c marinec oldtreec;
foss13c*foss1c foss13c*foss2c marine13c*marinec oldtree13c*oldtreec;
foss15n*foss1n foss15n*foss2n marine15n*marinen oldtree15n*oldtreen;
1 1 1 1 ]

Y = [ datan;
datac;
data13c*datac;
data15n*datan;
1]

# Solve by dividing matrices

allendmembers = X\Y

C = [ foss1c;
foss2c;
marinec;
oldtreec ]
N = [ foss1n; foss2n; marinen; oldtreen ]

# Transform output values into concentrations
sum(allendmembers)

propcarbon = allendmembers.*C

propnitrogen = allendmembers.*N

totalcarbon = sum(propcarbon)
datac

totalnitrogen = sum(propnitrogen)
data

perccarbon = propcarbon./totalcarbon*100

save -ascii octavedata.txt allendmembers
save -ascii octavedata2.txt propcarbon
save -ascii octavedata3.txt perccarbon
save -ascii octavedatac.txt totalcarbon datac totalnitrogen datan

EOF

# Make output text files, move on to the next sample

echo -n "$1" >> analysedoctavesamples—proportionmaterial.txt
awk '{ printf "%f", $1 }' octavedata.txt >> analysedoctavesamples—proportionmaterial.txt
awk '{ printf "%f", $1, $2 }' octavedatac.txt >> analysedoctavesamples—proportionmaterial.txt
echo "—" >> analysedoctavesamples—proportionmaterial.txt
A.3. 4-COMPONENT ENDMEMBER UNMIXING SCRIPT

```bash
echo -n "$1" >> analysedoctavesamples-amountcarbon.txt
awk '{ printf "%f", $1 }' octavedata2.txt >> analysedoctavesamples-amountcarbon.txt
awk '{ printf "%f", $1, $2, $3, $4 }' octavedatac.txt >> analysedoctavesamples-amountcarbon.txt
echo "$1" >> analysedoctavesamples-amountcarbon.txt

echo -n "$1" >> analysedoctavesamples-proportioncarbon.txt
awk '{ printf "%f", $1 }' octavedata3.txt >> analysedoctavesamples-proportioncarbon.txt
awk '{ printf "%f", $1, $2 }' octavedatac.txt >> analysedoctavesamples-proportioncarbon.txt
echo "$1" >> analysedoctavesamples-proportioncarbon.txt

shift 5

else
return
fi
done

process 'awk '{ print $1, $2, $2*$3, $4, $5 }' 13cdata.txt'

echo Done It!

rm *octavedata*.txt

awk '{ print $1, $2+$3 }' analysedoctavesamples-amountcarbon.txt > analysedoctavesamples-amountcarbon2.txt
awk '{ print $1, $4+$5 }' analysedoctavesamples-amountcarbon.txt > analysedoctavesamples-amountcarbon3.txt

echo Sample $name1 $name2 $name3 $name4 MixModelCarbon MeasuredTOC MixModelNitrogen MeasuredTON TotalFossil > ${plotname}results.txt
awk '{ print $1, $2, $3, $4, $5, $6, $7, $8, $9, ($2+$3) }' 
```
analysedoctavesamples−amountcarbon.txt >> ${plotname}_results.txt

# Plot the results

gnuplot −persist < <EOF

set term wxt font "arial,6"
set multiplot

set size 0.5,0.5
set origin 0,0.5
set xzeroaxis lt −1
set title "Amount of Carbon provided by each endmember"
plot "analysedoctavesamples−amountcarbon.txt" using 2:xticlabels(1) with lines title "$name1", "analysedoctavesamples−amountcarbon.txt" using 3:xticlabels(1) with lines title "$name2", "analysedoctavesamples−amountcarbon.txt" using 4:xticlabels(1) with lines title "$name3", "analysedoctavesamples−amountcarbon.txt" using 5:xticlabels(1) with lines title "$name4", "analysedoctavesamples−amountcarbon2.txt" using 2:xticlabels(1) with lines title "Total Fossil", "analysedoctavesamples−amountcarbon3.txt" using 2:xticlabels(1) with lines title "Total Other"

set size 0.5,0.5
set origin 0,0.5
set xzeroaxis lt −1
set title "Proportion of Carbon provided by each endmember"
plot [***] [-50:100] "analysedoctavesamples−proportioncarbon.txt" using 2:xticlabels(1) with lines title "$name1", "analysedoctavesamples−proportioncarbon.txt" using 3:xticlabels(1) with lines title "$name2", "analysedoctavesamples−proportioncarbon.txt" using 4:xticlabels(1) with lines title "$name3", "analysedoctavesamples−proportioncarbon.txt" using 5:xticlabels(1) with lines title "$name4"

set size 0.5,0.5
set origin 0,0
set xzeroaxis lt −1
set title "Proportion of each endmember in sample"
A.3. 4-COMPONENT ENDMEMBER UNMIXING SCRIPT

plot "analysedoctavesamples−proportionmaterial.txt" using 2:xticlabels(1) with lines title "name1", "analysedoctavesamples−proportionmaterial.txt" using 3:xticlabels(1) with lines title "name2", "analysedoctavesamples−proportionmaterial.txt" using 4:xticlabels(1) with lines title "name3", "analysedoctavesamples−proportionmaterial.txt" using 5:xticlabels(1) with lines title "name4"

set size 0.5,0.5
set origin 0.5,0

set title "Measured Carbon vs Carbon from Mixture"
plot [0:1.5] [0:1.5] "analysedoctavesamples−proportionmaterial.txt" using 6:7 with points notitle, "0022.xy" with lines notitle

unset multiplot

set term png font "arial,5" size 1000,800
set output '13 cmixing{name1}{name2}{name3}{name4}{plotname}.png'

set size 1,1
set origin 0,0

set multiplot

set size 0.5,0.5
set origin 0,0.5
set xzeroaxis lt −1
set title "Amount of Carbon provided by each endmember"
plot "analysedoctavesamples−amountcarbon.txt" using 2:xticlabels(1) with lines title "name1", "analysedoctavesamples−amountcarbon.txt" using 3:xticlabels(1) with lines title "name2", "analysedoctavesamples−amountcarbon.txt" using 4:xticlabels(1) with lines title "name3", "analysedoctavesamples−amountcarbon.txt" using 5:xticlabels(1) with lines title "name4", "analysedoctavesamples−amountcarbon2.txt" using 2:xticlabels(1) with lines title "Total Fossil"
APPENDIX A. COMPUTER SCRIPTS

```bash
set size 0.5,0.5
set origin 0.5,0.5
set xzeroaxis lt -1
set title "Proportion of Carbon provided by each endmember"
plot [**:] [−50:100] "analysedoctavesamples−proportioncarbon.txt" using 2:xticlabels(1) with lines title "$\text{name1}$", "analysedoctavesamples−proportioncarbon.txt" using 3:xticlabels(1) with lines title "$\text{name2}$", "analysedoctavesamples−proportioncarbon.txt" using 4:xticlabels(1) with lines title "$\text{name3}$", "analysedoctavesamples−proportioncarbon.txt" using 5:xticlabels(1) with lines title "$\text{name4}$"

set size 0.5,0.5
set origin 0,0
set xzeroaxis lt -1
set title "Proportion of each endmember in sample"
plot "analysedoctavesamples−proportionmaterial.txt" using 2:xticlabels(1) with lines title "$\text{name1}$", "analysedoctavesamples−proportionmaterial.txt" using 3:xticlabels(1) with lines title "$\text{name2}$", "analysedoctavesamples−proportionmaterial.txt" using 4:xticlabels(1) with lines title "$\text{name3}$", "analysedoctavesamples−proportionmaterial.txt" using 5:xticlabels(1) with lines title "$\text{name4}$"

set size 0.5,0.5
set origin 0.5,0
set xzeroaxis lt -1
set title "Measured Carbon vs Carbon from Mixture"
plot [0:1.5] [0:1.5] "analysedoctavesamples−proportionmaterial.txt" using 6:7 with points notitle, "0022.xy" with lines notitle
unset multiplot

set term post landscape color 10
set output '13cmixing\${\text{name1}}\${\text{name2}}\${\text{name3}}\${\text{name4}}\{\text{plotname}\}.ps'
set size 1,1
```
A.3. 4-COMPONENT ENDMEMBER UNMIXING SCRIPT

set origin 0,0

set multiplot

set size 0.5,0.5
set origin 0,0.5
set xzeroaxis lt -1
set title "Amount of Carbon provided by each endmember"
plot "analysedoctavesamples-amountcarbon.txt" using 2:xticlabels(1) with lines title "$\text{name1}$", "analysedoctavesamples-amountcarbon.txt" using 3:xticlabels(1) with lines title "$\text{name2}$", "analysedoctavesamples-amountcarbon.txt" using 4:xticlabels(1) with lines title "$\text{name3}$", "analysedoctavesamples-amountcarbon.txt" using 5:xticlabels(1) with lines title "$\text{name4}$", "analysedoctavesamples-amountcarbon2.txt" using 2:xticlabels(1) with lines title "Total Fossil"

set size 0.5,0.5
set origin 0.5,0.5
set xzeroaxis lt -1
set title "Proportion of Carbon provided by each endmember"
plot [\*:\*] [-50:100] "analysedoctavesamples-proportioncarbon.txt" using 2:xticlabels(1) with lines title "$\text{name1}$", "analysedoctavesamples-proportioncarbon.txt" using 3:xticlabels(1) with lines title "$\text{name2}$", "analysedoctavesamples-proportioncarbon.txt" using 4:xticlabels(1) with lines title "$\text{name3}$", "analysedoctavesamples-proportioncarbon.txt" using 5:xticlabels(1) with lines title "$\text{name4}$"

set size 0.5,0.5
set origin 0,0
set xzeroaxis lt -1
set title "Proportion of each endmember in sample"
plot "analysedoctavesamples-proportionmaterial.txt" using 2:xticlabels(1) with lines title "$\text{name1}$", "analysedoctavesamples-proportionmaterial.txt" using 3:xticlabels(1) with lines title "$\text{name2}$", "analysedoctavesamples-proportionmaterial.txt" using 4:xticlabels(1) with lines title "$\text{name3}$", "analysedoctavesamples-proportionmaterial.txt" using 5:xticlabels(1) with lines title "
APPENDIX A. COMPUTER SCRIPTS

```plaintext
$\text{name4}$

\textbf{set} size 0.5,0.5
\textbf{set} origin 0.5,0

\textbf{set} title "Measured Carbon vs Carbon from Mixture"
\textbf{plot} [0:1.5] [0:1.5] "analysedoctavesamples-proportionmaterial.txt"
\hspace{1cm} using 6:7 with points notitle, "0022.xy" with lines notitle

\textbf{unset} multiplot

EOF

\texttt{ps2pdf 13 cmixing$\{\text{name1}\}$$\{\text{name2}\}$$\{\text{name3}\}$$\{\text{name4}\}$$\{\text{plotname}\}$.ps}
```
Appendix B

Geochemical Data

<table>
<thead>
<tr>
<th>Key</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{CO_3}$</td>
<td>Proportion Carbonate (loss on decarbonation)</td>
</tr>
<tr>
<td>MTOC</td>
<td>Measured Total Organic Carbon (wt %)</td>
</tr>
<tr>
<td>CTOC</td>
<td>TOC corrected for carbonate dissolution (wt %)</td>
</tr>
<tr>
<td>TON</td>
<td>Measured Total Organic Nitrogen (wt %)</td>
</tr>
<tr>
<td>N/C</td>
<td>Nitrogen - Carbon ratio</td>
</tr>
<tr>
<td>$\delta^{13}C$</td>
<td>Carbon isotopic ratio ($%$) relative to VPDB</td>
</tr>
<tr>
<td>$\delta^{15}N$</td>
<td>Nitrogen isotopic ratio ($%$) relative to air</td>
</tr>
</tbody>
</table>

B.1 Taiwan

B.1.1 Plio-Pleistocene Formations

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_{CO_3}$</th>
<th>MTOC</th>
<th>CTOC</th>
<th>TON</th>
<th>N/C</th>
<th>$\delta^{13}C$</th>
<th>$\delta^{15}N$</th>
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<tbody>
<tr>
<td>01</td>
<td>0.10</td>
<td>0.1915</td>
<td>0.1721</td>
<td>0.0278</td>
<td>0.145</td>
<td>-24.99</td>
<td>2.76</td>
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<tr>
<td>02</td>
<td>0.23</td>
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<td>0.0468</td>
<td>0.049</td>
<td>-26.49</td>
<td>3.15</td>
</tr>
<tr>
<td>03</td>
<td>0.09</td>
<td>0.2206</td>
<td>0.2003</td>
<td>0.0170</td>
<td>0.077</td>
<td>-26.18</td>
<td>1.06</td>
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<td>04</td>
<td>0.08</td>
<td>0.1942</td>
<td>0.1783</td>
<td>0.0382</td>
<td>0.197</td>
<td>-24.94</td>
<td>4.00</td>
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<td>0.08</td>
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<td>0.1387</td>
<td>0.0222</td>
<td>0.147</td>
<td>-25.30</td>
<td>3.17</td>
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<tr>
<td>06</td>
<td>0.06</td>
<td>0.1196</td>
<td>0.1125</td>
<td>0.0282</td>
<td>0.236</td>
<td>-24.74</td>
<td>4.32</td>
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<td>0.09</td>
<td>0.2079</td>
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<td>0.0296</td>
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<td>-25.73</td>
<td>2.94</td>
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<td>0.1681</td>
<td>0.0323</td>
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<td>-25.21</td>
<td>3.53</td>
</tr>
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### APPENDIX B. GEOCHEMICAL DATA

<table>
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<tr>
<th>Sample</th>
<th>P(_{\text{CO}_3})</th>
<th>MTOC</th>
<th>CTOC</th>
<th>TON</th>
<th>N/C</th>
<th>(\delta^{13}\text{C})</th>
<th>(\delta^{15}\text{N})</th>
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<td>0.1251</td>
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<td>0.0372</td>
<td>0.104</td>
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<td>0.1532</td>
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<td>0.1767</td>
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<td>3.48</td>
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<td>27.1639</td>
<td>0.2003</td>
<td>0.006</td>
<td>-26.77</td>
<td>1.03</td>
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<tr>
<td>16</td>
<td>0.11</td>
<td>0.2359</td>
<td>0.2101</td>
<td>0.0509</td>
<td>0.216</td>
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<td>3.44</td>
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<td>17</td>
<td>0.23</td>
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<td>46.0215</td>
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<td>0.016</td>
<td>-27.53</td>
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<td>0.0399</td>
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<td>0.1487</td>
<td>0.0379</td>
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<td>-25.32</td>
<td>3.61</td>
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#### B.1.2 Gaoping River

<table>
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<th>Sample</th>
<th>P(_{\text{CO}_3})</th>
<th>MTOC</th>
<th>CTOC</th>
<th>TON</th>
<th>N/C</th>
<th>(\delta^{13}\text{C})</th>
<th>(\delta^{15}\text{N})</th>
</tr>
</thead>
<tbody>
<tr>
<td>KP1A</td>
<td>0.09</td>
<td>0.2721</td>
<td>0.2468</td>
<td>0.0643</td>
<td>0.236</td>
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<td>KP1B</td>
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<td>0.3766</td>
<td>0.0915</td>
<td>0.216</td>
<td>-23.58</td>
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<td>KP1C-ACID</td>
<td>0.00</td>
<td>32.3887</td>
<td>32.3887</td>
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<td>KP1C-ACID</td>
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<td>KP2A</td>
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<td>0.2051</td>
<td>0.1867</td>
<td>0.0542</td>
<td>0.264</td>
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</tr>
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<td>KP2B</td>
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<td>0.2767</td>
<td>0.2522</td>
<td>0.0754</td>
<td>0.272</td>
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<td>KP2C</td>
<td>0.07</td>
<td>0.2667</td>
<td>0.2491</td>
<td>0.0698</td>
<td>0.262</td>
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</tr>
<tr>
<td>KP3A</td>
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#### B.1.3 Post-Morakot Cores

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<th>MTOC</th>
<th>CTOC</th>
<th>TON</th>
<th>N/C</th>
<th>(\delta^{13}\text{C})</th>
<th>(\delta^{15}\text{N})</th>
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<td>K1-0</td>
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<td>0.6954</td>
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<td>Sample</td>
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<td>CTOC</td>
<td>TON</td>
<td>N/C</td>
<td>$\delta^{13}C$</td>
<td>$\delta^{15}N$</td>
</tr>
<tr>
<td>--------</td>
<td>-----------</td>
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<td>------</td>
<td>-----</td>
<td>-----</td>
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APPENDIX B. GEOCHEMICAL DATA

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**B.2 Pyrenees**

**B.2.1 Aren Formation**

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APPENDIX B. GEOCHEMICAL DATA

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B.3 Apennines

B.3.1 Marnoso Arenacea Formation

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