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Elucidation of different forms of organic carbon in marine sediments from the Atlantic coast of Spain using thermal analysis coupled to isotope ratio and quadrupole mass spectrometry

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Abstract

Analysis of river, estuary and marine sediments from the Atlantic coast of Spain using thermogravimetry–differential scanning calorimetry–quadrupole mass spectrometry–isotope ratio mass spectrometry (TG–DSC–QMS–IRMS) was used to (a) distinguish bulk chemical hosts for C within a sediment and humic acid fraction, (b) track C pools with differing natural C isotope ratios and (c) observe variation with distance from the coast. This is the first application of such a novel method to the characterisation of organic matter from marine sediments and their corresponding humic acid fractions. Using thermal analysis, a labile, a recalcitrant and a refractory carbon pool can be distinguished. Extracted humic fractions are mainly of recalcitrant nature. The proportion of refractory carbon is greatest in marine sediments and humic acid fractions. Quadrupole mass spectrometry confirmed that the greatest proportion of m/z 44 (CO_2) and m/z 18 (H_2O) were detected at temperatures associated with recalcitrant carbon (510–540 °C). Isotope analysis detected progressive enrichment in $\delta^{13}C$ for the sediment samples with an increase in marine influence. Isotopic heterogeneity in the refractory organic matter in marine sediments could be due to products of anthropogenic origin or natural combustion products. Isotope homogeneity of humic acids confirms the presence of terrigenous C in marine sediments, allowing the terrestrial input to be characterised.

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1. Introduction

The principal transport pathways that supply material derived from the continental crust to the oceans are river run-off and atmospheric deposition (Chester, 2000). Fluxes of carbon linking land and sea include those of dissolved and particulate

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Abbreviations: Exotot, total TG weight loss for the temperature interval 200–600 °C.

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organic matter (POM; Alongi, 1998). POM is deposited in sediments, which rapidly accumulate in continental shelves. Due to its reduced reactivity and bioavailability the organic matter reveals a high preservation potential in marine sediments (Holtvoeth et al., 2005). Severe recycling mechanisms occur in the sea (Smith and Mackenzie, 1987). Whatever processes are involved, they must allow extensive remineralization of intrinsically resistant terrigenous organic matter and subsequent preservation of seemingly more labile marine derived counterparts (Mayer et al., 1998). Thus, to understand global cycles of carbon and oxygen it is important to identify the mechanisms by which OM is preserved in near-shore marine sediments.

Soil organic matter (SOM) decomposition can be represented by three carbon pools. These include a labile [which includes cellulose (Lopez-Capel et al., 2005a)], a recalcitrant [including lignin (Leinweber et al., 1992)] and a refractory pool [including chars (Kaloustian et al., 2001] as well as aromatic carbon (Lopez-Capel et al., 2006)]. Decomposition models (such as ROTH-C) identify them respectively as ‘microbial biomass’, ‘humified organic matter’ and ‘inert’. Various thermal analysis techniques have been used to characterise SOM (Turner and Schnitzer, 1962; Leinweber et al., 1992), to estimate the thermal stability of the pools (Dell’Abate et al., 2003) and to relate their thermal properties to biological decomposability (Lopez-Capel et al., 2005a; Plante et al., 2005). While the labile C pool is reactive (Sohi et al., 2001) and susceptible to degradation (Lopez-Capel et al., 2006), the recalcitrant C pool has a low degradation rate, and the refractory C may remain in soil and sediments from centuries to millennia (González-Pérez et al., 2004).

The determination of refractory forms of organic matter in sediments is relevant in order to improve current estimates of carbon fluxes from the biosphere to the sedimentary C pool. Refractory forms of organic matter, such as humic-like materials and black carbon, can represent a significant sink for CO_2 due to the transfer of carbon from the relatively fast biological-atmosphere carbon cycle to the long term geological carbon cycle (Middelburg et al., 1999; Gustafsson et al., 2001). Due to their important geochemical and environmental implications, there is increasing interest in the study of the different forms of refractory organic matter (ROM) widely dispersed in soils, water and sediments.

The labile SOM fraction decomposes during thermal analysis at ca. 300–350 °C while the more recalcitrant SOM decomposes at ca. 400–500 °C (Lopez-Capel et al., 2005a,b). ROM has been reported to decompose at 430–530 °C and is composed of either artificial chars (Kaloustian et al., 2001) or natural aromatic compounds (Lopez-Capel et al., 2006). Inorganic C, such as carbonate, can also be determined from decomposition between 700 and 900 °C.

Extending the capability of thermal analysis, the coupling of an isotope ratio mass spectrometer (IRMS) and a quadrupole mass spectrometer (QMS) to a thermal analysis system (TG–DSC) allows the proportions of the major components, evolved gas composition and carbon isotope ratios of composite organic/inorganic materials to be determined during a single heating experiment. Distinction of the isotope signatures of labile, recalcitrant and refractory components can provide new insights into the dynamics of organic matter in sediments.

The study area is of environmental interest due to deposition of river-derived sediments over a surface of 90,000 km^2. Deep Mediterranean currents affect sediment accumulation and are partly responsible for the mobilisation, transport and deposition of large amounts of detritus on the continental shelf and slope, favouring turbidite formation (Bonnin et al., 1975; Martínez de Olmo et al., 1984; Flinch et al., 1996; Somoza et al., 1994; Berástegui et al., 1998; Battista et al., 2000). Middelburg et al. (1999) quantified the ROM in marine sediments (between 175 and 4909 m water depth) near the study area, detecting between 16% and 29% ROM in total organic carbon (TOC).

Sedimentary organic matter is characterised by organic geochemical methods, such as elemental analysis, stable carbon isotope analysis, Rock-Eval pyrolysis and lignin chemistry (Holtvoeth et al., 2005). This is the first application of thermal analysis coupled to quadrupole and isotope ratio mass spectrometry to the characterisation of organic matter in marine sediments from the Atlantic coast of Spain.

The aim was to determine carbon fluxes from the continent to the ocean using thermal analysis coupled to IRMS to discriminate organic fractions of differing biological origins, that cannot be distinguished using bulk analysis methods.

2. Materials and methods

2.1. Materials

During the 2000 and 2001 BACH Project cruise (BC, REN 2002-04602-C02), surface sediment samples (20 cm) were taken from the internal continental platform and from the Guadiana estuary coast, as part of the "Environmental geochemistry of sediments from the Huelva coast" project. Within the sampling area (Fig. 1), >200 samples, representing the estuary area, were taken. They were thought to have high OM content and to contain high amounts of ROM, such as black carbon.

To minimise variation, each sample was a composite made up from 5 sub-samples taken from the sampling plot. The samples were stored frozen in glass containers to avoid microbial growth. Before analysis they were freeze dried, ground thoroughly in a mortar mill and homogenised to reduce variability between replicates. For the study of ROM, humic acid (HA), humin (HU) and the ROM were extracted and isolated.

Humic substances were extracted with aqueous NaOH, followed by precipitation of HAs at low pH (McCarthy and Malcolm, 1979). Standard HA/fulvic acid (FA) separation includes an acid treatment, producing carbonate-free HA and FA. The insoluble fraction was further demineralised. The following treatments were successively applied: (i) lipid extraction at 40–60 °C with CH_2Cl_2/MeOH (3:1) for 16 h, (ii) removal of extractable HA/FA fractions by successive extraction with 0.1 M $Na_4P_2O_7$ and 0.1 M NaOH (×5) and separation of the dark brown supernatant solution (total humic extract) from the insoluble fraction (humin) by centrifugation at 15,000 rpm, 15 min; (iii) demineralization of the humin fraction in 6 M HCl and then 6 M 1:1 HCl/HF (Lim and Cachier, 1996).

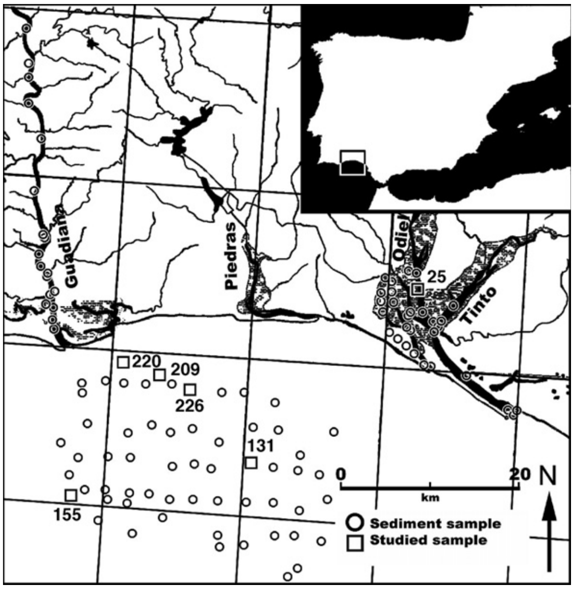

Fig. 1. Sampled area in the South West Iberian Peninsula with indication of sediments used.

A set of sub-samples, representing the area of study, were selected on the basis of total organic matter content and distance from the coast. They consist of 1 river (R25), 3 estuary (E209, E220, E226) and 2 marine (M131, M155) samples. Bulk sediments (R25S, E209S, E220S, E226S, M131S, M155S) and HAs (R25HA, E209HA, E220HA, E226HA, M131HA, M155HA) were analyzed using thermogravimetry–differential scanning calorimetry–quadropole mass spectrometry–isotope ratio mass spectrometry (TG–DSC–QMS–IRMS). Preliminary thermal analysis of the HU fractions showed the presence of quartz, with only 5–10% weight loss. Because of low reactivity (i.e. very low HU content), the HU fraction was not studied further.

2.2. Analysis

TG–DSC–QMS–IRMS evolved gas analysis was carried out by simultaneously coupling the TG–DSC system through an adapter head in the STA 449C Jupiter gas outlet (a) via a heated (200 °C) capilliary to a Netzsch Aeolos QMS 403C MS system (m/z 10–300) and (b) by a separate capilliary via a PDZ ANCA S/L interface module to a PDZ Europa 20:20 IRMS system (Lopez-Capel et al., 2005b, 2006).

An aliquot of sediment (30 mg) or of HA (10 mg) in an Al_2O_3 crucible was heated at 20 °C min^{-1}, from ambient temperature to 650 °C under a flow of 20% O_2 in He (50 cm^3 min^{-1}) and from 650 to 1000 °C under a flow of He only (for carbonate analysis).

For QMS analysis the evolved gas was sampled and analyzed with the mass spectrometer throughout the course of the desorption process. A range from m/z 10 to 300 was scanned and ion intensities of interest [12 (C), 18 (H_2O), 26 (CN), 27 (HCN), 30 (NO), 44 (CO_2 and N_2O), 45 ($^{13}C^{16}O_2$) and 46 (NO_2)] are reported. These species have previously been detected in evolved gases derived during thermal analysis of humic substance (Dell'Abate et al.,

2003) and coal samples (Varey et al., 1996). The number of m/z signals selected gave a temporal resolution of 10 s, corresponding to a temperature change of approximately 2 °C. The signals were exported to the NETZSCH software for analysis vs. temperature. In order to compare the relative intensity of m/z peaks for different samples, the signals from the QMS were normalised to the total intensity (Arenillas et al., 1999).

For IRMS analysis, 6 gas samples were taken during the TG–DSC heating profile between 290 and 900 °C for sediments and between 290 and 600 °C for HAs. These samples correspond to the gas evolved at 350, 510, 540, 620, 700 and 740 °C for sediments and 350, 430, 510, 540, 596 and 620 °C for HAs. These temperatures correspond to reactions detected using DSC. Reference CO_2 gas ($\delta^{13}C$ −29.88‰) was sampled (×3) at the beginning and end of each run.

Bulk carbon isotope values were obtained using off-line measurements with an ANCA S/L Prep unit attached to a PDZ Europa 20/20 isotope ratio spectrometer. Isotope values ($\delta^{13}C$) are expressed in per mil (‰) notation relative to the Pee Dee Belemnite (PDB) standard.

Total carbon (TC), total organic carbon (TOC) and total nitrogen (TN) of bulk sediments and HAs were determined with a Carlo-Erba Elemental Analyser.

To examine sediment mineralogy, samples were analysed with X-ray diffraction using a Phillips – binary XRD with an Xpert MPD diffractometer, scanning from 7° to 70° 2θ.

3. Results and discussion

3.1. Thermal analysis (TG–DSC)

Thermogravimetric (TG) mass loss was observed over various temperature ranges, as shown by more negative slopes in the TG thermograms. The mass loss can be associated with the decomposition of different carbon groups (Lopez-Capel et al., 2005a; Manning et al., 2005; Plante et al., 2005; Dell'Abate et al., 2003) as follows: labile C (200–400 °C), recalcitrant C (400–550 °C), refractory C (550–650 °C) and carbonate (650–900 °C; Fig. 2a).

TG parameters for the sediments and HA samples are summarised in Table 1 and bulk composition parameters are given in Table 2. From the weight losses the relative proportions of labile, recalcitrant and refractory carbon can be estimated. Using Dell' Abate and colleagues (2000) terminology in Table 1, stability indices (Exo 1, Exo 2, and Exo 3) are calculated from the % weight loss corresponding to the first exotherm (aliphatic C and carbohydrate – predominantly cellulose), second exotherm (aromatic C, predominantly lignin and recalcitrant C) and third exotherm (polycondensed forms of lipids and aromatic C) normalised to the total weight loss between 200 and 650 °C (Exotot).

Table 1 shows that the % labile C (Exo1) in sediments decreases, while the percentage of refractory C (Exo3) increases from river to marine samples. The greatest weight loss (46%), is associated with the recalcitrant C (Exo2). Carbonate content was greatest in the two marine sediment samples (M131S and M155S). There was little variation between weight losses for river, estuary and marine (Exo1, 2 and 3) HA fractions. The major weight loss was again associated with recalcitrant organic matter (Exo 2).

The highest amount of refractory carbon was present in the marine samples (M131S, M131HA, M155S and M155HA). Artificial char, from the combustion of labile materials during thermal analysis, could contribute to Exo 3 (Kaloustian et al., 2001; Varey et al., 1996; Lopez-Capel et al., 2006). Soot, originating from fossil fuel and biomass burning, has been found to dominate the black carbon (BC) input in open shelf sediments (Gustafsson and Gschwend, 1998). BC has been detected in HAs before, although concentrations were generally low (2–22%) (Sympson and Hatcher, 2004). It is possible that the high thermal stability of HAs, such as M131HA and M155HA, could result from BC (charred plant materials, soot) and not from native plant material (Haumaier and Zech, 1995).

DSC traces for sediments and HAs (Fig. 2b and c, respectively) showed changes in the contributions of labile C (300–350 °C), recalcitrant C (480–520 °C) and refractory C (560–590 °C) within the samples (riverine, estuarine and marine). The sediments have two exothermic peaks at 340 °C and 510–526 °C. The two marine ones also have an endothermic peak at 690 °C. Most HAs showed a main exothermic peak at 490–520 °C followed by a shoulder at 520–594 °C.

The first DSC exothermic peak for the sediment samples is attributed to decomposition of labile materials, such as cellulose (Kaloustian et al., 2001). Peaks at 300–350°C have previously been observed for soils (Satoh, 1984; Dell'Abate et al., 2002; Lopez-Capel et al., 2005a). This first DSC

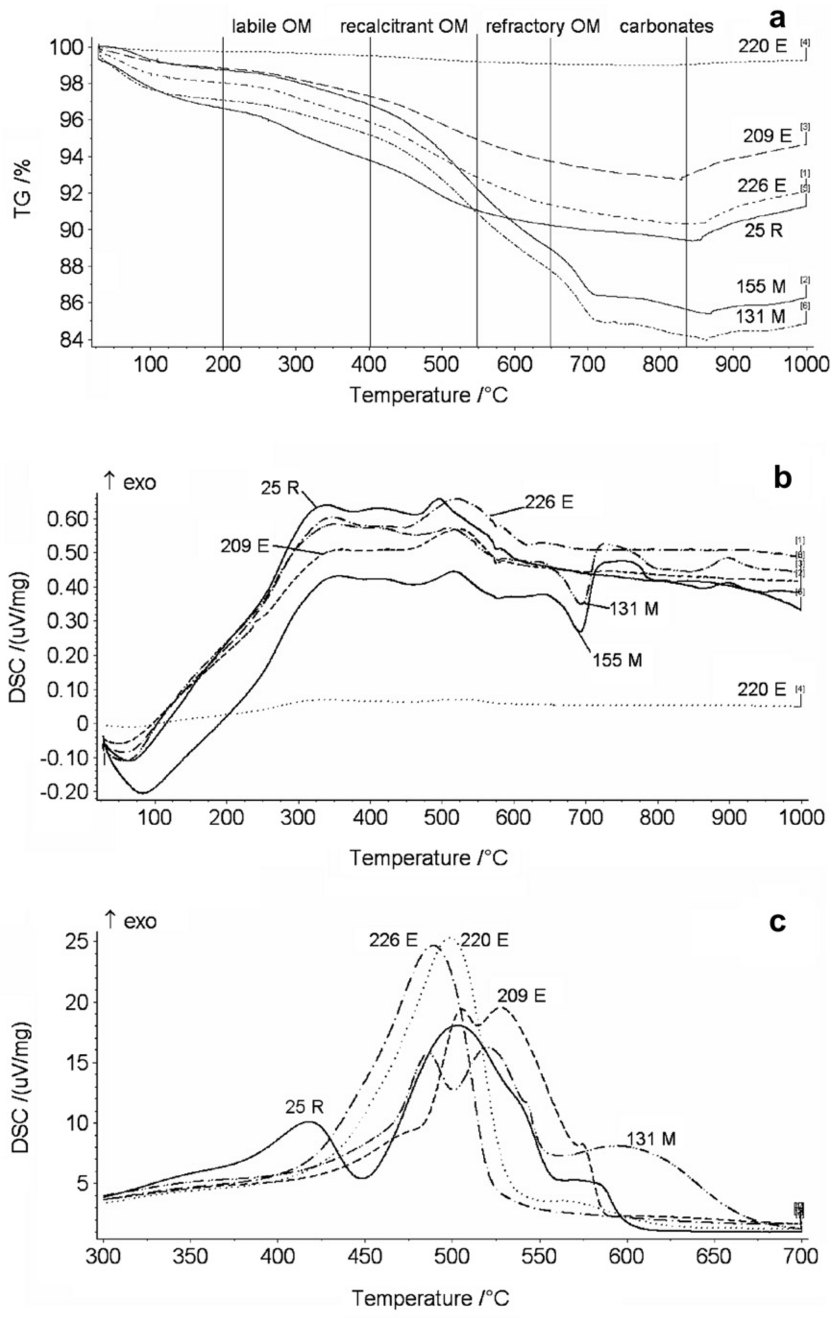

Fig. 2. Thermogravimetric (TG) traces from sediments (a) and differential scanning calorimetric (DSC) traces for sediments (b) and humic acids (c).

peak was not present for the HA samples. This could be due to the extraction procedure. Lipids were extracted prior to HA extraction and may account for a high proportion of the labile material. The lipid content decreased in the same order as Exo1: river < estuary < marine (Table 2). R25HA is the only sample showing a peak at 417 °C which, for solid samples, is attributed to lignin (Lopez-Capel et al., 2006). A shoulder at around 400–450 °C is possibly attributable to recalcitrant material in the sediments. However, this reaction could have been affected by mineral dilution. The second peak

Table 1
Thermogravimetry (TG) and differential scanning calorimetry (DSC) parameters for sediments and humic acids

	Exo 1[a] (%)	Exo 2[b] (%)	Exo 3[c] (%)	Exotot[d] (%)	CaCO3[e] (%)	1st DSC exotherm (°C)	2nd DSC exotherm(°C)	1st DSC endotherm (°C)
Sediment								
R 25S	44.29	43.19	12.52	7.23	1.84	342	496	
E 209S	29.72	47.24	23.03	5.96	1.23	356	524	
E 220S	35.29	47.06	17.65	0.76	0.02	336	526	
E 226S	31.78	46.03	22.19	7.71	2.36	346	522	
M 131S	20.24	46.47	33.30	12.97	8.25	349	512	693
M 155S	19.25	47.45	33.30	13.25	7.77	347	515	690
								3rd DSC exotherm (°C)
Humic acid								
R 25HA	35.23	58.80	5.97	82.53		417	503	584
E 209HA	30.41	59.32	10.27	78.82		None	505	527
E 220HA	33.01	64.87	2.12	82.58		None	499	564 (s)
E 226HA	33.40	65.77	0.83	77.29		None	489	None
M 131HA	32.60	51.09	16.31	85.07		486	520	594
M 155HA	29.08	17.65	53.27	71.02		None	544 (s)	670

[a] Relative weight loss for interval 200–400 °C.

[b] Relative weight loss for interval 400–550 °C.

[c] Relative weight loss for interval 550–650 °C.

[d] Total weight loss for interval 200–650 °C.

[e] Calculated from: mass of calcite = wt. loss (%) from release of CO_2 (650–850 °C) × 100/44 where $CaCO_3$(100RMM) → CaO(56RMM) + CO_2(44RMM).

Table 2
Proportions (±5%) of composition parameters for sediments and humic acids

Sediment	TC[a] (%)		TOC[c] (% C_{org})	TIC[d] (% C_{in})	C_{org}/N_{tot}	Lipids (%)	Humic acids (%)	Humin (%)	Humic acid	TC[a] (%)	TN[b] (%)
R25S	1.84	0.13	1.75	0.11	13.46	0.33	0.53	27.8	R25HA	49.50	4.30
E209S	1.69	0.16	0.77	0.92	4.81	0.16	0.46	51.9	E209HA	49.29	4.07
E220S	1.74	0.19	1.43	0.31	7.53	0.16	0.49	36.7	E220HA	47.31	4.52
E226S	1.19	0.10	1.16	0.03	11.60	0.12	0.58	44.6	E226HA	45.93	4.67
M131S	3.11	0.16	1.17	1.94	7.31	0.07	0.42	40.5	M131HA	49.12	4.66
M155S	3.11	0.15	1.09	2.02	7.27	0.07	0.40	41.7			

[a] Total carbon.

[b] Total nitrogen.

[c] Total organic carbon.

[d] Total inorganic carbon.

at 450–550 °C, in sediments and HAs, is attributed to combustion of the recalcitrant OM and/or char material (Lopez-Capel et al., 2005a,b, 2006). A third exothermic peak was detected for HAs at 550–650 °C, which could be attributed to refractory forms of organic matter. This third peak may reflect decomposition of materials such as BC and/or kerogen; further pyrolytic analysis of this fraction would, however, be needed to confirm this possibility. Exothermic peaks between 507 and 570 °C have been observed for HAs extracted from soils (Dell'Abate et al., 2002) and coal (Varey et al., 1996). Marine sediments (M131S and M155S) had a further endothermic peak at 690 °C, which could be attributed to calcium carbonate.

Proportions of C and N composition parameters for sediments and HAs are summarised in Table 2. There is little variation in TOC and total nitrogen (TN) for both sediment and HA fractions. Thermal analysis was able to differentiate carbon groups in the samples. Exothermic ratios Exo1/Exo2 have been related to C/N ratios (Dell'Abate et al., 2003;

Lopez-Capel et al., 2006). The sediment recalcitrant fraction (Exo 2) negatively correlates with C/N ratio ($r^2 = 0.7518$), TOC ($r^2 = 0.6103$) and lipid content ($r^2 = 0.7042$). There was no correlation between the HA fractions and other parameters in Table 2. C/N ratios from bulk organic matter have been used in many studies to distinguish between phytoplankton and land plant sources, with the former typically yielding low values (4–10) and the latter tending to have ratios >20 (Meyers, 1994, 1997).

Marine systems close to land, and lakes, generally show intermediate C/N values, reflecting mixing of terrestrial and aquatic organic matter (Prahl et al., 1994; Silliman et al., 1996). Increasing or decreasing ratios have therefore been used to infer relative change in organic matter sources for both marine (Calvert et al., 2001; Jasper and Gagosian, 1993) and lacustrine (Kaushal and Binford, 1999; Talbot and Johannessen, 1992) sediments, even though the ratio can increase somewhat upon degradation (Thornton and McManus, 1994).

The range of C/N ratios for all the samples includes values that characterise both aquatic phytoplankton and land plants, but for most suggests that the organic matter represents a mixture of marine and terrestrial carbon. Consequently, proximity to sources of land plant debris, and marine organic productivity should be important controls. This would imply that samples R25S and E226S have a higher terrigenous contribution, while samples E209S, E220S, M131S and M155S have a higher contribution of marine C.

3.2. XRD analysis of sediments

River and estuary particulate material (RPM and EPM) contain aluminosilicate minerals (such as clays), quartz and carbonate. The presence of clay minerals and carbonate may affect the TG–DSC trace for sedimentary organic matter but not for the isolated HA fractions. XRD analysis was used to examine the clay mineralogy of the sediment samples. The resulting diffractograms were compared with those of reference materials and indicated the presence of kaolinite, illite–muscovite, quartz and calcite in all the sediment samples. Dolomite was also detected in riverine and marine sediments and the feldspar albite in estuarine sediments. Although clay minerals were detected in marine sediments, amounts were low and the diffractograms were dominated by quartz and calcite. In order to assess the contribution of the thermal decomposition of

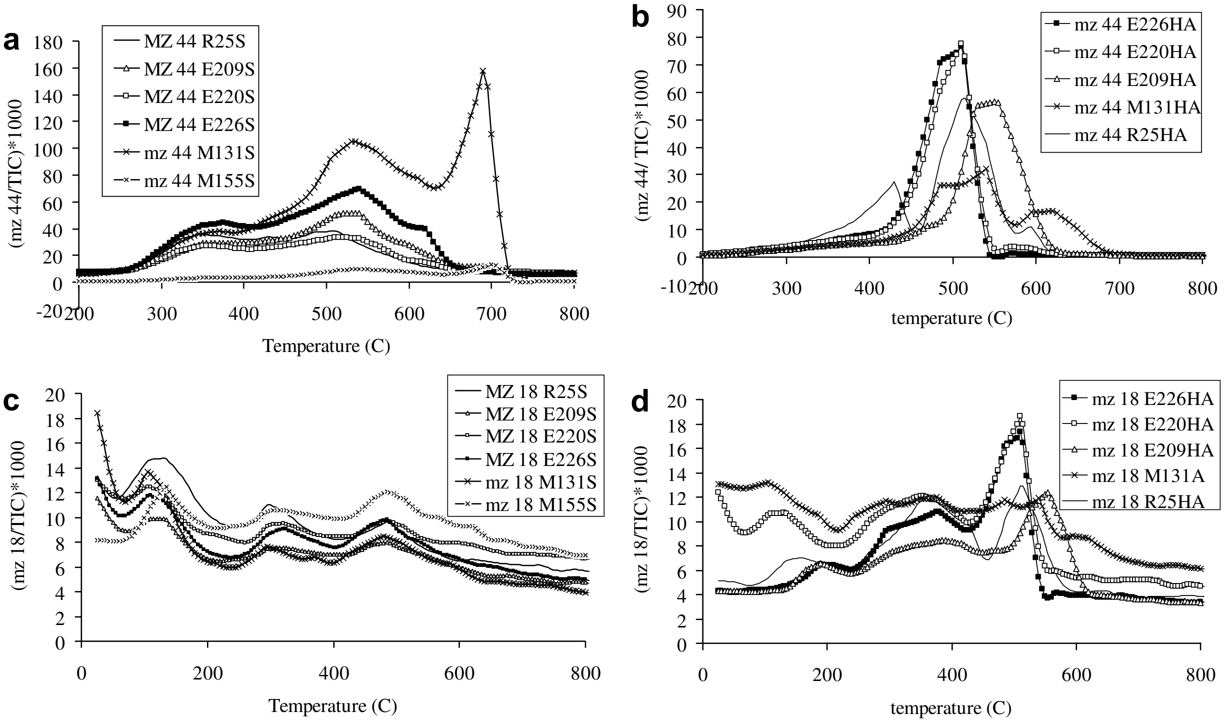

Fig. 3. Thermograms of ion current m/z 44 for (a) sediments and (b) humic acids and m/z 18 for (c) sediments and (d) humic acids.

clay minerals to the exothermic peaks in the temperature ranges 300–650 °C, reference samples of clay minerals known to be present in sediments (determined using XRD) were analysed using TG–DSC under the same analytical conditions as for the sediments. Illite releases water at 440–460 °C and kaolinite at 510–530 °C in endothermic reactions. Quartz undergoes a phase transition at 573 °C as an endothermic reaction with no associated weight loss. TG–DSC of calcite releases CO_2 at 680–700 °C in an endothermic reaction.

3.3. QMS analysis

Sediments and HAs were analyzed using QMS to assess the evolution of gas species which may relate to C dynamics in the sedimentary organic matter (OM) fraction. The only degradation products detected consistently for all samples were CO_2 (m/z 44) and H_2O (m/z 18). Volatiles were released at the lowest temperature (~350 °C), followed by decomposition of recalcitrant OM (450 °C) and refractory OM (500 °C). Similar findings have been reported for soils (Dell'Abate et al., 2003; Lopez-Capel et al., 2005b) and compost (Lopez-Capel et al., 2006).

The relative ion intensities for CO_2 (m/z 44) and H_2O (m/z 18) observed during thermal analysis are presented in Fig. 3. QMS analysis showed that the maximum amount of gas (CO_2) evolved from the combustion was at 510–540 °C followed by a shoulder at 600–620 °C. The exceptions were the river sediment, with maximum amount of CO_2 at 350 °C, and the marine sediments (131 and 155) with the greatest evolution of CO_2 at 700–720 °C. The maximum amounts of evolved H_2O (m/z 18) were at 510–540 °C and at 350 °C for the river sediment samples (Fig. 3). Traces of H_2O were detected at 100–120 °C, 300–350 °C, 510–540 °C and 600–620 °C for all the samples and also at 700–720 °C for the marine sediments 131 and 155.

Gas evolution peaks at the temperature ranges mentioned are associated with the release of free H_2O at 120 °C, with reaction of labile C at 350 °C, recalcitrant C at 510 °C, refractory C at 620 °C and carbonate decomposition at 700 °C. There would also be release of H_2O from sediments at 440 and 520 °C from the decomposition of clay minerals, such as illite and kaolinite, respectively. These may further release OM physically trapped in clay particles (Plante et al., 2005).

3.4. IRMS analysis

There is progressive ^{13}C enrichment for the sediment samples with an increase in marine influence (Fig. 4). Table 3 summarises the $\delta^{13}C$ values of sediments and HAs at various temperature ranges. In general, bulk $\delta^{13}C$ values are approximately 4‰ more negative than those determined using TG–DSC–IRMS (Lopez-Capel et al., 2005b). The isotope ratio for C_3 biomass ranges from −23‰ to −34‰, with an average of ca. −27‰ (Meyers, 1997), while typical marine end member values are −18‰ to −20‰ for $\delta^{13}C_{org}$ (Holtvoeth et al., 2005). Taking into account the systematic 4‰ difference between the TAIRMS methodology and bulk analysis, the river sediments have a terrestrial signal, marine sediments a marine signal and estuary sediments are a mixture of both. All HA fractions have

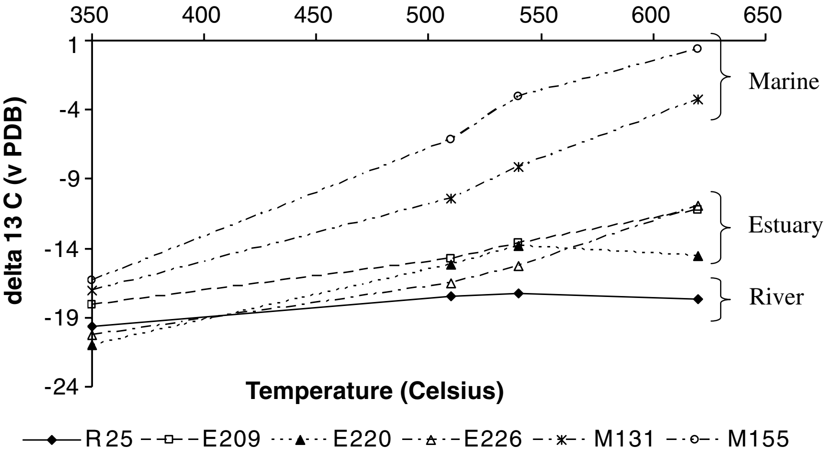

Fig. 4. $\delta^{13}C$ values of sediments during thermal degradation.

Table 3
$\delta^{13}C$ values for sediments and humic acid fractions at various temperatures during thermal degradation

Sample	350 °C	510 °C	540 °C	620 °C	700 °C	720 °C	bulk d 495 13 C
R25S	−19.7	−17.5	−17.2	−17.7	−21.0	−20.9	−23.8
E209S	−18.1	−14.7	−13.6	−11.2	−11.9	−13.5	−19.9
E220S	−20.9	−15.1	−13.8	−14.6	−23.4	−23.5	−22.7
E226S	−20.3	−16.5	−15.3	−10.9	−15.8	−16.5	n.d.
M131S	−17.1	−10.4	−8.17	−3.24	−2.02	−2.02	−9.77
M155S	−16.3	−6.13	−3.01	0.34	−6.20	−7.15	−9.75
	350 °C	430 °C	510 °C	540 °C	595 °C	620 °C	bulk d 495 13 C
R25HA	−18.7	−19.9	−20.5	−20.4	−20.7	−20.9	−24.9
E209HA	−19.9	−20.7	−22.1	−22.1	−21.9	−21.8	−25.4
E220HA	−20.4	−21.1	−22.6	−22.3	−22.1	−22.1	−25.3
E226HA	−18.5	−20.5	−21.7	−21.7	−21.8	−21.8	n.d.
M131HA	−16.2	−17.6	−19.3	−19.3	−19.4	−19.5	−23.0
M155HA	−12.8	−17.4	−19.8	−19.4	−17.7	−16.9	n.d.

n.d. = not determined.

a terrestrial signal, irrespective of the sample type. It is possible that the TG–DSC–IRMS data for whole samples include a contribution from anthropogenic BC or natural combustion products, for which $\delta^{13}C$ values are reported to range from −22.5‰ to −26.5‰ (Glaser et al., 2005).

There is great isotopic variability among the sediments (mean TAIRMS – 12.8‰ ± 4.5) but little variability among the HAs (mean TAIRMS −20.2‰ ± 1.7). Bulk ANCA isotopic values agree with this observation, with mean sediment values of −17.1‰ ± 6.9 and mean HA values of −24.7‰ ± 1.13. Notice that the bulk values for marine sediments were affected by carbonate content and that there is −4.41‰ difference between the ANCA bulk analysis and TAIRMS values. Such a difference between the methodologies has been observed before (Lopez-Capel et al., 2005b, 2006).

Sediments at 350 °C show $\delta^{13}C$ enrichment with an increase in marine influence, which could be partitioned into that due to local high plant input and that due to mineral, algal and non-local macrophyte inputs (Middelburg et al., 1997). Values for marine sediments (M131S, M155S) at 350 °C could be attributed to algal (−17‰) and plankton derived material (e.g. Middelburg et al., 1997). Sediments show $\delta^{13}C$ enrichment with an increase in decomposition temperature (from 350 to 620 °C) for river and estuarine sediments.

The greatest $\delta^{13}C$ difference between the samples was at 540 °C, by way of 14.0‰ between river and marine. This temperature corresponds to the maximum amount of CO_2 evolved from sediment combustion. The river sample $\delta^{13}C$ values range between −17.2‰ and −17.7‰, the estuary ones between −16.5‰ and −13.6‰ and the marine ones between −8.2‰ and −3.0‰. The isotopic enrichment in marine sediments (M131S and M155S) is greater than values reported for marine vegetation. It is possible that isotopic variability in

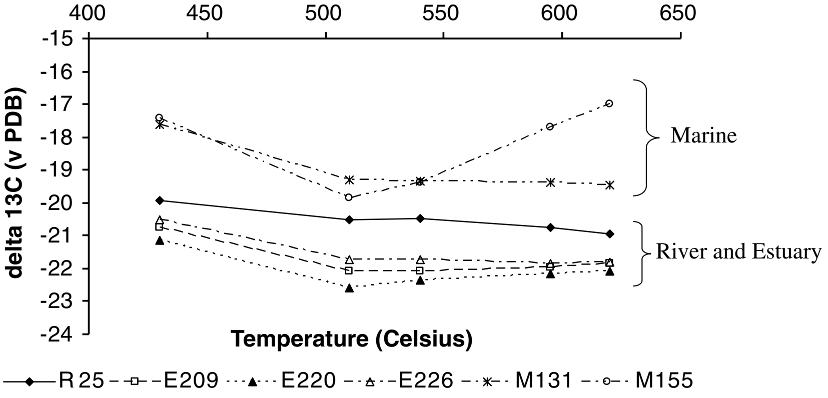

Fig. 5. $\delta^{13}C$ values of humic acid fractions during thermal degradation.

the marine samples could be due to microbial methanogenesis of ROM, probably kerogen. Clayton (1991) described differing isotopic fractionation for the formation of CH_4 from labile and refractory kerogen. When CH_4 formation occurs during OM oxidation, two metabolic pathways operate. The process is kinetically controlled, enriching ^{13}C in the residual CH_4 and ^{12}C in the respired CO_2 (the opposite of CH_4 generation). The fractionation ranges from 1.002 to 1.014, with $\delta^{13}C$ CO_2 values ranging from $-33‰$ to $+18‰$ (Whiticar et al., 1986). This may account for the observed enrichment in ^{13}C. Additionally, carbonate-derived contributions were detected at 700–720 °C for marine samples ($-2.0‰$ for M131S and $-6.2‰$ for M155S), with isotopic values in the range associated with marine carbonate (Gawenda et al., 1999).

The $\delta^{13}C$ values for the HAs show little variation for samples analysed using TG–DSC–IRMS (Fig. 5), with a mean of $-20.2 \pm 1.7‰$. This is consistent with a homogeneous input of terrestrial origin. The HAs from the marine sediment samples are slightly more enriched in $\delta^{13}C$, bearing in mind that values for gas samples at 350 °C are less reliable as the yields were very low at this temperature.

4. Conclusions

In the Huelva coast region, systematic changes have been observed in the proportions and bulk characteristics of sedimentary organic matter. Terrestrial influences, in terms of proportions of labile organic matter and $\delta^{13}C$ values, decrease towards the ocean. In contrast, the extracted humic acids show very consistent compositions in terms of thermal behaviour through the system and have constant $\delta^{13}C$ values.

We conclude that terrestrial humic acids, derived from soils, retain their carbon isotopic composition irrespective of their location in the system. The relative contributions of soil organic matter vary according to the amount of marine input, which includes carbonate minerals in fully marine systems.

This study demonstrates that humic acids can be recognised as a homogeneous C pool within marine sediments, allowing the terrestrial input to be characterised.

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References

Alongi, D.M., 1998. Coastal Ecosystem Processes. CRC Press, Boca Raton, FL.

Arenillas, A., Rubiera, F., Pis, J.J., 1999. Simultaneous thermogravimetric-mass spectrometric study on the pyrolysis behaviour of different rank coals. Journal of Analytical and Applied Pyrolysis 50, 31–46.

Battista, B.M., Lowrie, A., Makarov, V., Moffett, S.J., Somoza, L., 2000. Lateral tectonics in the Gulf of Mexico, Gulf of Cadiz, and the Middle America Trench: impacts on hydrocarbon accumulations. In: Deep-Water Structure and Stratigraphy as a Paired Process/Response System, Expanded Abstracts. American Association of Petroleum Geologists and Society of Economic Paleontologists and Mineralogists (AAPG), Tulsa.

Berástegui, X., Banks, C.J., Puig, C., Taberner, C., Waltham, D., Fernández, M., 1998. Lateral diapiric emplacement of Triassic evaporates at the southern margin of the Guadalquivir Basin, Spain. In: Mascle, A., Puigdefabregas, C., Luterbacher, H.P., Fernández, M. (Eds.), Cenozoic Foreland Basins of Western Europe, vol. 134. Geological Society Special Publications, pp. 49–68.

Bonnin, J., Olivet, J.L., Auzende, J.M., 1975. Structure en nappe a l'ouest de Gibraltar. Comptes Rendus de L'Academie des Sciences 280, 559–562.

Calvert, S.E., Pedersen, T.F., Karlin, R.E., 2001. Geochemical and isotopic evidence for post-glacial palaeoeceanographic changes in Saanich Inlet, British Columbia. Marine Geology 174, 287–305.

Chester, R., 2000. Marine Geochemistry. Blackwell, Oxford, p 506.

Clayton, C., 1991. Carbon isotope fractionation during natural gas generation from kerogen. Marine and Petroleum Geology 8, 232–240.

Dell'Abate, M.T., Benedetti, A., Trinchera, A., Dazzi, C., 2002. Humic substances along the profile of two Typic Haploxerert. Geoderma 107, 281–296.

Dell'Abate, M.T., Benedetti, A., Brookes, P.C., 2003. Hyphenated techniques of thermal analysis for characterisation of soil humic substances. Journal of Separation Science 26, 433440.

Flinch, J., Bally, A., Wu, S., 1996. Emplacement of a passive-margin evaporitic allochthon in the Betic Cordillera of Spain. Geology 24, 6770.

Gawenda, P., Winkler, W., Schmitz, B., Adatte, T., 1999. Climate and bioproductivity control on carbonate turbidite sedimentation (Paleocene to earliest Eocene, Gulf of Biscay, Zumaia, Spain. Journal of Sedimentary Research 69, 1253–1261.

Glaser, B., Dreyer, A., Bock, M., Fiedler, S., Mehring, M., Heitmann, T., 2005. Environmental Science and Technology 11, 3911–3917.

González-Pérez, J.A., González-Vila, F.J., Gonzalo Almendros, G., Knicker, H., 2004. The effect of fire on soil organic matter – a review. Environment International 30, 855–870.

Gustafsson, Ö., Gschwend, P.M., 1998. The flux of black carbon to surface sediments on the New England continental shelf. Geochimica et Cosmochimica Acta 62, 465–472.

Gustafsson, O., Bucheli, T.D., Kukulska, S., Anderson, M., Largeau, C., Rouzaud, J.N., Reddy, J.M., Eglinton, T.I., 2001. Evaluation of a protocol for the quantification of black carbon in sediments. Global Biochemistry 15, 881–890.

Haumaier, L., Zech, W., 1995. Black carbon-possible sources of highly aromatic components of soil humic acids. Organic Geochemistry 23, 191196.

Holtvoeth, J., Kolonic, S., Wagner, T., 2005. Soil organic matter as an important contributor to late Quaternary sediments of the tropical West African continental margin. Geochimica et Cosmochimica Acta 69, 2031–2041.

Jasper, J.P., Gagosian, R.B., 1993. The sources and deposition of organic matter in the Late Quaternary Pygmy Basin, Gulf of Mexico. Geochimica et Cosmochimica Acta 54, 117–132.

Kaloustian, J., Pauli, A.M., Pastor, J., 2001. Kinetic study of the thermal decompositions of biopolymers extracted from various plants. Journal of Thermal Analysis and Calorimetry 63, 7–20.

Kaushal, S., Binford, M.W., 1999. Relationship between C:N ratios of lake sediments, organic matter sources, and historical deforestation in Lake Pleasant, Massachusetts, USA. Journal of Paleolimnology 22, 439–442.

Leinweber, P., Schulter, H.R., Horte, C., 1992. Differential thermal analysis, thermogravimetry and pyrolysis-field ionisation mass spectrometry of soil organic matter in particle-size fractions and bulk soil samples. Thermochimica Acta 194, 175–187.

Lim, B., Cachier, H., 1996. Determination of black carbon by chemical oxidation and thermal treatment in recent marine and lake sediments and Cretaceous–Tertiary clays. Chemical Geology 131, 143–154.

Lopez-Capel, E., Sohi, S., Gaunt, J.L., Manning, D.A.C., 2005a. Use of thermogravimetry–differential scanning calorimetry to characterize modelable soil organic matter fractions. American Journal of Soil Science Society. 69, 136–140.

Lopez-Capel, E., Bol, R., Manning, D.A.C., 2005b. Application of simultaneous thermal analysis mass spectrometry and stable carbon isotope analysis in a carbon sequestration study. Rapid Communications in Mass Spectrometry 19, 3192–3198.

Lopez-Capel, E., Abbott, G.D., Thomas, K.M., Manning, D.A.C., 2006. Coupling of thermal analysis with quadrupole mass spectrometry and isotope ratio mass spectrometry for simultaneous determination of evolved gases and their carbon isotopic composition. Journal of Analytical and Applied Pyrolysis 75, 82–89.

Manning, D.A.C., Lopez-Capel, E., Barker, S., 2005. Seeing soil carbon: use of thermal analysis in the characterization of soil C reservoirs of differing stability. Mineralogical Magazine 69, 425–435.

Martínez de Olmo, W., García-Mallo, J., Leret, G., Serrano, A., Suárez, J., 1984. Modelo tectosedimentario del Bajo Guadalquivir. Proceedings of the II Spanish Geological Meeting 1, 199–213.

Mayer, L.M., Keil, R.G., Macko, S.A., Joye, S.B., Ruttenberg, K.C., Aller, R.C., 1998. Importance of suspended particulates in riverine delivery of bioavailable nitrogen to coastal zones. Global Biogeochemical Cycles 12, 573–579.

McCarthy, P., Malcolm, R.L., 1979. The need to establish a reference collection of humic substances. In: Chesier, S.N., Hertz, H.S. (Eds.), Trace Organic Analysis: A New Frontier in Analytical Chemistry. US National Bureau of Standards, pp. 519–793.

Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. Chemical Geology 114, 289–302.

Meyers, P.A., 1997. Organic geochemical proxies of palaeooceanographic, palaeolimnological, and palaeoclimatic processes. Organic Geochemistry 27, 213–250.

Middelburg, J.J., Nieuwenhuize, J., Lubberts, R.K., Van de Plassche, O., 1997. Organic carbon isotope systematics of coastal marshes. Estuarine, Coastal and Shelf Science 45, 681–687.

Middelburg, J.J., Nieuwenhuize, J., Breugel, P., 1999. Black carbon in marine sediments. Marine Chemistry 65, 245–252.

Plante, A.F., Pernes, M., Chenu, C., 2005. Changes in clay-associated organic matter quality in a C depletion sequence as measured by differential thermal analyses. Geoderma 129, 186–199.

Prahl, F.G., Ertel, J.R., Goni, M.A., Sparrow, M.A., Eversmeyer, B., 1994. Terrestrial organic carbon contributions to sediments in the Washington margin. Geochimica et Cosmochimica Acta 58, 3048–3055.

Satoh, T., 1984. Thermal nature of organo-mineral complex particles and their humic substances. Soil Science and Plant Nutrition 30, 95–104.

Silliman, H.E., Meyers, P.A., Bourbonniere, R.A., 1996. Record of postglacial organic matter delivery and burial in sediments of Lake Ontario. Organic Geochemistry 24, 463–472.

Smith, S.V., Mackenzie, F.T., 1987. The ocean as a net heterotrophic system: Implications for the carbon biogeochemical cycle. Global Biogeochemical Cycles 1, 187–198.

Sohi, S.P., Mahieu, N., Arah, J.R.M., Powlson, D.S., Madari, B., Gaunt, J.L., 2001. A procedure for isolating soil organic matter fractions suitable for modeling. Soil Science Society of America Journal 65, 1121–1128.

Somoza, L., de Andres, J.R., Rey, J., Hernandez-Molina, J., Rodriguez-Vidal, J., Clemente, L., Rodriguez-Ramirez, A., Diaz-del-Rio, V., 1994. Morpho-depositional evolution of the Cadiz Gulf continental shelf: Golca project. In: Proceedings del 1° Simpósio Sobre A Margen Continental Ibérica Atlántica, Lisboa, Portugal.

Sympson, M.J., Hatcher, P.G., 2004. Determination of black carbon in natural organic matter by chemical oxidation and solid-state ^{13}C nuclear magnetic resonance spectroscopy. Organic Geochemistry 35, 923935.

Talbot, M.R., Johannessen, T., 1992. A high resolution palaeoclimatic record for the last 27,500 years in tropical West Africa from the carbon and nitrogen isotopic composition of lacustrine organic matter. Earth and Planetary Science Letters 110, 23–37.

Thornton, S.F., McManus, J., 1994. Application of organic carbon and nitrogen stable isotope and C/N ratios as sources indicators of organic matter provenance in estuarine systems: evidence from the Tay Estuary, Scotland. Estuarine, Coastal and Shelf Science 38, 219–233.

Turner, R.C., Schnitzer, M., 1962. Thermogravimetry of the organic matter of a Podzol. Soil Science 93, 225–232.

Varey, A., Hindmarsh, C.J., Thomas, K.M., 1996. The detection of reactive intermediates in the combustion and pyrolysis of coals, chars and macerals. Fuel 75, 164–176.

Whiticar, M.J., Faber, E., Schoell, M., 1986. Biogenic methane formation in marine and fresh water environments: CO_2 reduction vs acetate fermentation isotope evidence. Geochimica et Cosmochimica Acta 5, 693–709.