A review of coastal palaeoclimate and relative sea-level reconstructions using $\delta^{13}C$ and C/N ratios in organic material

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Abstract

Holocene reconstructions of relative sea-level (RSL) and environmental change in the coastal zone have become progressively more numerous since the importance of assessing possible future sea-level rises has become apparent. Traditionally this has been achieved using a combination of biological and physical indicators (e.g. pollen, diatoms, foraminifera, grain size, etc.). In some circumstances, microfossils can be rare or absent from Holocene sediments and in these cases carbon isotope ratios ($\delta^{13}C$) and organic carbon to total nitrogen ratios (C/N) can be used because they have the potential to provide information as to the origin of organic material preserved in coastal environments. The distinction in $\delta^{13}C$ and C/N of the various sources of carbon to estuarine sediments has led to its wide use as a tracer of carbon pathways and storage in estuaries. More recently these techniques have been applied to Holocene sediments to decipher changes in palaeocoastal environments and thus position relative to sea-level and/or palaeoriver discharge, which have direct relevance to palaeoclimate. This paper reviews the studies that have utilised this technique and explores examples from a wide range of coastal environments (saltmarshes, estuaries, lagoons, isolation basins and fjords). It also discusses the potential alteration of geochemical signatures as a result of decompositional processes. Organic matter decomposition has been shown to change sediment $\delta^{13}C$ and C/N values and thus an understanding of the processes involved is necessary in order to have confidence in the palaeoenvironmental interpretation of Holocene $\delta^{13}C$ and C/N. Decompositional shifts in C/N, and particularly $\delta^{13}C$, can occur over a relatively short time-period, however it is the direction of change in $\delta^{13}C$ and C/N, rather than absolute values, that is key for interpreting changes in relative sea-level and thus such changes are commonly preserved.

1. Introduction

Sheltered coastal environments (e.g. estuaries, lagoons, bays, inlets, rias, isolation basins) commonly preserve thick sequences of Holocene sediments, offering the opportunity to investigate past climate, sea-level and land-level changes, as well as more local environmental changes. The sediment characteristics of tide-dominated environments, such as organic content (Long et al., 1999), particle size (Tanner, 1991), geochemistry (Freitas et al., 2003) and luminescence properties (Plater and Poolton, 1992) are commonly related to altitude within and above the tidal frame. Traditionally, wide use has been made of microfossils to reconstruct past sea-level changes and palaeoenvironments in coastal areas. The distribution of pollen (Innes et al., 1996), diatoms (Zong and Horton,

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1998), foraminifera (Horton, 1999) and testate amoeba (Charman et al., 2002) in the contemporary inter-tidal zone is largely governed by ground elevation within the tidal frame (Zong and Horton, 1998; Horton, 1999). Many microfossils are spatially restricted in the coastal zone (e.g. Shennan et al., 2000); foraminifera are restricted to the inter-tidal and sub-tidal zones, pollen to inter-tidal and supra-tidal zones, and diatoms (although occupying all three zones) tend to be sparse in some supra-tidal environments. Additionally, as microfossils are susceptible to chemical and mechanical damage, it is not uncommon to encounter sediment deposits containing a discontinuous microfossil record that is in various stages of preservation, restricting coastal palaeoenvironmental reconstructions (e.g. Shennan et al., 1999; Gonzalez et al., 2000; Wilson et al., 2005b). The absence of microfossils in sediments seriously hinders Holocene RSL reconstructions.

Emery et al. (1967) were among the first to use carbon isotope ratios to distinguish between saltmarsh sediments and freshwater peats in the coastal zone. They analysed freshwater peat from sequences in the northeastern United States and compared the $\delta^{13}C$ ratios to modern saltmarsh sediments at nearby Cape Cod, demonstrating that there was a significant difference in $\delta^{13}C$ values (~12‰) [carbon isotope ratios ($^{13}C/^{12}C$) are usually presented as per mille (‰) deviations ($\delta^{13}C$) from (V)PDB; (Vienna)Pee Dee Belemnite]. At this time, the processes creating the differences in $\delta^{13}C$ were poorly understood (see Chmura and Aharon, 1995, for review). Later, as it was realised that the isotope composition of organic carbon varies between a wide range of sources (e.g. Megens et al., 2002), focus switched to the application of carbon isotopes to identify different sources of carbon input to coastal and marine environments. For example, estuarine saltmarshes and tidal flats receive sediment from several different sources, including fluvial- and marine-derived minerogenic sediment and particulate organic matter (POM), organic matter from saltmarsh plants and other biota (Luternauer et al., 1995). This has resulted in the widespread use of $\delta^{13}C$ analysis in saltmarsh sediment provenance studies (e.g. Haines, 1976; Ember et al., 1987; Chmura and Aharon, 1995), carbon budget determinations (e.g. Middelburg et al., 1997; Andrews et al., 2000) and studies that aim to assess the origin of marine sediments (e.g. Torgersen and Chivas, 1985; Bird et al., 1995). The weight ratio of organic carbon to total nitrogen (C/N) is normally measured alongside $\delta^{13}C$, and can also help to distinguish carbon sources. Occasionally, the weight ratio is converted into an atomic/molar ratio by multiplying by

1.17; however, the ratio used is not always stated. Here, C/N refers to the weight ratio unless stated otherwise. As coastal deposits form a significant proportion of global carbon storage (Bauer and Druffel, 1998), such sediment provenance studies have dominated the literature (e.g. Fry and Sherr, 1989; Middelburg et al., 1997; Andrews et al., 2000).

One complication that may affect the reliability of $\delta^{13}C$ and C/N as faithful recorders of the source of organic material in sediments is the process of decomposition. Early loss of labile material in vascular vegetation detritus can lead to significant changes to $\delta^{13}C$ in sediments but is usually insufficient to prevent the distinction between organic sources. The loss of organic carbon in sediments as decomposition progresses may eventually complicate the use of C/N ratios (Sampei and Matsumoto, 2001), as small changes in %C or %N will cause relatively large changes in C/N ratios. The extension of the $\delta^{13}C$ and C/N technique to reconstruct changes in sea-level and palaeoclimate is relatively new and this review aims to explore the use of carbon isotopes and C/N ratios as an alternative proxy for such studies in coastal environments.

2. $\delta^{13}C$ and C/N values in coastal environments

Coastal sediments receive organic material from autochthonous sources (derived from in situ sources, such as plants growing on the sediment surface) and allochthonous sources (organic material transported to the sediment from elsewhere, such as with the tide or a river). For example, in saltmarsh sediments the dominant autochthonous component is derived from in situ vascular plant material. Highly organic-rich surface sediments develop at the most landward limit, where infrequent tidal inundation allows extensive vegetation cover. In contrast, tidal flats are frequently inundated for lengthy periods, vascular vegetation is absent, and allochthonous, tidal-derived POM is the dominant source of organic material in the surface sediments (Fig. 1). Allochthonous sources include fluvial and marine particulate organic carbon (POC; mainly derived from freshwater or marine phytoplankton and terrigenous organic matter) and dissolved organic carbon (DOC). The provenance of organic matter sources will be environment-dependent; for example, phytoplankton may be an allochthonous source to saltmarshes but an autochthonous source in tidally restricted environments (such as lagoons). This aside, the main sources of organic matter have distinctly different $\delta^{13}C$ and C/N compositions (see below). Bulk organic $\delta^{13}C$ and C/N should therefore in theory reflect the relative amounts of the sources of organic matter (Fry and Sherr,
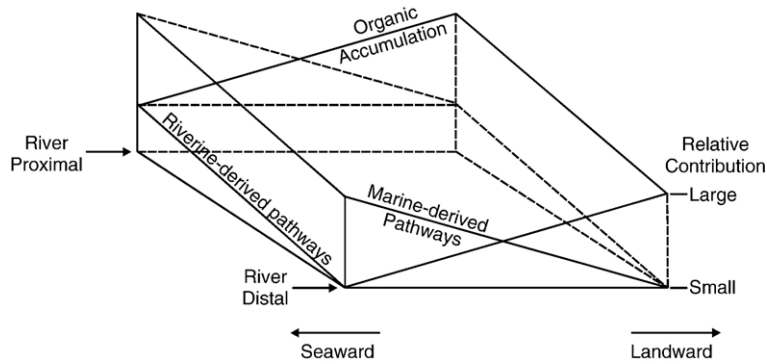
Fig. 1. Relative contributions and provenance of sediments on an estuarine saltmarsh (reproduced with permission from Elsevier from Luternauer et al., 1995).

1989). Much work has focused on saltmarshes, estuarine saltmarshes in particular, where the mixing of terrestrial plant input and marine input is key (e.g. Middelburg et al., 1997). In environments that are not regularly flushed by fresh and/or marine water, such as lagoons or isolation basins, autochthonous sources of carbon will dominate the supply to the sediments rather than the balance between autochthonous and allochthonous, unless

there are regular breaches of the basin by the sea. The range in $\delta^{13}C$ and C/N values of the main sources is discussed below (Fig. 2).

2.1. Terrestrial plants

During CO_2 fixation, plants preferentially take up ^{12}C by diffusion resulting in organic matter that is
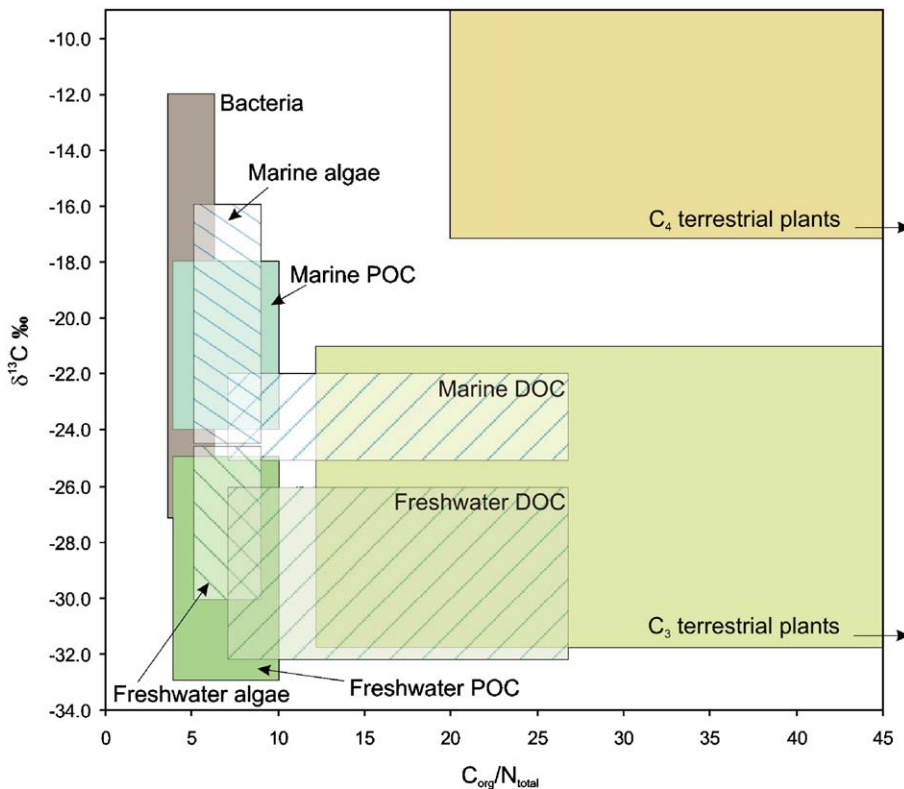

Fig. 2. Typical $\delta^{13}C$ and C/N ranges for organic inputs to coastal environments (data compiled from: Bordovskiy, 1965a; Haines, 1976; Deines, 1980; Sherr, 1982; Schidlowski et al., 1983; Meyers, 1994; Peterson et al., 1994; Schleser, 1995; Tyson, 1995; Middelburg and Nieuwenhuize, 1998; Chivas et al., 2001; Raymond and Bauer, 2001; Cloern et al., 2002; Goñi et al., 2003; and references therein).

depleted in ^{13}C compared to the atmosphere (current atmospheric CO_2 $\delta^{13}C_{PDB} = -8‰$, Keeling et al., 1995). Terrestrial plants that use the C_3 photosynthetic pathway constitute about 90% of all plants, and typically have $\delta^{13}C$ values that range between $-32‰$ and $-21‰$ (Deines, 1980), with freshwater aquatic plants typically having values that range from $-50‰$ to $-11‰$ (Osmond et al., 1981; Keeley and Sandquist, 1992). C_4 plants have $\delta^{13}C$ values of around $-13‰$ (range $= -17‰$ to $-9‰$; Deines, 1980) resulting from a much smaller fractionation (5.7‰) associated with CO_2 fixation by the enzyme phosphoenol pyruvate carboxylase (PEP) (e.g. O'Leary et al., 1992). A third group of plants, CAM photosynthesisers (crassulacean acid metabolism; this includes most succulents), are able to incorporate inorganic carbon using both the C_3 photosynthetic pathway and a C_4-like pathway, typically resulting in a wide range of $\delta^{13}C$ values ($-11‰$ to $-28‰$; Schleser, 1995), depending on which pathway is dominant.

The type of plant present on a sediment surface will to some degree depend on elevation above the tidal frame and clearly defined vegetation zones are common in coastal environments (Gray, 1992). Saltmarsh species vary with elevation within the tidal frame as a function of their salinity tolerance. On European marshes, salt-tolerant species such as *Puccinellia maritima* and *Salicornia europaea* are able to survive on lower saltmarshes, with less salt tolerant species such as *Phragmites australis* and *Agrostis stolonifera* preferring marsh areas above high water. In North America, common lower saltmarsh, salt-tolerant plants include *Spartina alterniflora* in particular, and on the upper saltmarsh various *Typha* sp. and *Scirpus* sp. (e.g. Middelburg et al., 1997). Plants that have adapted to tolerate very saline conditions are commonly of C_4 or CAM type.

Terrestrial vegetation normally has relatively high C/N ratios of >12 (Prahl et al., 1980) as it is composed predominantly of lignin and cellulose, which are nitrogen poor. C_3 vascular plant material has C/N ratios of around 12 and over (Tyson, 1995), where as C_4 grasses typically have C/N ratios of above 30 (Meyers, 1994). Plant C/N values can be highly variable in a small area mostly due to large fluctuations in the nitrogen content of plants.

2.2. Aquatic plants, bacteria and algae

The largest control on aquatic plant $\delta^{13}C$ is whether the plant utilises bicarbonate (HCO_3^-) or dissolved CO_2 (Benedict et al., 1980). Dissolved CO_2 has lower $\delta^{13}C$ values ($-8‰$ if in equilibrium with atmospheric CO_2) than HCO_3^- ($\sim 0‰$) (Keeley and Sandquist, 1992) and phytoplankton will preferentially take up CO_2 until this source is exhausted (Degens et al., 1968; Falkowski, 1991). Because the ratio of CO_2 to HCO_3^- is a function of ambient pH, there is consequently less CO_2 available in the marine environment than in freshwater, hence marine plankton will have higher $\delta^{13}C$ values, as it will need to utilise predominantly HCO_3^- (Fig. 2).

Some studies have suggested that in addition to vascular plant material, algae and bacteria may also have an impact on the $\delta^{13}C$ and C/N of coastal sediments (e.g. Malamud-Roam and Ingram, 2001). Peterson et al. (1980) argue that the $\delta^{13}C$ values of living *S. alterniflora* ($-11‰$ to $-13‰$) and underlying surface sediments ($-18‰$ to $-24‰$) are different in some saltmarshes of the eastern USA because of the presence of bacteria in the sediment. Cloern et al. (2002) analysed a cyanobacterial bloom in San Francisco Bay saltmarsh sediments, which had a $\delta^{13}C$ range of $-26.6‰$ to $-28.0‰$, suggesting that bacteria in large quantities is likely to lower sediment $\delta^{13}C$ values in environments that contain some C_4 plants. Although bacteria found on saltmarshes typically have relatively low $\delta^{13}C$ values, bacteria found in other coastal environments can have $\delta^{13}C$ values ranging from $-12‰$ to $-27‰$ depending on their origin (Coffin et al., 1989). If algae are abundant they can also have significant effects on the bulk $\delta^{13}C$ ratio, but as algae also have a large range in $\delta^{13}C$ values, their significance can be difficult to assess (also see Section 2.3). Freshwater algae in C_3-dominated environments tend to have lower $\delta^{13}C$ values ($-26‰$ to $-30‰$; Schidlowski et al., 1983; Meyers, 1994) than marine algae ($-16‰$ to $-23‰$; Haines, 1976; Meyers, 1994) but algae in C_4-vegetation catchments can have relatively high $\delta^{13}C$ values ($\leq 16‰$) (Chivas et al., 2001). As the range in $\delta^{13}C$ values between 'end-member' environments in coastal zones without C_4 vegetation is just a few ‰, the presence of bacteria and algae may affect the ability to distinguish organic carbon sources, and ultimately affect coastal palaeoenvironmental reconstructions. Some workers have attempted to overcome this by using compound-specific $\delta^{13}C$ in sediments (e.g. Bull et al., 1999).

C/N is usually analysed alongside $\delta^{13}C$ and provides an additional indication of the relative contributions of organic matter from contrasting sources, as bacteria and algae have C/N ratios that are distinct from terrestrial vegetation. Bacterial action can introduce N to the sediment and thus decrease C/N ratios (Rice and Hanson, 1984). However, bacteria and algae contain a high

level of labile compounds and decompose more rapidly than vascular plants (Valiela et al., 1985) and therefore become less significant to bulk organic δ^{13}C and C/N (e.g. Andrews et al. 1998). Bacteria and algae typically have low C/N ratios of 4–6 and <10, respectively (Meyers, 1994; Tyson, 1995). In coastal areas with high algal production, distinguishing between organic matter sources based on δ^{13}C can be difficult even with the help of C/N (see Chmura and Aharon, 1995; Chivas et al., 2001).

2.3. Particulate organic carbon

POC is a broad term that encompasses suspended organic matter such as phytoplankton (e.g. diatoms, dinoflagellates, green algae, euglenoides), and to a lesser extent, zooplankton. This is mixed with terrestrial organic matter of both natural (e.g. plant detritus) and anthropogenic origin (e.g. sewage) in coastal environments. Fluvial $\delta^{13}C_{POC}$ values are a reflection of the relative contributions from freshwater phytoplankton ($-25‰$ to $-30‰$) and particulate terrestrial organic matter ($-25‰$ to $-33‰$) (e.g. Salomons and Mook, 1981; Barth et al., 1998; Middelburg and Nieuwenhuize, 1998), in these examples reflecting the prevalence of C_3 vegetation in the catchment. Slightly higher $\delta^{13}C_{POC}$ values occur in catchments with a mixture of C_3 and C_4 vegetation. Indeed, $\delta^{13}C_{POC}$ is highly responsive to seasonal changes in the relative proportions of C_3 and C_4 catchment vegetation (Weiguo et al., 2003). Marine POC typically ranges from $-21‰$ to $-18‰$ (Peters et al., 1978; Wada et al., 1987; Middelburg and Nieuwenhuize, 1998), reflecting marine phytoplankton (Yamaguchi et al., 2003). Because of this, suspended $\delta^{13}C_{POC}$ values commonly increase systematically towards the mouth of an estuary (Section 3.1). In addition to variations in phytoplankton δ^{13}C from the differing sources of inorganic carbon utilised in marine and freshwater environments, phytoplankton δ^{13}C may also vary as a result of temperature, availability and partial pressure of CO_2 (Fontugne and Duplessy, 1981; Bentaleb et al., 1996) and by species (Wong and Sackett, 1978). Phytoplankton, which tends to be nitrogen rich, has relatively low C/N ratios of between 5 and 7 (Meyers, 1994; Tyson, 1995) resulting in marine organic C/N values typically <8 (Bordovskiy, 1965a).

2.4. Dissolved organic carbon

Most of the carbon in the oceans occurs in the form of dissolved organic carbon (DOC) (Hedges et al.,

1997). In rivers and estuaries, on average, 60% of carbon transported is in solution, whilst 40% is in the particulate phase (Raymond and Bauer, 2001). DOC is principally derived from phytoplankton in the marine environment and a mixture of terrigenous organic matter and phytoplankton in the fluvial environment (Rashid, 1985). In a study of $\delta^{13}C_{DOC}$ in several estuaries in the US, Peterson et al. (1994) found that the marine end-members had $\delta^{13}C_{DOC}$ values of between $-22‰$ and $-25‰$, whereas the freshwater end-members were between $-26‰$ and $-28‰$. This pattern of $\delta^{13}C_{DOC}$ in estuarine waters, reflecting fluvial and marine source material, has been observed by others, for example, Van Heemst et al. (2000), Goñi et al. (2003) and Otero et al. (2003). Otero et al. (2003) found that humic substances accounted for 50% to 80% of riverine DOC and 5% to 15% of marine DOC in the Altamaha and Satilla Estuaries in southeastern USA. Although the processes involved in the formation of humic and fulvic acids are not sufficiently understood (Hatcher and Spiker, 1988; Hedges, 1988; Gleixner et al., 2002), the provenance of humic substances may be determined by their δ^{13}C values. Terrigenous humic substances will retain δ^{13}C values in the C_3 plant range for C_3 plant-dominated catchments, whilst the δ^{13}C value of marine humic substances will reflect their phytoplankton precursors (Harvey and Boran, 1985).

3. Palaeoenvironmental applications

3.1. Estuarine environments

3.1.1. Saltmarsh C_3/C_4-based palaeosalinity

Estuarine salinity can be related to relative sea-level height during the Holocene and to regional rainfall, resulting in changes to river discharge and thus freshwater input. As an evolutionary adaptation to water stress and high salinity, some grasses have evolved to photosynthesise using the C_4 pathway, enabling them to survive on brackish/saline marshes. Such C_4 grasses include: *Spartina patens*, *S. alterniflora*, *S. foliosa* and *Distichlis spicata*. In regions where both C_3 and C_4 plants are native to coastal marshes, the sediment δ^{13}C composition can directly relate to the ratio of C_3/C_4 plants and thus provide a proxy for Holocene palaeoenvironmental change (Fry et al., 1977; Ember et al., 1987; Middelburg et al., 1997).

The application of these relationships to past variations in sea-level and river discharge has been particularly successful in the San Francisco Basin (Chmura

and Aharon, 1995; Byrne et al., 2001; Malamud-Roam and Ingram, 2004). The estuary is large and the watershed takes in 40% of the State of California, fed by the Sacramento and San Joaquin Rivers (Ingram et al., 1996a). Here, following the rapid postglacial sea-level rise culminating ~6000 ^{14}C yr BP, thick sequences of estuarine marsh sediments have accumulated in the bay and record interchanging phases of saltmarsh and freshwater marsh deposition in response to variations in mid/late Holocene sea-levels and river discharge (Byrne et al., 2001; Ingram et al., 1996a,b). Early studies sought to demonstrate that the δ^{13}C composition of the surface soil organic matter (SOM) on the marsh reflected the distribution of C_3 and C_4 plants growing in the local area (Stout et al., 1975; Chmura et al., 1987; Chmura and Aharon, 1995). Malamud-Roam and Ingram (2001) calculated that there was a direct correlation between the proportion of C_4 plants growing on a marsh and the $\delta^{13}C_{SOM}$ of the surface sediment ($R^2 = 0.75$) in San Francisco Bay. If the relative proportions of modern C_4 saltmarsh and C_3 freshwater marsh plants are reflected in surface sediment δ^{13}C (e.g. McPherson et al., 1993; Boutton et al., 1998), then a record of marsh

palaeovegetation and associated palaeosalinity will be contained in downcore changes in δ^{13}C (e.g. DeLaune, 1986; Byrne et al., 2001).

Byrne et al. (2001) compared bulk organic δ^{13}C values in a 3.5-m core from a brackish tidal marsh in the north of San Francisco Bay with the diatom and pollen record (Fig. 3). This multi-proxy study of the conditions in the bay over the last 3000 yr, enabled them to distinguish changes in δ^{13}C due to climatic (salinity), human and ecological effects. Changes in the amount of freshwater discharge flowing into the bay were identified as the key reason for changes in salinity and thus vegetation type on the marshes. There is a clear transition in the bay between marine water at the Golden Gate Bridge (33‰ salinity) to the freshwater input in the upper estuary (0‰ salinity), hence salinity anywhere in the estuary is primarily a function of both variations in river discharge and RSL.

Such studies assume that the vegetation preserved in the SOM has its origins in the plants growing in the area local to the SOM. Malamud-Roam and Ingram (2004) tried to strengthen this assumption by only measuring the organic fraction greater than 125 μm,
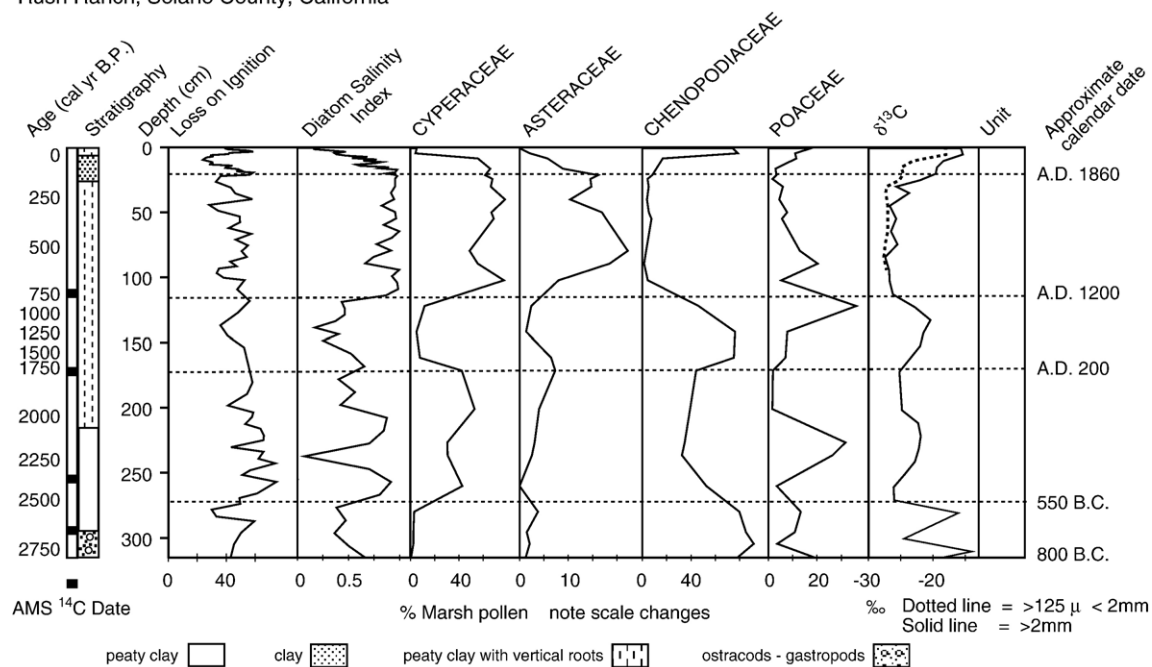

Fig. 3. % Loss on ignition, diatom salinity index (low values suggest high salinity), selected pollen taxa (% of total marsh pollen) and bulk organic δ^{13}C values from Rush Ranch core, San Francisco Bay. This research was able to distinguish between periods of high salinity (and thus low river discharge/low rainfall), e.g. 2750 to 2500 cal. yr BP; 1700 to 730 cal. yr BP and since 1930 AD and intermediate periods of low salinity and high discharge/rainfall. During high salinity periods, relatively high δ^{13}C values (c. −15‰) suggest the presence of C_4 grasses such as *Spartina foliosa* and salinities of 15–20‰. The most recent dry period may be due to water management related to agriculture and the diversion and storage of water further up the basin. Reproduced with permission from Elsevier from Byrne et al. (2001).

assuming that smaller sized organic fragments may have travelled considerable distances to the site of SOM. Contrary to this, Byrne et al. (2001) analysed fine (125 μm–2 mm) and coarse (>2 mm) bulk organic fractions and found that it was the coarse fraction that may have contained organic material that had been transported from elsewhere. Down-core trends in coarse sample $\delta^{13}C$ were vertically offset from fine fraction $\delta^{13}C$ trends, which they interpreted as evidence for *Distichlis* (C_4 taxon) root penetration from above (Fig. 3). *Distichlis* has resistant roots and thus will be present in the coarse but not the fine fraction, thus causing an offset between the grain sizes.

There are some problems with the simple C_3/C_4 mixing model that may interfere with its use as a palaeoenvironmental indicator (Chmura and Aharon, 1995). Some C_4 plants inevitably grow on freshwater marshes as well as on saline marshes, for example, *Spartina cynosuroides*. Also CAM plants will complicate bulk $\delta^{13}C$ mixing models as they can have $\delta^{13}C$ values inter-

mediate to C_3 and C_4 end-members or will reflect the dominant form of metabolism used. *Salicornia* sp., for example, is a common CAM plant in hypersaline environments which can have $\delta^{13}C$ values of $-25‰$ to $-27‰$, suggesting it predominantly utilises the C_3 pathway (Kwak and Zedler, 1997). However, these problems can commonly be overcome by pollen analysis (e.g. Malamud-Roam and Ingram, 2004). Hypersaline environments can also encourage edaphic algal growth (including diatoms and a variety of green, blue-green and yellow-green algae) and this can lead to algae forming a significant proportion of autochthonous carbon input (at least 60–70% in some cases, Zedler, 1980; Sullivan and Moncreiff, 1990). Finally, where sediments receive a significant proportion of allochthonous material (such as tidal-derived phytoplankton), then this could decrease sedimentary $\delta^{13}C$ values (marine $\delta^{13}C$ values generally range from $-21‰$ to $-18‰$), making it difficult to use vegetation-mixing models on saline marshes (Chmura and Aharon, 1995).

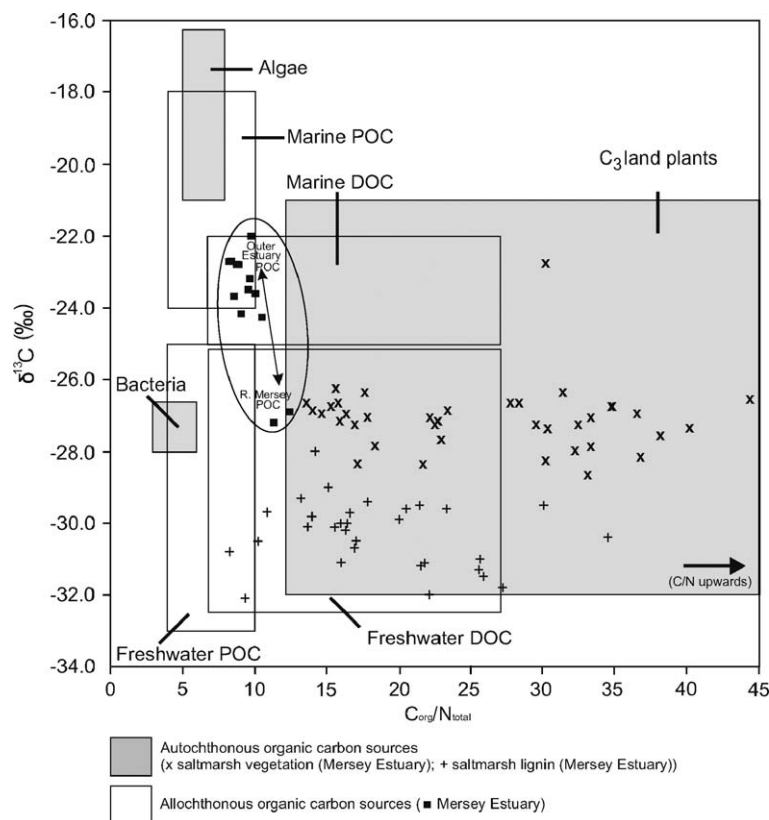Fig. 4. $\delta^{13}C$ and C/N ratios of autochthonous (C_3 vascular vegetation, marine algae and saltmarsh bacteria) and allochthonous (marine and freshwater POC and DOC) organic matter sources in saltmarsh sediments from the Mersey Estuary. The data fields are compiled from various saltmarsh studies (Haines, 1976; Deines, 1980 (and references therein); Salomons and Mook, 1981; Sherr, 1982; Peterson et al., 1994; Tyson, 1995 (and references therein); Twiddy, 1996; Barth et al., 1998; Middelburg and Nieuwenhuize, 1998; Raymond and Bauer, 2001 (and references therein); Cloern et al., 2002; Goñi et al., 2003) . Adapted from Wilson et al. (2005a) with permission from Elsevier.
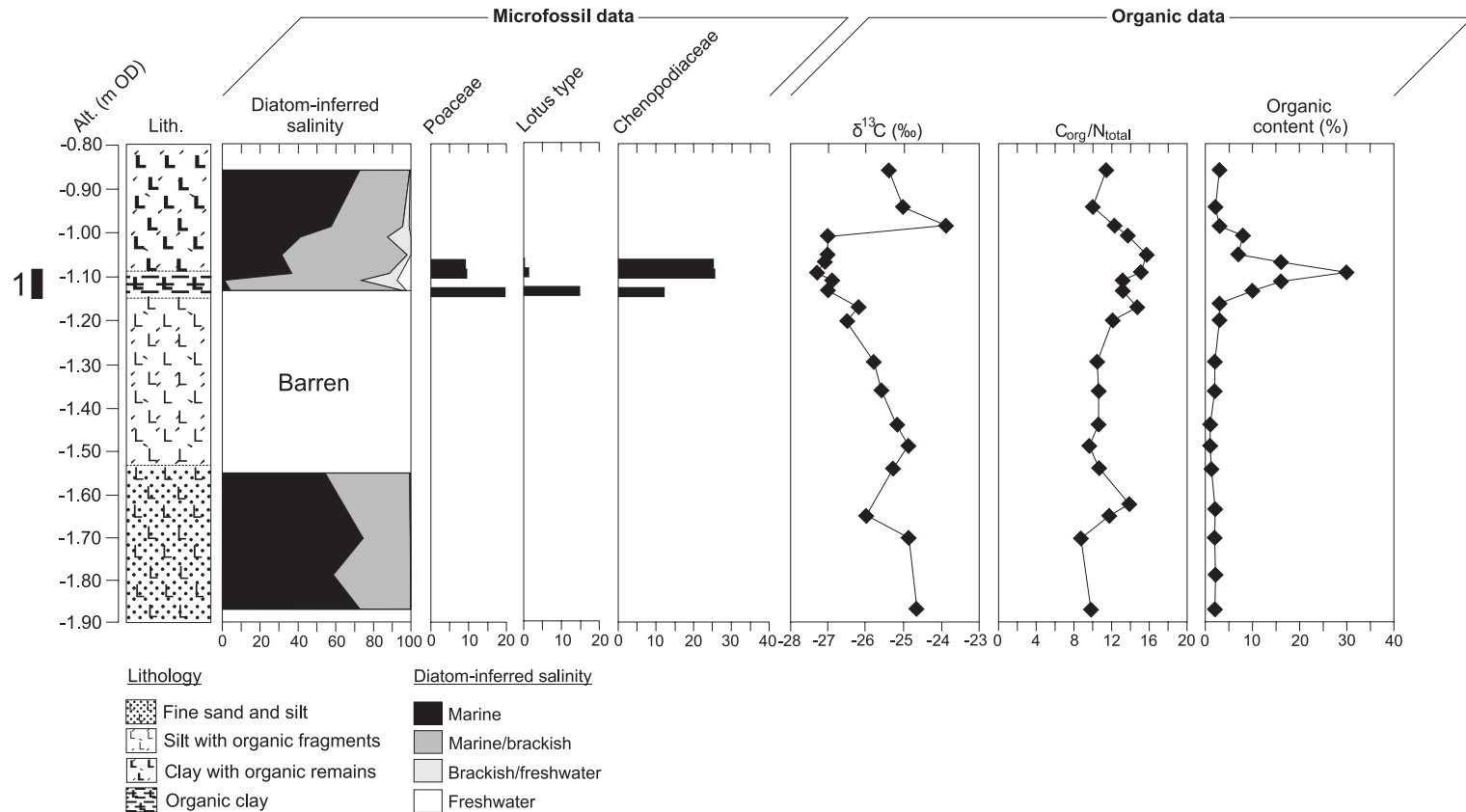
Fig. 5. Holocene sediment core section from Ince Marshes (black bar marked 1 = 7430–7250 cal. yr BP). Diatoms are summarised into the categories outlined in Vos and De Wolf (1993) and are presented as a percentage. Pollen abundance is expressed as a percentage of total land pollen, excluding aquatics, Pteriodophytes and *Sphagnum*. Only key pollen taxa are shown. The microfossil record is incomplete due to poor preservation, with the transition from sub-tidal channel conditions between −1.87 m and −1.55 m above ordnance datum (OD) and saltmarsh conditions between −1.13 m and −1.01 m OD unresolved. The absence of microfossils in sediments adjacent to saltmarsh units has important implications for Holocene RSL reconstruction. Saltmarsh sediments are invaluable as sea-level index points (e.g. Peltier et al., 2002) because they occur between distinctive tidal zones, but their integrity as a sea-level index point partly relies on the evidence of a gradual increase, or removal, of marine conditions in the adjacent sediments, otherwise an eroded contact, or a depositional hiatus, is indicated. Interpreted within the context of the changing lithology, the δ^{13}C and C/N data reveal a gradual reduction in tidal-derived POC and a greater contribution of organic carbon from C_3 vascular vegetation leading up to the saltmarsh sediment unit, as δ^{13}C decreases from −24.9‰ to −26.2‰ and C/N increases from 10.7 to 14.7. This change in the source of organic carbon is consistent with an increase in ground elevation within the tidal frame, which may have resulted from a fall in RSL (Wilson et al., 2004, Wilson et al., 2005a). Reproduced from Wilson et al. (2005a) with permission from Elsevier.

3.1.2. Saltmarsh C_3-based palaeosalinity

In many mid or high latitudes, including much of northern Europe, C_4 saltmarsh vegetation has either been relatively recently introduced or is rare (e.g. Preston et al., 2002). Consequently, the range in organic matter $\delta^{13}C$ values in coastal deposits is greatly reduced, hindering the use of $\delta^{13}C$ as a coastal change and sea-level indicator. Wilson et al. (2005a,b) provide an alternative isotope-based method for identifying changes in relative sea-level from regions without native C_4 coastal vegetation communities. In the Mersey Estuary, UK, they measured the $\delta^{13}C$ and C/N ratios of C_3 saltmarsh plants and suspended estuarine POC; the two main sources of organic carbon in inter-tidal sediments (Fig. 4). They showed that ground elevation in relation to the tidal frame was a key factor controlling bulk surface inter-tidal sediment $\delta^{13}C$ and C/N. Supra-tidal and high saltmarsh sediments consisted almost entirely of organic carbon derived from the overlying C_3 vegetation, and sub-tidal and tidal-flat sediments consisted almost entirely of tidal-derived POC. The different sources of organic carbon in high saltmarsh and sub-tidal sediments resulted in differing bulk sediment $\delta^{13}C$ values ($-27.8‰$ and $-22.8‰$, respectively) and C/N ratios (11.6 and 9.3). In light of these modern observations, $\delta^{13}C$ and C/N analysis can be applied to coastal sediment cores from regions without native C_4 saltmarsh vegetation communities (e.g. Northern Europe) to determine changes in Holocene RSL. This is demonstrated in a sediment core taken from the Mersey Estuary (Fig. 5).

As well as changes in the relative proportions of different organic matter sources, there are environmental variables that can affect C_3 plant $\delta^{13}C$ such as drought stress (Farquhar et al., 1989), salinity stress (Seemann and Critchley, 1985), vapour pressure deficit (Turney et al., 1999) and a small temperature fractionation effect. Many of the established relationships between C_3 plant $\delta^{13}C$ and exogenous factors have direct application to palaeoenvironmental and palaeo-climatic reconstructions (e.g. Krishnamurthy and Epstein, 1990; Turney et al., 1999). For example, studies have demonstrated a significant relationship between soil salinity and C_3 halophyte $\delta^{13}C$ at inland sites and under laboratory conditions. Neales et al. (1983) found a maximum shift in $\delta^{13}C$ from $-26.1‰$ to $-20.0‰$ in the leaves of *Disphyma clavellatum*, a succulent halophyte endemic to southern Australia, as the salinity of the root environment was increased. Inter-tidal salinity gradients result in a clearly defined zonation of vegetation communities in saltmarshes (Gray, 1992). Twiddy (1996) suggested that an inter-tidal salinity gradient might cause a systematic reduction of $\delta^{13}C$ in C_3 plant communities with increasing elevation within the tidal frame. If so, measurement of plant macrofossil $\delta^{13}C$ in Holocene coastal sediment cores may be used to reconstruct changes in saltmarsh communities, and thus salinity. However, an investigation into the $\delta^{13}C$ composition of saltmarsh vegetation zones at Kentra Bay, Scotland, found no such relationship between $\delta^{13}C$ of C_3 saltmarsh plant species and salinity and large variations in $\delta^{13}C$ between species (up to 4‰) in the same saltmarsh zones, together with significant seasonal variations in individual species (Twiddy, 1996). This disparity is most probably a reflection of the degree of exposure to salinity, with plants in inland saline areas (e.g. saline lakes) subject to continued exposure, whereas saltmarsh plants are subject only to periodic fluctuations in salinity. Twiddy (1996) reasoned that for the higher saltmarsh plants from Kentra Bay, photosynthesis may have been restricted to periods when precipitation had reduced the concentration of marine-derived salts in the local sediment. In light of these findings, this technique may produce more promising results for saltmarshes in coastal areas with lower precipitation, although the value of this technique in reconstructing coastal palaeoenvironments and RSL change is questionable when changes in palaeoprecipitation are considered.

In terms of coastal palaeoenvironmental reconstruction, the application of isotopes to distinguish palaeoenvironments in the sediment record has had mixed results (Andrews et al., 2000; Wilson et al., 2005b). Although a relatively simple task in areas with C_4 and C_3 plants, there is a lower range of $\delta^{13}C$ values in C_3 marshes, and decompositional-induced alteration of bulk sediment $\delta^{13}C$ values becomes a greater complication (Wilson et al., 2005b; Section 4). However, Andrews et al. (2000) demonstrated that the environmental facies present in the sediment deposits of the Humber Estuary, UK, had diagnostic geochemical (carbon, nitrogen and sulphur) signatures and $\delta^{13}C$ values (Fig. 6). In the Mersey Estuary, $\delta^{13}C$ and C/N values were measured for a range of Holocene coastal palaeoenvironments, identified through microfossil analysis, and the data showed a good correspondence between the microfossil, geochemical and isotopic data (Wilson et al., 2005b). However, the Holocene $\delta^{13}C$ values differed from modern environment equivalent values by up to 3.7‰, presumably because of decomposition (Section 4), suggesting that 'signature' $\delta^{13}C$ and C/N values could not be assigned to environmental facies.
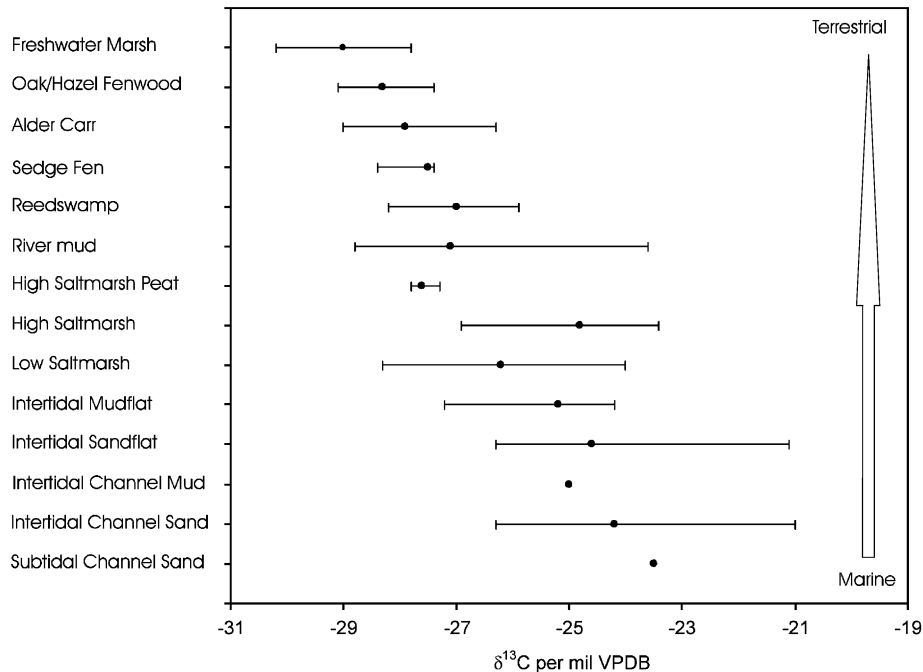
Fig. 6. Mean $\delta^{13}C_{org}$ and range of Holocene environmental facies from Humber estuarine sediment deposits. Redrawn from Andrews et al. (2000).

3.1.3. River-dominated estuaries

A gradient of suspended POM $\delta^{13}C$ and C/N commonly occurs along the axis of poorly mixed estuaries (Section 2.3). For example, in the Schelde Estuary on the Netherlands–Belgium border, upper and lower estuarine $\delta^{13}C$ differs significantly ($-28.9‰$ and $-20.1‰$, respectively; Middelburg and Nieuwenhuize, 1998). Similar values have been observed in the Great Ouse Estuary and the Mersey Estuary, UK (e.g. Fichez et al., 1993; Wilson et al., 2005a). In contrast to $\delta^{13}C$, POM C/N tends to decrease systematically towards the mouth of an estuary. For example, in the Mersey Estuary, outer estuarine POM C/N (8.3) is much lower than POM C/N just beyond the tidal limit (11.3). Slightly higher fluvial C/N (12.4) and outer estuarine C/N (8.7) are observed during the following low tide, highlighting the greater reach of freshwater phytoplankton and terrigenous POM.

Despite early decomposition of planktonic material (Section 4), the systematic shift in $\delta^{13}C$ and C/N along the axis of poorly mixed estuaries is commonly preserved in the sedimentary record. Moreover, analysis of the sediments will represent average $\delta^{13}C$ and C/N over several years at each location along the axis, depending on the depth of the surface sediment sample, thus integrating seasonal fluctuations in $\delta^{13}C$ and C/N. For example, Hunt (1970) measured surface sediment $\delta^{13}C$ in the rivers and estuaries along the entire Atlantic Coast of the United States. He also measured near-shore and continental shelf sediments and found that in most of the 32 rivers studied, river mouth sediment $\delta^{13}C$ was around $-20‰$, whilst for sediments several kilometres upstream, $\delta^{13}C$ was around $-26‰$. Furthermore, Shultz and Calder (1976) demonstrated a correlation between the reach of terrigenous organic carbon from the river mouth, manifest in near-shore sediments in the form of lower $\delta^{13}C$, and the volume of river discharge. This gradient in $\delta^{13}C$ and C/N between fluvial and marine sediments is well established. For example, in the Winyah Bay Estuary, USA, Goñi et al. (2003) showed that suspended POM atomic C/N fell from 13 in Upper Winyah Bay to 6 in Lower Winyah Bay. This gradient in C/N was retained in the sediments, which dropped from 14 to 6 between the upper and lower bay. In contrast, sediment $\delta^{13}C$ rose from $-26.3‰$ to $-22.7‰$ between these two zones (Goñi et al., 2003). Similar patterns in $\delta^{13}C$ and C/N have been observed in numerous estuaries across the world (e.g. Sackett and Thompson, 1963; Salomons and Mook, 1981; Thornton and McMannus, 1994; Ruttenberg and Goñi, 1997; Andrews et al., 1998; Middelburg and Nieuwenhuize, 1998; Zong et al., in press). The gradient in $\delta^{13}C$ and C/N may be absent in some estuaries for a number of reasons, including efficient sediment mixing (Graham et al., 2001), or the presence of numerous organic matter sources with differing $\delta^{13}C$

values, such as C_4 plant detritus in terrigenous POM (Ruttenberg and Goñi, 1997). Consequently, a comprehensive survey of estuarine suspended and surface sediment $\delta^{13}C$ and C/N is a prerequisite for successful palaeoenvironmental investigations.

The existence of a gradient in sediment $\delta^{13}C$ and C/N along the axis of many poorly mixed estuaries has enormous potential for palaeoenvironmental reconstruction. For example, bulk sediment $\delta^{13}C$ and C/N analysis of estuarine core material may be employed to determine changes in Holocene RSL. Alternatively, in estuaries with a large fluvial input, $\delta^{13}C$ and C/N may be used in combination to reconstruct Holocene palaeoriver discharge. This approach has already been adopted using both strontium and oxygen isotopes (which exhibit distinct marine and fluvial end-member values) in numerous estuaries around the world with impressive results (e.g. Ingram and Sloan, 1992; Ingram and DePaolo, 1993; Ingram et al., 1996a,b; Aguirre et al., 1998; Parra et al., 1998; Ricken et al., 2003). However, $\delta^{13}C$ and C/N has only very recently been applied in estuaries to reconstruct palaeoriver discharge (Zong et al., in press), and is yet to be employed in this fashion for Holocene RSL reconstruction.

Zong et al. (in press) analysed $\delta^{13}C$ and C/N alongside diatom distributions in surface sediments along the axis of the Pearl River Estuary in southern China. The gradual transition from diatom flora characteristic of fully marine conditions at the margins of the South China Sea to flora characteristic of near fully freshwater conditions in the inner estuary was mirrored in sediment $\delta^{13}C$ and C/N. Based on the strong relationship between modern diatom flora, $\delta^{13}C$, C/N and water salinity; Zong et al. (in press) were able to reconstruct the Holocene palaeodischarge history of the Pearl River Estuary by applying these techniques to an estuarine sediment core (Fig. 7).

3.2. Lagoons

Organic $\delta^{13}C$ and C/N values have been successfully applied to lagoonal deposits to detect palaeoenvironmental changes as a result of Holocene RSL fluctuations (Müller and Mathesius, 1999; Müller and Voss, 1999; Yamamuro, 2000). Lagoons are typically shallow water bodies partially separated from the sea by a physical barrier (sandbanks, shingle bars, etc.) and most are highly sensitive to sea-level changes. Most lagoons will receive freshwater via river inflow and seawater through narrow inlets, but unlike estuaries, lagoons are not continuously flushed by fresh and marine water and therefore autochthonous organic matter (in situ plankton,

macrophytes and marginal terrestrial plants) is often the most significant organic source to the sediments. There may be some problems specific to lagoons and similar environments where autochthonous input is dominant. For instance, Yamamuro (2000) examined a series of surface sediments from two large connected brackish lagoons (both c. 80 km^2) in southwestern Japan using C, N and phosphorus (P) concentrations (atomic) and $\delta^{13}C$ and $\delta^{15}N$. The eutrophic conditions gave C/N ratios of 8.7 to 11.4 in the surface sediments; suggesting a high proportion of plankton input relative to terrestrial plants. The $\delta^{13}C$ values in surface sediments decreased with increasing distance from the only seawater inlet to the lagoon ($p < 0.001$). For example, surface sediment $\delta^{13}C$ was $-21.7‰$, 2.4 km from the inlet and $-23.9‰$, 32.1 km from the inlet. Yamamuro (2000) postulated that the $\delta^{13}C$ results indicated freshwater end-member mixing with the seawater, either from freshwater plankton using ^{13}C-depleted dissolved inorganic carbon (DIC) or terrestrial plant material. In order to test this, he measured N/P ratios for a range of phytoplankton found currently growing in each lagoon and compared this to the surface sediment N/P ratios. The dominant, bloom-forming phytoplankton in each lagoon had very similar N/P ratios to the surface sediment, suggesting that the dominant freshwater carbon input was from phytoplankton. The phytoplankton $\delta^{13}C$ values were salinity dependent in these environments, varying due to the source of the DIC that was fixed by the phytoplankton (Section 2.3). As C/N ratios were not directly affected by DIC and marine and freshwater phytoplankton have similar C/N ratios, C/N and $\delta^{13}C$ surface sediment values did not correlate in this study ($p > 0.2$). In estuaries, the mixing of terrestrial plant input and marine input is frequently more important to the carbon supply to the sediments than variation within autochthonous sources alone and thus C/N and $\delta^{13}C$ commonly correlate (e.g. Thornton and McManus, 1994).

Other problems with using C/N in lagoonal environments are highlighted by a study of a 20 m sediment core from the Nakaumi Lagoon, southwest Japan. Here, Sampei and Matsumoto (2001) investigated the effect of inorganic N levels on C/N as most studies assume that the commonly measured C_{org}/N_{total} is roughly equivalent to C/N_{org} and thus % N_{inorg} is minor. The c. 8000 ^{14}C yr C/N curve has two peaks of >15, whereas the rest of the values lie between 8 and 12. Under normal circumstances, this could be interpreted as two periods where terrestrial input increased relative to plankton-dominated conditions. However, the C/N ratios vary from other measured organic proxies: C/N_{org} and % N_{inorg}, but show similar trends to % C_{org} and
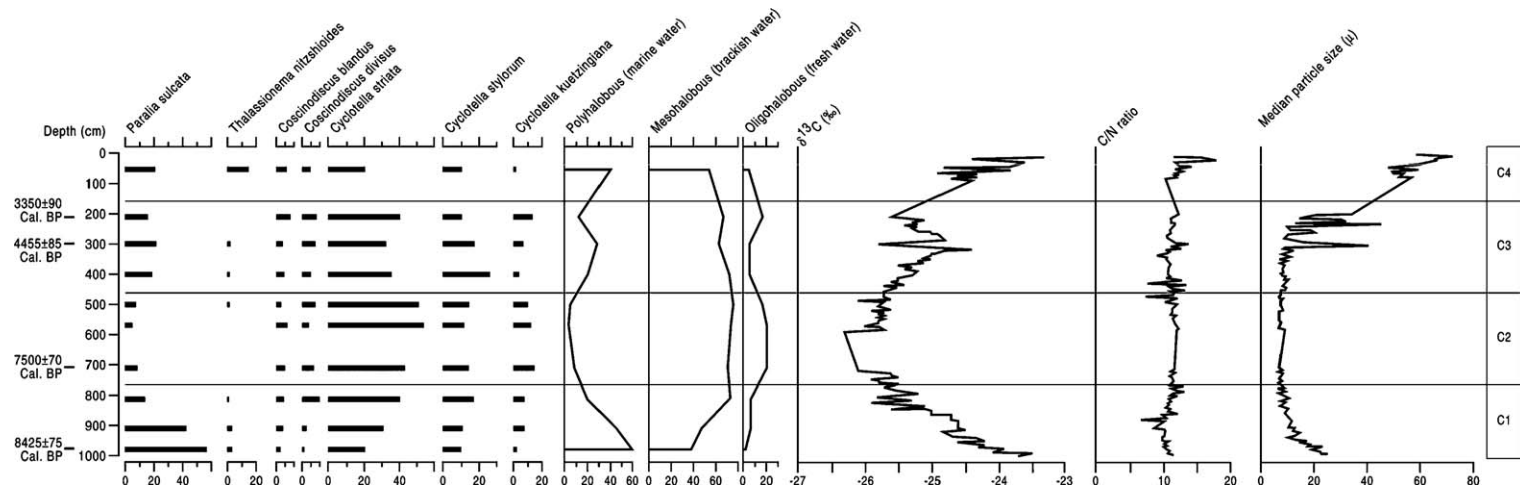
Fig. 7. Diatom distribution (%), median particle size, $\delta^{13}C$ and C/N from a sediment core from the Pearl River Estuary, southern China reveal an increase in freshwater flux from 8425 to 7500 cal BP, with a strong freshwater flux continuing into the middle Holocene, before weakening throughout the middle to late Holocene. There is a close agreement between the $\delta^{13}C$ and C/N record and the diatom record, despite their responding to different variables (organic source as opposed to salinity), thus allowing greater confidence in palaeoenvironmental interpretations. © 2002 Edward Arnold (Publishers) Ltd. (Zong et al., in press, www.hodderarnoldjournals.com).

% N_{total}. High levels of N_{inorg} throughout the core (~0.04 wt.%) have the effect of lowering the C/N ratio to a point where it decreases when either N_{total} or C_{org} decreases and this is especially effective when C_{org} is less than 1%. These circumstances led Sampei and Matsumoto (2001) to argue that C/N was unreliable as a source indicator when % organic C was low. These findings stress the importance of multi-proxy carbon and nitrogen indices in trying to separate out the variations in particular components.

High levels of phytoplankton also led to problems when using C/N as an indicator of changes in organic sources in the lagoon. By modelling the relationship between the relative proportions of terrestrial and planktonic organic matter and C/N ratios, Sampei and Matsumoto (2001) were able to demonstrate clearly that the relationship was nonlinear and C/N is much less sensitive to changes in planktonic input in environments where it is proportionately high (Fig. 8). Clearly, these findings have far reaching consequences for the use of C/N as a source indicator in other coastal environments.

Müller and Mathesius (1999) and Müller and Voss (1999) compared the C/N and $\delta^{13}C$ of modern plants, macrophytes and plankton to Holocene sediments for a chain of coastal lagoons (and lagoonal basins) in the southern Baltic Sea region. The lagoons are currently separated from the Baltic Sea by low barrier islands, which have developed since the mid-Holocene. Breaches of the lagoons by the sea occasionally occur via sills or outlets. They measured C/N and $\delta^{13}C$ in the western and eastern parts of the 1000 km² Oder Estuary lagoon (approximately the last 8000 yr of sedimentation). C/N was generally >12 for both parts of the estuary, typical of terrestrial organic material dominance (Müller and Mathesius, 1999), and together with low $\delta^{13}C$ values of between −25‰ and −30‰, is indicative of freshwater-derived organic material (Müller and Voss, 1999). As seen in the previous examples, coastal lagoons can also have macrophytes and plankton as sources of autochthonous input in addition to terrestrial plant inputs. As macrophytes have relatively high C/N and $\delta^{13}C$ ratios and plankton correspondingly low ratios, Müller and Mathesius (1999) and Müller and Voss (1999) found it difficult to assess intermediate sedimentary $\delta^{13}C$ values. Lower C/N and $\delta^{13}C$ in the mid to late Holocene are interpreted as an increase in freshwater algae in the lagoon, coinciding with a quiescent phase following sand spit development. Particularly low C/N values in the upper 70 cm of the western estuary core are postulated as being linked to less macrophyte input but increasingly more phytoplankton input due to eutrophication, seen elsewhere along the Baltic coastal lagoons (Müller and Mathesius, 1999). Although they attached little confidence to such conclusions, the studies were successful in distinguishing between different environments during the Holocene, which included lacustrine peat phases ($\delta^{13}C=-29.1‰$, Eastern Oder Estuary 6500 BP), sandy shallow lake environments with some aquatic macrophyte input ($\delta^{13}C$ −24.8‰, high C/N ratios >12: Greifswalder Bodden core, Late Glacial) and lagoonal phases following sand spit formation (see above). Although similar patterns were seen in different lagoons, many behaved differently (Müller, 2002), suggesting that individual studies need careful calibration work to be able to relate them to regional RSL changes.

3.2.1. Isolation basins

The ability of $\delta^{13}C$ and C/N to record changes in the source of organic matter in C_3-dominated systems has resulted in their application to isolation basin sediments as a proxy of shoreline displacement during the Late Quaternary (e.g. Chivas et al., 2001; Westman and Hedenström, 2002; Mackie et al., 2005). Isolation basins are natural rock depressions that have been separated from the sea due to falls in RSL. They are extremely important as they provide long, high-resolution records of RSL change reaching back to the Late Devensian (e.g. Shennan et al., 1999), and contribute to isostatic adjustment models. In a similar way to lagoons, isolation basins may be connected to the sea intermittently over a period of time depending on their height relative to sea-level.

As in UK estuaries, isolation basins (common on the west coast of Scotland), are naturally C_3-vegetated environments and Holocene RSL studies have traditionally relied on microfossil-based palaeoenvironmental reconstructions (e.g. Shennan et al., 2000). Mackie et al. (2005) measured a range of plants, freshwater aquatics and surface sediment samples from around marine and freshwater contemporary isolation basins in western Scotland to characterise end-member values for $\delta^{13}C$ and C/N ratios. They found that the surface sediment values reflected a mixture of the end-member ratios from the range of modern inputs measured and thus concluded that the dominant controlling variable on $\delta^{13}C$ and C/N surface sediment was carbon source. $\delta^{13}C$ and C/N should therefore be a reliable proxy for past changes in basin salinity and RSL. This was tested by comparing a Holocene profile of $\delta^{13}C$ and C/N from bulk organics with published diatom analyses from Upper Loch nan Eala, an infilled isolation basin (Fig. 9). By making reference to the contemporary

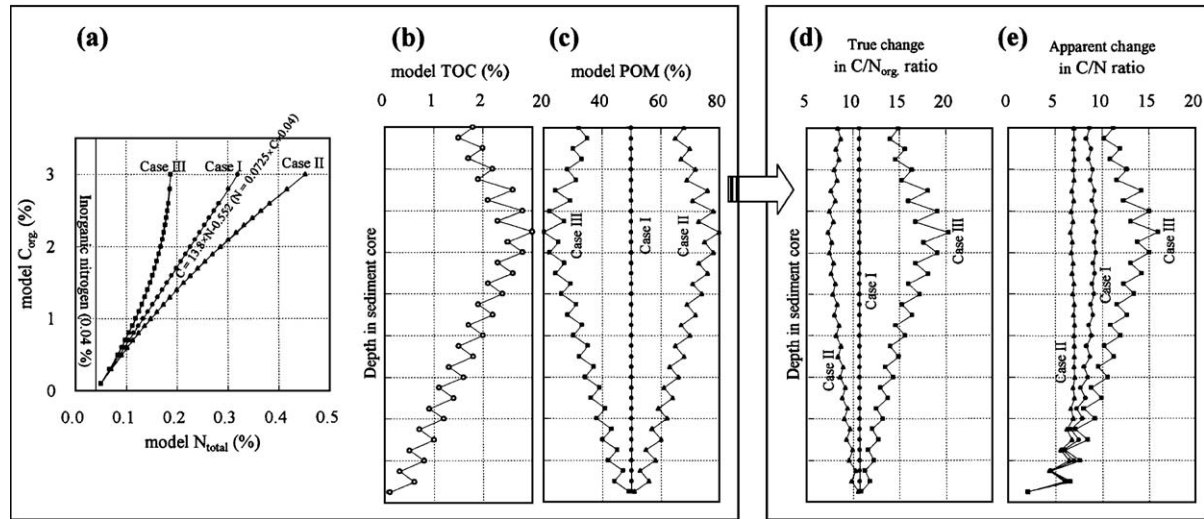Fig. 8. Nakaumi Lagoon, southwest Japan. (a) Model plots of sediment C_{org} content vs. sediment N_{tot} including 0.04% N_{inorg}. (b) Modelled % TOC vs. depth. (c) Modelled % planktonic organic matter (POM) vs. depth, expressed by proportion of carbon. (d) True change in C/N of the modelled sediment. (e) Apparent change in C/N of the modelled sediment (the C/N ratios of POM and terrestrial organic matter (TOM) were assumed to be 6 and 50, respectively). Changes in proportion of POM were simulated at rates of 0/0.1% C_{org} (case I), 1/0.1% C_{org} (case II) and −1/0.1% C_{org} (case III) from the base of the modelled sediment core from a starting POM/TOM ratio of 1. For example, increasing the proportion of planktonic OM from 10% to 20% leads to a decrease in C/N of 8, whereas increasing the proportion of planktonic OM from 80% to 90% leads to a decrease in C/N of only 1.2. Reproduced with permission from Sampei and Matsumoto (2001).
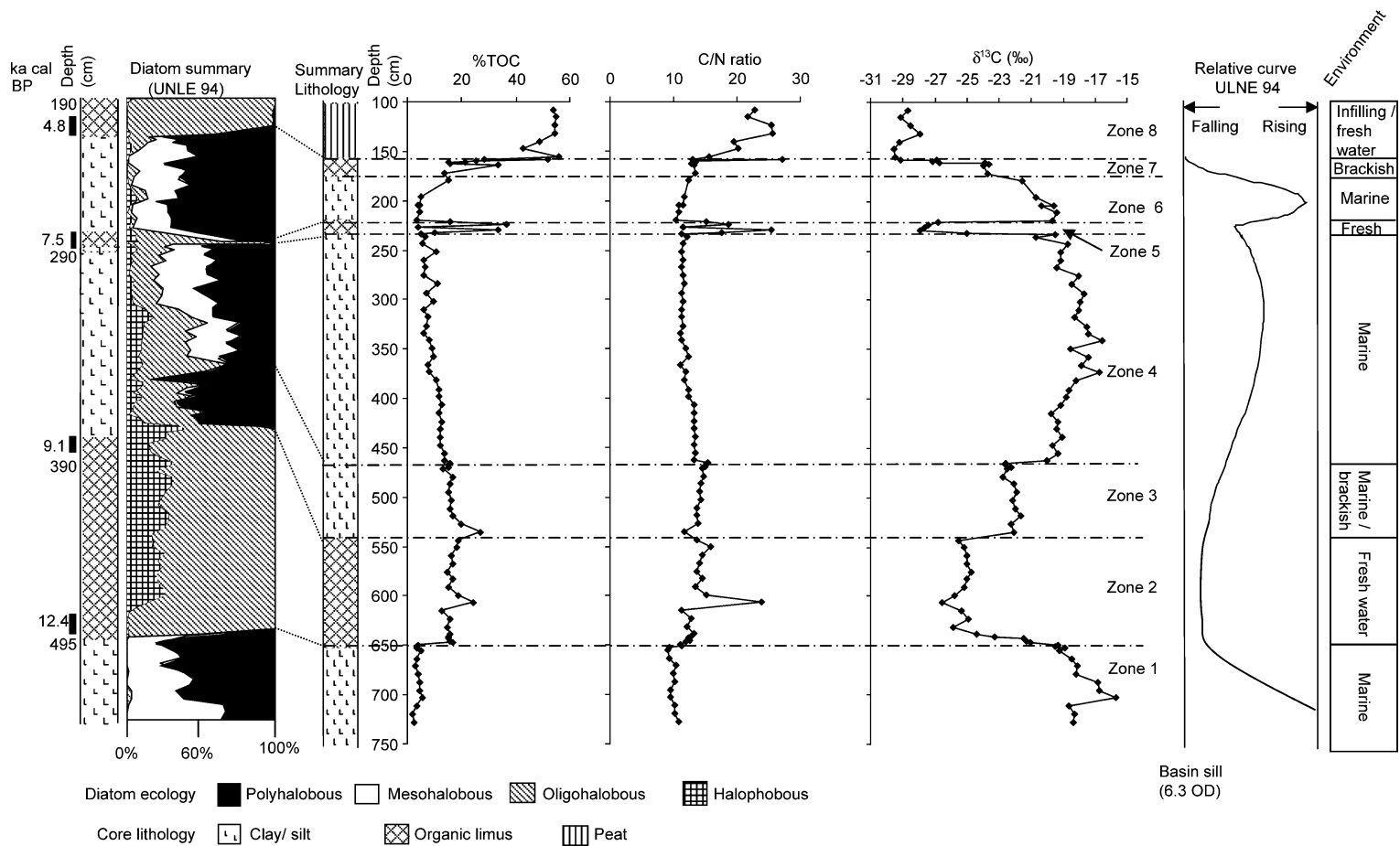
Fig. 9. Diatom palaeosalinity reconstruction, %TOC, C/N ratios, and $\delta^{13}C$ from the Upper Loch nan Eala (ULNE) sediment core, western Scotland. The sequence is divided into eight subdivisions (zones) based on changes in the $\delta^{13}C$ and C/N data. These zones closely correlate with changes in the diatom flora, suggesting a strong salinity control on the type of the organic material entering the basin. Adapted from Mackie et al. (2005) with permission from Elsevier.

end-member values, they were able to define a variety of conditions in the basin from full marine, through to transitional/brackish and freshwater loch. The palaeo-environmental changes inferred from the core $\delta^{13}C$ and C/N data coincide well with the diatom-inferred environments and with previously interpreted changes in RSL (Shennan et al., 2000), confirming that $\delta^{13}C$ values provide an effective RSL curve (Fig. 9). They conclude that changes in the balance between marine input and freshwater input (ultimately controlled by RSL) is the main factor governing $\delta^{13}C$ and to a lesser extent, C/N. The relationship is not perfect, however, as around 6000 cal yr BP the diatoms indicate relatively high salinity and full marine conditions, whereas $\delta^{13}C$ and C/N are lower than in other parts of the core with lower RSL. They suggest several possible reasons for this including varying amounts of marine plankton input during the marine periods, or a change in temperature or CO_2 concentration at 6000 cal. ^{14}C yr BP (compared to Late glacial marine conditions) that would affect the fractionation of $\delta^{13}C$. These results emphasise that although the technique appears to work, it is important to use a multiproxy approach.

The technique has also been successfully applied in regions where C_4 grasses naturally occur. The Gulf of Carpentaria, which lies between Australia and New Guinea, has periodically been cut off from the Indian and Pacific Oceans during the Late Quaternary, forming Lake Carpentaria (Chivas et al., 2001). During periods of low RSL, the isolation basin has an outlet channel into the Arafura Sea and as the surrounding sea is relatively shallow, Lake Carpentaria is particularly sensitive to changes in RSL. A multi-proxy study of several sediment cores from the lake (the longest stretching back to 130,000 ^{14}C yr BP), was used to attempt to identify past occurrences of marine and non-marine phases, including various microfossils (ostracoda, foraminifera, charophyta and pollen) (Chivas et al., 2001). It was clear from these results that there had been periods of sub-aerial exposure, open ocean conditions, estuarine conditions and lacustrine conditions during the Late Quaternary. In order to further examine the most recent non-marine/marine transition identified (9700 ^{14}C yr BP), $\delta^{13}C$ and atomic C/N were measured on the bulk organic fraction in the top 1 m of all cores (Fig. 10). C/N was predominantly higher in the non-marine facies in most of the cores but the distinction was not unequivocal. The $\delta^{13}C$ values, however, did show marked and consistent changes between the non-marine (-14‰ to -15‰) and marine (-19‰ to -21‰) phases. The non-marine $\delta^{13}C$ values reflect the abundance of C_4 savannah grasses growing around Lake Carpentaria during periods of low RSL. In several of the cores the C/N ratios change from ~10 to ~30, which supports the increase in C_4 terrestrial plants. Chivas et al. (2001) explain the fact that C/N values were not higher in some cores when $\delta^{13}C$ was high (indicating relatively low RSL), by the presence of algae in those cores (MD 28, 29, 32, 33; Fig. 10). Lacustrine algae may have similar $\delta^{13}C$ to the surrounding C_4 vegetation, but relatively low C/N ratios, similar to marine plankton.

3.3. Fjords

Although there are relatively few examples (Bird et al., 1991; St-Onge and Hillaire-Marcel, 2001; Smittenberg et al., 2004), $\delta^{13}C$ and C/N techniques can also be applied to sediments preserved in fjords. Fjords are normally glacially over-deepened submerged valleys, which commonly reach in excess of 1000 m in depth. As with estuaries, mixing occurs between the terrestrial inflow of plant material and POM with tidal-derived OM; although due to their depth, tidal-derived water can also enter a fjord through deep-water inflows that can reach as far as the fjord head.

Particularly high sedimentation rates over the Holocene (up to a few cm/yr) and relatively organic sediments at Saguenay Fjord in southeastern Canada prompted St-Onge and Hillaire-Marcel (2001) to investigate the degree of carbon storage in the fjord using $\delta^{13}C$ and atomic C/N ratios in four sediment cores along the fjord axis. The cores are characterised by several large-scale events (e.g. a landslide deposit formed in 1971) used both to correlate cores and to estimate sedimentation rates. Apart from the major event layers, the background sediments in each core show relatively unvarying $\delta^{13}C$ from an average of -26.7‰ in the inner basin, -26.8‰ and -26.1‰ in the middle basin and -25.9‰ in the outer basin. Deep saline landward flowing water can introduce higher $\delta^{13}C$ and lower C/N values to the sediments (-21.5‰ and 8.5–12.7, respectively, for contemporary data) but the core values suggest that this is negligible here. The unvarying $\delta^{13}C$ values prevent the establishment of marine and terrestrial end members in this fjord and thus the extent of a brackish water layer at the top of the water column, produced by the mixing of marine and freshwater, is difficult to assess. This mixing is likely to contribute to the small increase in $\delta^{13}C$ seen towards the fjord mouth. The C/N ratios did show more variation than $\delta^{13}C$, and the modern upper water layer POM had low C/N values of around 5, suggesting a
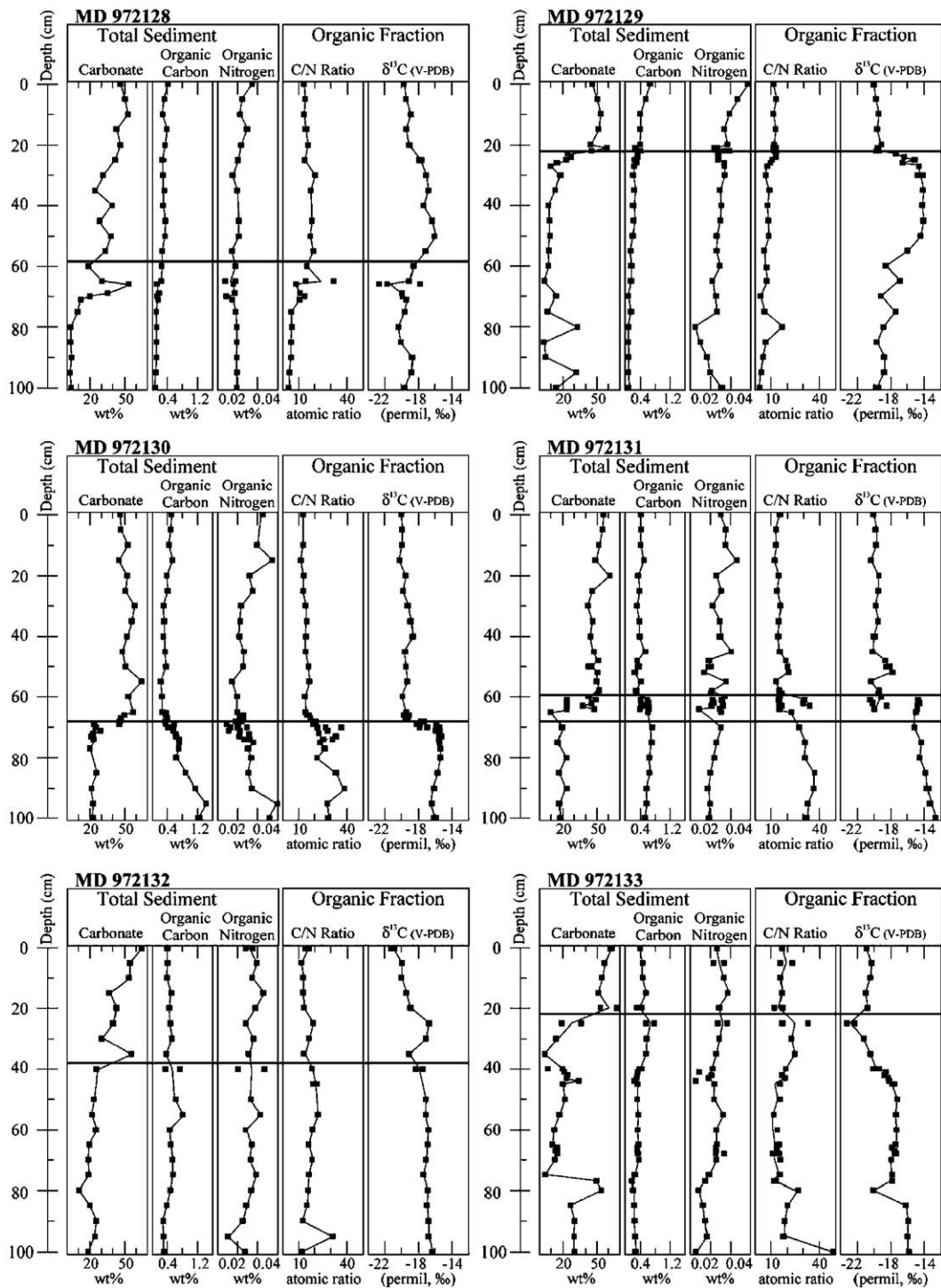
Fig. 10. Total carbonate, organic carbon and organic nitrogen content (wt.%) and organic atomic C/N and $\delta^{13}C$ values for the top metre of six cores from the Gulf of Carpentaria. Horizontal lines mark inferred positions of non-marine/marine transitions. Reproduced with permission from Elsevier from Chivas et al. (2001).
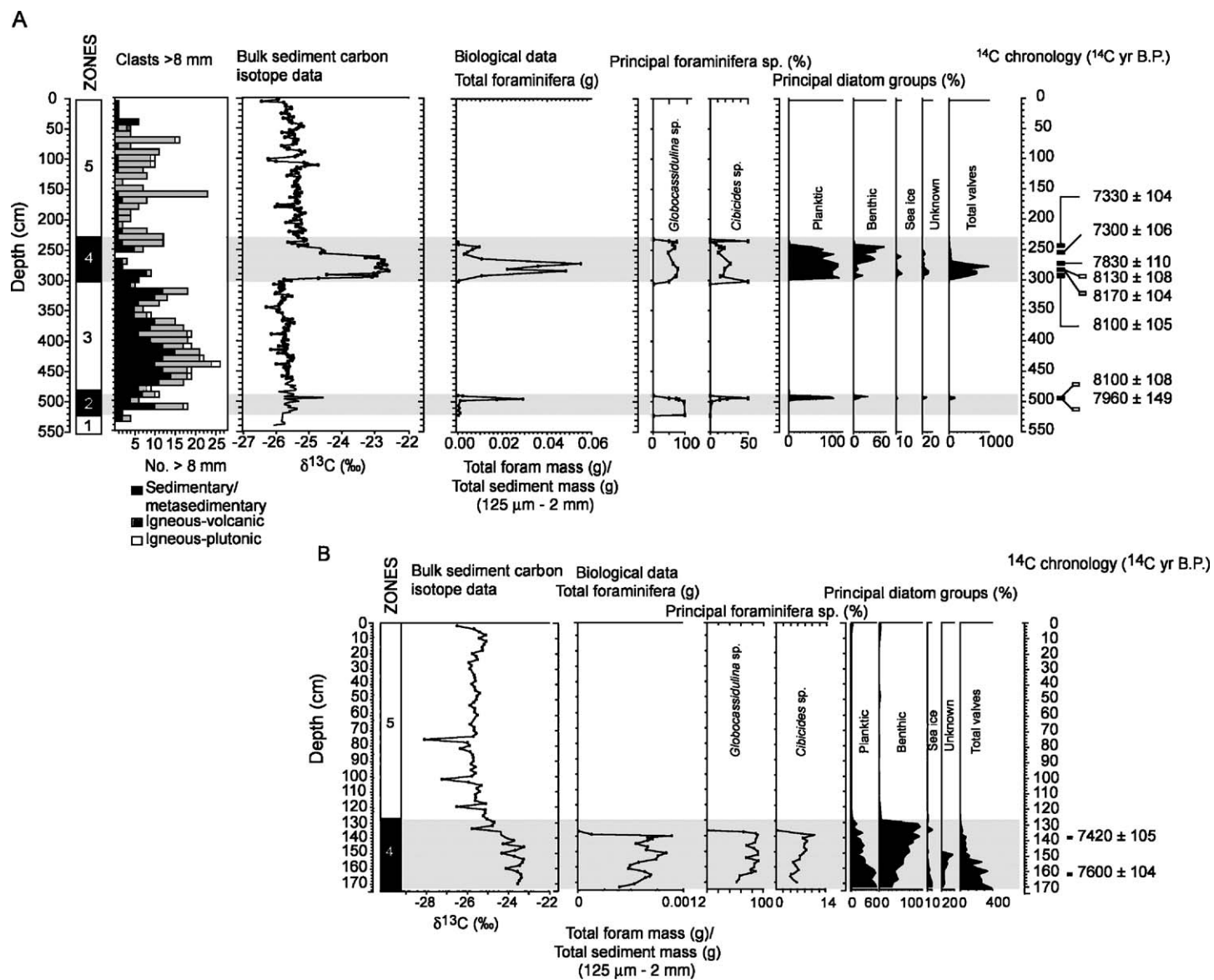
Fig. 11. Multiproxy studies of sediment cores from (A) Moutonnée Lake and (B) Moutonnée Lake North Basin, Alexander Island, Antarctica including number and lithology of clasts >8 mm, bulk $\delta^{13}C_{org}$ and foraminiferal and diatom assemblages. Zones 1, 3 and 5 (A) and zone 5 (B) were devoid of diatoms and foraminifera. Adapted with permission from Bentley et al. (2005).

marine POM source; whereas surface sediments from the inner fjord basin had values of >12 suggesting more terrestrial POM and less marine sources in the upper water column.

More recently, bulk organic δ^{13}C analyses have been applied to cores from two Antarctic marine embayments lying between the Antarctic Peninsula and Alexander Island (Bentley et al., 2005). Currently, the embayments are ice damned by the 100–500 m thick George VI Ice Shelf, forming the Moutonnée and Ablation Lakes, which are tidal and have a deep marine connection under the ice shelf and an upper layer of freshwater. The collapse of other Antarctic Peninsula ice shelves in recent years is thought to be linked to twentieth century warming and there is some evidence to suggest that this may have also occurred during warmer phases of the Holocene. Bentley et al. (2005) hypothesised that sediments preserved in Moutonnée and Ablation Lake would reflect a dominant freshwater input when the ice shelf was present, but a marine-dominated ecology when the ice was absent. They used a multiproxy approach to investigate Holocene sediment cores including various microfossils, the composition of ice-rafted debris (IRD) and bulk organic δ^{13}C. Two marine zones occur (radiocarbon dated at 9595 and 7945 cal. ^{14}C yr BP), identified by marine diatoms and forams, diverse IRD (indicative of open water conditions) and relatively high δ^{13}C (Fig. 11). Away from the marine layers, bulk organic δ^{13}C plot around −26‰, which reflects a significant freshwater component to the waterbody and is similar to modern surface sediment δ^{13}C values. The marine layers have δ^{13}C values between −23‰ and −22‰ suggesting a greater marine inflow that could be explained by the collapse of the ice shelf barrier. There is good correspondence between the microfossil evidence and the δ^{13}C evidence, and as the microfossils only occur in the marine layers, δ^{13}C is able to give a continuous Holocene record of ice shelf existence, whereas interpreting the presence of the ice shelf by the absence of microfossils alone is equivocal for reasons described earlier. Bentley et al. (2005) were able to successfully date the Holocene collapse of the ice shelf and link it to a period of known warmer temperatures, suggesting that Holocene natural temperature variability is currently greater than anthropogenically induced warming.

4. Organic matter degradation: implications for δ^{13}C and C/N ratios

Changes in bulk sediment organic δ^{13}C and C/N over time due to decomposition is an important consideration in coastal palaeoenvironmental research (e.g. Fogel et al., 1989; Müller and Mathesius, 1999; Müller and Voss, 1999; Byrne et al., 2001; Wilson et al., 2005b). Shifts in δ^{13}C can be particularly significant and can occur over relatively short time-periods. In the coastal wetlands of Louisiana, USA, for example, bulk organic surface sediment δ^{13}C had shifted on average between −0.5‰ and −3.3‰ from that of the above vegetation (Chmura et al., 1987). Similar results have been found in other marshes around the U.S.A. coastline (e.g. Ember et al., 1987; Chmura and Aharon, 1995; Malamud-Roam and Ingram, 2001). Significant changes in C/N can also occur during decomposition, particularly in the early stages (Valiela et al., 1985). In inter-tidal and supra-tidal sediments, this may result in much lower surface sediment C/N compared with the overlying vegetation (e.g. Wang et al., 2003; Wilson et al., 2005a), whereas in sub-tidal sediments, C/N is commonly slightly higher than in the suspended sediment phase (e.g. Cifuentes, 1991; Middelburg and Nieuwenhuize, 1998). In the following discussion, a distinction is made between sediments accumulating in the higher inter-tidal or supra-tidal zone and sediments accumulating in the lower inter-tidal or sub-tidal zone owing to the different character of organic detritus in these environments.

4.1. Upper inter-tidal and supra-tidal environments

In European saltmarshes, closed vegetation cover occurs relatively high in the inter-tidal zone, usually well above mean high water of neap tides (MHWN) (Beeftink, 1977). Due to the reduced frequency and duration of tidal flooding, and the relatively small herbivore consumption in saltmarshes (Teal, 1962), the detritus of much of the organic matter produced in the middle and high saltmarsh zones is allowed to accumulate in situ (Bouchard et al., 1998; Bouchard and Lefeuvre, 2000) resulting in organic-rich sediments. This is in contrast to most North American saltmarshes. Here, closed vegetation stands of *S. alterniflora* occur below mid-tide level (McKee and Patrick, 1988), resulting in sediment deposits rich in organic matter at much lower elevations within the tidal frame compared with most European saltmarsh sediments at equivalent ground elevations. In addition, *Spartina* detritus may be exported on the tide to coastal waters (e.g. Haines, 1977; Bouchard and Lefeuvre, 2000). In view of this, decomposition is a potentially significant factor affecting δ^{13}C and C/N in North American saltmarsh deposits, and in European saltmarsh deposits above MHWN.

The relative concentrations of C and N in decaying saltmarsh plant litter changes during three phases of decomposition (Valiela et al., 1985), although not all of these phases may be seen in practice (e.g. Haynes, 1986). Leaching of soluble compounds is the first phase and leads to a rapid loss of mass in vascular plant detritus within days (Rice and Tenore, 1981; Valiela et al., 1985) or months (Benner et al., 1991; White and Howes, 1994) of decomposition beginning, depending on the detritus involved and local conditions. During this initial phase, the C/N ratio of decaying vascular plant litter commonly increases, as nitrogen is lost more rapidly than carbon (e.g. Rice and Tenore, 1981; White and Howes, 1994; Benner et al., 1991; Fig. 12). However, a large quantity of carbon is also leached from the detritus, sometimes within days. For example, S. alterniflora was observed to lose approximately 10% of its original mass of carbon in the first 10 days of leaching (Rice and Tenore, 1981).

Microbial degradation of organic matter, principally by bacteria (Benner et al., 1984b), with leaching of decay products, is the second phase of decomposition and can last up to a year (Valiela et al., 1985). An increase in nitrogen concentrations has commonly been observed during this phase (e.g. Rice and Tenore, 1981; Valiela et al., 1985; Benner et al., 1991; White and Howes, 1994; Fig. 12) that may occur through fixation of external nitrogen sources (Glenn, 1976; Rice, 1982; Benner et al., 1991). In addition to further carbon loss through respiration, leaching, or particulate transport, the increased nitrogen concentration results in a fall in plant detrital C/N (Fig. 12). Due to the enhanced nutrient quality of the detritus during this phase, decomposition rates may increase (Lillebø et al., 1999). The decay of

detritus under anaerobic conditions, such as in saltmarsh sediments for example, is much slower than under aerobic conditions (Benner et al., 1984a) allowing a greater accumulation of refractory organic matter, which may lead to peat accumulation (Valiela, 1995).

The third phase of decomposition is the refractory phase, where only relatively refractory material, such as lignin, remains and decomposition rates are very slow (Valiela et al., 1985; Benner et al., 1991). During this phase, C/N usually stabilises as carbon and nitrogen is lost at approximately the same rate (Melillo et al. 1989; White and Howes, 1994; Fig. 12).

The early loss of nitrogen and the stabilisation of C/N in the refractory phase in sediment is a common observation on coastal marshes. Wang et al. (2003) compared bulk sediment atomic C/N ratios in both freshwater marsh and saltmarsh sediment cores with that of the dominant plant species in Plum Island marsh in Massachusetts, USA. They found that the C/N ratios of the near surface marsh sediments (14–18) were much lower than the average C/N of the overlying vegetation (50) and that no further changes of any significance occurred in C/N downcore. Wilson et al. (2005a) obtained similar results in a saltmarsh fringing the Mersey Estuary. Here, surface saltmarsh sediments had C/N ratios of 10–12, much lower than the mean value of the overlying vegetation (29).

Wilson et al. (2005b) measured bulk sediment C/N in sub-tidal, inter-tidal and supra-tidal deposits over a much longer timescale (extending back to 8330–8010 cal. yr BP), and compared these with C/N measurements from equivalent modern environments in the Mersey Estuary (Fig. 13). They found that mean early–mid Holocene saltmarsh sediment C/N (13.3) was higher than mean
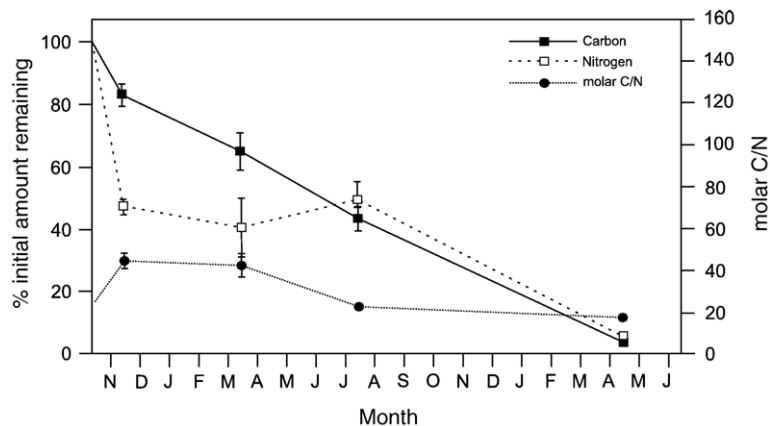

Fig. 12. Changes in detrital organic carbon and total nitrogen, expressed as a percent of initial amount remaining (± 1 S.D.) and changes in atomic C/N through time in decaying *Spartina alterniflora* in litter bags placed on the surface of Great Sippewissett saltmarsh, Massachusetts, USA (1986–1989). Redrawn with permission from White and Howes (1994). Copyright, 2002 by the American Society of Limnology and Oceanography, Inc.
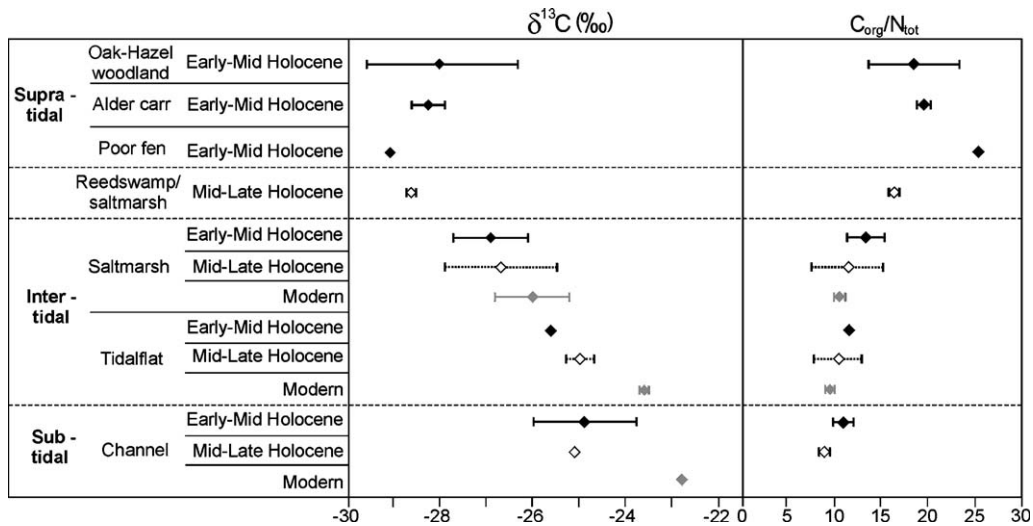
Fig. 13. Mean early-mid Holocene $\delta^{13}C$ and C/N (◆), mean mid-late Holocene $\delta^{13}C$ and C/N (◇) and mean modern $\delta^{13}C$ and C/N (◆) values of supra-tidal, inter-tidal and sub-tidal environments in the Inner Mersey Estuary, UK. The standard deviation (1σ error bars) of the group of $\delta^{13}C$ and C/N values measured for each environment are also shown. Data points without error bars indicate $\delta^{13}C$ and C/N measurements of insufficient number to assign errors. The low nitrogen content of modern sub-tidal sediments prevented C/N measurement. Reproduced with permission from Elsevier from Wilson et al. (2005b).

modern saltmarsh sediment C/N (10.6). Mean mid–late Holocene saltmarsh C/N gave intermediate values of 11.3. This pattern of increasing C/N of saltmarsh sediment with age is consistent with further decomposition of organic matter and the concentration of carbon-rich refractory organic compounds.

Changes in the $\delta^{13}C$ of bulk organic sediment also occur during decomposition, and this is due to the differing $\delta^{13}C$ composition of labile and refractory plant compounds. Park and Epstein (1961) demonstrated that lipids were up to 8‰ enriched in ^{12}C relative to the whole plant, and research since this seminal work has shown that several other plant compounds have different $\delta^{13}C$ values. For example, cellulose and hemi-cellulose, which make up between 57% and 77% of herbaceous and woody plant tissues respectively, are enriched in ^{13}C by 1‰ to 2‰ relative to the whole plant (Benner et al., 1987). Lignin, which is only found in vascular plants, accounts for between 17% to 31% and 4% to 9% of woody and herbaceous plant tissues respectively, and is depleted in ^{13}C by 2‰ to 6‰ relative to the whole plant, and 4‰ to 7‰ relative to cellulose (Benner et al., 1987). Lignified macrophyte detritus is the single most refractory particulate organic component in sediments (Tyson, 1995). Incubation experiments and studies in saltmarshes have demonstrated the preferential decay of hemi-cellulose and cellulose (e.g. Maccubbin and Hodson, 1980; Wilson, 1985; Benner et al., 1987; Fogel et al., 1989; Melillo et al., 1989), with bulk $\delta^{13}C$ values of the whole plant

approaching those of lignin over time (Ember et al., 1987; Benner et al., 1987, 1991). It is this shift in bulk organic sediment $\delta^{13}C$, reflecting the relative concentration in lignin, that is thought to account for some of the difference between surface sediment $\delta^{13}C$ and over-lying vegetation $\delta^{13}C$ in saltmarshes (e.g. Chmura et al., 1987; Chmura and Aharon, 1995; Mallamud-Roam and Ingram, 2001).

Since up to 90% of plant material is composed of hemi-cellulose, cellulose and lignin, changes in the relative abundance of these plant compounds during decomposition of organic-rich high inter-tidal and supra-tidal sediments have obvious implications for bulk sediment $\delta^{13}C$ analysis. Nevertheless, the magnitude of change in the $\delta^{13}C$ of bulk organic sediment is insufficient to prevent the distinction of C_3 and C_4 peats in the sediment record (e.g., Byrne et al., 2001; Mala-mud-Roam and Ingram, 2004). Furthermore, the direction of shift in $\delta^{13}C$ as decomposition progresses in coastal sediments is known, because $\delta^{13}C$ increasingly reflects the more refractory compounds such as lignin.

For coastlines where C_4 vegetation has been absent or rare throughout the Holocene, the smaller range in $\delta^{13}C$ between organic matter sources means that changes in $\delta^{13}C$ due to decomposition become much more significant. In the Mersey Estuary, a large variability in $\delta^{13}C$ exists in the modern and Holocene saltmarsh deposits, and Holocene high saltmarsh sediments had $\delta^{13}C$ values up to 3.7‰ lower than modern high saltmarsh sediment $\delta^{13}C$, whereas Holocene low

saltmarsh sediments have $\delta^{13}C$ values up to 3.2‰ lower than modern low saltmarsh sediment (Wilson et al., 2005b). Based on similar differences in $\delta^{13}C$ between contemporary Mersey Estuary saltmarsh whole plant and plant lignin, Wilson (2004) and Wilson et al. (2005a) reasoned that the difference in $\delta^{13}C$ between some Holocene and contemporary equivalent saltmarsh sediment samples may be largely explained by the selective preservation of ^{13}C depleted refractory material, such as lignin, in the sediments over time. Despite these decompositional effects, Wilson et al. (2005b) concluded that $\delta^{13}C$, together with C/N, could be used to distinguish between supra-tidal, inter-tidal and sub-tidal sediments in Holocene deposits. Furthermore, because $\delta^{13}C$ and C/N appears to be governed by ground elevation within the tidal frame in this environment (Section 3.1); it is the direction of change in $\delta^{13}C$ and C/N that is important in detecting changes in RSL. This relationship is retained in Holocene sediments (Fig. 13) and is unaffected by decomposition. Therefore, $\delta^{13}C$ and C/N can be employed effectively, even in dynamic coastal environments like saltmarshes.

4.2. Lower inter-tidal and sub-tidal environments

Organic matter in sub-tidal sediments (e.g. estuarine, lagoonal) and lower inter-tidal sediments (e.g. tidal flats and European lower saltmarshes) is mostly derived from suspended POM from riverine and marine sources (e.g. Sampei and Matsumoto, 2001; Wilson et al., 2005a). Much of the terrigenous component of riverine POM may have already been extensively degraded on land or further upstream and should be relatively resistant to further degradation (Hedges and Keil, 1995). Phytoplankton has a high protein content (up to 34%, Bordovskiy, 1965b), which is relatively rich in nitrogen (15% to 19% on average, Bordovskiy, 1965b), and is therefore an attractive food source for consumers. Furthermore, together with protein, carbohydrates account for between 63% and 93% of phytoplankton biomass. Consequently, phytoplankton undergoes considerable degradation in the water column and only a few percent of the organic matter of plankton may be incorporated into the sedimentary record in coastal areas (Bordovskiy, 1965a; Meyers, 1997). The C/N ratio of phytoplankton detritus changes as degradation proceeds in the water column, although unlike vascular plant detritus, nitrogen does not increase in phytoplankton detritus during decay (Valiela, 1995). The $\delta^{13}C$ value of phytoplankton (~ -21‰) also alters in the water column. This is due to the preferential degradation of ^{13}C-enriched compounds, such as carbohydrates and pro-

teins, and the subsequent increasing concentration of the more refractory ^{12}C-enriched lipid fraction.

Cifuentes (1991) compared atomic C/N ratios in suspended and deposited sediments in the Delaware Estuary, southeastern USA. Suspended POC exhibited C/N ratios of 6.4, compared with 11.1 for surface sediments. This is consistent with the breakdown of nitrogen-rich compounds of plankton in the water column prior to deposition. Middelburg and Nieuwenhuize (1998) observed a similar change in atomic C/N between the suspended and surface sediments in the Schelde Estuary, located on the border of the Netherlands and Belgium. Here, the C/N ratio of suspended sediment (8.9) was much lower than surface sediment C/N (17.0) in the upper estuary, although no appreciable difference was measured between the two phases in the lower estuary (9.1 and 10.3, respectively). The $\delta^{13}C$ values also differed between the two phases, and this difference was present in both estuarine zones. In the upper estuary, the $\delta^{13}C$ value of suspended sediment (-28.9‰) was lower than surface sediment $\delta^{13}C$ (-26.3‰), whilst in the lower estuary; suspended sediment $\delta^{13}C$ (-20.1‰) was higher than surface sediment $\delta^{13}C$ (-23.5‰). Seasonality may partly account for this apparent disparity in C/N and $\delta^{13}C$ changes between the suspended and surface sediment phases in the upper and lower estuarine zones. Differential decomposition of organic detritus may also partly explain these observations. In the Schelde Estuary, for example, atomic C/N ratios indicate that suspended organic sediment is dominantly phytoplankton, with little terrestrial organic matter present. In contrast, in the surface sediments, the more labile phytoplankton is preferentially degraded, leading to a relative increase in the concentration of the more refractory terrestrial organic matter (Middelburg and Nieuwenhuize, 1998).

Arzayus and Canuel (2004) measured atomic C/N and $\delta^{13}C$ in estuarine sediment cores from the York River Estuary, a sub-estuary of the Chesapeake Bay on the eastern USA seaboard. C/N and $\delta^{13}C$ remained largely unchanged below 15 cm, indicating little further diagenetic alteration in the sediment column, and only modest (~ 1‰) diagenetic alteration in the surface sediments. In contrast to observations in the York River Estuary, Wilson et al. (2005b) did observe further changes in both $\delta^{13}C$ and C/N in sub-tidal and lower inter-tidal deposits (Fig. 13). For example, C/N increased from 8.9 in the mid–late Holocene to 10.9 in the early–mid Holocene in sub-tidal sediments, whereas in tidal flat sediments, $\delta^{13}C$ decreased from -25.0‰ in the mid–late Holocene to -25.6‰ in the early–mid Holocene. This is supported by independent evidence

from diatoms, which rule out coastal palaeoenvironmental changes, and thus a change in organic carbon source, as a causal factor. Indeed, decompositionally induced changes in $\delta^{13}C$ and C/N were not sufficient to mask the source of organic matter in sub-tidal and lower inter-tidal sediments. In certain circumstances, it may be difficult to distinguish between the effects of decomposition and changes in carbon source when interpreting down-core changes in bulk $\delta^{13}C$ and C/N. For example, both decompositional processes and increases in palaeoriver discharge will result in an observed down-core decrease in $\delta^{13}C$ and increase in C/N in estuarine sub-tidal sediments. In the absence of lithological changes, it is necessary to compare the data with independent proxies, such as diatoms, to achieve a robust interpretation. The reliability of C/N as an organic matter source indicator may be reduced considerably in sediments with very low levels of organic carbon (Section 3.2), such as highly degraded subtidal and lower inter-tidal sediment.

Further degradation of phytoplankton and vascular vegetation detritus (both labile and refractory) leads to the formation of the highly structurally and biochemically altered refractory organic materials humin and humic and fulvic acids. Humic substances and humin may represent a substantial proportion of carbon contained in sediments. For example, humic substances in well-developed soils may constitute up to 91% of the organic matter present (Rashid, 1985) and 35% in peats (Nissenbaum and Schallinger, 1974). Estuarine sediments commonly contain humic substances in the range of 10–65% (Mayer, 1985), whilst in marine sediments sensu stricto and continental shelf sediments, humic substances constitute 25–50% and 49% of the carbon, respectively (Ertel and Hedges, 1984). These concentrations of humic substances may vary widely in the sediments, within each of the above environments, based on variations in physico-chemical conditions. Nevertheless, humic substances and humin appear to be significant components of sediments and will, therefore, impact on bulk sediment $\delta^{13}C$ values.

In terrestrial soils and sediments, degraded plant material is the precursor of humic substances and humin. In estuarine sediments, humic substances may have a range of sources, including deposition of terrestrially derived detritus, marine and fluvial phytoplankton and flocculated organic and organo-clay complexes. Humic substances and humin exhibit $\delta^{13}C$ values in the range of their precursors. Loss of ^{13}C-enriched material during humic substance formation is evident, however. Alberts et al. (1988) found that humic substances extracted from *S. alterniflora* were 2‰ to 3‰ lower

than the parent plant material. In addition, surface sediment humic substance extracts were a further 3‰ lower than the plant humic extracts. Although the processes involved in the generation of humic substances and humin are not sufficiently understood (Hatcher and Spiker, 1988; Hedges, 1988; Gleixner et al., 2002), a decrease in $\delta^{13}C$ remains a consistent observation.

5. Summary

The sediment deposits that are preserved in sheltered coastal environments (e.g., estuaries, lagoons, bays, inlets, rias, and isolation basins) offer a valuable opportunity to investigate past climate, sea-level and land-level changes. Where microfossils are poorly preserved or absent, $\delta^{13}C$ and C/N analysis offers an alternative method that can be applied to any sediments that contain some organic material. This review assesses the application of $\delta^{13}C$ and C/N-based studies to palaeoenvironmental reconstructions in a wide range of coastal environments. In some of the examples highlighted, $\delta^{13}C$ and C/N have provided a reliable palaeoenvironmental proxy but also many examples stress the need to include a wide range of other proxies to enable an accurate palaeoenvironmental reconstruction. What is also evident is the importance of completing systematic isotope and geochemical measurements of organic matter sources in modern environments before palaeoenvironmental interpretations can be attempted. The wide range of $\delta^{13}C$ and C/N-based carbon budget studies that exist provide a database of examples of different coastal conditions that are useful when selecting appropriate environments for study.

Perhaps most successful have been studies that utilise the relationship between C_3 and C_4 plant distribution and salinity in coastal environments and apply this relationship to Holocene sediment cores. Early studies in the San Francisco Basin demonstrated that the relative proportions of C_3 and C_4 plants growing in an area were preserved in the $\delta^{13}C$ composition of the underlying surface sediment and thus past changes in salinity could be interpreted by observing sedimentary changes in $\delta^{13}C$. Where there are no native C_4 plants, $\delta^{13}C$ and C/N have also been successfully used as a palaeoenvironmental indicator as bulk inter-tidal sediment $\delta^{13}C$ and C/N can reflect elevation within the tidal frame. Several examples have shown supra-tidal and high salt-marsh sediments to consist almost entirely of organic carbon derived from the overlying C_3 vegetation, and sub-tidal and tidal-flat sediments of tidal-derived POM. The different sources of organic carbon resulting in differing bulk sediment $\delta^{13}C$ and C/N values.

Away from estuarine environments, successful carbon-based palaeoenvironmental reconstructions have been achieved from lagoons, fjords and isolation basins. In these cases, it is the change in dominant carbon source from terrestrial to marine (or vice-versa), that is observed in the sedimentary record, like for example, an isolation basin is breached by the sea during a RSL rise. It is clear from the examples that plankton-dominated environments may pose several problems to potential $\delta^{13}C$ and, in particular, C/N studies of RSL change. As plankton has variable $\delta^{13}C$, it may be difficult to interpret in environments where it dominates input to the sediments. Where there is more of a balance between terrestrial inputs and phytoplankton, variations in their relative proportions can be deduced successfully using C/N and $\delta^{13}C$.

Shifts in bulk organic sediment $\delta^{13}C$ due to decomposition are thought to account for differences between surface sediment $\delta^{13}C$ and overlying vegetation $\delta^{13}C$ in some environments (e.g. Malamud-Roam and Ingram, 2001). Other factors, such as the introduction of tidal-derived sediment with distinctly different organic $\delta^{13}C$ (e.g. Wilson et al., 2005a), bacteria in the surface sediments (Peterson et al., 1980), and algae (Fogel et al., 1989) may also account for some of the differences between surface sediments and overlying vegetation.

Organic matter decomposition can have a potentially significant influence on both sediment $\delta^{13}C$ and C/N, and therefore using either proxy in isolation may produce misleading results in many coastal environments. Early loss of labile material in vascular vegetation can lead to significant changes to $\delta^{13}C$ in saltmarshes but is usually insufficient to prevent the distinction between sediments from C_3 and C_4 vegetated marshes (e.g. Malamud-Roam and Ingram, 2004), and $\delta^{13}C$ remains a faithful indicator of its precursor. The loss of organic carbon in sediments as decomposition progresses may eventually complicate the use of C/N ratios (Sampei and Matsumoto, 2001), as an increase in inorganic nitrogen relative to organic nitrogen may prevent accurate identification of organic matter source. The direction of change in $\delta^{13}C$ and C/N, rather than absolute values, is frequently more important for detecting changes in RSL. Relative changes are commonly retained in Holocene sediments being little affected by decomposition, suggesting that $\delta^{13}C$ and C/N can be employed even in the most dynamic of coastal environments. The close agreement commonly seen between diatom records and $\delta^{13}C$ and C/N records (e.g. Mackie et al., 2005; Wilson et al., 2005b; Zong et al., in press), despite their responding to different variables (organic

source as opposed to salinity), allows greater confidence in palaeoenvironmental interpretations using $\delta^{13}C$ and C/N.

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