Below are the two reviews, our responses (***bold italics***), and changes made to the manuscript in response (***bold red italics***). The new revision also contains minor editorial changes made throughout the manuscript that show up on the marked copy but are not included in our responses to the reviewers given below.

Review 1, with our responses in bold italics; red indicates the changes that will be made upon revision:

This manuscript discusses the sources of organic carbon in surface sediments of Black Sea, Arabian Sea and Ross Sea. Contributions of 'marine biomass, terrigenous vascular plant, and relict sources' are evaluated using lipid biomarkers, stable carbon and radiocarbon analysis. To better understand the global carbon cycle and its impact on climate change, it is important to learn sources of OC in marine sediments, which is still not well-studied. Radiocarbon analysis of specific lipid biomarkers is a powerful tool for marine OC sources apportionment in the past 15 years and it is applied in this study. I realize that nice samples and data were obtained in this work, but the authors fail to show an interesting story. Some terms are not defined, some conclusions are not easy to understand because a lack of detailed explanation. The key points of some sections are not clear that I need to read several times to have an idea what valuable information I can obtain. The manuscript needs to be reorganized to make the manuscript easily understandable to the reader and highlighted the key points.

Specific comments:
Title: P9761: I suggest modification of the title. As mentioned in the abstract, the manuscript focuses on the sources of OC, but not lipid biomarker. Lipid biomarker is a tool for OC source apportionment.
Ok, we will modify the title slightly to: "Transfer of organic carbon through marine water columns to sediments – insights from stable and radiocarbon isotopes of lipid biomarkers".

Abstract: P9762 Line7: What's the definition of 'relict sources'?
"Relict" is a commonly used term in geology, but to clarify we have changed "relict sources" to "relict kerogen sources." See also lines 3-6, p 9765.

P9762 Line7: 'sediment trap material'. It takes me some time to remember that 'sinking particulate matter', 'sediment trap material', 'particulate organic matter/POM/bulk POM' used in this manuscript are the same thing.
We agree that these terms are interchangeable, as are sediment organic matter, SOM etc used throughout. Actually "bulk POM" and "bulk SOM" are used to specifically distinguish the unfractionated material from the extracted SLE (see comment below) or specific isolated biomarkers. We do not feel that these need to be changed. POM and SOM were first defined on p 9764, line 27.

P9762 Line7-11: 'Marine biomass in. . .respectively.' P9762 Line15- 18: 'These results. . .marine POC.' I suggest you explain a little about how you get these conclusions, even though you have mentioned in the text. I feel that's more important than or as important as the conclusion itself.

We are not sure what is requested here. Since this is in the abstract, it is a summary of results and discussion that follow and are developed in the main body, from which the abstract is derived. However, we will modify (changes in color) the abstract to:

…"The goal was to develop a multi-parameter approach to constrain relative inputs of organic carbon (OC) from marine biomass, terrigenous vascular plant, and relict kerogen sources. Using an isotope mass balance, we calculate that marine biomass in sediment trap material from the Black Sea and Arabian Sea accounted for 66-100% of OC, with lower terrigenous (3-8%) and relict (4-16%) contributions. Marine biomass in sediments constituted lower proportions of OC (66-90%), with consequentially higher proportions of terrigenous and relict carbon (3-17% and 7-13%, respectively). Ross Sea data were insufficient to allow similar mass balance calculations. These results suggest that whereas particulate organic carbon is overwhelmingly marine in origin, pre-aged allochthonous terrigenous and relict OC becomes proportionally more important in sediments, consistent with pre-aged OC being better preserved during vertical transport to and burial at the seafloor than the upper ocean-derived marine OC."

By the way, what's the definition of 'pre-aged OC'? ***"Pre-aged OC" is a term commonly used in the radiocarbon literature to designate allochthonous OC that has been aged prior to being delivered to its present depositional setting. Since it is widely used, we do not think a definition is needed here. But see line 10, p 9764 and lines 3-6, p 9765.***

Introduction:
P9763 Line9: "marine OC' may contain 'terrigenous plant and relict sediment OC'. So what's the real meaning of 'marine OC' herein?
Again, we are not sure what the reviewer is asking. "Marine OC" is a commonly used term for autochthonous OC, as opposed to allochthonous terrigenous and relict kerogen OC. It is true that OC in the ocean will be a mix of autochthonous marine and allochthonous terrestrial and relict OC, but we do not feel that changing the terminology here is needed.

One extra question: Are there any previous studies on sources of marine OC in the same study areas? Without statement of historical work, it is not clear what knowledge the present work will added. At least, I know Eglinton et al., 1997, Science also 'combined biomarker/stable carbon/radiocarbon studies of marine particulate matter', studying the sample area (e.g. Black Sea and Arabian Sea).
To our knowledge, there are no comparable sediment trap OM-sediment SOM compound-specific biomarker/stable C/ radiocarbon isotope studies in the literature, especially not for these areas. The Eglinton et al paper 1997 cited here and on p 9764 line 7 does indeed give from 14C data for sedimentary lipids in the Black Sea and Arabian Sea, but not in sediment trap material (marine particulate matter as the reviewer suggests), which is the novel feature of this paper. Kusch et al (cited p 9782) report radiocarbon data for some alkenes in several core tops (no trap material) in the western Black Sea.

But we will add the following to p 9778, line 12: "A similar spread in $\delta^{13}C$ and $\Delta^{14}C$ values for marine, vascular plant and relict hydrocarbon biomarkers had been previously reported for Black Sea and Arabian Sea sediments (Eglinton et al., 1997)."

Results and discussions:

P9772-4 Section3.2-3.3: When compound-specific stable carbon/radiocarbon analysis of sources biomarkers is used to estimate sources of OC, why it is still necessary to measure stable carbon/radiocarbon of bulk OC? ***There is a tremendous literature on isotope compositions of bulk POM and SOM, so by including these here, it puts these samples into a wider perspective. Further, we use the compound-specific results as proxies for bulk OC, which really is what is of importance to biogeochemists.***

In this section, sometimes abbreviated names of the seas (BS, AS and RS) are used, sometimes non-abbreviated names are used. It takes me some time to remind what the abbreviation means, because they are not as commonly used as 'OC'. I suggest avoid using abbreviated names of the seas since the names are actually not long. ***We feel that the abbreviations are not a problem and they have been defined when first used.***

Several points make Section 3.3 difficult to follow:

1) The discussion starts from BS and AS, switch to RS, back to BS and AS, again switch to RS, then to AS and RS. ***To us, this order of the two paragraphs in this section labeled "bulk radiocarbon isotopes" is logical as we are taking about two separate sample sets (OC vs SLE): paragraph 1) presents radiocarbon of bulk BS, AS and RS trap and sediment OC; paragraph 2) then gives radiocarbon for BS, AS and RS trap and sediment SLE's.***

2) DIC probably means dissolve inorganic carbon, but it is not introduced in the text above, and the authors also don't mentioned DIC was measured before this data is showed. It is confusing that why the discussion switch to DIC herein. ***Yes, DIC does mean dissolved organic carbon; we thought the term was widely accepted. But we will change to "pre-bomb and post-bomb mixed layer DIC (dissolved inorganic carbon)… these values determine the*** Δ^{14}***C of autochthonous marine biomass." DIC was not measured in this paper, so it was not included in methods; the values given are from the literature as cited. But mixed layer DIC is important for setting the*** ^{14}***C of the autochthonous marine OC component, effectively one end-member.***

By the way, what's SLE (P9774, Line12 and also P9773, Line5). ***SLE was defined when first used on p 9769 line 6.***

3) There is no prior explanation of 'pre-bomb and post-bomb' (P9773, Line25). Even though I know the change about atmospheric 14C concentrations before and after nuclear weapon test, it is still not easy to make clear what the authors intend to tell herein. ***Again "pre-bomb" and "post-bomb" are widely used terms in the radiocarbon community and we do not fell that they need to be redefined here. Pre- and post-bomb terms are related to the DIC question noted above.***

P9780 Section3.6: Components of OC can vary a lot in radiocarbon age, why the radiocarbon ages of bulk OC can be used in the mass balance method***? The goal of this paper was to use lipid biomarkers to tease apart the isotopic contributions from the marine, terrestrial, and***

relict components, and then to try to apportion sources and show how the relative contributions from each changes between the water column POM and the underlying sediments, i.e. bulk OC. Using the biomarkers, we thought would give a better opportunity to determine the relevant endmembers, given that, as the reviewer points out, components of OC can vary a lot in radiocarbon age. Thus the ^{14}C of the biomarkers is used to estimate the relative inputs from the different OC sources.

Review 2, with our responses in bold italics; red indicates the changes that will be made upon revision:

The Wakeham and McNichol paper examines the stable and radiocarbon composition of a quite wide range of lipid biomarkers from a unique set of marine particulate samples, including both water column particles and surface sediments from the Black Sea, Arabian Sea and Ross Sea with contrasting oceanic settings. Both the sample set and the compound-specific 14C data are very precious, given the laborious nature and stringent analytical standard required for this type of analysis. Some of the results are the first attempt applied to the specific environment and will add valuable information on the source and fate of lipid compounds in the ocean. In this regard, the paper is very worthy of publication.

The authors further attempt to constrain the relative inputs of marine, terrigenous, and relict OC sources by utilizing a multiparameter mixing model. While this approach has been used in quite many papers previously, it is not very clearly explained here, particularly the end-member values. For instance, both Cadded and Cother are mentioned. What's the difference? Does Cadded include both CT and CR? If so, why is _14Cadded assumed to equal _14Crelict? I think this needs to be clarified as it has a decisive effect on the result of the mixing model solution. ***Our model differs from many that have been used because we are not able to use the δ^{13}C values (see comment below). This forces us to make assumptions that are not necessary in other models. The mention of both C_{added} and C_{other} is an editing mistake; C_{other} will be edited to C_{added}. Clarification of the confusion is attempted with the following editing of the text between lines 554-557 and 570-574.***

554-557 For each sample, there is a Δ^{14}C value assigned to the bulk SLE extract, fresh marine, fresh terrestrial and a relict/terrestrial mix. Bulk material is assumed to be a mixture of fresh marine and other "added" material, where the added material refers to the fresh terrestrial and relict/terrestrial mix. Given this, we can derive an equation the relative amounts of marine and "added" material.

570-574 Truly relict material has a Δ^{14}C value of -1000 ‰ and fresh terrigeneous material has the values determined in this study ($\Delta^{14}C_T$, Table 5). As stated earlier, the measured value of $\Delta^{14}C_R$ appears to be a mixture of truly relict material and terrigeneous material with a suite of ages. If we assume that the value we measured for "relict" material (Table 5) is a good representation of $\Delta^{14}C_{added}$, then we can assign a unique solution to the mass balance.

Also, on Page 9780, it says “the small differences in δ13C coupled with significant error make it difficult to use the stable isotopic composition as a discriminating factor in determining the sources of the bulk material”. But it seems that δ 13C values in Table 4 are still used for the calculations. Why so? How are the δ 13C values chosen? ***^{13}C values, obtained by the same averaging as for ^{14}C, are indeed included in Table 4, but as stated in the text their range was small and as such they were not helpful in distinguishing OC source so they were not used in mass balance.***

Finally, as compared with marine-derived lipids, terrestrially derived lipids are relatively poorly represented in Tables 1-3 with only 3 compound classes, although they are probably the most abundant and workable types in the solvent extractable lipids. But considering the large range of Δ14C values found for various marine lipids (in Arabian Sea, for example), how much confidence do you have in having these three types of lipids to represent the average 14C content terrestrial OC? As compared with marine biota, lipids are a relatively smaller component in the terrestrial biomass or OC. Some recent work has shown that other major terrestrial biopolymers (lignin) may have different 14C ages in surface sediments. How will this affect the end-member values and hence the result of the mixing model? ***We don’t know how to answer this except to say that we had to work with what we were able to measure. Other compounds like lignin would indeed have been helpful, but in most of the samples available, there would have been too little lignin to work with as the trap and several sediments would have contained little lignin, and in any event at the time of analysis compound-specific lignin methods were not available. The results of the mixing model are not presented as the absolute answer but as an indication of what the data suggest is happening.***

Specific comment: Page 9771, Line 15: Pearson and Eglinton (2000) is not found in the references. ***Yes, it will be added.*** ***Pearson, A., and Eglinton, T. I.: The origin of n-alkanes in Santa Monica Basin surface sediment: a model based on compound-specific Δ^{14}C and δ^{13}C data. Org. Geochem. 31, 1103-1116, 2000.***

Transfer of organic carbon through marine water columns to sediments – Insights from stable and radiocarbon isotopes of lipid biomarkers

Deleted: lipids

S. G. Wakeham[1,*] and A. P. McNichol[2]

[1]Skidaway Institute of Oceanography, 10 Ocean Science Circle, Savannah, GA 31411
USA

[2]National Ocean Sciences Accelerator Mass Spectrometer Facility (NOSAMS),
Woods Hole Oceanographic Institution, McLean Laboratory, Mail Stop #8,
266 Woods Hole Road, Woods Hole, MA 02543-1539 USA

Key words: marine sediments, sediment traps, lipid biomarkers, stable carbon isotopes, radiocarbon, Black Sea, Arabian Sea, Ross Sea

[*]Corresponding author: email stuart.wakeham@skio.usg.edu

Abstract

Compound-specific ^{13}C and ^{14}C compositions of diverse lipid biomarkers (fatty acids, alkenones, hydrocarbons, sterols, and fatty alcohols) were measured in sinking particulate matter collected in sediment traps and from underlying surface sediments in the Black Sea, the Arabian Sea and the Ross Sea. The goal was to develop a multi-parameter approach to constrain relative inputs of organic carbon (OC) from marine biomass, terrigenous vascular plant, and relict kerogen sources. Using an isotope mass balance, we calculate that marine biomass in sediment trap material from the Black Sea and Arabian Sea accounted for 66-100% of OC, with lower terrigenous (3-8%) and relict (4-16%) contributions. Marine biomass in sediments constituted lower proportions of OC (66-90%), with consequentially higher proportions of terrigenous and relict carbon (3-17% and 7-13%, respectively). Ross Sea data were insufficient to allow similar mass balance calculations. These results suggest that whereas particulate organic carbon is overwhelmingly marine in origin, pre-aged allochthonous terrigenous and relict OC become proportionally more important in sediments, consistent with pre-aged OC being better preserved during vertical transport to and burial at the seafloor than the upper ocean-derived marine OC.

Deleted: M

Deleted: biomarkers

Deleted: It is apparent

Deleted: there are also significant proportions of

Deleted: that

Deleted: . These results indicate that

Deleted: is

Deleted: and/or it reaches the sediment by lateral advection rather

Deleted: only by the vertical sinking/biological pump that affects

Deleted: P

1 Introduction

The dynamics of sources, sinks and processes that control burial of organic carbon (OC) in marine sediments have important implications for the global carbon cycle, paleoceanographic reconstructions and understanding climate variability (Berner, 1982; Hedges and Keil, 1995; Burdige, 2007; Zonneveld et al., 2010). Assigning the provenance of sedimentary OC remains a difficult task. Most burial occurs on continental margins where terrigenous material constitutes a significant proportion of the burial flux (Hedges et al., 1997; Burdige, 2005). But even at open ocean locations remote from the continents where marine OC dominates the water column flux via the biological pump, a terrigenous component delivered by long-range aeolian transport (Zafiriou et al., 1995; Gagosian and Peltzer, 1986; Eglinton et al., 2002; Kawamura et al., 2003) is still recognizable in sediments (Prahl et al., 1989; Wakeham et al., 2002; Zonneveld et al., 2010). Myriad biogeochemical and sedimentological processes during transport through the marine water column and at the sediment-water interface affect the quantity and nature of sedimentary OC. Structural characterization of most marine organic matter is incomplete (Hedges et al., 2000; Lee et al., 2004), but it is generally thought that marine OC is more reactive than terrigenous plant and relict sediment OC (Cowie and Hedges, 1984; Wakeham et al., 1997). Even a small fraction of the most recalcitrant relict carbon is amenable to bacterial assimilation (Petsch et al., 2001, 2003; Pearson et al., 2005; Wakeham et al., 2006). Selective enrichment of terrigenous OC in marine sediments over what is observed in the water column may result from differences in the intrinsic reactivity of the organic molecules themselves, protection by degradation-resistant macro-organic matrices and mineral surfaces, or environmental conditions (oxygen availability, oscillating redox, microbial consortia present) (Hedges and Keil, 1995; Hedges et al., 2001; Aller, 1994; Wakeham and Canuel, 2006; Burdige, 2007).

A suite of geochemical tools are applied to characterize the source(s) and fate of OC in the marine water column and sediments. Elemental compositions and ratios (e.g., OC/N) are often combined with carbon isotope analyses at the bulk level. Natural abundance stable carbon isotopes ($\delta^{13}C$) give insight into carbon source, carbon assimilation pathways and carbon flow in marine ecosystems and food webs (Hayes, 1993; Fry and Sherr, 1994; Freeman, 2001; Pearson, 2010). Natural-abundance radiocarbon analyses ($\Delta^{14}C_{OC}$ or fraction modern f_m) add the dimension of “age” to the character of organic matter and help define the residence time and redistribution of OC (Blair et al., 2003; Ingalls and Pearson, 2005; Griffith et al., 2010). Molecular analyses of biomarkers can distinguish between marine (e.g., sterols, alkenones), terrigenous (plant waxes and lignin phenols) and relict (alkanes with a carbon preference index of ~1 and often an unresolved complex mixture) materials in the heterogeneous mixture that is sedimentary OC. But biomarker compounds are often present at low concentrations, and extrapolations to bulk OC are formidable. Single-compound (compound-specific) isotope analyses help in this respect because they combine the source-specificity of biomarkers with $\delta^{13}C_{biomarker}$-derived information on carbon flow (Freeman et al., 1990; Hayes, 2001; Freeman, 2001) and $\Delta^{14}C_{biomarker}$-derived ages that indicate mixing of old with modern OC (Eglinton et al., 1997; McNichol and Aluwihare, 2007; Ingalls and Pearson, 2005). Early investigations in the marine water column showed that whereas sinking particulate OC comprised of fresh planktonic detritus has a young radiocarbon age, surface sedimentary OC has older ages of a “pre-aged” and/or relict terrigenous component (Druffel et al., 1996; Wang et al, 1998; Hwang et al., 2010). Compound-specific radiocarbon measurements confirm pre-aged biomarkers in sedimentary OC (review by Ingalls and Pearson, 2005), and compound-class radiocarbon analyses have subsequently shown pre-aged OC in water column particulate matter (Wang et al., 2001; review by McNichol and Aluwihare, 2007). However, to date combined biomarker/stable carbon/radiocarbon studies of marine particulate matter are few (an exception being Ingalls et al., 2006), largely due to sample size limitations.

The present investigation attempts to fill this gap. The combination of lipid biomarker composition with molecular stable- and radio-carbon isotopes offers a three-dimensional approach for investigating OC sources and transport and alteration processes in the ocean. In this study, compound-specific stable carbon and radiocarbon isotopes were measured on multiple lipid biomarkers in sinking particulate matter collected in sediment traps and from underlying surface sediments to evaluate the provenance of sedimentary organic matter. Three sets of paired sediment trap-surface sediment samples (POM – particulate organic matter; SOM – sedimentary organic matter) from the Black Sea, Arabian Sea and Ross Sea were investigated as representatives of oceanic regions characterized by widely disparate OC sources and depositional environments. Organic carbon content (%OC), atomic C/N ratios ($C/N_{(a)}$), $\delta^{13}C$ and $\Delta^{14}C$ of bulk materials and individual biomarkers (fatty acids, hydrocarbons, alkenones, alcohols, and sterols) were measured to identify major molecular and isotopic compositions, and thereby shifts in relative amounts of marine, terrigenous (pre-aged vascular plant-derived with continental residence times of decades to centuries) and relict (derived from eroded ancient sedimentary rocks and petrogenic material) carbon, in POM and underlying SOM.

Throughout this discussion it is important to remember that the sediment trap samples are short snap-shots in time (up to 6 months) whereas the surface sediments may represent centuries.

2 Materials and Methods

2.1 Study sites and samples

Paired sediment trap and surface sediment (~0-2 cm) samples from three settings (Fig. 1) were studied: Black Sea (anoxic water column; high biogenic and high terrigenous OC); Arabian Sea (oxygen minimum zone; high biogenic OC, low terrrigenous OC); Ross Sea, Antarctica (high biogenic flux, relict continental OC). The choice of these locations was predicated in part on the availability of large amounts of archived sinking particulate matter to facilitate compound-specific radiocarbon analyses.

2.1.1 Black Sea

The Black Sea site was in southwestern Black Sea (42°N, 32°E), at station BS of the joint U.S. Turkish/German sediment trap program 50 km north of Asmara and 15 km from the base of the continental slope (Hay and Honjo, 1989; Hay et al., 1990). Anoxic conditions prevail below ~120-150 m water depth (Sorokin, 1983). Underlying sediments contain up to ~6% OC (Ross and Degens, 1974; Premuzic et al., 1982; Calvert et al., 1991). Biogenic and lithogenic particle fluxes and sediment accumulation have been reported by Hay (1987) and Hay et al. (1990). The site is offshore of the rugged Pontic Mountains on the north-Anatolian coastline and the continental margin is particularly steep, typically 6° between 100 and 2000 m depths (Ross et al., 1974).

Lithogenic material delivered by the Sarkarya Nehri, Filyos and Kocacay Rivers, usually during winter/spring, is deposited on the shelf, is frequently resuspended by storms, and is subsequently transported off-shore as either surface, mid-water (~150 m depth) or bottom water nepheloid layers and turbidites; a surface plume extending out to the study site is sometimes visible on LANDSAT imagery (Hay, 1987). Sedimentation of lithogenic material out of the water column is enhanced by biogenic material derived from the annual succession of blooms of the coccolithophoride *Emiliania huxleyi* (spring) and pennate diatoms *Rhizosolenia* sp. (summer), producing the characteristic light-dark laminae (varve couplets) of Black Sea sediments (Hay, 1987; Hay et al., 1991). White laminae are comprised almost exclusively of coccolithophores of *E. huxleyi*, whereas dark laminae are predominately terrigenous clay minerals.

Formatted: Font: Italic

Sediment trap material (18.5 g dry weight) from the moored BS trap at ~250 m depth under strongly anoxic conditions is a composite of a seven month-long time-series collection (October 1985-April 1986). Trap material was preserved with buffered formalin and stored refrigerated at 4ºC. Surface sediment (0-2 cm; 109.7 gdw) was composited from multicores collected at 2200 m water depth during the 1988 Black Sea Expedition (Murray and Izdar, 1989; Hay and Honjo, 1989) at approximately the same location as the trap mooring. Sediments were stored frozen. Radiocarbon dating of sediments near the study site gave a sedimentation rate of 26 cm/kyr (Arthur and Dean, 1998). Thus the 0-2 cm sediment interval represents approximately one century.

2.1.2 Arabian Sea

Arabian Sea samples were collected at mooring site MS-1 in the northwestern Arabian Sea (Oman Margin) during the U.S. JGOFS Arabian Sea Process Study (ASPS) in 1994-1995 (Smith et al., 1998). MS-1 was approximately 160 km from the Oman coast off Ra’s Sharbatat (17°41’N, 58°51”E) at a water depth of 1445 m. High seasonal productivity during monsoon-driven upwelling enhances export into deep waters where remineralization of sinking organic matter depletes dissolved oxygen down to levels of ~5 µM, producing the world’s largest open ocean oxygen minimum zone (OMZ) (Smith et al., 1998). Greater than 50% of the annual particle flux in the central Arabian Sea occurs during the boreal summer southwest monsoon. Biogenic material, primarily diatom-derived, dominates over lithogenic material (Haake et al., 1996; Honjo et al., 1999), but some terrigenous material is delivered to the northwestern Arabian Sea as dust from the Horn of Africa (Somalia and Ethiopia) and from the Arabian Peninsula by strong summer monsoon winds (Ramage et al., 1972; Sirocko and Sarnthein, 1989; Dahl et al., 2005).

Sediment trap material (35.5 gdw) was a composite of material collected in time-series traps deployed in the OMZ at ~500 and ~900 m between May 1995 and January 1996, covering the southwest monsoon period (Wakeham et al., 2002). Mercuric chloride was used as a biocide. Upon recovery, trap samples were sealed and stored refrigerated at 4°C. Surface sediments (0-2 cm) were composited (142.7 gdw) from multicores collected in 1995 at the same location as the trap deployment and stored frozen. Passier et al. (1997) have estimated the sedimentation rate for this part of the Oman Margin at 5 cm/kyr; the sediment sample thus represents about 400 years.

2.1.3 Ross Sea

The Ross Sea site was in the southwestern Ross Sea where diatoms, primarily *Nitzschia* sp., and *Phaeocystis antarctica*, dominate the phytoplankton community and vertical flux during the austral summer bloom (Arrigo et al., 2002; Dunbar et al., 2003). Sediments are largely biogenic oozes (biogenic silica 10-30%) with low OC (0.1-3%, averaging 1.5%) and negligible biogenic carbonate (Dunbar et al., 1985; 1989). Terrigeneous material, primary lithogenics with low OC content, is delivered by glaciers that drain the polar plateau and by aeolian transport from the ice-free Dry Valleys and accounts for 2-25% of the vertical flux through the water column. In the western Ross Sea, ice-rafted debris constitutes ~10% of sediments (Anderson et al., 1984) and aeolian sedimentation (either through sea ice or directly onto the sea surface) could be up to 50% of sediments in nearshore areas with limited glacial ice cover (Bentley, 1979, cited in Dunbar et al., 1989). Nonetheless, sedimentary OC is dominated by biogenic water column sources. Sediments are resuspended, mixed and redistributed within a pervasive nepheloid layer.

Deleted: *A*

Ross Sea samples were collected during 1998 cruises of the ROAVERRS (Research on Ocean-Atmosphere Variability and Ecosystem Response in the Ross Sea) program (Dunbar et al., 2003). Trap material (48.2 gdw) came from Gentoo and Adelie time-series traps located at about 76° S, 172 E in the southwestern Ross Sea and deployed ~50 m above the sea floor in 650-m deep water (Dunbar et al., 2003). Trap material was preserved with 3% formalin and stored at 4ºC. Surface sediments (515.1 gdw) were obtained from box cores (Ohkouchi et al., 2003) and stored frozen.

Sedimentation rate determinations for the Antarctic margin often use acid-insoluble organic carbon (AIOC) due to lack of calcareous formaninifera (Domack et al. 1989; Licht et al. 1996; Harris et al. 1996; Andrew et al. 1999). DeMaster et al. (1996) reported AIOC-derived sedimentation rates in this region of the Ross Sea at ~4.5 cm/kyr. AIOC-based chronology, however, is complicated by "contamination" by unknown amounts of relict OC (Sackett et al. 1974). To overcome this problem, Ohkouchi et al. (2003) applied compound-specific radiocarbon analysis of sedimentary fatty acids for cores from the Gentoo and Adelie sites and found a 1200-2000 year offset between ages of fatty acids and AIOC. The fatty acid-derived sedimentation rate was 7.5 cm/kyr vs. an AIOC-derived rate of 15 cm/kyr. The sediment sample therefore represents 130-250 years of deposition.

2.2 Elemental analysis

Freeze-dried and acidified (Hedges and Stern, 1984) trap material (bulk POM) and sediments (bulk SOM) were analyzed for organic carbon (%OC) and total nitrogen (TN) with a Fisons CHN analyzer (Model EA 1108) elemental analyzer.

2.3 Lipid analysis

Extraction, cleanup and isolation of fatty acids, hydrocarbons, alcohols and sterols by preparative capillary gas chromatography (PCGC; Eglinton et al., 1996) are outlined in Fig. 2. All laboratory glassware and SiO_2were precombusted at 500 °C for 8 hr before use. Freeze-dried POM and SOM were Soxhlet-extracted with methylene-chloride:methanol (DCM:MeOH, 2:1 v/v) for 72 hr. Extracts were washed with 5%

NaCl solution and solvent lipid extracts (SLEs) were partitioned into DCM, after which the DCM fraction was dried over Na_2SO_4. SLEs were saponified using 0.5 N KOH at 100º C for 2 hr, and nonsaponifiable lipids were extracted out of the alkaline mixture with hexane after which the pH was adjusted to <2 with 6N HCl and acids were extracted with hexane. Non-saponifiable lipids were fractionated on 5% deactivated silica gel into a hydrocarbon fraction eluted with hexane, an alkenone fraction eluted with 10% ethylacetate in hexane and an alcohol/sterol fraction eluted with 25% ethylacetate in hexane. Straight-chained hydrocarbons were separated from branched and cyclic hydrocarbons by urea adduction. Alkenones were isolated by sequential silica gel, $AgNO_3$/silica gel chromatography and urea adduction after Ohkouchi et al. (2005). Alcohols and sterols were acetylated with pyridine and acetic anhydride. Acids were methylated with BF_3:MeOH and the fatty acid methyl esters (FAMEs) were purified on columns of activated SiO_2.

2.4 Stable and Radiocarbon Analysis

Isolation of purified individual hydrocarbons, sterol acetates, alcohol acetates and FAMEs was by preparative capillary gas chromatography (PCGC; Eglinton et al., 1996; Wakeham et al., 2006). An HP 5980II GC equipped with an HP 7673 autoinjector, a Gerstel CIS-3 cooled injection system and a Gerstel preparative fraction collector (PFC) was fitted with RTX-1 megabore (60 m x 0.53 mm id x 0.5μm film) capillary column. The GC temperature program was 60°C (1 min), 20°C/min to 160°C, 4°C/min to 300°C and isothermal at 300°C for 20 min. An effluent splitter directed 1% of the column effluent to the FID and the remaining 99% was sent to the zero-dead-volume splitter of the PFC. The PFC was operated at 320°C and U-tube traps were held at room temperature. Purified fractions were checked for purity and quantified by gas chromatography-mass spectrometry (Agilent 6890 gas chromatograph, Agilent 5793 mass spectrometer, 30 m x 0.25 mm i.d. J&W DB-5 capillary column). Individual, composited compounds or operational classes were transferred to glass ampules and flame-sealed for isotope analysis.

Stable and radio-carbon isotope measurements were made at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility at the Woods Hole Oceanographic Institution. $\delta^{13}C$ values are reported relative to the VPDB (precision ±0.2 ‰) and $\Delta^{14}C$ values are reported according to Stuiver and Polach (1977) using the year of sample collection for age correction. Acidified POM and SOM were transferred to pre-combusted Vycor tubes containing CuO and Ag powder. Sample extracts and isolated biomarkers were transferred with solvent to pre-combusted Vycor tubes, and after evaporating the solvent, 100 mg pre-combusted CuO was added to the tube. Samples were combusted to CO_2 at 850°C for 5 hours. After purification and quantification, a split of the CO_2 was analyzed for $\delta^{13}C$ on a VG Micromass Optima isotope ratio mass spectrometer. The remaining CO_2 was reduced to filamentous graphite over either Fe or Co powder. Radiocarbon analyses of both large and small samples were performed using standard NOSAMS procedures (McNichol et al., 1994; von Reden et al., 1998; Pearson et al., 1998). Processing and combustion blanks of a hydrocarbon fraction isolated from a south Louisiana crude oil had replicate $\Delta^{14}C$ values between –980 and –998 ‰ (f_m 0.03 and 0.001, respectively). Contributions of added methyl carbon derived from methanol in FAMEs and acetyl carbons from acetic anhydride in alcohol and sterol esters were

Deleted:

Deleted: 01-

Deleted: 3

removed by isotopic mass balance (Pearson, 2000; Wakeham et al., 2006). The $\delta^{13}C$ and $\Delta^{14}C$ values of carbon in the BF_3:MeOH and acetic anhydride reagents were calculated by measuring the $\delta^{13}C$ and $\Delta^{14}C$ values of palmitic acid and cholesterol standards and of methylpalmitate and cholesteryl acetate prepared using the same lots of BF_3-MeOH and acetic anhydride, respectively, and isolated by PCGC.

Several FA had unusually high $\Delta^{14}C$ values and were not used in subsequent calculations of ranges, means and standard deviations of radiocarbon data (shown in bold italics in Tables 1-3). The reasons for these enrichments are unknown (see Wakeham et al., 2006 for additional discussion). Radiotracers had never been used in the SkIO laboratory that was thoroughly checked for any radiocarbon contamination and crude oil process blanks were free of modern carbon. The most enriched FA (most often but not always 16:0, 18:1 and 18:0) were compounds isolated in the highest concentrations and thus for which larger amounts of carbon were analyzed by AMS rather than the less-abundant compounds. Such enrichments were not systematic, and in several cases replicate AMS analyses from splits of the same isolates were made, but with similar results indicating that any contamination must have occurred prior to or during PCGC workup. However, Levin and Kromer (1997) suggested that the average ^{14}C of atmospheric CO_2 between 1980 and present may have been ~200 ‰ whereas analysis of post-bomb sediment from the Santa Monica Basin by Pearson and Eglinton (2000) indicates an average ^{14}C of atmospheric CO_2 around 1960 may have been ~400 ‰. Thus while it is not possible to completely rule out incorporation of higher amounts of post-bomb ^{14}C into these biomarkers $\Delta^{14}C$, other marine biomarkers and bulk OC are not consistent with such a scenario.

3 Results and discussion

3.1 Bulk elemental compositions

Organic carbon contents (%OC) of POM (Fig. 3a) were 8.7 % in the Black Sea (BS), 6.4 % in the Arabian Sea (AS) and 5.5 % in the Ross Sea (RS). Total nitrogen (%TN) contents were 1.1, 0.86, and 0.92 %, respectively, for the BS, AS and RS trap material. Thus atomic C/N ratios were 7.7, 7.4, and 5.9 (Fig. 3b). Sediment %OC and %TN were lower: 1.8, 2.3, and 0.54 % OC for the BS, AS, and RS, respectively; 0.20, 0.29, and 0.08 % TN for the BS, AS, and RS, respectively. $C/N_{(a)}$ ratios for sediments were somewhat higher (9.4, 7.7, 6.5 for BS, AS, and RS, respectively) than for POM. Except for the BS sediment, $C/N_{(a)}$ ratios of the other trap and sediment samples were sufficiently Redfield-like to indicate the predominance of marine OC. The higher $C/N_{(a)}$ ratio of the BS sediment suggests a somewhat higher component of terrigenous OC; alternately the higher $C/N_{(a)}$ ratio could result from preferential loss of nitrogen during degradation of OC, but this process is likely limited by the anoxic water column of the BS.

3.2 Bulk stable carbon isotopes

BS and AS POM $\delta^{13}C_{OC}$ values were typical for marine dominated OC: –22.9 ‰ and –22.4 ‰ for the Black Sea and Arabian Sea, respectively (Fig. 4a). $\delta^{13}C_{OC}$ values for the corresponding SOM were both slightly more negative (BS –25.3 ‰) and more positive (AS –20.8 ‰) compared to the corresponding POM. The ^{13}C-depletion in the BS sediment could reflect a greater long-term/time-averaged terrigenous C_3-plant OC component (Collister et al., 1994; Conte and Weber, 2002; Chikaraishi et al., 2004) from the heavily wooded Anatolian coast than was present in the short-term trap sample. The relative enrichment of the AS sediment compared to the trap material could be the result of the addition of isotopically-enriched aeolian-transported OC derived from C_4-grasses in the arid Horn of Africa and Arabian Peninsula (Parker et al., 2004; Dahl et al., 2005), but again sampling time-scales for trap and sediment are different.

The Ross Sea is a very different environment. Both POM and SOM had $\delta^{13}C_{OC}$ values of –27.9 ‰, significantly isotopically depleted compared to BS and AS samples. Algal biomass at high latitudes is typically depleted in ^{13}C relative to algal OC at lower latitudes (Rau et al., 1991a,b; DeHairs et al., 1997; Freeman, 2001). Several factors may be involved in this differential photosynthetic isotope fractionation, including high algal growth rates, higher dissolved CO_2 concentrations associated with low seawater temperatures, and carbon assimilation mechanism (Rau et al., 1991a,b; DeHairs et al., 1997; Freeman, 2001). In the open southwest Ross Sea, diatom and *Phaeocystis* biomass is –28 ‰ to –27 ‰ (Villinski et al, 2000). Sea-ice algae would add ^{13}C-enriched OC (Gleitz et al., 1996; Gibson et al., 1999; Villinski et al., 2000) but is not a significant source of algal OC at the study site. Antarctic kerogen and coal have $\delta^{13}C_{OC}$ values of –22 ‰ and –24 ‰, respectively (Sackett, 1986; Burkins et al., 2000), and soils from the McMurdo Dry Valley region have a wide range of $\delta^{13}C_{OC}$ values, ~–30 ‰ to ~–18 ‰ (and C/N(a) of 11±4) (Burkins et al., 2000).

Deleted:

Solvent lipid extracts (SLE) would help bridge the gap between bulk OC and individual biomarkers. In all three sample pairs, SLE's were depleted by up to 4 ‰ in ^{13}C compared with the respective bulk OC's (Fig. 4b). $\delta^{13}C_{SLE}$ values for both traps and sediments followed the same trend among samples as $\delta^{13}C_{OC}$: $\delta^{13}C_{AS\text{-}SLE} > \delta^{13}C_{BS\text{-}SLE} > \delta^{13}C_{RS\text{-}SLE}$. Lipids are a relatively abundant fraction of OC in phytoplankton and zooplankton but are usually only a few percent of OC in particulate matter and sediments (Wakeham et al., 1997; Wang and Druffel, 2001). They would thus not be major contributors to particulate and sedimentary $\delta^{13}C_{OC}$ compared to more abundant proteins and carbohydrates that are ~4-6 ‰ enriched in ^{13}C relative to lipids. Intra-class comparisons of isotopic compositions in marine systems are few. A study of $\delta^{13}C$ of particulate and sedimentary OC in the northeast Pacific and Southern Oceans found that total hydrolysable amino acids (THAA) and total carbohydrates (TCHO) in phytoplankton, zooplankton and sediments were enriched in ^{13}C by about ~2 ‰ and ~3 ‰, respectively, relative to OC whereas lipids were depleted ~4 ‰ relative to OC (Wang et al., 1998; Wang and Druffel, 2001).

3.3 Bulk radiocarbon isotopes

Radiocarbon isotopic values for BS and AS trap OC ($\Delta^{14}C_{OC}$) were 21 ‰ and 14 ‰ and for BS and AS sediments were −199 ‰ and −138 ‰, respectively (Fig. 4c and Tables 1-3 which also lists radiocarbon ages and fraction (%) modern, f_m). RS POC and SOC were depleted in ^{14}C (−208 ‰ and −355 ‰, respectively) relative to the two other sites. $\Delta^{14}C_{DIC}$ values for pre-bomb and post-bomb mixed-layer DIC (dissolved inorganic carbon) in the Black Sea are ~−70 ‰ and 100 ‰, respectively (Jones and Gagnon, 1994) and in the AS are ~−60 ‰ and ~70 ‰ (Stuiver and Östlund, 1983; Southon et al., 2002); these values determine the $\Delta^{14}C$ of autochthonous marine biomass. Pre-bomb and post-bomb $\Delta^{14}C_{DIC}$ values in the Ross Sea are lower than elsewhere, −130 ‰ and −100 ‰, respectively (Berkman and Forman 1996; Gordon and Harkness 1992; Hall et al., 2010). In the AS and RS, upwelling of ^{14}C-depleted deep-waters and the short residence time of surface waters lead to the high surface-water reservoir ages (~700 yr and ~1100 yr for AS and RS, respectively vs. ~400 yr for open ocean locations, including the BS; Stuiver and Braziunas, 1993; Siani et al., 2000; Southon et al., 2002; Key, 2004; Hall et al., 2010). Thus trap OC displayed post-bomb signatures for their respective regions but additionally contained older carbon, especially in the Ross Sea. Sediments contained significant contributions of old carbon, and corrected $^{14}C_{OC}$-ages (Tables 1-3) are significantly older than estimated geological ages (100-400 yr, admittedly based on $^{14}C_{OC}$-derived sedimentation rates).

Trap and sediment SLE's for the BS and RS had higher $\Delta^{14}C_{SLE}$ values than corresponding $\Delta^{14}C_{OC}$ values (Fig. 4d): $\Delta^{14}C_{SLE}$ values were −96 ‰ and −150 ‰ for BS trap and sediment, respectively; −154 ‰ and −211 ‰ for RS trap and sediment. That the BS and RS trap lipid fractions had lower $\Delta^{14}C_{SLE}$ values than $\Delta^{14}C_{OC}$ values indicates that some old carbon was extractable (e.g., plant waxes and petroleum hydrocarbons). But the higher sediment $\Delta^{14}C_{SLE}$ values than sediment $\Delta^{14}C_{OC}$ suggested that residual OC remaining after solvent extraction must be, by extension, still older, such as non-extractable kerogen, especially in the RS sediment. On the other hand, $\Delta^{14}C_{SLE}$ of the AS trap material was enriched (66 ‰) compared to $\Delta^{14}C_{OC}$ value, but the sediment was depleted (−173 ‰) relative to its $\Delta^{14}C_{OC}$ value. Thus solvent extraction of the AS trap material released a greater proportion of fresh, young algal lipid into the SLE but extraction of the sediment recovered an SLE with a greater proportion of older lipid. In the only other reports to our knowledge that measured $\Delta^{14}C_{SLE}$ (Wang et al., 1998; Wang

Deleted: OC, as lipid,

Deleted: left behind

Deleted: non-extractable,

Deleted: OC

and Druffel, 2001), plankton and sedimentary lipids in the northeastern Pacific and Southern Ocean were similar to or lower than, respectively, $\Delta^{14}C$ of total OC. Lipids, THAA and TCHO all had similar $\Delta^{14}C$ values in plankton, but in sediments lipids usually had lower $\Delta^{14}C$ signatures than THAA and THCO.

3.4 Biomarker molecular compositions

Biomarker analyses focused on fatty acids, alkenones, fatty alcohols, sterols, and hydrocarbons (Figs 5-7). In the following discussion, the operational distinction is made between biomarkers of marine origin (hereafter termed "marine OC"), those derived from pre-aged terrestrial vascular plants ("terrigenous OC") and compounds originating from eroded ancient sediment or petrogenic sources ("relict OC"). In all POM samples, short-chain C_{14}-C_{24} *n*- and methyl-branched *iso*- and *anteiso*-C_{15} and C_{17} compounds of marine biomass dominated fatty acid distributions (Volkman, 2006). Long-chain, even-carbon number predominant C_{24}-C_{30} terrestrial vascular plant *n*-fatty acids were ~10-fold less abundant. Sediments contained similar fatty acid distributions but with higher relative abundances (but still ~3-5-fold less abundant) of long-chain compounds. Long-chain C_{37}-C_{39} alkenones derived from the haptophyte, *Emiliania huxleyi* (Volkman et al., 1980), were abundant in BS (where coccoliths of *E. huxleyi* constitute the light laminae) and AS traps and sediments, but absent from the RS. Low levels of hydrocarbons, a mix of C_{15}-C_{36} *n*-alkanes and an unresolved complex mixture (UCM) in the C_{14} –C_{22} carbon number range were present in BS and AS samples at levels ~10-fold lower than fatty acids; none above blanks were detected in the RS. Short-chain *n*-alkanes (C_{16} –C_{22}) showed no odd-over-even carbon number predominance (CPI ~1) and were underlain by

Deleted:

an unresolved complex mixture (UCM), whereas long-chain *n*-alkanes (C_{25} – C_{31}) were odd-carbon predominant (CPI > 5). C_{25}-highly branched isoprenoid (HBI) alkenes of diatom origin were the dominant hydrocarbons in AS POM but were only minor components in BS POM and sediments and AS sediments. No hydrocarbons (above blanks) were detected in RS samples. All POM samples contained abundant *n*-hexadecanol (16 ROH, assumed derived primarily from zooplankton wax esters) and C_{27}-C_{30}-Δ^{5}, $\Delta^{5,22}$, $\Delta^{5,24(28)}$ sterols [e.g., cholest-5-en-3β-ol (cholesterol), abbreviated as 27Δ^{5}; 24-methylcholesta-5,22-dien-3β-ol, 28$\Delta^{5,22}$; 24-methylcholesta-5,24(28)-dien-3β-ol, 28$\Delta^{5,24(28)}$; and in the BS, a significant amount of 4,23,24-trimethylcholest-22-en-3β-ol (dinosterol), 30Δ^{22}], all of marine origin (Volkman, 2006). POM contained only low amounts of even-carbon number predominant C_{24}-C_{30} *n*-alcohols produced by vascular plants, but sediments contained higher abundances of terrestrial *n*-alcohols than sterols.

3.5 Biomarker isotopic compositions

PCGC isolation for compound-specific isotope analyses targeted the most abundant biomarkers of marine, terrigenous plant and relict origins. Short-chain *n*-fatty acids (C_{14}-C_{24}, abbreviated as 14:0 FA, etc), C_{37}+C_{38}-alkenones, a short-chain *n*-fatty alcohol [16ROH (*n*-hexadecanol)] and sterols [cholest-5-en-3β-ol (cholesterol), abbreviated as 27Δ^{5}; 24-methylcholesta-5,22-dien-3β-ol, 28$\Delta^{5,22}$; and 4,23,24-trimethylcholest-22-en-3β-ol (dinosterol), 30Δ^{22}], were designated as marine biomarkers. Long-chain even-carbon number *n*-acids (C_{26}-C_{30}) and *n*-alcohols (C_{24}-C_{28}) and long-chain odd-carbon numbered *n*-alkanes (C_{27}, and C_{29}) were tagged as terrigenous, vascular plant markers; in some cases the long-chain fatty acids could be isolated individually but

Deleted:

Deleted:

in other cases composites (e.g. C_{24}+C_{26}+C_{28} fatty acids) were required. Long-chain even-carbon numbered *n*-alkanes (composited C_{24}+C_{26}+C_{28}) and, in the AS sediment, short-chain C_{15}+C_{16}+C_{17}+C_{18} alkanes (and including some unresolved complex mixture that could not be removed) were used as relict markers since these alkanes are not abundant in marine or terrestrial biomass. As will be shown below, using long-chain *n*-alkanes as either terrigenous plant or relict markers is problematic because in the present samples there is overlap between odd- vs even-chain lengths and plant vs. relict sources. Thus it is possible that long-chain *n*-alcohols, if present in sufficient abundances, may represent the best "terrigenous" biomarkers since they would have neither modern marine (major alcohols in wax esters are C_{16} and C_{18}; Wakeham, 1982) nor relict sources. Highly branched C_{25} alkenes (HBI) of diatom origin (Belt et al., 2000) were the most abundant hydrocarbons in AS trap material, less so in AS sediments, but they were underlain by a UCM that could not be removed, thus yielding unrealistically ^{14}C depleted results. In the RS POM and SOM, only fatty acids, 16 ROH, and sterols (cholest-5-en-3β-ol and 24-methylcholesta-5,22-dien-3β-ol) could be isolated. Stable carbon and radiocarbon isotope results were weighted according to their abundance within each sample to give means for each of the three sources (marine, terrigenous, and relict) that are designated below as $\delta^{13}C_M$ and $\Delta^{14}C_M$, $\delta^{13}C_T$ and $\Delta^{14}C_T$, and $\delta^{13}C_R$ and $\Delta^{14}C_R$.

Deleted:

3.5.1 Black Sea

For the Black Sea POM, short-chain fatty acids, long-chain alkenones, and sterols had $\delta^{13}C$ values between –26.1 ‰ to –23.2 ‰ (Fig. 8a and Table 1), generally 1-4 ‰ more ^{13}C-depleted than bulk POM (–22.9 ‰). Interestingly, alkenones were the most

Deleted:

Deleted:

^{13}C-depleted of this group. Overall these “marine” biomarkers had an abundance weighted average $\delta^{13}C_M$ of –25.3 ± 1.1 ‰ (Table 4), typical for marine lipids. Radiocarbon values for the marine biomarkers (excluding the highly ^{14}C-enriched 18:1 fatty acid outlier at 288 ‰) ranged from 65 ‰ to 146 ‰, giving $\Delta^{14}C_M$ of 92 ± 28‰, considerably enriched in ^{14}C relative to bulk POM ($\Delta^{14}C_{OC}$ –199 ‰) (Fig. 8b). Long-chain even-carbon number acids and alcohols and odd-carbon number alkanes had δ^{13}C values ranging from –30.1 ‰ to –27.0 ‰, yielding a mean $\delta^{13}C_T$ –28.7 ± 1.6 ‰, roughly 3‰ depleted in δ^{13}C compared to marine lipids. Terrigenous markers had a much greater range of Δ^{14}C values (1 ‰ for the fatty acids, –44 ‰ for the alcohols, and –181 ‰ for the alkanes) but a mean $\Delta^{14}C_T$ of –53 ± 60 ‰. It is possible that some fraction of the long-chain fatty acids are zooplankton (wax ester) derived young carbon whereas the long chain alkanes may contain a relict component. Thus the long-chain alcohols may represent the best “terrigenous” biomarkers since they would have neither modern marine (major alcohols in wax esters are C_{16} and C_{18}; Wakeham, 1982) nor relict sources with a Δ^{14}C of –1000 ‰. The single sample of “relict” biomarkers isolated by PCGC was a composite of C_{24}+C_{26}+C_{28} *n*-alkanes that had a $\delta^{13}C_R$ of –29.3 ± 0.2 ‰ and a $\Delta^{14}C_R$ of –677 ± 10‰; this Δ^{14}C value probably also reflects a mix of moderately pre-aged terrigenous (Δ^{14}C of –44 ‰ might be reasonable if the alcohols are a good representative of terrigenous OC) and radiocarbon-dead ($\Delta^{14}C_R$ of –1000) relict carbon.

Marine biomarkers in the BS sediment had δ^{13}C values ranging from –31.9 ‰ to –26.0 ‰ (mean $\delta^{13}C_M$ –28.8 ± 1.1‰), about 2.5 ‰ depleted in ^{13}C relative to both BS bulk SOM (–25.3 ‰) and the marine group of BS POM (also –25.3 ‰). Radiocarbon contents of marine biomarkers ranged from –46 ‰ to 75 ‰ (mean $\Delta^{14}C_M$ 2 ± 44 ‰,

Deleted:

Deleted: -

Deleted: likely

Deleted:

excluding 16:0 at 214 ‰ and 18:0 at 374 ‰), considerably enriched in ^{14}C relative to bulk POM ($\Delta^{14}C_{OC}$ –199 ‰) but depleted in ^{14}C compared to marine biomarkers in BS POM. Terrigenous biomarkers displayed $\delta^{13}C$ values between –31.9 ‰ to –29.7 ‰ (mean $\delta^{13}C_T$ –30.5 ± 0.65 ‰). Thus although there was a considerable overlap in $\delta^{13}C$ values for marine and terrigenous groups, concentration weighting yielded an offset of ~ 2 ‰ as would be expected. Plant-wax alkanes (C_{27} and C_{29}) and alcohols (C_{24} and C_{26}) were strongly depleted in $\Delta^{14}C$ relative to the marine lipids (range –231 ‰ to –100 ‰), with a mean $\Delta^{14}C_T$ of –171 ± 58 ‰. Long-chain even-carbon numbered [C_{24}+C_{26}+C_{28}] alkanes had a $\delta^{13}C$ value of –29.3 ‰ and a $\Delta^{14}C_R$ of –609 ‰, again suggesting they are pre-aged but not exclusively relict. A similar spread in $\delta^{13}C$ and $\Delta^{14}C$ values for marine, vascular plant and relict hydrocarbon biomarkers had been previously reported for Black Sea and Arabian Sea sediments (Eglinton et al., 1997).

3.5.2. Arabian Sea

The marine biomarkers in the AS trap POM had $\delta^{13}C$ values between –27.1 ‰ and –16.7 ‰ (mean $\delta^{13}C_M$ –23.5 ± 2.5) and $\Delta^{14}C$ contents ranging from –91 ‰ to 111 ‰ (Fig. 9a and b and Table 2) (mean $\Delta^{14}C_M$ –67 ± 40 excluding $C_{14:0}$ at 178 ‰ and HBI alkenes at –514 ‰). The negative $\Delta^{14}C$ value for the HBI alkenes is due inclusion of a UCM which could not be removed. The only vascular plant compounds in the AS trap in sufficient quantity for AMS analysis were analyzed as a composite of [C_{27}+C_{29}] *n*-alkanes, giving a $\delta^{13}C_T$ of –28.4 ‰ and a $\Delta^{14}C_T$ of –320 ‰. The single sample of [C_{24}+C_{26}+C_{28}] *n*-alkanes gave a $\delta^{13}C_R$ of –28.5 ± 0.2 ‰ and a $\Delta^{14}C_R$ of –731 ± 14 ‰.

Deleted: –

Deleted:

Formatted: Font: 12 pt, Not Bold, Not Italic, Font color: Black

Formatted: Font: 12 pt, Not Bold, Not Italic, Font color: Black, Superscript

Formatted: Font: 12 pt, Not Bold, Not Italic, Font color: Black

Formatted: Font: 12 pt, Not Bold, Not Italic, Font color: Black, Superscript

Formatted: Font: 12 pt, Not Bold, Not Italic, Font color: Black

The $\delta^{13}C$ values for marine biomarkers in AS sediments ranged from –26.8 ‰ to –18.2 ‰ ($\delta^{13}C_M$ mean –24.5 ± 2.1 ‰), and $\Delta^{14}C$ ranged from 104 to –171 ‰ ($\Delta^{14}C_M$ –59 ± 60 ‰, excluding 18:0 FA at 190 ‰ and HBI alkenes at –256 ‰). Vascular plant [C_{26}+C_{28}+C_{30}] *n*-alcohols had a $\delta^{13}C$ value of –24.1 ‰ and a $\Delta^{14}C$ value of –113 ± 13 ‰ and [C_{27}+C_{29}] *n*-alkanes displayed a $\delta^{13}C$ value of –27.7 ‰ and a $\Delta^{14}C$ value of –430 ± 11 ‰. Together, the terrigenous biomarkers had a concentration weighted $\delta^{13}C_T$ value of –27.7 ± 0.20 ‰ and a $\Delta^{14}C_T$ of –270 ± 110 ‰. Two groups of *n*-alkanes in AS sediments could be assigned to relict sources. Short-chain [C_{14}+C_{15}+C_{16}+C_{17}] alkanes and the UCM under this group of homologs had a $\delta^{13}C$ value of –29.4 ‰ and a $\Delta^{14}C$ value of –887 ‰. Long-chain [C_{24}+C_{26}+C_{28}] *n*-alkanes had a $\delta^{13}C$ value of –27.7 ‰ and a $\Delta^{14}C$ value of –430 ‰. Thus $\delta^{13}C_R$ and $\Delta^{14}C_R$ for the AS sediments would be –28.4 ± 0.2 ‰ and –879 ± 45 ‰, respectively.

Deleted:

Deleted:

3.5.3. Ross Sea

Ross Sea POM and SOM contained only marine-derived fatty acids (here C_{26} is considered marine assuming the absence of much terrigenous FA input to the RS) and alcohols/sterols in sufficient abundance for compound-specific isotopic analysis. In keeping with a ^{13}C isotope depletion in high latitude regions, noted above, fatty acids had $\delta^{13}C$ values ranging from –35.3 to –31.7 ‰ and alcohols/sterols values ranging from –35.4 to –31.8 ‰ (Fig. 10a and Table 3), together giving a mean $\delta^{13}C_M$ of –33.3 ± 1.8 ‰. Radiocarbon contents ranged from –216 to –100 ‰, with the alcohols/sterols slightly depleted relative to the fatty acids, for a $\Delta^{14}C_M$ –155 ± 47 ‰ (Fig. 10b).

Deleted:

Fatty acids and sterols/alcohols in RS sediments had δ^{13}C values ranging from –36.6 to –31.7 ‰ and –34.3 to –33.0 ‰, respectively, for a mean $\delta^{13}C_M$ of –34.3 ± 1.9 ‰. Radiocarbon contents of fatty acids from RS sediments were more variable than for RS POM, with values ranging from –302 to –83 ‰. Sterols from RS sediments were very unchanged from sterols in POM with Δ^{14}C values between –202 and –178 ‰ for sterols. Overall this gave a mean $\Delta^{14}C_M$ of –163 ± 77 ‰, also essentially the same as for $\Delta^{14}C_M$ of the trap material.

Deleted:

3.6 The provenance of POM and SOM in the Black Sea and Arabian Sea

Concentration-weighted isotope values (Table 4) can be used to constrain the ranges of isotopic compositions of marine, terrigenous and relict biomarkers, and by extension organic carbon, in Black Sea and Arabian Sea POM and SOM. Neither terrigenous nor relict biomarkers could be isolated from the Ross Sea in sufficient quantities for AMS analyses. Overall, $\delta^{13}C_M > \delta^{13}C_T \sim \delta^{13}C_R$ and $\Delta^{14}C_M > \Delta^{14}C_T >> \Delta^{14}C_R$ (Fig. 11). Furthermore, SOM biomarkers were generally ^{13}C-depleted and ^{14}C-depleted relative to their corresponding POM samples, indicative of higher proportions of ^{13}C depleted but older, pre-aged OC in sediments. The range of $\delta^{13}C_R$ was relatively small compared to $\delta^{13}C_M$ and $\delta^{13}C_T$ of POM and SOM, but the span of $\Delta^{14}C_R$ values was quite large since the odd carbon number hydrocarbons constituting these groups are a mix of old but not radiocarbon “dead” terrigenous vascular plant (Δ^{14}C values similar to average $\Delta^{14}C_T$ values) and truly relict (Δ^{14}C =1000 ‰) OC.

The relative contributions of marine, pre-aged terrigenous, and relict OC (f_M, f_T, and f_R) to sediment trap material and sediments can be estimated in the Black, Arabian,

Deleted: i

Deleted: e

and Ross Seas using an isotopic mass balance. Plots of $\delta^{13}C_{M,T,R}$ vs. $\Delta^{14}C_{M,T,R}$ in both the sediment traps and sediment (Fig. 11) show significantly different values for the radiocarbon content of the different carbon pools but relatively small differences in the stable isotopic content in the Black and Arabian Seas and in the Ross Sea sediments. The small differences in $\delta^{13}C$ coupled with significant error make it difficult to use the stable isotopic composition as a discriminating factor in determining the sources of the bulk material. However, the large differences observed in the $\Delta^{14}C$ values make it possible to use these data to constrain the relative amounts of relict, terrestrial and marine components.

For each sample, there is a $\Delta^{14}C$ value assigned to the bulk SLE, fresh marine, fresh terrestrial and a relict/terrestrial mix. Bulk material is assumed to be a mixture of fresh marine and other "added" material, where the added material refers to the fresh terrestrial and relict/terrestrial mix. Given this, we can derive the relative amounts of marine and "added" material.

Deleted: extract

Formatted: Font color: Black

Formatted: Font: Not Bold, Not Italic, Font color: Black

Deleted: Knowing that the bulk material is a mix of fresh marine and other "added" material,

Deleted: calculate

$$1 = f_M + f_{added} \qquad (1)$$

$$\Delta^{14}C_{bulk} = f_M\,(\Delta^{14}C_{mar}) + f_{added}\,(\Delta^{14}C_{added}) \qquad (2)$$

Solving this equation for f_{added}

$$f_{added} = \frac{D^{14}C_{bulk} - D^{14}C_M}{D^{14}C_{added} - D^{14}C_M} \qquad (3)$$

The value of $\Delta^{14}C_{added}$ can range from that for relict material (-1000 ‰) to that of the bulk material. Using this information, we can calculate the relative amounts of marine and "added" material as a function of the $\Delta^{14}C$ of the "added" material. Further, we can combine the radiocarbon value measured on the terrestrial portion with the value of truly relict material to calculate how much of the “added” material might come from fresh terrestrial material using the equations below.

Deleted: other

$$f_{added} = f_T + f_R \qquad (4)$$

$$\Delta^{14}C_{added} = f_T\,(\Delta^{14}C_T) + f_R\,(\Delta^{14}C_R) \qquad (5)$$

Truly relict material has a $\Delta^{14}C$ value of -1000‰ and fresh terrigenous material has the values determined in this study ($\Delta^{14}C_T$, Table 5). As stated earlier, the measured value of $\Delta^{14}C_R$ appears to be a mixture of truly relict material and terrigeneous material with a suite of ages. If we assume that the value we measured for “relict” material (Table 5) is a good representation of $\Delta^{14}C_{added}$, then we have a unique solution to the mass balance. This solution is indicated by the vertical lines in Figure 12 and the values listed in Table 5. Using this model, we force ourselves to an extreme situation where all the “added” material is either vascular or totally dead. Thus, the relative fractions of terrestrial and relict material must be considered maximum and minimum values, respectively.

Deleted: e

Formatted: Font color: Black

Formatted: Font: Not Bold, Not Italic, Font color: Black

Deleted: 9

For the calculations, concentration weighted $\delta^{13}C_M$, $\delta^{13}C_T$, $\delta^{13}C_R$, $\delta^{13}C_B$, $\Delta^{14}C_M$, $\Delta^{14}C_T$ and $\Delta^{14}C_B$ values listed in Table 4 were used. The relative fractions of marine, terrestrial and relict material (f_M, f_T, *and* f_R) as a function of $\Delta^{14}C_{added}$ are shown in Fig. 12. It is most likely that the marine component is dominant in both the trap and sediment samples, although the possible values range from >80 to 0%. Fresh vascular material can account for 0 up to almost 100%. The amount of relict material is constant at a low proportion, ranging from 0 to < 20% in both the trap and sediments. In the AS, the marine component is dominant in both the trap and sediments; the trap data indicate that there can be virtually no relict or vascular material input to this sample, while the

Deleted: s 3,

Deleted: and 5

Deleted: *other*

sediment data suggest that up to 30% of the material may come from either relict or vascular sources. In the RS sediment, marine material dominates in almost all instances, with possible values ranging from 90 to 30%. Relict material can account for >10 to 0% and vascular from 0 to <70%.

In the Black Sea and Arabian Sea cases here, it is likely that the marine component contributes the most material because a marine biogenic flux dominates at both sites. No comparable combined biomarker, ^{13}C, and ^{14}C studies of POM at other sites exist to our knowledge. But the high amounts of marine OC in the Black Sea and Arabian Sea sediments contrasts with other environments where similar biomarker-isotopic mass balances have been made, although using a narrower range of biomarkers. In nearshore sediments on the northern California Margin off the high-energy Eel River that erodes ancient sedimentary rocks in its watershed (Blair et al., 2003), fractional contributions from marine, terrestrial and relict components were estimated at 0-10, 50-75 and 30-50 % of total OC (Drenzek et al, 2009). On the Washington Margin off the lower-energy Columbia River, marine, terrestrial and relict OC contribute 2, 89-95 and 3-9 % of bulk sedimentary OC (Feng et al., 2013). Sediments in the Beaufort Sea had f_M, f_T and f_R values of 13-27, 36-42, and 34-37%, respectively, with the elevated f_R values consistent with the well-defined petrogenic signature of *n*-alkanes and polycyclic aromatic hydrocarbons in Mackenzie River and Beaufort Sea sediments (Yunker et al., 1993, 2002). For surface sediments in the southwest Black Sea near our study site, Kusch et al (2010) estimate a f_R of ~18% of TOC. In the Santa Monica Basin of the California Borderlands, 80-87% of the *n*-alkanes were of terrigenous plant origin whereas up to 20% of the alkanes were derived from petroleum or shales (Pearson and Eglinton,

Deleted:

2000), but since alkanes are not abundant in most marine biota, no estimation of the marine component was made.

For the Black Sea, the graphs for the relative contributions look similar for both the trap and sediment samples. A strict interpretation of these results suggests that there is a greater relative amount of non-marine material in the sediment trap than in the sediments themselves. Given the limitations of our data set, we believe that it is more likely that the relative amounts of material are actually very similar. This is somewhat surprising for two reasons. First, under a differential degradation/preservation case (Wakeham and Canuel, 2006), a more labile component of marine OC would be selectively degraded as POM moved between the trap depths and the surface sediments, leaving behind increased proportions of selectively preserved, more refractory terrigenous and relict components in sediments. Alternately, lateral advection of terrigenous and relict OC below the trap depths either by mid-depth or bottom currents might simply allow this pre-aged material to bypass the traps to be deposited directly on the sediments. At the Black Sea site, advective transport of continental material containing terrigenous and relict carbon to the study site is likely via surface, mid-water (~150 m depth) or bottom water nepheloid layers and turbidites. Surface and mid-water plumes moving offshore could carry some continental material to the shallow (~250 m) sediment trap. But a greater amount of terrigenous and relict carbon might, after temporary storage on the narrow continental shelf, be remobilized to move laterally down the steep continental slope under the trap. This type of advective remobilization of pre-aged material is well documented at other locations for both marine derived alkenones (e.g., Ohkouchi et al., 2002; Mollenhauer et al., 2003) and terrigenous/relict OC (e.g.,

Deleted: In

Aller et al., 2004; Mead and Goñi, 2006; Mollenhauer and Eglinton, 2007; Kusch et al., 2010; Hwang et al., 2010). Aeolian transport of leaf wax OC and petrogenic OC to the sediments of the central Black Sea have been reported (Wakeham 1996; Eglinton et al., 1997), but the importance of aeolian delivery to the southwestern Black Sea is unknown. Nonetheless, a small leaf wax/petrogenic signal was detected in the trap POM. Because the trap was already deployed within the anoxic zone (which starts at 120-150 m), OC degradation in the water column and surface sediments should be depressed, so that degradation might not be a significant cause for any reduction in f_M for the sediments.

In the Arabian Sea, the sediment trap material indicates the material is all marine while the sediments show a small influence of non-marine material. The Arabian Sea site was in an area of intense upwelling dominated by high export of diatomaceous material (Wakeham et al., 2002), remote from fluvial inputs but potentially affected by aeolian transport of pre-aged OC off the Arabian Peninsula and Horn of Africa during the windy monsoon periods (Dahl et al., 2005). The AS trap was deployed within the OMZ where organic matter degradation has reduced dissolved oxygen concentrations to ~5 μM (Smith et al., 1998), but AS sediments were collected at 1400 m water depth where bottom waters are oxygenated. Indeed within and below the OMZ, OC fluxes decreased 5-10 fold between the trap and surface sediments, even as %OC did not change as dramatically (Lee et al., 2000 for OC; Wakeham et al., 2002 for AS lipid fluxes). Comparative studies have shown conclusively that, among other things (e.g., intrinsic reactivity of organic molecules and protection by macromolecular organic matrices and mineral surfaces), oxygen availability is a key control on OC and lipid degradation/preservation water columns and sediments (e.g., Hedges and Keil, 1995;

Deleted: see

Gong and Hollander, 1997; Wakeham and Canuel, 2006; Burdige, 2007; Mollenhauer and Eglinton, 2007). Enhanced degradation (diminished preservation) in the oxygenated AS should be greater than in the anoxic Black Sea, and if marine OC is more labile than terrigenous/relict OC, f_M in the AS POM and SOM would, as observed, be higher than in the BS. Extensive production of petroleum reserves on the Arabian Peninsula and intense tanker traffic in the Arabian Sea is an additional source of refractory and radiocarbon-dead petrogenic OC to AS particulate matter and sediments.

The RS sediment results are consistent with previous studies suggesting that marine material is the most important source of organic matter to the sediments (Arrigo et al., 2002; Dunbar et al., 2003). The solutions that suggest a relatively large input of vascular plant material seem unrealistic given these prior studies. The Ross Sea data set is very limited and in fact does not include unambiguous lipids of either terrestrial or relict origins with which to constrain the isotopic compositions of these endmembers.

4 Conclusions

This study examined the compound-specific ^{13}C and ^{14}C compositions of diverse biomarker indicators of marine biomass, terrigenous vascular plant, and relict sources of organic carbon in sediment traps and underlying surface sediments in the Black Sea, the Arabian Sea and the Ross Sea. Using an isotopic mass balance approach, it was possible to constrain relative inputs from these three sources, with marine biomass accounting for 66-100% of extractable lipids and organic carbon in Black Sea and Arabian Sea sediment trap material. The remaining 3-8% derives from terrigenous and 4-16% from relict sources. Sediments contained lower proportions of marine biomarkers (66-90%) and consequentially higher proportions of terrigenous and relict carbon (3-17% and 7-13%, respectively). These results suggest that although particulate organic carbon is overwhelmingly marine in origin, there are significant proportions of pre-aged terrigenous and relict OC present. Because these latter fractions become proportionally more important in sediments, it is likely that they are better preserved than the marine component, and/or they reach the sediments by lateral advection rather than only by the vertical sinking that affects the upper ocean-derived marine POC. This approach demonstrates the strengths, and limitations, of such a multi-parameter approach for studying marine OC cycling and budgeting.

Acknowledgements

We thank Susumo Honjo and Steve Manganini for providing the Black Sea sediment trap material, Rob Dunbar Ross Sea trap material, and Tim Eglinton, Nao Ohkouchi and Jacqueline Grebmeier for providing the Ross Sea sediments. Michael Peterson helped with sediment trap and sediment collections in the Arabian Sea. Tamara Pease helped with initial analytical workup. NOSAMS personnel are thanked for assistance in sample processing there for ^{13}C and ^{14}C analyses. Grants OCE-9310364 and OCE-9911678 from the U.S. National Science Foundation (NSF), and the NSF Cooperative Agreement for the Operation of a National Ocean Sciences Accelerator Mass Spectrometry Facility (OCE-0753487 and OCE-123966) supported this research. SGW acknowledges the Hanse Wisseschaftskolleg (Hanse Institute for Advanced Studies), Delmenhorst, Germany, for a fellowship that supported writing of this manuscript.

Deleted: i

Deleted: e

References

Aller, R. C.: Bioturbation and remineralization of sedimentary organic matter: effects of redox oscillation, Chem. Geol., 114, 331-345, 1994.

Anderson, J. B., Brake, C., and Myers, N.: Sedimentation on the Ross Sea continental shelf, Mar. Geol., 57, 295 333, 1984.

Andrews, J. T., Domack, E. W., Cunningham, W. L., Leventer, A., Licht, K. J., Jull, A. J. T., DeMaster, D. J., and Jennings, A. E.: Problems and possible solutions concerning radiocarbon dating of surface marine sediments, Ross Sea, Antarctica, Quaternary Res., 52, 206–216, 1999.

Arrigo, K. R., DiTullio, G. R., Dunbar, R. B., Lizotte, M. P., Robinson, D. R., Van Woert, M., and Worthen, D. L.: Phytoplankton taxonomic variability and nutrient utilization and primary production in the Ross Sea, J. Geophys. Res., 105, 8827-8846, 2000.

Arthur M. A. and Dean W. E.: Organic-matter production and preservation and evolution of anoxia in the Holocene Black Sea, Paleoceanogr., 13, 395–411, 1998.

Belt, S.T., Allard, W. G., Massé, Robert, J.-M., and Rowland, S.J.: Highly branched isoprenoids (HBIs): Identification of the most common and abundant sedimentary isomers. Geochim. Cosmochim. Ac. 64, 3829-3851, 2000.

Bentley, P. N.: Characteristics and distribution of wind blown sediment, western McMurdo Sound, Antarctica, Thesis, Victoria Univ. Wellington, N.Z. 46 pp, 1979.

Deleted: ta

Berkman, P. A., and Forman, S. L.: Pre-bomb radiocarbon and the reservoir correction for calcareous marine species in the Southern Ocean, Geophys. Res. Lett., 23, 363–66, 1996.

Berner, R. A.: Burial of organic carbon and pyrite sulfur in the modern ocean – its geochemical and environmental significance, Am. J. Sci., 282, 451–473, 1982.

Blair, N. E., Leithold, E. L., Ford, S. T., Peeler, K. A., Holmes, J. C., and Perkey, D. W.: The persistence of memory: the fate of ancient sedimentary organic carbon in a modern sedimentary system, Geochim. Cosmochim. Ac., 67, 63– 73, 2003.

Burdige, D. J.: Burial of terrestrial organic matter in marine sediments: A re-assessment, Global Biogeochem. Cycles, 19, GB4011, doi:10.1029/2004GB002368, 2001.

Burdige, D. J.: Preservation of organic matter in marine sediments: controls, mechanisms, and an imbalance in sediment organic carbon budgets? Chem. Rev., 107, 467-485, 2007.

Burkins, M. B., Virginia, R. A., Chamberlain, R. A., and Wall D. H.: The origin of soil organic matter in Taylor Valley, Antarctica, Antarct. Ecol., 81, 2377-2391, 2000.

Chikaraishi, Y., Naraoka, H., and Poulson, S. R.: Hydrogen and carbon isotopic fractionations of lipid biosynthesis amount terrestrial (C3, C4, and CAM) and aquatic plants, Phytochem., 65, 1369–1381, 2004.

Collister, J. W., Rieley, G., Stern, B., Eglinton, G., and Fry, B.: Compound-specific ^{13}C analyses of leaf lipids from plants with differing carbon dioxide metabolisms, Org. Geochem., 21, 619-627, 1994.

Conte, M. H. and Weber, J. C.: Plant biomarkers in aerosols record isotopic discrimination of terrestrial photosynthesis, Nature, 417, 639–641, 2002.

Deleted:

Formatted: Font: (Default) Times New Roman

Deleted: ta

Cowie, G. L., and Hedges, J. I.: Biochemical indicators of diagenetic alteration in natural organic mixtures, Nature, 369, 304-307, 1994.

Dahl, K. A., Oppo, D. W., Eglinton, T. I., Hughen, K. A., Curry W. B., Sirocko, F.: Terrigenous plant wax inputs to the Arabian Sea: Implications for the reconstruction of winds associated with the Indian Monsoon, Geochim. Cosmochim. Ac, 10, 2547–2558, 2005.

Dehairs, F., Kopczynska, E., Nielsen, P., Lancelot, C., Bakker, D. C. E., Koeve, W., and Goyens, L.: δ^{13}C of Southern Ocean suspended organic matter during spring and early summer: Regional and temporal variability, Deep-Sea Res., Part II, 44, 129–142, doi:10.1016/S0967- 0645(96)00073-2, 1997.

DeMaster, D. J., Ragueneau, O., and Nittrouer, C. A.: Preservation efficiencies and accumulation rates for biogenic silica and organic C, N, and P in high-latitude sediments: the Ross Sea, J. Geophys. Res., 101, 18501–18518, 1996.

Domack, E. W., Jull, A. J. T., Anderson, J. B., Linick, T. W., and Williams, C. R.: Application of tandem accelerator mass-spectrometer dating to Late-Pleistocene–Holocene sediments of the East Antarctic continental shelf, Quaternary Res., 31, 277–287, 1989.

Drenzek, N. J., Montluçon, D. B., Yunker, M. B., Macdonald, R. W., and Eglinton, T. I.: Constraints on the origin of sedimentary organic carbon in the Beaufort Sea from coupled molecular ^{14}C and ^{13}C measurements, Mar. Chem., 103, 146–162, doi: 10.1016/j.marchem.2006.06.017, 2007.

Deleted: ¶

Deleted: ta

Deleted: ¶

Drenzek, N. J., Hughen, K. A., Montluçon, D. B., Southon, J. R., dos Santos, G. M., Druffel, E. R. M., Giosan, L., and Eglinton, T. I.: A new look at old carbon in active margin sediments, Geology, 37, 239–242, doi: 10.1130/G25351A.1, 2009.

Druffel, E. R. M., Bauer, J. E., Williams, P. M., Griffin, S., and Wolgast, D.: Seasonal variability of particulate organic radiocarbon in the northeast Pacific Ocean, J. Geophys. Res., 101:20,543-20,552, 1996.

Dunbar, R. B., Anderson, J. B., Domack, E. W.: Oceanographic influences on sedimentation along the Antarctic Continental Shelf, Antarctic Res. Ser., American Geophysical Union, 45, 291–312, 1985.

Dunbar, R. B., Leventer, A. R., and Stockton, W. L.: Biogenic sedimentation in McMurdo Sound, Antarctica, Mar. Geol., 85, 155-179, 1989.

Dunbar, R. B., Arrigo, K. R., Lutz, M., DiTullio, G. R., Leventer, A. R., Lizotte, M. P., Van Woert, M. P., and Robinson, D. H.: Non-Redfield production and export of marine organic matter: a recurrent part of the annual cycle in the Ross Sea, in: Biogeochemistry of the Ross Sea, Antarctic Research Series Monograph, 78,, edited by: DiTullio, G.R., and Dunbar, R.B., American Geophysical Union, 179-195, 2003.

Eglinton, T. I., Aliwihare, L. I, Bauer, J. E., Druffel, E. R. M. and McNichol, A. P.: Gas chromatographic isolation of individual compounds from complex matrices for radiocarbon dating, Anal. Chem., 68, 904-912, 1996.

Eglinton, T. I., Benitez-Nelson, B. C., Pearson, A., McNichol, A. P., Bauer, J. E., and Druffel, E. R. M.: Variability in radiocarbon ages of individual organic compounds from marine sediments, Science, 277, 796–799, 1997.

Deleted: ¶

Eglinton, T. I., Eglinton, G., Dupont, L., Sholkovitz, E. R., Montlucon, D. and Reddy, C. M.: Composition, age, and provenance of organic matter in NW African dust over the Atlantic Ocean, Geochem. Geophys. Geosys., 3, 1-27, doi:10.1029/2001gc000269, 2002.

Feng, X., Benitez-Nelson, B. C., Montluçon, D. B., Prahl, F. G., McNichol, A. P., Xu, L., Repeta, D. J., and Eglinton, T. I.: ^{14}C and ^{13}C characteristics of higher plant biomarkers in Washington margin surface sediments, Geochim. Cosmochim. Ac., 105, 14–30, 2013.

Freeman K. H., Hayes J. M., Trendel J.-M., and Albrecht P.: Evidence from carbon isotope measurements for diverse origins of sedimentary hydrocarbons, Nature, 343, 254-256, 1990.

Freeman K. H.: Isotopic biogeochemistry of marine organic carbon, in: Stable Isotope Geochemistry, Reviews in Mineralogy and Geochemistry, vol. 43, edited by Valley, J. W. and Cole, D. R., 579-605, 2001.

Fry, B., and Sherr, E. B.: δ^{13}C Measurements as indicators of carbon flow in marine and freshwater eosystems, Mar. Sci., 27, 13–47 1984.

Gagosian, R. B., and Peltzer, E. T.: The importance of atmospheric input of terrestrial organic material to deep sea sediments, Org. Geochem. 10, 661-669, 1986.

Gong, C., and Hollander, D. J.: Differential contribution of bacteria to sedimentary organic matter in oxic and anoxic environments, Santa Monica Basin, California, Org. Geochem., 26, 545-563, 1997.

D. R., Martin, W. R., and Eglinton, T. I.: The radiocarbon age of organic carbon in marine surface sediments, Geochim. Cosmochim. Ac., 74, 6788–6800, 2010.

Deleted: w

Deleted: o

Deleted: ta

Deleted: ta

Gibson, J. A. E., Trull, T., Nichols, P. D., Summons, R. E., and McMinn, A.: Sedimentation of C-13-rich organic matter from Antarctic sea-ice algae: A potential indicator of past sea-ice extent, Geology, 27, 331-334, 1999.

Gleitz, M., Kukert, H., Riebesell, U., and Dieckmann, G. S.: Carbon acquisition and growth of Antarctic sea ice diatoms in closed bottle incubations, Mar. Ecol. Prog. Ser., 135, 169-177, 1996.

Haake, B., Rixen, T., Reemtsma, T., Ramaswamy, V., and Ittekkot, V.: Processes determining seasonal variability and interannual variability of settling particle fluxes to the deep Arabian Sea, in: Particle Flux in the Ocean, SCOPE vol. 57, edited by Ittekkot, V., Schaefer, P., Honjo, S., and Depetris, P. J., 251-270, Wiley, New York, 1996.

Gordon, J. E., and Harkness, D. D.: Magnitude and geographic variation of the radiocarbon content in Antarctic marine life: implications for reservoir corrections in radiocarbon dating, Quaternary Sci. Rev., 11, 697-708, 1992.

Hall, B., Henderson, G., Baroni, C., and Kellogg, T.: Constant Holocene Southern Ocean ^{14}C reservoir ages and ice-shelf flow rates. Earth Planet. Sci. Lett., 296, 115-123, 2010.

Harris, P.T., O'Brien, P.E., Sedwick, P., and Truswell, E.M.: Late Quaternary history of sedimentation on the Mac. Robertson Shelf, East Antarctica: problems with ^{14}C-dating of marine sediment cores, Proc. Roy. Soc. Tasmania, 130, 47-53 1996.

Hayes, J.N.: Fractionation of the isotopes of carbon and hydrogen in biosynthetic processes, in: Stable Isotope Geochemistry, Reviews in Mineralogy and

Formatted: Allow hanging punctuation, Font Alignment: Auto

Deleted: ¶

Geochemistry, vol. 43, edited by: Valley, J.W. and Cole, D.R., 225-278, Mineralogical society of America, Washington DC, 2001.

Hay, B. J., Honjo, S, Kempe, S., Ittekkot, V., Degens, E. T., Konuk, T., and Izdar, E.: Interannual variability in particle flux in the southwestern Black Sea, Deep-Sea Res., 37, 911-928, 1990.

Hay, B. J., and Honjo, S.: Particle deposition in the present and Holocene Black Sea, Oceanogr., 2, 26-31, 1989.

Hay B. J.: Particle flux in the western Black Sea in the present and over the last 5000 years: Temporal variability, sources, transport mechanisms. Ph.D. thesis, WHOI·87-44. 201 pp .. MIT-WHOI Joint Program, 1987.

Hay, B. J., Arthur, M. A., Dean, W.: Sediment deposition in the Late Holocene abyssal Black Sea with climatic and chronological implications, Deep-Sea Res., 38, Suppl 2, S1211-S1235, 1991.

Hedges, J. I., Hu, F. S., Devol, A. H., Hartnett, H. E., Tsamakis, E., and Keil, R. G.: Sediment organic matter preservation; a test for selective degradation under oxic conditions, Am. J. Sci., 299, 529-555; doi:10.2475/ajs.299.7-9.529, 1999.

Hedges, J. I., Baldock, J. A., Gelinas, Y., Lee, C., Peterson, M. L., and Wakeham, S. G.: Non-selective preservation of organic matter in sinking marine particles, Nature, 409, 801-804, 2001.

Hedges J. I., and Keil R. G.: Sedimentary organic matter preservation: an assessment and speculative synthesis, Mar. Chem., 49, 81-115, 1995.

Hedges, J. I., Keil, R. G., and Benner, R.: What happens to terrestrial organic matter in the ocean? Org. Geochem., 27, 195-212, 1997.

Deleted: ¶

Formatted: Indent: First line: 0"

Hedges, J. I., Eglinton, G., Hatcher, P. G., Kirchman, D. L., Arnosti, C., Derenne, S., Evershed, R. P., Kögel-Knabner, I., de Leeuw, J. W., Littke, R., Michaelis, W. and Rullkötter, J.: The molecularly-uncharacterized component of nonliving organic matter in natural environments, Org. Geochem., 31, 945-958, 2000.

Honjo, S., Dymond, J., Prell, W., and Ittekkot, V.: Monsoon-controlled export fluxes to the interior of the Arabian Sea, Deep-Sea Res. II, 46, 1859-1902, 1999.

Hwang, J., Druffel, E., and Komada, T.: Transport of organic carbon from the California coast to the slope region: a study of $\Delta^{14}C$ and $\delta^{13}C$ signatures of organic compound classes, Global Biogeochem. Cycles, 19, GB2018, doi:10.1029/2004GB002422, 2005.

Hwang, J., Druffel, E. R. M., and Eglinton, T. I.: Widespread influence of resuspended sediments on oceanic particulate organic carbon: Insights from radiocarbon and aluminum contents in sinking particles, Global Biogeochem. Cycles, 24, GB4016, doi:10.1029/2010GB003802, 2010.

Ingalls A. E. and Pearson A.: Ten years of compound-specific radiocarbon analysis, Oceanography, 18, 18-31, 2005.

Jones, G. A. and Gagnon, A. R.: Radiocarbon chronology of Black Sea sediments, Deep-Sea Research, 41, 531-557, 1994.

Kawamura, K., Ishimura, Y., and Yamazaki, K.: Four years' observations of terrestrial lipid class compounds in marine aerosols from the western North Pacific, Global Biogeochem. Cycles, 17, 1003, doi:10.1029/2001GB001810, 2003.

Key, R. M., Kozyr, A., Sabine, C. L., Lee, K., Wanninkhof, R., Bullister, J. L., Feely, R. A., Millero, F. J., Mordy, C., and Peng, T.-H.: A global ocean carbon

Deleted: Key, R.M.: A global ocean carbon climatology: results from the Global Data¶
Analysis Project (GLODAP), Global Biogeochem. Cycles, 18, 10.1029/2004GB002247, 2004.

Formatted: Font: (Default) Times New Roman, 12 pt

Formatted: Font: (Default) Times New Roman, 12 pt

climatology: Results from Global Data Analysis Project (GLODAP), Global Biogeochem. Cy., 18, GB4031, doi:10.1029/2004GB002247, 2004.

Komada, T, Druffel, E., and Hwang, J.: Sedimentary rocks as sources of ancient organic carbon to the ocean: an investigation through $\Delta^{14}C$ and $\delta^{13}C$ signatures of compound classes, Global Biogeochem. Cycles, 19, GB2017, doi:10.1029/2004GB002347, 2005.

Deleted: ,

Kusch, S., Rethemeyer, J., Schefuß, E., and Mollenhauer, G.: Controls on the age of vascular plant biomarkers in Black Sea sediments, Geochim. Cosmochim. Ac, 74, 7031-7047, 2010.

Deleted: ta

Lee, C., Murray, D. W., Barber, R. T., Buesseler, K. O., Dymond, J., Hedges, J. I., Honjo, S., Manganini, S.J., Marra, J., Moser, C., Peterson, M. L., Prell, W. L., and Wakeham, S. G.: Particulate organic carbon fluxes: compilation of results from the 1995 US JGOFS Arabian Sea Process Study, Deep-Sea Res. II, 45, 2489-2501, 1998.

Lee, C., Wakeham, S. G., and Arnosti, C.: Particulate organic matter in the sea: the composition conundrum, Ambio, 33, 565-575, 2004.

Levin, I., and Kromer, B.; Twenty years of atmospheric $^{14}CO_2$ observations at Schauinsland, Radiocarbon, 39, 205-218, 1997.

Licht, K. J., Jennings, A. E., Andrews, J. T., and Williams, K. M.: Chronology of late Wisconsin ice retreat from the western Ross Sea, Antarctica, Geol., 24, 223-226, 1996.

McNichol A. P., Osborne E. A., Gagnon A. R., Fry B., and Jones G. A.: TIC, TOC, DIC, DOC, PIC, POC – unique aspects in the preparation of oceanographic samples for

^{14}C-AMS, Nucl. Instr. Meth. Phys. Res., Sect. B92, 162-165, 1994.

McNichol, A.P., and Aluwihare, L. I.: The power of radiocarbon in biogeochemical studies of the marine carbon cycle: Insights from studies of dissolved and particulate organic carbon (DOC and POC), Chem. Rev. 107, 443-466, 2007.

Mollenhauer, G., Eglinton, T. I., Ohkouchi, N., Schneider, R. R., Müller, P. J., Grootes, P. M., and Rullkötter, J.: Asynchronous alkenone and foraminifera records from the Benguela Upwelling System, Geochim. Cosmochim. Ac., 67, 2157-2171, 2003.

Mollenhauer, G., and Eglinton, T. I.: Diagenetic and sedimentological controls on the composition of organic matter preserved in California Borderland Basin sediments, Limnol. Oceanogr., 52, 558-576, 2007.

Ohkouchi, N., Eglinton, T. I., Keigwin, L. D., and Hayes, J. M.: Spatial and temporal offsets between proxy records in a sediment drift, Science, 298, 1224-1227, 2002.

Ohkouchi, N., Eglinton, T. I., and Hayes, J. M.: Radiocarbon dating of individual fatty acids as a tool for refining Antarctic Margin sediment chronologies, Radiocarbon, 45, 17-24, 2003.

Ohkouchi, N., and Eglinton, T. I.: Compound-specific radiocarbon dating of Ross Sea sediments: A prospect for constructing chronologies in high-latitude oceanic sediments, Quart. Geochronol., 3, 235-243, 2008.

Ohkouchi, N., Xu, L., Reddy, C. M., Montluçon, D., and Eglinton, T. I.: Radiocarbon dating of alkenones from marine sediments, I. Isolation protocol, Radiocarbon, 47, 401-412, 2005.

Deleted: ta

Deleted:

Deleted:

Passier, H. F., Luther, G.W, III., and de Lange, G. J.: Early diagenesis and sulfur speciation in sediments of the Oman Margin, northwestern Arabian Sea, Deep-Sea Res., 44, 1361-1380, 1997.

Pearson A.: Biogeochemical applications of compound-specific radiocarbon analysis, Ph.D. Thesis, Woods Hole Oceanographic Institution/Massachusetts Institute of Technology, Woods Hole, MA, 248 pp, 2000.

Pearson, A.: Pathways of carbon assimilation and their impact on organic matter values of $\delta^{13}C$, in: Handbook of Hydrocarbon and Lipid Microbiology: Microbial interactions with hydrocarbons, oils, fats, and related hydrophobic substrates and products, edited by: K. Timmis, 143-156, Springer-Verlag Berlin, DOI 10.1007/978-3-540-77587-4_9, 2010.

Pearson, A., and Eglinton, T. I.: The origin of *n*-alkanes in Santa Monica Basin surface sediment: a model based on compound-specific $\Delta^{14}C$ and $\delta^{13}C$ data. Org. Geochem. 31, 1103-1116, 2000.

Pearson A., McNichol A. P., Schneider R. J. and von Reden K. F.: Microscale AMS ^{14}C measurement at NOSAMS, Radiocarbon, 40, 61-76, 1998.

Pearson A., McNichol A. P., Benetiz-Nelson B. C., Hayes J. M., and Eglinton T. I.: Origins of lipid biomarkers in Santa Monica Basin surface sediment: A case study using compound-specific $\Delta^{14}C$ analysis, Geochim. Cosmochim. Ac., 65, 3123-3137, 2001.

Pearson A., Seewald J. S. and Eglinton T. I.:Bacterial incorporation of relict carbon in the hydrothermal environment of Guaymas Basin, Geochim. Cosmochim. Ac., 69, 5477-5486, 2005.

Deleted: -

Formatted: Font: (Default) Times New Roman, 12 pt

Formatted: Don't adjust space between Latin and Asian text, Don't adjust space between Asian text and numbers

Formatted: Font: (Default) Times New Roman, 12 pt, Italic

Formatted: Font: (Default) Times New Roman, 12 pt

Formatted: Font: (Default) Times New Roman, 12 pt

Formatted: Font: (Default) Times New Roman, 12 pt

Formatted: Font: (Default) Times New Roman, 12 pt, Superscript

Formatted: Font: (Default) Times New Roman, 12 pt

Formatted: Font: (Default) Times New Roman, 12 pt, Superscript

Formatted: Font: (Default) Times New Roman, 12 pt

Formatted: Font: (Default) Times New Roman, 12 pt

Formatted: Font: (Default) Times New Roman, 12 pt

Deleted: ¶

Deleted: ta

Deleted: ta

Petsch, S. T., Eglinton, T. I., and Edwards, K. J.: ^{14}C-dead living biomass: Evidence for microbial assimilation of ancient organic carbon during shale weathering, Science, 292, 1127-1131, doi: 10.1126/science.1058332, 2001.

Petsch, S. T., Edwards, K. J., and Eglinton, T. I.: Abundance, distribution, and δ^{13}C analysis of microbial phospholipid-derived fatty acids in a black shale weathering profile, Org. Geochem., 34, 731-743, doi: 10.1016/S0146–6380(03)00040–8, 2003.

Prahl F. G., Muehlhausen L. A., and Lyle, M.: An organic geochemical assessment of oceanographic conditions at MANOP Site C over the past 26,000 years, Paleoceanogr, 4, 495-510, 1989.

Premuzic E. T., Benkovitz C. M., Gaffney J. S., and Walsh J. J.: The nature and distribution of organic matter in the surface sediments of world oceans and seas, Org. Geochem., 4, 63-77, 1982.

Ramage C. S., Miller F. R., and Jeffries C.: Meteorological Atlas of the International Indian Ocean Expedition: The Surface Climate of 1963, 1964, U.S. National Science Foundation and India Meteorological Department, 1972.

Rau, G. H., Takahashi, T., Des Marias, D. J., and Sullivan, C. W.: Particulate organic matter $^{\delta}$C variations across the Drake Passage, J. Geophys. Res., 96, 15,131-15,135, doi:10.1029/91JC01253, 1991.

Rau, G. H., C. W. Sullivan, and L. I. Gordon (1991), δ^{13}C and δ^{15}N variations in Weddell Sea particulate organic matter, Mar. Chem., 35, 355–369, doi:10.1016/S0304-4203(09)90028-7, 1991.

Ross D. A., and Degens, E. T.: Recent sediments of the Black Sea, in: The Black Sea - Geology, chemistry, and biology, Memoirs of the American Association of Petroleum Geologists, 20, edited by: Degens, E. T., and Ross, D. A., 183-199, 1974.

Sackett, W. M., Poag, C.W., and Eadie, B. J.: Kerogen recycling in the Ross Sea, Antarctica, Science, 185, 1045-1047, 1974.

Siani, G., Paterne, M., Arnold, M., Bard, E., Métivie, B., Tisnerat, N., and Bassinot, F.: Radiocarbon reservoir ages in the Mediterranean Sea and Black Sea. Radiocarbon, 2, 271-280, 2000.

Sirocko F., and Sarnthein M.: Wind-borne deposits in the Northwestern Indian Ocean: Record of Holocene sediments versus satellite data, in: Paleoclimatology and Paleometeorology: Modern and Past Patterns of Global Atmospheric Transport, Vol. 282 in NATO ASI Series, Series C (edited by: Leinin, M., and Sarnthein, M., 401–433. Kluwer, 1989.

Smith, S. L., Codispoti, L. A., Morrison, J. M., and Barber, R.T.: The 1994-1996 Arabian Sea Expedition: an integrated, interdisciplinary investigation of the response of the northwestern Indian Ocean to monsoonal forcing, Deep-Sea Res II, 45, 1905-1915, 1998.

Southon, J., Kashgarian, M., Fontugne, M., Metivier, B., Yim, W.-S.: Marine reservoir corrections for the Indian Ocean and Southeast Asia, Radiocarbon, 44, 167–180, 2002.

Stuiver M., and Polach, H. A.: Discussion: Reporting of 14C data, Radiocarbon, 19, 355-363, 1977.

Deleted: o

Stuiver M., and Ostlund, H. G.: GEOSECS Indian Ocean and Mediterranean radiocarbon. Radiocarbon 25, 1–29, 1983.

Stuiver, M., and Braziunas, T. F.: Modelling atmospheric ^{14}C influences and ^{14}C ages of marine samples to 10,000 BP, Radiocarbon, 35, 137– 189, 1993.

Villinski, J. C., Dunbar, R. B., and Mucciarone, D. A.: Carbon 13/ Carbon 12 ratios of sedimentary organic matter from the Ross Sea, Antarctica: A record of phytoplankton bloom dynamics, J. Geophys. Res., 105(C6), 14,163–14,172, doi:10.1029/1999JC000309, 2000.

Volkman J. R, Eglinton G., Corner E. D. S. and Forsberg T. E. V.: Long-chain alkenes and alkenones in the marine coccolithophorid *Emiliania huxleyi.* Phytochem., 19, 2619-2622, 1980.

Volkman, J.K.: Lipid markers for marine organic matter, in: The Handbook of Environmental Chemistry, edited by: Hutzinger, O.; Vol 2: Reactions and processes, Part N, Marine organic matter: Biomarkers, isotopes and DNA, edited by Volkman, J.K. Springer, Berlin, 27-70, 2006.

von Reden K. F., Schneider R. F., McNichol A. P., and Pearson A.: ^{14}C-AMS measurements of < 100 μg samples with a high-current system, Radiocarbon 40, 247-253, 1998.

Wakeham, S. G.: Organic matter from a sediment trap experiment in the equatorial Atlantic: wax esters, steryl esters, triacylglycerols, and alkyldiacylglycerols, Geochim. Cosmochim. Ac, 46, 2239-2257, 1982.

Wakeham, S. G.: Aliphatic and polycyclic aromatic hydrocarbons in Black Sea sediments, Mar. Chem., 53, 187-205, 1996.

Deleted: ta

Wakeham, S. G., and Canuel, E. A.: Degradation and preservation of organic matter in marine sediments, in: The Handbook of Environmental Chemistry, Vol. 2, Reactions and Processes, edited by: Hutzinger, O.; Vol. 2. Marine Organic Matter: Biomarkers, Isotopes and DNA, edited by: Volkman, J. K., Springer-Verlag, Berlin, 295-321, 2006.

Wakeham, S. G., Beier, J. A., and Clifford, C. H.: Organic matter sources in the Black Sea as inferred from hydrocarbon distributions, in: Black Sea Oceanography, edited by: Izdar, E., and Murray, J. W., Kluwer, 319-341, 1991.

Wakeham, S. G., Lee, C., Hedges, J. I., Hernes, P. J., and Peterson, M. L.: Molecular indicators of diagenetic status in marine organic matter, Geochim. Cosmochim. Ac., 61, 5363-5369, 1997.

Wakeham, S. G., Peterson, M. L., Hedges J. I., and Lee, C.: Lipid biomarker fluxes in the Arabian Sea: with a comparison to the Equatorial Pacific Ocean, Deep-Sea Res. II., 49, 2265-2301, 2002.

Wakeham, S. G., McNichol, A. P., Kostka, J., and Pease, T. K.: Natural abundance radiocarbon as a tracer of assimilation of petroleum carbon by bacteria in salt marsh sediments, Geochim. Cosmochim. Ac., 70, 1761-1771, 2006.

Wang, X.-C., Druffel, E. R. M., Griffin, S., Lee, C., and Kashgarian, M.: Radiocarbon studies of organic compound classes in plankton and sediment of the northeastern Pacific Ocean, Geochim. Cosmochim. Ac., 62, 1365-1378, 1998.

Wang, X.-C., and Druffel, E. R. M.: Radiocarbon and stable carbon isotope compositions of organic compound classes in sediments from the NE Pacific and Southern Oceans, Mar. Chem., 73, 65-81, 2001.

Deleted:

Deleted: v

Deleted: ta

Deleted: ta

Deleted: ta

Yunker, M. B., Macdonald, R. W., Cretney, W. J., Fowler, B. R., and McLaughlin, F. A.: Alkane, terpene and polycyclic aromatic hydrocarbon geochemistry of the Mackenzie River and Mackenzie shelf: Riverine contributions to Beaufort Sea coastal sediment, Geochim. Cosmochim. Ac., 57, 3041-3061, 1993.

Yunker, M. B., Backus, S. M., Pannatier, E. G., Jeffries, D. S., and Macdonald, R. W.: Sources and significance of alkane and PAH hydrocarbons in Canadian arctic rivers, Estuar. Coast. Shelf S., 55, 1-31, 2002.

Zafiriou, 0. C., Gagosian, R. B., Peltzer, E. T., and Alford, J. B.: Air-to-sea fluxes of lipids at Enewetak Atoll, J. Geophys. Res., 90, 2409-2423, 1985.

Zonneveld, K. A. F., Versteegh, G. J. M., Kasten, S., Eglinton, T., Emeis, K.-C., Huguet, C., Koch, B., de Lange, G. J., de Leeuw, J. W., Middelburg, J. J., Mollenhauer, G., Prahl, F., Rethemeyer, J., and Wakeham, S.: Selective preservation of organic matter in marine environments; processes and impact on the fossil record, Biogeosci., 7, 483-511, 2010.

Deleted: ta

Table 1. Stable carbon and radiocarbon isotope data for Black Sea POM and SOM.

	source	ID #	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	*fm*	Age
		Black Sea Trap				
OC		OS-32870	–22.9	21 ± 2	1.026 ± 0.003	>Mod
SLE		OS-38316	–27.2	–96 ± 16	0.909 ± 0.016	770 ± 140
14:0 FA	M	OS-38328	–25.6	132 ± 13	1.064 ± 0.014	>Mod
b-15:0 FA	M	OS-38321	–25.3	90 ± 9	1.029 ± 0.011	>Mod
16:1 FA	M	OS-38327	–25.4	81 ± 11	1.025 ± 0.011	>Mod
16:0 FA	M	OS-38333	–24.3	***146 ± 9***	**1.086 ± 0.011**	**>Mod**
18:1 FA	M	OS-38318	–23.2	***288 ± 11***	**1.228 ± 0.008**	**>Mod**
18:0 FA	M	OS-38320	–23.9	77 ± 11	1.028 ± 0.011	>Mod
24+26+28 FA	T	OS-38331	–27.0	1 ± 16	0.967 ± 0.014	265 ± 110
alkenones	M	OS-39539	–26.6	87 ± 14	1.099 ± 0.014	>Mod
24+26+28 HC	R	OS-39911	–29.3	–677 ± 10	0.325 ± 0.009	9030 ± 210
27+29 HC	T	OS-39908	–30.0	–181 ± 14	0.825 ± 0.010	1550 ± 100
27Δ^{5} sterol	M	OS-53936	–26.4	79 ± 11	1.046 ± 0.011	>Mod.
28$\Delta^{5,22}$ sterol	M	OS-53934	–26.1	65 ± 9	1.034 ± 0.009	>Mod.
30Δ^{22} sterol	M	OS-53957	–25.7	69 ± 15	1.040 ± 0.015	>Mod.
24+26+28 ROH	T	OS-53956	–30.1	–44 ± 12	0.925 ± 0.012	625 ± 110
		Black Sea Sediment				
OC		OS-32871	–25.3	–199 ± 6	0.806 ± 0.004	1740 ± 35
SLE		OS-38309	–27.9	–150 ± 15	0.856 ± 0.008	1250 ± 80
14:0 FA	M	OS-38630	–28.6	18 ± 15	0.957 ± 0.016	350 ± 130
b-15:0 FA	M	OS-38632	–30.5	–27 ± 14	0.919 ± 0.019	680 ± 170
16:1 FA	M	OS-38628	–31.9	75 ± 14	1.019 ± 0.013	>Mod
16:0 FA	M	OS-38627	–29.1	***214 ± 18***	**1.151 ± 0.018**	**>Mod**
b-17:0 FA	M	OS-38642	–30.5	57 ± 20	1.006 ± 0.020	>Mod
18:1 FA	M	OS-38637	–27.0	–24 ± 20	0.999±0.020	5 ± 100
18:0 FA	M	OS-38636	–29.5	***374 ± 27***	**1.310 ± 0.023**	**>Mod**
22:0 FA	M	OS-38639	–28.9	–46 ± 26	0.919± 0.027	680 ± 230
24:0 FA	M	OS-38640	–29.2	–34 ± 26	0.934 ± 0.024	550 ± 220
26:0 FA	T	OS-38641	–30.5	–223 ± 31	0.754 ± 0.021	2270 ± 230
alkenones	M	OS-39536	–28.6	45 ± 13	1.069± 0.013	>Mod
24+26+28 HC	R	OS-39909	–29.2	–609 ± 11	0.393 ± 0.007	7500 ± 150
27 HC	T	OS-39907	–30.0	–231 ± 8	0.774 ± 0.011	2060 ± 110
29 HC	T	OS-39906	–31.0	–125 ± 8	0.880 ± 0.008	1020 ± 75
27Δ^{5} sterol	M	OS-53948	–27.0	–33 ± 12	0.937 ± 0012	520 ± 100
30Δ^{22} sterol	M	OS-53943	–26.0	–15 ± 9	0.942 ± 0.011	475 ± 95
24 ROH	T	OS-53951	–29.7	–176 ± 8	0.796 ± 0.011	1840 ± 110
26 ROH	T	OS-53958	–31.2	–100 ± 16	0.871 ± 0.018	1100 ± 160

M = marine; T = terrigenous; R = relict

FA = fatty acid; ROH = alcohol; HC = alkane

Deleted: 2

Deleted: 85

Deleted: 1

Deleted: –

Table 2. Stable carbon and radiocarbon isotope data for Arabian Sea POM and SOM.

Arabian Sea Trap						
	source	ID #	δ^{13}C (‰)	Δ^{14}C (‰)	*fm*	Age
OC		OS- 32868	–22.4	14 ± 13	1.020 ± 0.013	>Mod
SLE		OS- 38314	–24.7	66 ± 14	1.073 ± 0.014	>Mod
14:0 FA	M	OS- 37311	–25.7	***178 ± 17***	**1.107 ± 0.017**	**>Mod**
b-15:0 FA	M	OS- 37314	–23.2	56 ± 13	0.997 ± 0.014	25 ± 110
16:1 FA	M	OS- 37304	–24.0	55 ± 21	0.999 ± 0.014	5 ± 100
16:0 FA	M	OS- 37298	–23.8	97 ± 14	1.039 ± 0.013	>Mod
18:1 FA	M	OS- 37297	–23.1	38 ± 21	0.990 ± 0.013	80 ± 100
18:0 FA	M	OS- 37302	–23.8	111 ± 15	1.060 ± 0.015	>Mod
22:0 FA	M	OS- 37305	–23.8	51 ± 14	1.012 ± 0.014	>Mod
24:0 FA	M	OS- 37313	–24.7	69 ± 14	1.033 ± 0.013	>Mod
26:0 FA	M	OS- 37315	–25.2	80 ± 16	1.047 ± 0.016	>Mod
alkenones	M	OS-39910	–23.9	–6 ± 9	1.000 ± 0.011	>Mod
24+26+28 HC	R	OS-55323	–28.5	–731 ± 14	0.270 ± 0.013	10500 ± 390
HBI HC	M	OS-55248	–24.5	–514 ± 10	**0.488 ± 0.010**	5750 ± 160
27+29 HC	T	OS-55325	–28.4	–320 ± 24	0.684 ± 0.024	3050 ± 280
27Δ^{5} sterol	M	OS-56344	–16.7	–32 ± 12	0.939 ± 0.012	505 ± 100
28$\Delta^{5,22}$ sterol	M	OS-56348	–27.1	–86 ± 13	0.888 ± 0.013	955 ± 120
16 ROH	M	OS-56347	–22.5	–91 ± 12	0.861 ± 0.012	1200 ± 110
Arabian Sea Sediment						
OC		OS- 32869	–20.8	–138 ± 2	0.867 ± 0.003	1140 ± 30
LE		OS- 38322	–25.0	–173 ± 11	0.833 ± 0.011	1470 ± 100
14:0 FA	M	OS- 38332	–26.6	–10 ± 13	0.931 ± 0.013	575 ± 110
b-15:0 FA	M	OS- 38324	–24.5	–70 ± 11	0.878 ± 0.011	1040 ± 100
16:1 FA	M	OS- 38313	–26.0	–112 ± 7	0.842 ± 0.007	1380 ± 65
16:0 FA	M	OS- 38329	–25.0	104 ± 12	1.046 ±0.012	>Mod
18:1 FA	M	OS- 38334	–24.8	–171 ± 13	0.791 ± 0.013	1880 ± 140
18:0 FA	M	OS- 38325	–24.7	***190 ± 10***	**1.135 ± 0.010**	**>Mod**
22:0 FA	M	OS- 38326	–26.8	103 ± 12	0.864 ± 0.012	1180 ± 110
24:0 FA	M	OS- 38317	–25.4	–91 ± 7	0.879 ± 0.006	1040 ± 55
26:0 FA	M	OS- 38319	–24.7	–116 ± 7	0.858 ± 0.007	1230 ± 70
alkenones	M	OS- 39902	–24.1	–202 ± 7	0.803 ± 0.003	1760 ± 65
24+26+28 HC	R	OS-55329	–27.6	–805 ± 9	0.197 ± 0.008	13050 ± 340
HBI HC	M	OS-56341	–18.2	***–256 ± 8***	**0.748 ±0.008**	***2330 ± 85***
15+16+17+18 HC	R	OS-55251	–29.4	–887 ± 5	0.114 ± 0.004	17500 ± 250
27+29 HC	T	OS-55318	–27.7	–430 ± 11	0.573 ± 0.011	4470 ± 160
27Δ^{5} sterol	M	OS-56349	–24.0	–152 ± 13	0.822 ± 0.013	1570 ± 130
16 ROH	M	OS-56351	–23.3	–99 ± 13	0.853 ± 0.012	1270 ± 110
26+28+30 ROH	T	OS-56350	–24.1	–113 ± 14	0.861 ± 0.012	1200 ± 110

M = marine; T = terrigenous; R = relict

FA = fatty acid; ROH = alcohol; HC = alkane

Table 3. Stable carbon and radiocarbon isotope data for Ross Sea POM and SOM.

		Ross Sea Trap				
	source	ID #	δ^{13}C (‰)	Δ^{14}C (‰)	*fm*	Age
OC		OS-32872	–28.0	–208 ± 6	0.797 ± 0.004	1820 ± 40
SLE		OS-38330	–32.7	–154 ± 15	0.852 ± 0.015	1290 ± 140
14:0 FA	M	OS-38626	–34.9	–115 ± 14	0.831 ± 0.012	1490 ± 110
16:0 FA	M	OS-38624	–31.7	–100 ± 10	0.853 ± 0010	1270 ± 95
18:0 FA	M	OS-39272	–35.3	–105 ± 15	0.854 ± 0.015	1270 ± 140
22:0+24:0 FA	M	OS- 38635	–31.8	–175 ± 19	0.796 ± 0.019	1830 ± 190
$27\Delta^{5}$ sterol	M	OS-50105	–32.0	–216 ± 7	0.761 ± 0.007	2190 ± 75
$28\Delta^{5,22}$ sterol	M	OS-50107	–35.4	–180 ± 8	0.796 ± 0.007	1830 ± 70
14+16 ROH	M	OS-50100	–31.8	–191 ± 9	0.764 ± 0.008	2160 ± 80
		Ross Sea Sediment				
OC		OS-32873	–27.9	–355 ± 3	0.649 ± 0.003	3480 ± 35
SLE		OS-38323	–30.0	–211 ± 18	0.795 ± 0.018	1850 ± 180
14:0 FA	M	OS-38633	–36.6	–83 ± 5	0.862 ± 0.015	1190 ± 140
br-15:0 FA	M	OS-38625	–32.3	–128 ± 12	0.824 ± 0.012	1560 ± 120
16:0 FA	M	OS-39266	–32.5	***430 ± 11***	**1.439 ± 0.011**	**>Mod**
18:0 FA	M	OS-38644	–31.0	***189 ± 29***	**1.196 ± 0.029**	**>Mod**
24:0 FA	M	OS-38634	–33.5	–208 ± 22	0.765 ± 0.023	2150 ± 240
26:0 FA	M	OS-38645	–30.3	–302 ± 27	0.677 ± 0.029	3130 ± 340
$27\Delta^{5}$ sterol	M	OS-50108	–33.0	–178 ± 10	0.798 ± 0.010	1810 ± 95
$28\Delta^{5,22}$ sterol	M	OS-50106	–34.3	–202 ± 8	0.775 ± 0.007	2050 ± 70

FA = fatty acid; ROH = alcohol

Table 4. Abundance weighted mean table carbon and radiocarbon isotope values for composited marine, terrigenous, and relict biomarkers.

	$\delta^{13}C$ (‰) ± s.d.	$\Delta^{14}C$ (‰) ± s.d.	f_m ± s.d.	Age ± s.d.	n
BS trap					
marine	–25.3 ± 1.1	78± 9	1.110 ± 0.066	>Mod	7
terrigenous	–28.7 ± 1.6	–75 ± 94	0.930 ± 0.043	580 ± 360	3
relict	–29.1	–677 ± 9	0.325 ± 0.009	9030 ± 220	1
BS sediment					
marine	–28.8 ± 1.8	-30±10	0.970 ± 0.023	240 ± 56	6
terrigenous	–30.5 ± 0.7	–171 ± 58	0.833 ± 0.066	1470 ± 615	5
relict	–29.2	–609 ± 8	0.393 ± 0.007	7500 ± 150	1
AS trap					
marine	–23.5 ± 2.5	64 ± 20	1.071 ± .019	>Mod	7
terrigenous	–26.8 ± 2.3	–320 ± 24	0.684 ± 0.024	3050±280	2,1
relict	–28.5	–731 ± 13	0.270 ± 0.013	10140 ± 360	1
AS sediment					
marine	–24.5 ± 2.1	–63 ± 110	0.941 ± 0.110	490 ± 1440	8
terrigenous	–27.7	–430 ± 13	0.573 ± 0.011	4470 ± 150	1
relict	–28.5 ± 1.2	–846 ± 58	0.114 ± 0.004	17440 ± 270	1
RS trap					
marine	–33.3 ± 1.8	–155 ± 47	0.850 ± .045	1310 ± 420	7
terrigenous	nd*	nd*	nd*	nd*	nd*
relict	nd*	nd*	nd*	nd*	nd*
RS sediment					
marine	–33.2 ± 1.9	–105 ± 31	0.900 ± 0.030	850 ± 270	6
terrigenous	–31.8 ± 2.8	–255 ± 66	0.750 ± 0.056	2310 ± 560	2
relict	nd*	nd*	nd*	nd*	nd*

nd* not determined

Table 5. Isotopic values used in mass balance calculations. The values of f_M, f_T, *and* f_R are those values calculated assuming that the actual value of $\Delta^{14}C_{added}$ is that measured on the compounds defined as relict.

Sample	**$\Delta^{14}C_{bulk}$ (‰)**	**$\Delta^{14}C_{M}$ (‰)**	**$\Delta^{14}C_{T}$ (‰)**	**$\Delta^{14}C_{add}$ (‰)**	**f_M**	**f_T**	**f_R**
BS trap	-100	80	-75	-677	0.76	0.08	0.15
BS sed	-150	-30	-171	-609	0.79	0.1	0.11
AS trap	64	64	-320	-731	1	0	0
AS sed	-173	-63	-430	-846	0.86	0.04	0.1
RS sed	-210	-105	-255	--	--	--	--

Figure Captions

Figure 1. Sampling locations in the Black Sea, Arabian Sea and Ross Sea.

Figure 2. Scheme of extraction, isolation and analysis of biomarkers.

Figure 3. (a) Organic carbon (%OC) and (b) C/N(a) for bulk trap and sediments.

Figure 4. (a) The δ^{13}C and (b) Δ^{14}C values of bulk organic carbon (OC) and (c) δ^{13}C and (d) Δ^{14}C values solvent extractable lipids (SLE) for trap POM and sediments.

Figure 5. Histograms of relative abundances of (a) fatty acids, (b) hydrocarbons, and (c) sterols/alcohols POM and SOM from the Black Sea. Carbon numbers are given for fatty acids, alkanes, and alcohols; sterol abbreviations are 27D5,22 = $27\Delta^{5,22}$, etc.

Figure 6. Histograms of relative abundances of (a) fatty acids, (b) hydrocarbons, and (c) sterols/alcohols in POM and SOM from the Arabian Sea. Carbon numbers are given for fatty acids, alkanes, and alcohols; sterol abbreviations are 27D5,22 = $27\Delta^{5,22}$, etc.

Figure 7. Histograms of relative abundances of (a) fatty acids, (b) hydrocarbons, and (c) sterols/alcohols in POM and SOM from the Ross Sea. Carbon numbers are given for fatty acids, alkanes, and alcohols; sterol abbreviations are 27D5,22 = $27\Delta^{5,22}$, etc.

Figure 8. The (a) δ^{13}C and (b) Δ^{14}C values of bulk POC and SOC and individual biomarkers for trap and sediments from the Black Sea (see also Table 1). Filled symbols are trap biomarkers; open symbols are sediment biomarkers. All values have been corrected for procedural blanks and any derivative carbon, as needed. Dashed lines are pre-bomb (lower) and post-bomb (upper) mixed-layer $\Delta^{14}C_{DIC}$.

Formatted: Indent: Left: 0", Hanging: 0.5", Line spacing: Double

Deleted: ¶

Deleted: ¶

Deleted: ¶

Deleted: ¶

Deleted: . All values

Deleted: have been corrected for procedural blanks and any derivative carbon.¶

Formatted: Font color: Black

Formatted: Font: (Default) Times New Roman, Font color: Black

Formatted: Font color: Black

Formatted: Font: (Default) Times New Roman, Font color: Black

Formatted: Font color: Black

Formatted: Font: (Default) Times New Roman, Font color: Black

Formatted: Font: (Default) Times New Roman, 12 pt, Font color: Black, Superscript

Formatted: Font: (Default) Times New Roman, Font color: Black

Deleted: ¶

Formatted: Font color: Black

Formatted: Font color: Black, Superscript

Formatted: Font color: Black

Deleted: ¶

Formatted: Font color: Black

Formatted: Font color: Black, Superscript

Formatted: Font color: Black

Deleted: ¶

Formatted: Font color: Black

Formatted: Font: (Default) Times New Roman, Font color: Black

Formatted: Font color: Black

Formatted: Font: (Default) Times New Roman, Font color: Black

Deleted: ¶

Formatted: Font: (Default) Times New Roman, Font color: Black

Formatted ...

Formatted ...

Formatted ...

Formatted: Font color: Black

Figure 9. The (a) δ^{13}C and (b) Δ^{14}C values of bulk POC and SOC and individual biomarkers for trap and sediments from the Arabian Sea (see also Table 2). Filled symbols are trap biomarkers; open symbols are sediment biomarkers. All values have been corrected for procedural blanks and any derivative carbon, as needed. Dashed lines are pre-bomb (lower) and post-bomb (upper) mixed-layer $\Delta^{14}C_{DIC}$.

Figure 10. The (a) δ^{13}C and (b) Δ^{14}C values of bulk POC and SOC and individual biomarkers for trap and sediments from the Ross Sea (see also Table 3). Filled symbols are trap biomarkers; open symbols are sediment biomarkers. All values have been corrected for procedural blanks and any derivative carbon, as needed. Dashed lines are pre-bomb (lower) and post-bomb (upper) mixed-layer $\Delta^{14}C_{DIC}$.

Figure 11. Concentration weighted average δ^{13}C and Δ^{14}C values of marine (M), terrigenous (T) and relict (R) lipids in (a) Black Sea, (b) Arabian Sea, and (c) Ross Sea traps and sediments.

Figure 12. Relative amounts of marine (M, blue solid line), terrestrial (T, red dashed line) and relict (R, black small-dashed line) carbon as a function of $\Delta^{14}C_{add}$ in Black Sea and Arabian Sea trap material (a and c, respectively) and in Black Sea, Arabian Sea and Ross Sea sediments (b, d, and e, respectively). Only real solutions are depicted. The solid black line indicates the solution when $\Delta^{14}C_{added}$ is equal to the value measured on compounds defined as relict. There are not enough data to construct a graph for the Ross Sea sediment trap.

Formatted: Font color: Black

Deleted: ¶

Formatted: Font color: Black

Deleted: ¶

Formatted: Font color: Black

Deleted: , b)

Deleted: c,d

Deleted: e

Deleted: ¶

Deleted: ,

Deleted: , and Ross Sea

Deleted: material