

Early diagenesis of marine organic matter: Alteration of the carbon isotopic composition

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ABSTRACT

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In two distal carbonate turbidites (labelled *a* and *e*) from the Madeira Abyssal Plain oxidation of organic matter (OM) has been accompanied by a reduction in Hydrogen Index (HI) and change in the isotopic composition of carbon. Since the emplacement of turbidite *a* 0.5 ka ago 35% of the OM in the upper part has been oxidised by oxygen and nitrate diffusing from sea water into the sediment. There is an accompanying decrease of $\leq 0.3\%$ in $\delta^{13}\text{C}$ -OM, and a decrease of 25% in HI. Turbidite *e* was emplaced about 73 ka and was exposed to bottom water for 12.3 ka before being buried beneath later turbidites. During exposure oxygen and nitrate diffused into its upper part and oxidised 50% of the TOC without an accompanying change in isotopic composition; further oxidation of the more refractory organic components decreased TOC by a further 25% and decreased $\delta^{13}\text{C}$ by 2.5‰. Oxidation also reduced HI by 50% from originally low values. Unless corrected for, the isotopic changes accompanying extended oxic and suboxic degradation of organic matter in sediments will give rise to erroneous estimates of marine–terrestrial OM ratios.

Introduction

The isotopic composition of organic matter (OM) in marine sediments is often used to identify its source, and for oil/source-rock and similar correlations (Gearing et al., 1984; Sackett, 1989; Dean et al., 1986, and refs. therein). Many workers have determined the relative proportions of marine and terrestrial OM in sediments from a study of its isotopic composition (e.g. Hedges and Parker, 1976; Schultz and Calder, 1976; Gearing et al., 1977; Tan and Strain, 1979; Showers and Angle, 1986; Kennicutt et al., 1987; Cai et al., 1988). In such studies a value of about -21% is often

assumed for the $\delta^{13}\text{C}$ of Recent marine (non-seagrass) OM, and a value of about -26% for Recent terrestrial OM. A further assumption often made is that the isotopic composition of OM is a conservative property that is little affected by diagenetic fractionation. (e.g. Gearing et al., 1984; Lewan, 1986). Nevertheless, the isotopic composition of organic matter is an average of that of its components (e.g. lignins, lipids, proteins, carbohydrates, etc.), the isotopic composition of which may differ by as much as 5‰ (Deines, 1980; Spiker and Hatcher, 1984) and individual organic components, decaying at different rates during diagenesis, might be expected to change the isotopic composition of organic matter (Dean et al., 1986; Spiker and Hatcher, 1987). Downcore diagenetic fractionations of up to 4‰ caused by the selective degradation of carbohydrates have been documented in

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lacustrine settings (Hatcher et al., 1983; Spiker and Hatcher, 1984, 1987).

Although the general significance of such diagenetic effects remains controversial (e.g. Dean et al., 1986; Sackett, 1989) they have been recognised as a potentially significant source of error in determining marine-terrestrial OM ratios (Spiker and Hatcher, 1984; Jasper and Gagosian, 1990). The controversy stems from the difficulty of isolating or constraining non-diagenetic sources of isotopic variation that may influence the vertical changes seen in sediment cores, especially those due to variations in organic matter type, that may result from changes in productivity and the variable supply of terrestrial-OM. In this paper we attempt to analyse the problem of diagenetic fractionation by studying sediments that were uniform in composition when deposited and which have subsequently been altered by diagenetic processes alone. Such sediments occur as distal, carbonate-rich turbidites on the Madeira Abyssal Plain beneath the eastern Atlantic off NW Africa. (Weaver and Kuijpers, 1983; Searle et al., 1985; Weaver et al., 1986; Thomson et al., 1986, 1987; Jarvis and Higgs, 1987; De Lange et al., 1987).

Sample location and description

Samples were recovered from the Madeira Abyssal Plain beneath the NE Atlantic Ocean 800 km WNW of the Canary Islands (Fig. 1). Turbidite *a* was collected from the uppermost 60+ cm of box core BX 11327 taken from a depth of 5380 m at 31° 18.3' N, 25° 23.4' W. Turbidite *e* was sampled from piston core 11143, in which it was 270 cm thick, and occurred between 808 and 1078 cm sub-bottom depth. This core was recovered from 5424 m of water at 31° 12.0' N, 25° 11.4' W. Turbidite *a* contains 58% CaCO₃ and turbidite *e* contains 53% CaCO₃ (Jarvis and Higgs, 1987; McArthur, unpublished data).

In the study area turbidites on the Madeira Abyssal Plain, including *a* and *e*, are homogenous ungraded muds intercalated into a typical sequence of pelagic carbonate (Weaver et al., 1986; Thomson et al., 1988; Weaver et al., in press). Each turbidite, including *a* and *e*, is distinctive mineralogically and chemically (Jarvis and Higgs, 1987). Pelagic

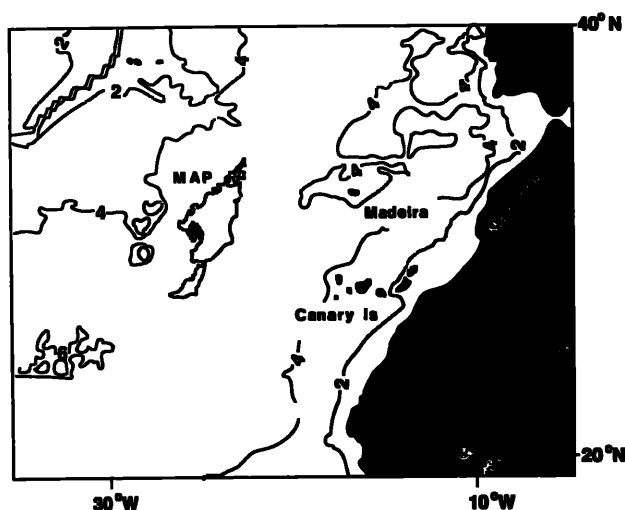


Fig. 1. Location of Madeira Abyssal Plain (MAP) shown stippled. Filled triangle show locations of core sites. Bathymetry in kilometres (adapted from Weaver et al., in press).

carbonate deposited subsequently to turbidite emplacement is mixed into turbidite tops by bioturbation. This has not altered the calcite contents of our samples from the upper part of turbidite *a* (Thomson et al., 1987; McArthur, 1989), but this process, or calcite dissolution, has reduced the calcite content of the the uppermost sample in turbidite *e* to 39%.

Diagenesis of OM is active now in turbidite *a*, which is currently exposed to bottom water, but has been arrested in turbidite *e* owing to its burial beneath later turbidites. As a consequence of this post-depositional oxic and post-oxic diagenesis turbidites *a* and *e* have different colours above and below their redox fronts. Turbidite *e* is light green in the upper 74 cm, darker green below 83 cm, and an intermediate but distinctive colour between 74 and 83 cm. The boundaries represent chemical interfaces and are termed redox fronts. They are caused by the progressive downward oxidation of the original OM by oxygen and nitrate diffusing into the turbidite when exposed to bottom water. The colour changes at 74 cm and 83 cm in turbidite *e* represent the maximum depths of penetration of O₂ and NO₃ respectively, prior to burial. Turbidite *a* is pale brown above 21 cm and light grey below. In this turbidite the oxygen and nitrate fronts are too close to be distinguished.

Analytical methods

Before analysis calcite was removed from all samples with 1 *M* HCl. Samples were then dried at 20°C. Methods of carbonate removal prior to isotopic analysis of OM vary widely (cf. Gearing et al., 1984; Lewan, 1986) and it seems that isotopic artefacts during sample preparation are not widely anticipated. We have tested superficially for such artefacts by analysing sub-samples of turbidite *a* from above (5–7 cm) and below (52–54 cm) the redox front following carbonate removal with 1 *M* HCl, 5 *M* HCl, and 8.5 *M* H₃PO₄, and drying at various temperatures (Table 1). Isotopic measurements were made on a VG Isotech Prism gas-source mass spectrometer after the oxidation of TOC to CO₂. About 10 mg of accurately weighed sediment was mixed with copper oxide and silver wire and combusted at 950°C for 10 h in a quartz tube sealed under vacuum. Yields of CO₂ were measured, using a capacitance manometer, to an accuracy of $\pm 3\%$. Accuracy of the isotopic analysis was monitored with twelve analyses of NBS 21 (graphite), which gave $-28.05 \pm 0.10\%$ (2σ) during the period of the analysis. Replicate sample analysis showed that the precision of the isotopic

analysis of samples was $\leq 0.1\%$; duplicates usually agreed to within 0.03‰ of a mean value. Measurements of carbonate-free TOC were made with a LECO C/S125 Determinator to a precision of $\pm 3\%$, and served as a check on the yield of CO₂ obtained by combustion during isotopic analysis; LECO data were systematically 0.07% lower than TOC measured from isotopic combustions. LECO data are reported here. The organic matter in four samples from above the redox boundaries of each core, and four from below, were subjected to examination by optical microscopy in order to determine the type of OM present. Samples were prepared for this examination by treatment with HCl and HF, and were then strewn-mounted on glass slides. Nineteen samples were analysed using a LECO THA-200 Thermolytic Hydrocarbon Analyser, to characterise the OM further. Between 60 and 120 mg of dry sample were pyrolysed and Hydrogen Indices (HI) measured (100S₂/TOC). Duplicates agreed to within 20% and the means are given in Table 2. The poor reproducibility results from the low TOC of the samples. Reported HI may be systematically low because of matrix absorption at low TOC (Peters, 1986).

Results

TABLE 1

$\delta^{13}\text{C}$ and carbonate-free TOC for samples given different preparations

Sample	Drying °C/h	Acid	¹ %TOC	$\delta^{13}\text{C}\%$
5–7	20/20	1 <i>M</i> HCl	0.81	–19.71
			0.80	–19.72
5–7	50/16	8.5 <i>M</i>	0.79	–19.92
		H ₃ PO ₄	0.80	–19.97
5–7	110/4	5 <i>M</i> HCl	0.83	–19.53
			0.84	–19.46
5–7	90/96	1 <i>M</i> HCl	0.82	–20.01
			0.83	–19.97
52–54	20/20	1 <i>M</i> HCl	1.29	–19.49
52–54	50/16	8.5 <i>M</i>	1.29	–19.53
		H ₃ PO ₄		
52–54	110/4	5 <i>M</i> HCl	1.28	–19.35
			1.28	–19.38
52–54	90/96	1 <i>M</i> HCl	1.24	–19.71
			1.25	–19.75

¹TOC on a carbonate-free basis.

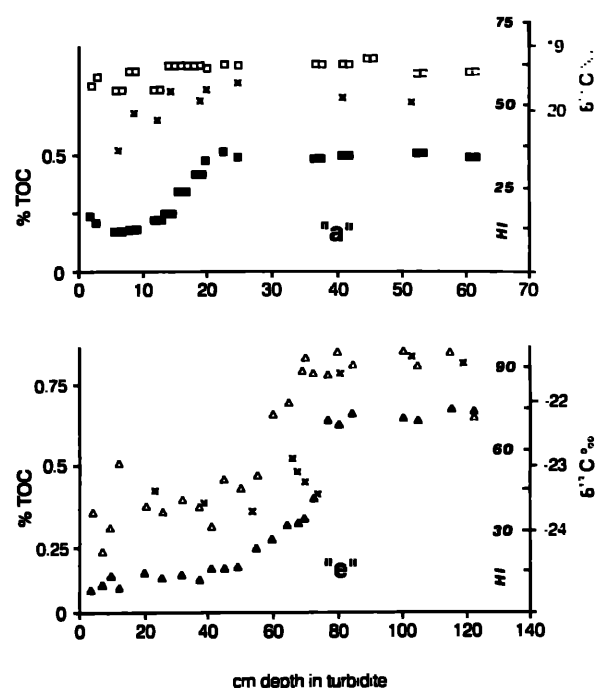
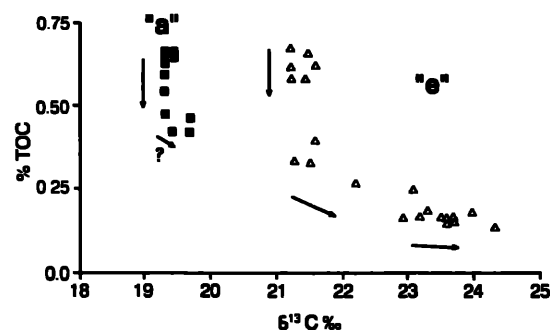
Table 1 gives isotopic data and TOC on replicates of turbidite *a* from 5–7 cm and 52–54 cm after carbonate removal with acids of different composition and strength, and different drying conditions. Table 2 presents the results of analysis for $\delta^{13}\text{C}$, TOC, and HI for depth profiles through turbidites *a* and *e*. TOC data are presented on a carbonate-free basis, and a whole-sediment basis (recalculated from the carbonate-free data). The $\delta^{13}\text{C}$, TOC and HI data for turbidites *a* and *e* are also shown in Figs. 2 and 3.

Optical microscopic examination of the organic matter residues from both turbidites showed it consisted of brown amorphous organic matter and some undigested clay minerals. Also present are rare angiosperm pollen and rare fragments of opaque phytoclasts, the latter probably wind-blown charcoal. In turbidite *a* there is no clear difference in the appearance of the organic matter above and below the redox front. In turbidite *e*

TABLE 2

%TOC, $\delta^{13}\text{C}$, S_2 , T_{max} and HI in turbidites *a* and *e*

¹ Depth (cm)	² %TOC	%TOC	$\delta^{13}\text{C}$	S_2 (mg/g)	T_{max}	³ HI
Turbidite a. Core 11327						
1-2	0.94	0.39	-19.6			
2-3	0.90	0.38	-19.5			
5-7	0.84	0.35	-19.7	0.13	376	37
7-9	0.86	0.36	-19.4	0.17	373	47
11-13	0.92	0.39	-19.7	0.17	376	44
13-15	0.96	0.40	-19.3	0.24	376	60
15-17	1.10	0.46	-19.3			
17-19	1.20	0.50	-19.3	0.28	379	55
19-20	1.29	0.54	-19.3	0.33	387	61
Redox front at 21 cm						
22-23	1.33	0.56	-19.3			
24-25	1.31	0.55	-19.3	0.36	404	66
36-38	1.30	0.55	-19.3			
40-42	1.32	0.55	-19.3	0.33	395	59
44-46	—	—	-19.2			
52-54	1.34	0.56	-19.4	0.32	408	56
60-62	1.32	0.55	-19.4			
Turbidite e. Core 11143						
1-2	0.26	0.16	-23.7			
4-5	0.29	0.14	-24.3			
7-8	0.32	0.15	-23.9			
10-11	0.27	0.13	-22.9			
18-19	0.34	0.16	-23.6			
23-24	0.31	0.15	-23.7	0.07	456	45
29-30	0.34	0.16	-23.5			
35-36	0.30	0.14	-23.6			
39-41	0.37	0.17	-23.9	0.07	397	40
43-44	0.36	0.17	-23.2			
47-48	0.38	0.18	-23.3			
53-54	0.50	0.24	-23.1	0.09	369	38
57-58	0.54	0.25	-22.2			
62-63	0.64	0.30	-22.0			
66-67	0.66	0.31	-21.5	0.18	382	58
68-69	0.68	0.32	-21.3	0.17	387	52
70-71	0.80	0.38	-21.6	0.18	377	47
Oxygen front at 74 cm						
74-75	1.27	0.60	-21.6	0.25	389	42
78-79	1.26	0.59	-21.2			
82-83	1.33	0.63	-21.4	0.55	416	88
Nitrate front at 83 cm						
98-90	1.29	0.61	-21.2			
103-104	1.29	0.61	-21.4	0.59	409	96
113-114	1.38	0.65	-21.2			
118-119				0.58	415	92
120-121	1.34	0.63	-22.2			

¹Accurate to ± 2 cm; bioturbation obscures the turbidite top.²%TOC on a carbonate-free basis.³ $100 \times (\text{mg hydrocarbons } [\text{S}_2]/\text{g TOC})$.Fig. 2. Variation of %TOC, $\delta^{13}\text{C}$ and HI with depth from turbidite top in turbidites *a* and *e*. Open symbols are $\delta^{13}\text{C}\text{‰}$ (PDB); filled symbols are %TOC. Crosses are HI.Fig. 3. Variation of $\delta^{13}\text{C}$ with TOC in turbidites *a* and *e*. Arrows highlight data trends. Uppermost two samples from turbidite *a* are not plotted as they are affected by bioturbation (see text).

that above the front is slightly darker in colour than that below. Our experience with ancient kerogens suggests such colour differences reflect partial oxidation, not a difference in organic matter type.

Characterisation of OM in both turbidites by pyrolysis showed it to have a Type IV, 'residual organic matter', inert or gas-prone composition (Tissot and Welte, 1984; Peters, 1986). This often consists of oxidised woody material, but it can also result from degradation of marine material, as is clearly the case in this study. The organic

matter type is the same above and below the redox fronts, but samples from below show higher HI, particularly in turbidite *e*, indicating that they are relatively less oxidised.

Discussion

Turbidite *a* was emplaced 0.5 ka ago (Thomson et al., 1988) and is at present undergoing oxic diagenesis. The sharp interface between oxic and anoxic parts of the turbidite is at 21 cm. Turbidite *e* was emplaced about 73 ka, at the boundary between Oxygen Isotope Stages 4 and 5 (Weaver et al., in press) and suffered oxic diagenesis for 12.3 ka (see later sections), during which time the redox front reached a depth of 74 cm below the sediment–water interface. The turbidite was then buried beneath 8 m of later turbidites and pelagic sediments. Burial terminated the supply of oxygen to the turbidite and oxic diagenesis ceased. Subsequently, anoxic conditions prevailed but sulphate reduction does not seem to occur in either turbidite (De Lange et al., 1987).

Source of the organic matter

Turbidites *a* and *e* are classified as organic-rich and have unusually high values of TOC for deep-sea sediments (Tables 1 and 2; De Lange et al., 1987; Jarvis and Higgs, 1987; Weaver et al., in press). This reflects their derivation from the NW African continental margin north of 20° N (Weaver and Kuijpers, 1983; De Lange et al., 1987; Weaver et al., in press), a region of upwelling where the OM in sediments is largely amorphous organic matter (AOM) derived predominantly from marine phytoplankton. A small amount of windblown charcoal is the only terrestrial input from the arid hinterland (Caratini et al., 1979; Summerhayes, 1983; De Leeuw et al., 1982, in De Lange et al., 1987). Organic matter does not accumulate on the continental shelf where the currents are strong but instead concentrates below 500 m at the first down-slope occurrence of fine sediment (Diester-Haas and Müller, 1979; Diester-Haas, 1982; Fütterer, 1983; Summerhayes, 1983). Slumping on the margin triggers turbidity currents which lead to periodic re-sedimentation of the organic-rich slope

sediment on the Madeira Abyssal Plain. AOM might be expected to concentrate in the upper portion of turbidites owing to its low density, but TOC profiles (Fig. 2; Jarvis and Higgs, 1987) suggest that it originally had a uniform vertical distribution in Madeira turbidites. The absence of appreciable woody input, the limited variation in grain size, and the overwhelming predominance of marine OM in the source area, are the main reasons for this uniformity.

In contrast to turbidites on the Madeira Abyssal Plain, many elsewhere show strong vertical variations, especially where terrestrial phytoclasts are concentrated in the coarser lower divisions because of their hydraulic equivalence to fine sand and silt grade clastics. The lower parts of many, even carbonate-rich, turbidites are thus woody, whilst the upper parts are richer in OM of algal origin (Tyson, 1984; Nwachukwu and Barker, 1985). Our optical characterisation of the organic matter as 'amorphous' is rather imprecise. Although AOM in marine settings may have a number of origins its isotopic composition usually indicates derivation from phytoplankton (Lewan, 1986). In view of our optical study, and the isotopic composition of AOM in the unoxidised part of the turbidites ($-19.3 \pm 0.1\text{‰}$, $-21.4 \pm 0.2\text{‰}$) we feel confident in ruling out other sources. Other studies have also indicated that the OM in the MAP turbidites is predominantly marine (De Leeuw et al., 1982, in De Lange et al., 1987).

Despite rapid deposition, and the large amounts of marine OM, sulphate reduction does not occur in most of the turbidites on the Madeira Abyssal Plain (Wilson et al., 1985; De Lange et al., 1987); only trace consumption of sulphate has been demonstrated, and this at depths below 17 m (De Lange, 1988). Reduction of iron and manganese do occur (Wilson et al., 1985, 1986; Thomson et al., 1986). Significant reduction of sulphate in deep-water sediments is often absent because the reactivity of OM is reduced by oxidation, prior to deposition (Jørgensen, 1982, 1983). Slow sulphate reduction has been noted in slope sediments at 2500 m of NW Africa (Hartmann et al., 1973), but only half the pore-water sulphate is reduced at 8 m below the sediment surface, despite the sediment containing 3–4% TOC. The slowness of this sul-

phate reduction probably reflects rapid transformation of much of the original AOM into stable humic substances (cf. Cronin and Morris, 1982), and also its partial oxidation during winnowing from the shelf and transport downslope (as noted earlier). Its partial oxidation is suggested by the high C/N weight ratios (mean 15, Hartmann et al., 1973), which are twice that of fresh planktonic detritus. An average C/N ratio of 17 has also been reported as characteristic of buried turbidites (5–18 m) from the Madeira Abyssal Plain (De Lange, 1988). The C/N ratios in the sandier shelf sediments, has been interpreted as being due to dilution by terrestrial OM (e.g. Diester-Haas and Muller, 1979; Stein et al., 1989), but in view of our optical observations and the low potential of the arid hinterland for supplying such an input, we consider partial oxidation more likely. Davis et al. (1988) suggest that significant sulphate reduction does not occur in sediments where the Hydrogen Index is less than 150. In our turbidites even the least oxidised organic matter, in the lower part of the units, has HI values less than 100 (Table 2). Thus it is not surprising that little sulphate reduction is seen in turbidites on the Madeira Abyssal Plain.

Sample preparation artefacts

Table 1 shows that variations in $\delta^{13}\text{C}$ OM of up to 0.5‰ can result from simple variations in the conditions of sample preparation prior to analysis. Similar responses to preparation method are seen in oxidised samples from above the redox front and in reduced samples from below it. In both cases the shortest drying time yields the heaviest samples (4 h at 110°C) and the most extreme drying conditions yields the lightest samples (96 hrs. at 90°C). The chemical methods used to separate organic matter from sediments differs between authors and are sometimes more severe than those reported here (cf. Lewan, 1986 and Dean et al., 1986). Sample preparation artefacts may therefore induce noise on isotopic signals of OM that may be larger than the 0.5‰ reported here.

Pyrolysis, TOC and $\delta^{13}\text{C}$ analysis

In both turbidites the first down-core colour change is taken to mark the position of maximum penetration of O_2 . More deeply buried redox fronts mark the position at which NO_3 is completely reduced and reduction of Fe(III) begins (Potter et al., 1980; Lyle, 1983). In turbidite *a* these redox fronts are not separable. Below this joint redox front (at 21 cm) in turbidite *a* the TOC has a concentration of 0.55%–0.56%. In the oxic region of the turbidite TOC decreases exponentially to a minimum of 0.36% at about 5 cm after which it increases slightly in the 0–5 cm region because pelagic sedimentation and bioturbation are adding new organic matter from the sediment-water interface. In all, 35% of the TOC is oxidised. Values of $\delta^{13}\text{C}$ in Turbidite *a* are $-19.3 \pm 0.1\text{‰}$ below the redox front and no more negative than -19.6‰ above it (Figs. 2 and 3). The oxidation of 35% of the TOC does not alter the carbon isotope composition of the OM by more than 0.3‰. In turbidite *e* about 75% of the TOC has been lost from above the upper redox front (at 74 cm) and this loss has been accompanied by a shift of about 2.5‰ in $\delta^{13}\text{C}$. The consumption of OM and the isotopic change in $\delta^{13}\text{C}$ do not coincide. At 66 cm, about 8 cm above the upper redox front, TOC has decreased by about 50% (from 0.61 to 0.31%) without an accompanying isotopic fractionation. A further decrease of TOC to 0.16% (i.e. a further decrease of 25% of the original amount) in the upper part of the turbidite is accompanied by an isotopic shift of 2.5‰. This is best seen in Fig. 3 where the co-variation of TOC and $\delta^{13}\text{C}$ is shown. The isotopic change is not coincident with the change in TOC, but the change in TOC is coincident at 74 cm with the upper of the two colour changes in this turbidite. There is no observable change in either TOC or $\delta^{13}\text{C}$ in the interval 74–83 cm; metabolism of OM by NO_3 reducing bacteria is therefore not an important influence in our samples on either of these parameters.

The greater isotopic fractionation in turbidite *e* compared to turbidite *a*, and the greater loss of TOC is probably due to the difference in exposure time to oxic conditions experienced by the two

sediments. The O_2 redox front moves down in the cores at a rate that is diffusion-limited and decreases with depth. The O_2 front in turbidite *a* took 0.5 ka to reach its present depth of 21 cm (Thomson et al., 1988). Using the approximation $t_z = z^2/2D$ (McCorkle et al., 1985, where t_z is time to depth z and D is sediment bulk density), and also allowing for the different amounts of organic carbon consumed above the redox fronts in the turbidites, it can be calculated that the redox front in turbidite *e* took 12.3 ka to reach 74 cm. This calculation assumes that the concentration of dissolved oxygen in bottom water was the same during oxidation of both turbidites, which may not be correct. This estimate of time greatly exceeds the estimate of 4.5 ka made by Buckley and Crans-ton (1988), but is consistent with the observation that most of Isotope Stage 4 (12 ka) appears to be preserved in pelagic sediment overlying turbidite *e* (Weaver and Kuijpers, 1983; Jarvis and Higgs, 1987; Weaver et al., in press). Oxidation would have continued throughout this time interval, before being terminated by the emplacement of the overlying turbidite.

In turbidite *e* there is a 65% change in TOC and HI across the full thickness of the redox front. Hydrogen Index is normalised to TOC, so both independently indicate a similar magnitude of oxidation. The change in HI in turbidite *a* is about 30%. This data confirms that, above the redox front, turbidite *e* apparently suffered more oxidation than turbidite *a*.

It is clear that turbidite *e* was exposed to oxidation at least 20 times longer than turbidite *a*. This leads us to suggest that the OM in turbidite *a* had sufficient time to partially oxidise, but insufficient time for oxidation to cause isotopic fractionation. In turbidite *e* the offset step-functions in TOC and $\delta^{13}C$ (Figs. 2 and 3) suggest that above 66 cm enough time elapsed for both processes to occur; and that between 66 cm and 74 cm, a distance equivalent in time to 2.4 ka, oxidation occurred without isotopic fractionation. This time is longer than the time oxidation took to reach 21 cm in turbidite *a* because of the higher amount of reactive OM in turbidite *e* and the greater depth to the redox front.

The $\delta^{13}C$ data for turbidite *e* show a 2–3‰ shift

in $\delta^{13}C$ from values of about –21.4‰ in the lower part to –23.8‰ in the upper oxidised part. The values below the redox front are typical for marine sediments at these latitudes (Newman et al., 1973; Dean et al., 1986), whilst those above the redox front are similar to those recorded from wood-rich marine deltaic sediments. A trend of $\delta^{13}C$ and TOC similar to that seen in turbidite *e* has been reported in a core from the Hatteras Abyssal Plain that contained a turbidity unit (Sackett, 1964). The OM in the core was not characterised and it was assumed that the turbidite introduced marine OM into a terrestrially dominated basin, thus explaining the lighter $\delta^{13}C$ at the top of the core. In view of the sharp decrease in TOC in the upper part of the core, we suspect that post-depositional oxic diagenesis is a viable alternative explanation of the chemical trends. Conversely, isotopic values similar to those seen in the upper part of turbidite *e* have been reported in turbiditic muds from the Gulf of Mexico (Newman et al., 1973). In view of the different nature of the sediment sources in the two areas, however, the isotopic similarity is probably fortuitous; sediments in the Gulf of Mexico are probably enriched in terrestrial OM, whilst those on the Madeira Abyssal Plain are not.

For turbidite *e* the $\delta^{13}C$ -OM is about –21.4‰ in the lower part and –23.8‰ in the upper oxidised part. Conventional calculations of marine–terrestrial ratios of OM, based on isotopic data and using marine and terrestrial end-member values of –21 and –26‰, respectively (Popp et al., 1989; Sackett, 1989), suggest that the upper oxidised layer of the turbidite contains 50% terrestrial OM and the bottom very little. This is a trend opposite to that expected from hydraulic sorting of OM during deposition. Even if an unusually light value of –30‰ is assigned to a putative terrestrial component conventional calculation suggests 28% of terrestrial OM should be present in the upper part of the turbidite. Optical microscopy of OM residues failed to reveal any significant vertical change in the abundance of terrestrially-derived OM, and certainly none of the magnitude required to match a conventional isotopic interpretation of marine–terrestrial OM proportions. Thus the isotopic shift in turbidite *e* must result from the selective degradation of an isotopi-

cally heavy component of the marine organic matter which has left the residue isotopically light.

The isotopic composition of OM below the redox fronts in the turbidites is -21.4‰ in turbidite *e* and -19.3‰ in turbidite *a*. The 2‰ difference encompasses the range of $\delta^{13}\text{C}$ in planktonic OM at these latitudes. As the optical microscopy showed no real difference between the OM in the cores the $\delta^{13}\text{C}$ may have changed in the time between their deposition. Whether these values represent isotopic fractionations from the original AOM is not clear, but the degree of further oxidation in the turbidites needed to change $\delta^{13}\text{C}$ suggests not. Also, the OM in turbidite *e* (-21.4‰) may have experienced an isotopic shift (of about 2‰) prior to re-sedimentation on the abyssal plain, making the total isotopic fractionation as potentially as great as 4.5‰ . A final complication in interpreting the 2‰ difference is that it might result from the mixing of AOM in the turbidite with AOM entrained from the sediment surface by passage across the abyssal plain.

Consequences of isotopic fractionation

The isotopic composition of dissolved inorganic carbon (DIC) in pore water is strongly influenced by inputs of CO_2 and HCO_3^- produced by oxidation of organic matter. The relation between $\delta^{13}\text{C}$ of OM in sediments and $\delta^{13}\text{C}$ of DIC in marine pore water in abyssal sediments is not well described by available pore-water models, which assume a bulk OM value for $\delta^{13}\text{C}$ in their calculations (McCorkle et al., 1985, 1988; Sayles and Curry, 1988; McArthur, 1989). Isotopic fractionation of organic matter during diagenesis may lead to DIC inputs with $\delta^{13}\text{C}$ different to that in bulk OM and enable measured and modelled values to be reconciled. Isotopic fractionation of OM was rejected by McArthur (1989) as a viable explanation for differences between measured and modelled values of $\delta^{13}\text{C}$ -DIC in pore waters from turbidite *a* but on the basis of only a small number of analyses of $\delta^{13}\text{C}$ -OM. The additional data presented here confirms the previous finding that little ($\leq 0.3\text{‰}$) isotope fractionation is now manifest in the isotopic composition of the OM, but does not prove that it is not occurring. Isotopic

fractionation in the solid phase would not yet be too apparent if the OM in turbidite *a* is only now entering a period of isotopic change after a prolonged period (0.5 ka) of oxidation without fractionation, as the step functions in $\delta^{13}\text{C}$, HI and TOC show happened in turbidite *e*.

Isotopic fractionation of OM may well be applicable to modelling $\delta^{13}\text{C}$ -DIC in turbidites and in slowly accumulating pelagic sediments (McCorkle et al., 1985; Sayles and Curry, 1988). In slowly accumulating sediments (sedimentation rates of the order of 1 cm/ka) and sediments exposed to oxidation for long periods ($> 10^3$ yrs), OM would have sufficient time to undergo isotopic fractionation. In turbidite *e* an isotopic fractionation of 2.5‰ accompanies the TOC decrease from 0.31 to 0.16% in the upper regions of the turbidite. The DIC added to pore water over this interval must have had an isotopic composition of -18.4‰ , about 2‰ heavier than the OM. The fractionation required by McCorkle et al. (1985) to match measurement to modelled $\delta^{13}\text{C}$ in DIC was 1.5‰ , (a figure well within the range our turbidite data suggests) and achievable by oxidation of OM. Furthermore, Sayles and Curry (1988) suggest that isotopic fractionation cannot easily explain the difference in measured and modelled values for DIC in their sediments because less than 2% of the OM reaching the sediment was preserved and buried. Our data suggest extensive oxidation can occur without fractionation, and be followed by a period of small loss in TOC but high isotopic fractionation. Isotopic fractionation of organic matter should be re-examined as a possible cause of the discrepancies between modelled and measured values of DIC in abyssal pore-waters.

We infer from our data that oxidation may be a significant source of variation of $\delta^{13}\text{C}$ in the OM of pelagic and turbiditic sediments. It certainly needs to be taken into account when calculating marine-terrestrial ratios of OM in slowly or discontinuously accumulating oxic facies. Long-term variation in bottom water oxygenation may also be a significant variable in determining whether oxidation is sufficiently intense to result in isotopic fractionation.

The possible time-variant nature of isotopic fractionation may introduce 'noise' into the iso-

topic record of marine-OM and hamper identification of trends in the data. $\delta^{13}\text{C}$ of terrestrial and marine OM differ by between 0 and 7‰ for different periods in the Phanerozoic (Dean et al., 1986; Hayes et al. 1989; Popp et al., 1989); the change in $\delta^{13}\text{C}$ we see on oxidation of OM in turbidite *e* is 35% of the maximum difference. The degree of isotopic fractionation may depend on concentrations of dissolved oxygen and these have not always been similar to those of today. Lower concentrations in the past may have resulted in different degrees of isotopic fractionation during oxic respiration.

Finally, the influence of time on isotopic fractionation of organic matter may be one reason (out of many) for the variety of conflicting reports in the literature regarding the occurrence, or non-occurrence of isotopic fractionation of organic matter during degradation. Published reports carry too little data to permit this idea to be tested.

Summary

Preparing samples for isotopic analysis by different methods can result in differences of up to 0.5‰ in $\delta^{13}\text{C}$, so caution must be exercised when comparing $\delta^{13}\text{C}$ data from different authors using different sample preparation techniques. Isotopic fractionation of marine-derived OM requires >0.5 ka to occur at abyssal temperatures and bacterial populations. A substantial component of OM can be oxidised without isotopic fractionation. Continued exposure to oxygen causes further degradation and substantial isotopic fractionation. This isotopic fractionation may be the reason why isotopic modelling of marine abyssal pore-water fails to predict their isotopic compositions. The time-variant nature of isotopic fractionation may partly explain some of the conflicting reports in the literature regarding the extent of isotopic fractionation on degradation of organic matter. Isotopic fractionation on organic matter degradation may also introduce noise into the isotopic record and obscure temporal trends in the isotopic composition of OM. In slowly, or discontinuously accumulating marine sediments oxidation of OM may result in isotopic compositions appearing terrestrial rather than marine. As with other bulk

geochemical techniques (such as elemental analysis and pyrolysis) source characterisation with stable isotopic signatures of partially degraded marine organic matter may yield erroneous interpretations unless integrated with optical methods.

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