An assessment of geochemical preparation methods prior to organic carbon concentration and carbon isotope ratio analyses of fine-grained sedimentary rocks

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[1] This study summarizes organic carbon isotope (δ^{13}C) and total organic carbon (TOC) data from a series of tests undertaken to provide an appropriate methodology for pre-analysis treatment of mudstones from an Upper Carboniferous sedimentary succession, in order to develop a consistent preparation procedure. The main treatments involved removing both inorganic carbonate and hydrocarbons (which might be extraneous) before δ^{13}C and TOC analysis. The results show that decarbonating using hydrochloric acid causes significant reduction in δ^{13}C and total carbon (TC) of the bulk material due to the removal of inorganic carbonate. These changes are most pronounced where soluble calcium carbonate (rather than Ca-Mg-Fe carbonate) is present. Deoiled samples show only slightly higher mean δ^{13}C where visible bitumen was extracted from the bulk sample. Moreover, the isotopic signatures of the extracts are closely correlated to those of their respective bulk samples, suggesting that small yields of hydrocarbons were generated in situ with no isotopic fractionation. In addition, further δ^{13}C and TC analyses were performed on samples where mixing of oil-based drilling mud with brecciated core material had been undertaken. Brecciated mudstone material did not display distinct isotopic signals compared to the surrounding fine-grained material. Overall we show that the most accurate assessment of bulk organic carbon isotopes and concentration in these samples can be achieved through decarbonating the material prior to measurement via the 'rinse method'. However, our results support recent findings that pre-analysis acid treatments can cause variable and unpredictable errors in δ^{13}C and TOC values. We believe that, despite these uncertainties, the findings presented here can be applied to paleoenvironmental studies on organic matter contained within sedimentary rocks over a range of geological ages and compositions.

Theme: Development of Isotopic Proxies for Paleoenvironmental Interpretation: A Carbon Perspective (DIPPI-C)

1. Introduction

[2] The dependence of organic carbon isotope ratios ($\delta^{13}C$) and percent total organic carbon (TOC) content on the preparation method for geological materials has been previously demonstrated [*King et al.*, 1998; *Midwood and Boutton*, 1998; *Larson et al.*, 2008; *Brodie et al.*, 2011a, 2011b]. Pre-analysis treatment through acidification, designed to remove inorganic carbon is routinely undertaken on modern and ancient organic matter (OM). A variety of protocols are used with different acid reagents in varying strengths to fully digest carbonate minerals. While it is widely assumed that calcite can be dissolved by small amounts of dilute acid [*Kennedy et al.*, 2005], the elimination of dolomite or siderite, due to their slower reaction with acid is more problematic, and may require higher acid concentrations and longer duration of treatment [e.g., *van Kaam-Peters et al.*, 1997] and/or heating [*Huon et al.*, 2002; *Kennedy et al.*, 2005; *Galy et al.*, 2007; *Larson et al.*, 2008]. The effect of acidification on organic matter vary with the lithology, depositional environment and geological age of the samples, however, intrinsic controls are poorly constrained. *Brodie et al.* [2011a, 2011b] show nonlinear and unsystematic offsets of carbon concentration and $\delta^{13}C$ data within and between different pre-treatment methods. Three different methods are common: (I) The 'rinse method' which involves the dissolution of carbonate in the powdered material in acid followed by discarding of the solution and rinsing with deionized water; (II) in situ acidification during which sample material is placed into a silver capsule (occasionally wrapped in a tin capsule for better combustion) and acid is added and evaporated ('capsule method'); and (III) the fumigation method in which the sample material is subjected to acidic vapor in a desiccator. Most studies involving the 'rinse method' testify underestimation of TOC due to the discarding of the supernatant containing acid soluble OM, although proportions of lost OM vary between negligible values [*Midwood and Boutton*, 1998], to 14–19% [*Galy et al.*, 2007] and

up to 44% [*Roberts et al.*, 1973; *Froelich*, 1980]. As a result, the organic material may be depleted in $\delta^{13}C$, reflecting the more acid-resistant fractions of the OM pool [*Fernandes and Krull*, 2008; *Brodie et al.*, 2011a], although sometimes $\delta^{13}C$ remains relatively unchanged [*Midwood and Boutton*, 1998; *Schubert and Nielsen*, 2000]. However, *Brodie et al.* [2011b] also found an artificial concentration of TOC in samples after acid treatment following the 'rinse method' relative to untreated aliquots or materials which were acidified following the 'capsule method'. This was attributed to the loss of fine-grained inorganic sediment suspended in the supernatant [*Brodie et al.*, 2011a]. The fact that these discrepancies were unproportional and were only observed in some of the samples analyzed by *Brodie et al.* [2011a], indicate that even within methods variable and unsystematic errors occur, thus adding uncertainties to environmental interpretations based on TOC and $\delta^{13}C$ values. In situ acidification and fumigation minimize the loss of both inorganic and organic material, but there are significant issues with samples with high carbonate content. In the capsule method the sample material is prone to spills during the reaction and CO_2 bubbles may protect carbonate from dissolution, while in the fumigation method the vapor may not attack all of the carbonate [*Brodie et al.*, 2011a]. In addition, in situ acidification of carbonate produces hygroscopic salts (e.g., calcium chloride) which not only impede on mass balance calculations for total carbon (TC) analysis, but also represent a hazard to the carbon analyzer over prolonged periods [*Schubert and Nielsen*, 2000; *Fernandes and Krull*, 2008; *Larson et al.*, 2008].

[3] All the experiments presented here were conducted on mudstones of Serpukhovian (Namurian, Upper Carboniferous) age following the 'rinse method'; with all geological organic carbon we assume that the OM is consolidated and tightly bound to the mineral matrix, and contains therefore less hydrolysable components compared to OM in recent sediments and soils [*Roberts et al.*, 1973;

Durand and Nicaise, 1980], particularly if a non-oxidizing reagent such as HCl is used [*King et al.*, 1998]. In addition, decanting and rinsing the sample with deionized water after treatment with HCl avoids the formation of calcium chloride.

[4] In contrast to decarbonating, hydrocarbon removal is seldom undertaken, with the exception of, for example, by *Stephenson et al.* [2005]. Oil and gas molecules are generally ^{13}C depleted compared to the source kerogen in Phanerozoic systems [*Radke et al.*, 1997], therefore hydrocarbon-saturated samples overall have lower $\delta^{13}C$, but higher TOC, particularly when significant amounts of the hydrocarbons are migrated into the sediment from other sources. It has been recognized that extraneous (i.e., migrated) bitumen can cause negative excursions of bulk $\delta^{13}C$ which might lead to errors in the interpretation of the in situ OM composition [*Stephenson et al.*, 2005].

[5] Here, we test material from the Upper Carboniferous of Northern and Central England, where we intend to use $\delta^{13}C$ and TOC of sedimentary OM for paleoenvironmental reconstruction. We expect that variations in bulk $\delta^{13}C_{org}$ can be attributed to mixing of different proportions of marine and terrigenous OM in a variety of geological settings [cf. *Stephenson et al.*, 2008]. Previous studies on Upper Paleozoic OM have noted that terrestrially influenced kerogen dominated by plant and woody debris has typically lower $\delta^{13}C$ than marine kerogen. *Peters-Kottig et al.* [2006] found a medium value of $-23.5‰$ for Carboniferous land plant OM, similar isotopic ratios are reported by *Wenger et al.* [1988] ($-22.9‰$) and for the Permian by *Gorter et al.* [1995] ($-23.5‰$ to $-24.8‰$). In contrast, marine (presumably algal-derived) OM is characterized by $\delta^{13}C$ of around $-28.0‰$ [*Lewan*, 1986] to $-27.8‰$ (maximum value [*Wenger et al.*, 1988]).

[6] The organic matter contained within the sediments is composed of kerogen and bitumen. The latter is composed of hydrocarbon compounds and represents the fraction of OM which can be extracted by organic solvents (e.g., chloroform and benzene [*Durand*, 1980]). Within this fraction we consider hydrocarbons that are formed and retained in the OM in situ and possible contributions from hydrocarbons of extraneous sources. Kerogen, in turn, is the insoluble fraction of OM, composed of high molecular weight geopolymers [*Durand*, 1980; *Brooks*, 1981]. This study aims to reconstruct the $\delta^{13}C_{org}$ composition of the bulk sedimentary organic carbon which includes the kerogen fraction and all bitumen formed in situ. For convenience, we

label this entity 'organic matter' as opposed to 'extraneous hydrocarbons'.

[7] Few studies have compared results of different pre-analysis treatments on deep-time OM preserved in sedimentary rocks. Here, we present a pre-analysis method for the 7 different lithofacies recognized during sedimentological core-logging of an Upper Carboniferous succession (see Table 1 and Figure 1). The lithofacies range from clay-dominated mudstones and plant debris-bearing sandstones to calcareous mudstones. The samples contain different proportions of inorganic carbon and (potentially) extraneous hydrocarbons and hence measurement of the sedimentary OM requires removal of these additional carbon sources. In addition, we investigate the possible contamination of core material with drilling mud used as a lubricant during the core drilling.

2. Study Site

[8] The analyses used samples derived from core material of the Carsington Reconstruction Dam C4 Borehole in Derbyshire, UK, housed at the British Geological Survey. The core covers a 40 m thick mudstone-dominated succession of Arnsbergian (Serpukhovian) age. In the upper part two stratigraphic markers are present, the *Ct. edalensis* and the *E. yatesae* 'marine bands' which many authors have interpreted as widespread horizons deposited during phases of high sea level and fully marine conditions [*Trewin and Holdsworth*, 1973; *Ramsbottom*, 1977]. Two major lithological units have been identified (Figure 1): a lower series of clay-dominated mudstones interbedded with thin silt-bearing mudstones and centimeter-scale silt- and sandstones, which is overlain by a partly calcareous and fossil-bearing unit of clay-dominated mudstones and silty mudstones. The latter is characterized by sometimes abundant bivalve and less common goniatite calcitic and aragonitic shell material. In addition, two distinct 15 cm thick tough calcareous mudstone concretionary horizons were recognized in the upper unit. The lower unit, however, displays abundant plant and occasional woody debris which is mostly associated with erosive bases of graded silt-rich mudstone and sand- and clay-bearing siltstone beds. In contrast to the carbonate- and fossil-bearing unit, the more siliciclastic lower unit has presumably been deposited by distant pro-delta turbidity currents laden with silt- and sand-sized terrigenous material and interturbidite hemipelagic settling of clays during periods of

Table 1. Carbon Isotope and Concentration Data for Different Subsample Aliquots From Carsington C4 Borehole[a]

Sample	British Geological Survey Reference Number	Depth (m)	Lithofacies	$\delta^{13}C$ (‰PDB)/TC (%)					
				a	b	c[1/2]	c[2/2]	d	e
1	SSK4529	16.57	Ib	−20.7 / 12.3		−28.0 / 6.4	−27.8 / 6.9	−27.8 / 6.2	
2	SSK4525	18.18	III			−21.4 / 13.6	−21.4 / 13.2		
3	SSK4520	20.48	Ib			−28.1 / 4.5	−28.5 / 4.0	−28.2 / 4.1	
4	SSK4506	26.90	III	−18.9 / 13.2		−18.2 / 11.4			
5	SSK4504	27.42	Ia (brecciated)			−27.9 / 2.2	−28.8 / 1.7	−27.2 / 2.4	
6	SSK4499	29.04	Ib	−18.6 / 6.2	−18.9 / 6.3	−27.7 / 4.6	−28.0 / 4.3	−27.6 / 4.7	−29.6
7	SSK4471	38.73	IVb	−14.2 / 12.9	−16.1 / 14.6	−23.5 / 9.8	−23.3 / 9.6	−22.8 / 10.0	−29.3
8	SSK4470	38.95	IVa	−25.3 / 1.3	−25.3 / 1.0	−26.3 / 1.4	−26.7 / 1.0	−26.1 / 1.2	−29.8
9	SSK4452	44.16	Ia	−28.8 / 1.6	−28.6 / 1.6	−28.8 / 2.5	−29.3 / 2.3	−28.6 / 2.5	−30.6
10	SSK4407	45.01	IIb (brecciated)	−27.4 / 2.9	−27.5 / 2.1	−28.7 / 2.7	−28.7 / 2.6	−27.7 / 2.2	−31.6
11	SSK4401	47.51	IVb	−24.2 / 10.9	−23.6 / 9.4	−25.9 / 7.4	−26.0 / 6.9	−25.1 / 12.2	−30.7
12	SSK4387	52.64	IIa	−15.9 / 6.4	−16.2 / 6.8	−27.9 / 6.5	−28.1 / 6.3	−27.7 / 6.1	−30.2
$\delta^{13}C$ means				−21.6 ± 5.1	−22.2 ± 5.3	−26.0 ± 3.3	−26.9 ± 2.5	−26.9 ± 1.8	−30.3 ± 0.8
Shapiro–Wilk p-value				0.72	0.28	0.01	0.01	0.03	0.82

Sample From 'Brecciated Intervals'	British Geological Survey Reference Number	Depth (m)	Lithofacies	Bulk	Mudstone	Drill Mud
MB1	SSK4518	20.77	Ib	−28.1 / 2.4	−27.6 / 2.0	−29.1 / 2.9
MB2	SSK4517	20.95	Ib	−30.0 / 4.4	−30.6 / 6.0	−30.0 / 4.7
MB3	SSK4502	28.42	Ia	−28.7 / 2.6	−28.5 / 2.6	−28.7 / 2.5
MB4	SSK4479	36.09	Ia	−26.5 / 1.7	−26.7 / 1.1	−28.3 / 1.2

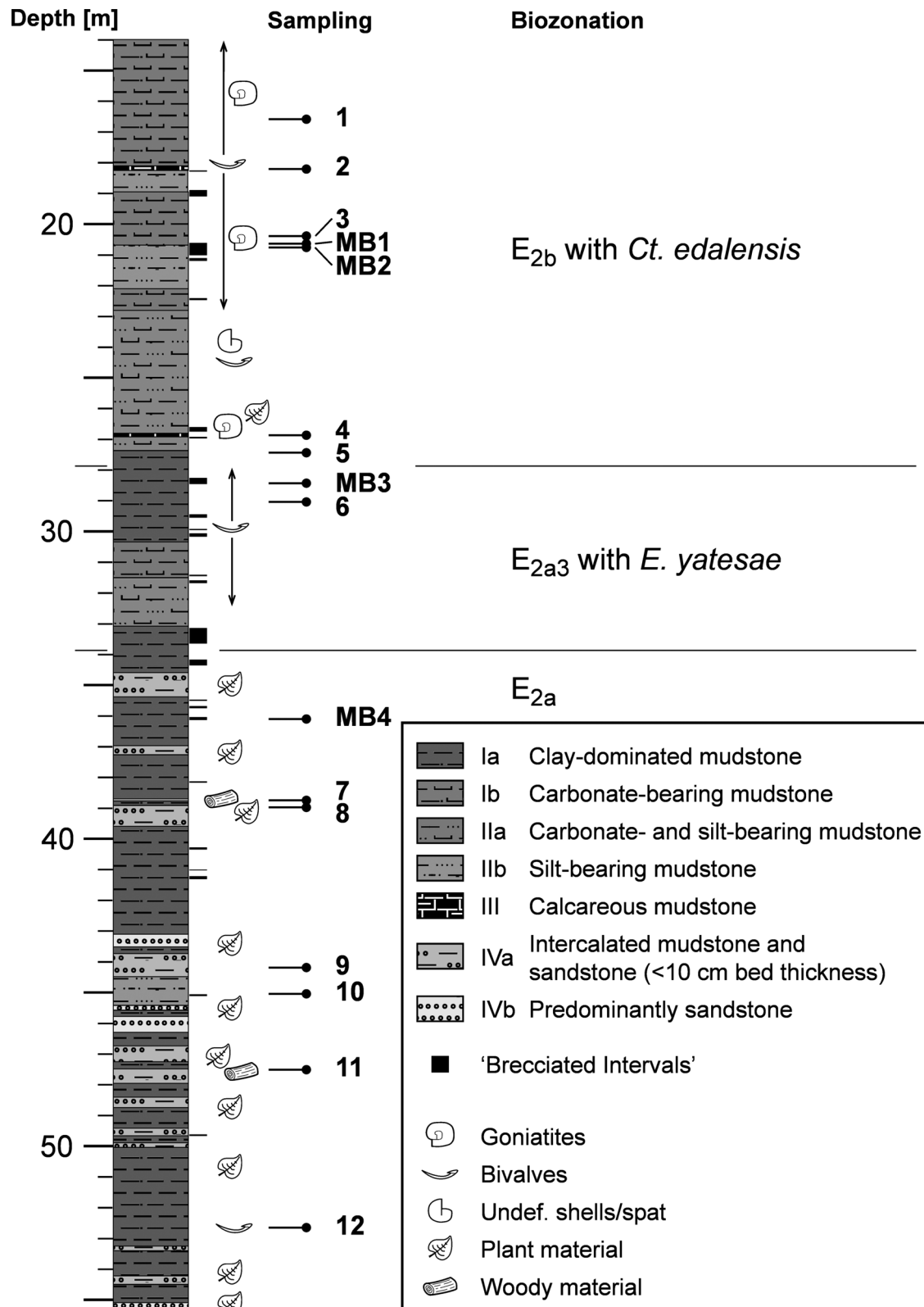[a]a, raw; b, deoiled; c, decarbonated; d, decarbonated + deoiled; e, extracts.

Figure 1. Lithofacies distribution and sample locations (1–12, MB1–4) in the Carsington C4 borehole.

Table 2. Mineralogical Composition of Decarbonated Samples 2, 6 and 7, Determined by Semiquantitative XRD Analysis

	Sample 2/SSK4525[a]	Sample 6/SSK4499[a]	Sample 7/SSK4471[a]
Lithofacies	III	Ib	IVb
Major constituents	Calcite	Quartz	Quartz
Minor constituents	Pyrite	Pyrite, Muscovite, Kaolinite	Pyrite, Kaolinite, Plagioclase, Muscovite
Possible traces	Dolomite, Quartz	–	Siderite

[a]British Geological Survey reference number.

lower sea level [*Trewin and Holdsworth*, 1973; *Aitkenhead*, 1977]. Time-equivalent successions from Northumberland have shown that OM from coarsening-upward deltaic cycles is dominated by terrestrial plant material while the marine intervals, expressed as fossiliferous limestones, contain predominantly amorphous OM of presumably algae origin [*Stephenson et al.*, 2008]. TOC contents average 2.8% in fossil-barren mudstones intercalated with silt-bearing mudstones and sandstones, and 5.3% in marine fossil-bearing intervals [*Spears and Amin*, 1981].

[9] Some intervals within the core section are composed of millimeter- to centimeter-sized angular mudstone pieces surrounded by fine consolidated muddy material. These are suspected to represent zones of fragile sediment which disintegrated during the coring and handling process rather than actual sedimentary breccias. In this case, mixing of cored sediment and drilling fluid (possibly oil-based) cannot be excluded.

[10] The thermal maturity of Serpukhovian sediments in the Carsington area does not exceed the immature to early oil window stage [*Department of Energy and Climate Change*, 2010], therefore only minor amounts of hydrocarbons generated in situ are anticipated.

3. Methods

3.1. Sample Preparation

[11] Twelve samples were selected, comprising of an example from all the seven main lithological units, plus replicates from the carbonate-bearing lithofacies (Table 1 and Figure 1). Based on thin section observation and the cessation of reaction with acid, we estimate that lithofacies Ia, IIb and IV (except sample 7) are virtually free of carbonate, lithofacies Ib and IIa contain few percent of calcite and aragonite, and lithofacies III (samples 2 and 4) is predominately made up of calcite. About 20–30 g of rock fragments per sample were crushed in a fly press and ground in an agate mortar and pestle. For

the drilling mud experiment, 4 samples from 'brecciated intervals' (denoted 'MB') were selected; both 'pure mudstone' and 'drilling mud' samples were separated as far as possible. In total, we present 5 measurements from each of the 12 samples plus 4 measurements from 4 'brecciated intervals'.

[12] Decarbonating experiments were performed following the 'rinse method'. Approximately 3–6 g of sample powder was placed into a 500 ml glass beaker with approximately 100 ml of 5% HCl. This amount represents excess acid with respect to the amount of carbonate present in all samples except for samples 2 and 4 (calcareous mudstones). After 24 h, the solution was diluted using 400 ml of deionized water and left for a further 24 h. This was followed by decanting the supernatant and care was taken not to lose any visible amount of sample. The beaker was then refilled with 500 ml of deionized water, and decanted 3 times at 24 h intervals. After the final decant the beaker was placed in a drying cabinet at 50°C to evaporate the remaining water (<50 ml). Finally, the dry sample was removed from the beaker with a metal spatula and reground to a powder. The presence of residual carbonate after acid treatment was investigated in three known carbonate-bearing samples by semiquantitative XRD: Sample 2 (calcareous mudstone), sample 6 (shell-bearing clay-dominated mudstone) and sample 7 (plant debris-bearing sandstone with carbonate recrystallization), and the findings are summarized in Table 2. For the two samples from the calcareous mudstone facies (2 and 4) which contain abundant calcite, the procedure was repeated using ca. 1 g of material. The sample weight was recorded before and after treatment, and TOC was calculated taking into account the loss of carbonate. In addition, the supernatant was tested with universal indicator to ensure full dissolution of carbonate. The δ^{13}C value of the carbonate fraction in both samples was determined following standard carbonate isotope methods.

[13] Removal of bitumen constituents (deoiling) was conducted in a Dionex ASE 200 Solvent
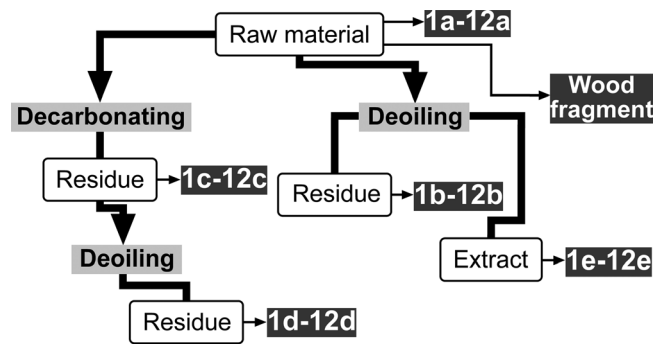
Figure 2. Workflow of sample treatment and subsequent analyses.

Extractor, using a 90:10 mixture of dichloromethane and methanol which was flushed through the extraction cylinders at 175°C and 2,000 psi. A silica wool plug prevented flushing of the powder. Extracts were concentrated through part-evaporation of the solvents and filled into 10 ml glass vials after which the mixture was dried down. The sample residue underwent sieving with deionized water at 80 μm in order to remove any fragments of silica wool; the <80 μm fraction was used for TC and δ^{13}C measurement.

[14] TC and δ^{13}C were thus analyzed for five subsample aliquots (Figure 2): (a) untreated (raw), (b) deoiled, (c) decarbonated, (d) decarbonated and deoiled, and (e) the extract (bitumen), which was separated from (b). Samples 1–4 only provided enough sample material to process subsamples for (c) and (d). The subsamples from 'brecciated' intervals were analyzed as decarbonated only, as these were small samples and the analysis of the 12 samples suggested in situ oil contamination was minor. Weighed quantities of powder were poured into tin (Sn) capsules which were then crimped and squashed to exclude air. TC and δ^{13}C analyses were performed by combustion in an online system comprising a Costech ECS4010 elemental analyzer (EA) coupled with a VG TripleTrap and a VG Optima dual-inlet mass spectrometer at the NERC Isotope Geosciences Laboratory. ^{13}C/^{12}C ratios (δ^{13}C values) were calculated to the VPDB scale using a within-run laboratory standards calibrated against NBS18, NBS-19 and NBS-22. Each analytical run contained well-mixed control material samples: 10 replicates of the internal NIGL standard BROC2 and 2 replicates of the external standard SOILB, which indicated a precision of ±<0.1‰ (1 SD).

[15] We use the following nomenclature to describe the data: TC and δ^{13}C are used for the bulk sample analysis, i.e., when the analysis may have involved

OM as well as inorganic and extraneous hydrocarbon contaminants. TOC and δ^{13}C$_{org}$ refer to data that are considered to represent the properties of the in situ OM only.

3.2. Statistical Data Analysis

[16] The sample populations of δ^{13}C derived from each method were examined for normality through a Shapiro-Wilk test, with a significance level of $p(z) < 0.05$ indicating that a normal distribution cannot be assumed (Table 1). Due to the evident non-normality of data from decarbonated and decarbonated + deoiled aliquots (which could not be improved through logarithmic transformation) and the limited sample size, a two-sided sign test (testing the equality of related pairs of data) was applied to compare samples from each method. Thus we test the null hypothesis that no significant difference exists between the samples with different pre-treatment at a significance level of 0.05 (p-value). The decarbonated samples were analyzed in duplicates to allow estimation of the sample reproducibility. The duplicate analysis (the sample precision) is given as the standard deviation of the two measurements.

4. Results

4.1. Isotopic Composition and TOC Content

[17] The δ^{13}C of the samples covers the range from −29.3‰ to −14.2‰ (Table 1 and Figure 3). A fairly typical range given for organic matter consisting of mixtures of geological marine and terrestrially derived material is −28.0‰ to −23.5‰ [*Lewan*, 1986; *Peters-Kottig et al.*, 2006]. A wood fragment from sample 11 was analyzed separately and has a δ^{13}C composition of −25.1‰ (Figure 3). In particular, the very high δ^{13}C produced by some
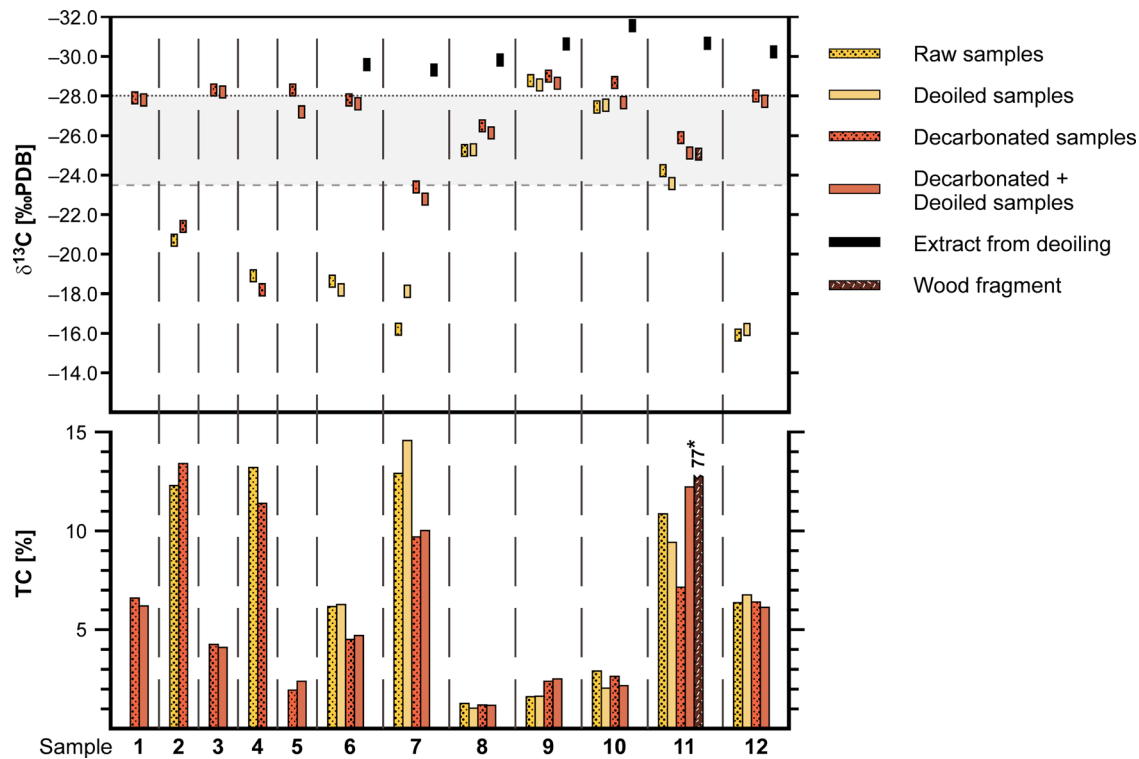
Figure 3. δ^{13}C and TC data from samples 1–12. Values for decarbonated aliquots are displayed as the average of the two measurements. Length of bars for δ^{13}C corresponds to the sample precision (± 0.3‰). Dotted line represents approximation of marine OM end-member after *Lewan* [1986]; dashed line for mean of plant material after *Peters-Kottig et al.* [2006]. TOC of extracted oils are not displayed. Only decarbonated and deoiled + decarbonated aliquots were generated from sample 1, 3 and 5. Sample 2 and 4 were only used for decarbonating experiments. Asterisk indicates TOC percentage for wood fragment.

of the raw samples (up to -14.2‰), demonstrate that some of the raw and deoiled materials contain carbonate minerals (rich in ^{13}C) as well as the organic matter. The carbonate-bearing samples 2, 4, 6, 7 and 12 all have higher δ^{13}C compared to the wood end-member, indicating possible contamination by inorganic carbon. This includes fossil shell material (mainly bivalves and goniatites) as well as post depositional carbonate cements (e.g., some of the plant tissue in sample 7 is replaced by carbonate minerals).

[18] In contrast, δ^{13}C from decarbonated and decarbonated + deoiled subsamples fit well into the expected range of OM (Figure 3), with the exception of samples 2 and 4, which were decarbonated twice. After the standard decarbonating procedure, semiquantitative XRD analysis indicated residual calcite in sample 2 (Table 2), suggesting that the acid was exhausted before all the carbonate was dissolved. Complete calcite removal was achieved during the second decarbonating step using approximately 1 g of powder with 100 ml of 5% HCl. The residues had lower δ^{13}C (-29.4‰ and -29.9‰

respectively) and these values are taken as the 'primary' $\delta^{13}C_{org}$. Separate analysis of the inorganic carbonate after leaching of the OM produced -21.0‰ for sample 2 and -18.5‰ for sample 4. The analysis was undertaken to show the isotopic difference between inorganic and organic carbon. These values are higher than for the OM but unusually low for typical Carboniferous marine carbonate components which are around -2.0‰ to $+3.0$‰ [e.g., *Brand*, 2004]. However, as most of the calcite appears to be authigenic rather than primary, *Mozley and Burns* [1993] have documented that δ^{13}C ratios of calcite concretions often are as low as -22.0‰, resulting from sulfate reduction of OM and subsequent calcite precipitation.

[19] The acidified aliquot of sample 6, however, was free of residual carbonate as shown by XRD analysis (Table 2). Sample 7, which contains macroscopic woody debris, revealed possible traces of siderite, which is relatively insoluble within 5% HCl. This might account for higher δ^{13}C (-23.3‰ to -23.5‰) compared to the wood fragment (-25.1‰). Except for sample 9 and 10, which are

Table 3. Sample Weights and Carbon Content for Repeated Decarbonating Experiment of Samples 2 and 4

	Sample 2/ SSK4525[a]	Sample 4/ SSK4506[a]
Initial sample weight (mg)	1,029.9	1,049.2
Sample weight after decarbonating (mg)	46.2	45.9
TC after decarbonating	7.33	6.17
$\delta^{13}C$ after decarbonating (‰PDB)	−29.4	−29.9
TOC corrected for weight loss (%)	0.33	0.27

[a]British Geological Survey reference number.

presumed to have no carbonate content, all decarbonated samples show a depletion in $\delta^{13}C$ (mean reduction = 3.6‰ ± 4.6‰) beyond the sample precision (0.3‰) compared to raw samples. This suggests that the depletion of $\delta^{13}C$ is primarily a result of carbonate loss, whereas hydrolyzing effects on the OM are relatively low. A fractionation of the organic matter through decarbonating cannot be ruled out but seems to affect the isotopic signals to a lesser extent.

[20] Deoiling of raw samples yielded only minor alterations in the isotopic composition (difference of means between raw and deoiled samples is 0.2‰). Presumably, the removal of hydrocarbon compounds from the raw samples was insignificant in comparison to inorganic carbon effects in the residues. Only the deoiled residues of 7 and 11 were enriched in ^{13}C beyond the sample precision, and their respective bulk samples produced significantly more visible extract than the other samples. For the deoiling of decarbonated samples, Figure 3 shows some trend toward higher $\delta^{13}C$. Decarbonated and deoiled subsamples are, on average, 0.5‰ higher in $\delta^{13}C$ than samples which have undergone decarbonating only. This reflects the removal of small amounts of hydrocarbons with low $\delta^{13}C$. In fact, the $\delta^{13}C$ of the extracted oils (mean value of −30.3‰) are lower than both the raw material and the deoiled residues, which is consistent with other findings that oil and gas, especially those fractions formed during early catagenesis, have lower isotope values than their source kerogen, while the organic residue only shows slight changes in the isotope geochemistry [*Radke et al.*, 1997].

[21] Carbon concentrations are very slightly more variable for the raw samples (mean value 7.5% ± 4.9%) compared with decarbonated samples (6.5% ± 4.3%) and mean values in the decarbonated subsamples are reduced (6, 7 and 11, but not 12; Table 1 and Figure 3). This indicates that through carbonate

removal, the carbon concentration in the decarbonated residues can be regarded as TOC. As a result of the high carbonate content in sample 2 and 4, the material was apparently enriched in OM after decarbonating but this is a consequence of the carbonate removal. The TOC content of the bulk samples was therefore calculated taking into account the weight of lost material during decarbonating (Table 3).

[22] Results from the data analysis show that in most cases statistically significant differences exist between treatments (Table 4). However, the outcomes from the sign test are less meaningful than for a parametric test, due to the constraints of the data. Most importantly, the data indicate that the decarbonating step from untreated and deoiled aliquots creates samples with significantly different isotopic composition. The deoiling step, on the contrary, does not systematically change the carbon isotope composition, at least from untreated aliquots ($p = 0.69$). It is therefore likely that any bitumen which was extracted from bulk samples had been generated from the in situ OM, rather than migrated from extraneous source rocks.

4.2. Drilling Mud Experiment

[23] Finally, the four samples analyzed to see if lubrication mud has affected $\delta^{13}C$ show no systematic offset in $\delta^{13}C$ or TC in their non-brecciated neighboring sample material (Table 1). Isotopic signals were significantly higher in the fine-grained material ('drill mud') in MB1 and MB4, however only in MB1 the bulk sample (−28.1‰) can be described as a mixture of the mudstone and the drill mud (−27.6‰ and −29.1‰ respectively). In the other samples MB2 and MB3, the bulk samples are no different with respect to the 'pure mudstone' samples. Additionally, carbon concentrations are

Table 4. Results for the Two-Sided Sign Test Obtained for Different Sample Aliquots ($\delta^{13}C$ Only)[a]

	N	+	−	*p*-Value
Raw − deoiled	7	4	2	0.69
Raw − decarbonated	9	8	0	*0.01*
Raw − decarb. + deoiled	7	6	1	0.13
Raw − extracts	7	7	0	*0.02*
Deoiled − decarbonated	7	7	0	*0.02*
Deoiled − decarb. + deoiled	7	6	0	*0.03*
Decarbonated − decarb. + deoiled	10	0	10	*0.00*

[a]Significant differences exist where $p < 0.05$ (in italics). N, number of observations; +, number of observations with a positive difference; −, number of observations with a negative difference.

similar between the subsamples. Although deoiling of the decarbonated aliquots from sample 5 and 10 which were also derived from brecciated core material, results in depleted δ^{13}C (by -0.7‰ and -1.0‰ respectively), these alterations may as well have been caused by removal of hydrocarbon compounds, as in the other residues. A contamination of core sediment with oil-based drilling mud therefore seems unlikely.

5. Discussion

[24] Overall, the decarbonated samples show trends according to the perceived changes in the type of organic material. Samples 1–6 were obtained from the upper section of the borehole, which comprises mainly fossil-bearing mudstones with some calcareous mudstone horizons and has relatively low δ^{13}C (between -27.7‰ and -29.9‰), consistent with a marine origin of the organic matter. In the samples 7–11, silt- and sand-bearing lithofacies and partly abundant macroscopic plant debris suggest much higher allochtonous terrestrial input, which is expressed in relatively high δ^{13}C values (-23.3‰ and -26.0‰ respectively). The interturbidite mudstones (e.g., samples 9, 10 and 12) within the bottom section of the borehole have low isotope values (from -27.7‰ to -28.6‰) and therefore the OM is thought to have a marine signature.

[25] Although decarbonating, in this case applied through the 'rinse method', is therefore clearly necessary to obtain reliable information on the organic carbon composition, this study, among others [*Roberts et al.*, 1973; *Froelich*, 1980; *Ryba and Burgess*, 2002; *Fernandes and Krull*, 2008; *Brodie et al.*, 2011a, 2011b], shows that acid treatment reduces the precision of TOC and δ^{13}C$_{org}$ data. The additional uncertainties associated with the 'rinse method' are threefold:

[26] (a) There is a potential for residual inorganic carbon, when insoluble carbonate phases (e.g., dolomite, siderite) are present. Additionally, traces of inorganic carbon may be protected from acid attack by surrounding organic or mineral matter [*King et al.*, 1998]. HCl has been shown to be the most efficient reagent in removing high relative amounts of CaCO$_3$ [*Kennedy et al.*, 2005; *Fernandes and Krull*, 2008], as long as excess acid with respect to the amount of carbonate is used (at least 15 ml of 5% HCl are required to dissolve 1 g of calcite). This is important because small amounts of residual calcite (as in samples 2 and 4) with unusually low δ^{13}C may not be recognized in the

total residue if there are small differences between organic and inorganic carbon [cf. *Brodie et al.*, 2011b]. Our results indicate that calcium carbonate was fully removed and should therefore not affect the TOC and δ^{13}C$_{org}$ analyses of decarbonated samples. However, Ca-Mg-Fe carbonate such as dolomite and siderite will not be eliminated by 5% HCl, as shown by sample 7. Other studies reported that the removal of dolomite can be achieved through treatment with 20% HCl [*van Kaam-Peters et al.*, 1997] or with low acid concentrations at high temperatures [*Huon et al.*, 2002]. *Larson et al.* [2008] found that siderite was removed after immersion for 3 days in 20% HCl at 50°C. However, sample heating bears the risk of OM volatilization, although investigation of the effects of higher acid concentration on organic carbon yielded no evident trend as shown in *Brodie et al.* [2011a].

[27] (b) Mass balance variations can occur affecting the TOC analysis, as a result of discarding suspended clay and dissolved carbonate with the supernatant. This appears to be the case with samples 9 (clay-dominated mudstone) and 2 (calcareous mudstone), respectively, which exhibit a potentially artificial enrichment in total carbon after decarbonating. *Brodie et al.* [2011a] have suggested a centrifugation step to reduce this source of error.

[28] (c) The loss of organic carbon is possible (e.g., acid- and water-soluble portions of OM), with a potential for isotopic fractionation [*Froelich*, 1980; *Kennedy et al.*, 2005; *Fernandes and Krull*, 2008] in all samples. Organic matter in sedimentary rocks is presumed to be relatively resistant against HCl attack, nonetheless some organic carbon might be lost as material adsorbed to clay particles or as bituminous compounds at the top of the supernatant due to their low density. This can be partly compensated for by analyzing the dissolved carbon content in the supernatant [*Galy et al.*, 2007; *Brodie et al.*, 2011a].

[29] *Brodie et al.* [2011b] have demonstrated that, as a result, samples from a down-core sedimentary sequence which have undergone pre-analysis acid treatment are affected by non-proportional, and therefore unpredictable bias in carbon concentration and isotopic composition. The offsets due to acid treatment vary from sample to sample with no emergent relationship between inorganic or organic carbon content of the sample and the extent of the alteration. Ultimately, this bias can be considerably greater than the instrument precision (here ± 0.1‰ for δ^{13}C) and probably also greater than the sample precision (± 0.3‰). While this

makes the interpretation of small differences in $\delta^{13}C$ ratios highly questionable, our data from decarbonated samples has shown to be robust enough for paleoenvironmental interpretations, which are consistent with lithofacies observations.

[30] We believe that the 'rinse method' can be applied to a range of other materials from sedimentary rocks including both carbonate-rich and carbonate-poor samples. A thorough understanding of the inorganic carbon phase in the sample material is needed in order to recognize potential contamination caused by residual carbonate, so that the error associated with inorganic carbon can at least be accounted for.

[31] Deoiling with subsequent $\delta^{13}C$ analysis has the potential to identify extraneous hydrocarbon effects. In the sample material investigated here, extraneous hydrocarbons could be excluded on the basis of the small difference between undeoiled and deoiled aliquots. In general, samples from thick sedimentary sequences containing multiple TOC-rich intervals should be tested via deoiling (solvent extraction), to exclude migrated hydrocarbons. Nevertheless, an understanding about the thermal maturity of the organic matter is required for the estimation of hydrocarbon recovery during deoiling. With increasing maturity, growing amounts of hydrocarbons (with low $\delta^{13}C$ ratios) are formed in situ [Radke et al., 1997] which, if extracted, might be misinterpreted as extraneous hydrocarbons.

6. Conclusions

[32] For the best approximation of bulk $\delta^{13}C_{org}$ and TOC in fine-grained sedimentary rocks, a preparation method which involves acid treatment for 24 h in 5% HCl with subsequent decanting and refilling with deionized water is proposed. The method described efficiently removes soluble carbonate (mainly calcite and aragonite shelly material) from powdered sample material that would otherwise cause increased carbon isotope ratios and carbon concentrations. Care must be undertaken with calcite-rich samples to ensure full dissolution of inorganic carbon by using excess acid. Small amounts of hydrocarbons (bitumen) were detected in extracts derived from deoiling of sample material, but are most likely generated from the organic matter in situ. Therefore, analyses of bulk organic carbon should include this fraction for these particular samples. Separated subsamples from brecciated core material, which are thought to be a function of penetration of the drilling mud into weak

mudstones, displayed no systematic differences from the bulk sample, hence gave no evidence for contamination of the core by oil-base drilling mud. We find that while decarbonating of the samples is required, this process imparts errors on $\delta^{13}C_{org}$ and TOC values, which are greater than the instrument precision, but vary from sample to sample. This is the result of potential influences from residual carbonate, loss of inorganic material and, to a lesser extent, loss of organic carbon. Overall, we conclude that despite these uncertainties, results obtained here from our decarbonating method can be used for paleoenvironmental interpretation and reconstruction of sedimentary organic matter source and applied to a wider range of samples from sedimentary rocks of different geological ages and compositions.

Acknowledgments

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