

Highly branched isoprenoids as proxies for variable sea ice conditions in the Southern Ocean

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Abstract: Concentrations of a highly branched isoprenoid (HBI) diene determined in over 200 sediment samples from the Arctic co-vary with those of an HBI monoene (IP₂₅) shown previously to be a sedimentary sea ice proxy for the Arctic. The same diene, but not monoene IP₂₅, occurred in nine sea ice samples collected from various locations around Antarctica. The diene has been reported previously in Antarctic sea ice diatoms and the ¹³C isotopic compositions of the diene determined in two Antarctic sea ice samples were also consistent with an origin from sea ice diatoms ($\delta^{13}\text{C}$ -5.7 to -8.5‰). In contrast, HBIs found in two Antarctic phytoplankton samples did not include the diene but comprised a number of tri- to pentaenes. In sediment samples collected near Adélie Land, East Antarctica, both the diene and the tri- to pentaenes often co-occurred. ¹³C isotopic compositions of the tri- to pentaenes in three sediment samples ranged from -35 to -42‰ whereas that of the diene in a sediment sample was -18‰. We propose the presence of this isotopically ¹³C enriched HBI diene in Antarctic sediments to be a useful proxy indicator for contributions of organic matter derived from sea ice diatoms. A ratio of the concentrations of diene/trienes might reflect the relative contributions of sea ice to phytoplanktonic inputs of organic matter to Antarctic sediments.

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Introduction

Reconstruction of the historical and palaeoenvironmental occurrence of sea ice is a key component of efforts to understand climate change (Polyak *et al.* 2010). Since sea ice is obviously a transient indicator of climate, numerous sediment proxies of historical and palaeosea ice occurrence have been proposed and used (Armand & Leventer 2010, Polyak *et al.* 2010). Amongst these proxies is a hydrocarbon designated IP₂₅ (I, Fig. 1), which is a mono-unsaturated C₂₅ highly branched isoprenoid (HBI monoene). Highly branched isoprenoids are secondary metabolites synthesized by a limited number of diatom species (e.g. Rowland *et al.* 2001, Damsté *et al.* 2004). A large number of studies have described the widespread occurrence of di- to penta- (and occasionally mono-) unsaturated HBIs from freshwater, brackish or marine settings ranging from low to high latitudes. However, IP₂₅ has to date only been reported in Arctic sea ice, sediments and sedimenting particles (Brown *et al.* 2010 and references therein). Belt *et al.* (2007) described the structure of (I) isolated from both sea ice and sediments collected from the

Canadian Arctic. The relative abundances of (I) in sections of a sediment core collected from the north Icelandic shelf showed a strong correlation with documented historical sea ice occurrences (Massé *et al.* 2008). Belt *et al.* (2008) measured the ¹³C composition of various HBI isomers (including IP₂₅) isolated from sea ice, trap samples and sediments collected from a wide range of locations across the Canadian Arctic with IP₂₅ values ranging between -23.2 and -16.3‰, consistent with an origin from sea ice derived organic matter (Schubert & Calvert 2001). In contrast, the $\delta^{13}\text{C}$ values of more unsaturated HBIs were between -35 and -42.2‰ (Belt *et al.* 2008) consistent with an origin from phytoplankton or freshwater plankton. Using the results of an examination of grain size, benthic foraminiferal composition, $\delta^{18}\text{O}$ ratios, sediment mineral composition and magnetic properties, in conjunction with abundances of IP₂₅ for sediment samples from a core collected off the north-westernmost coast of Iceland, Andrews *et al.* (2009) documented sea ice and marine climate variability over the last 2000 years. Recently, Vare *et al.* (2009) and Belt *et al.* (2010) reconstructed the Holocene (0–10 kyr BP) sea ice

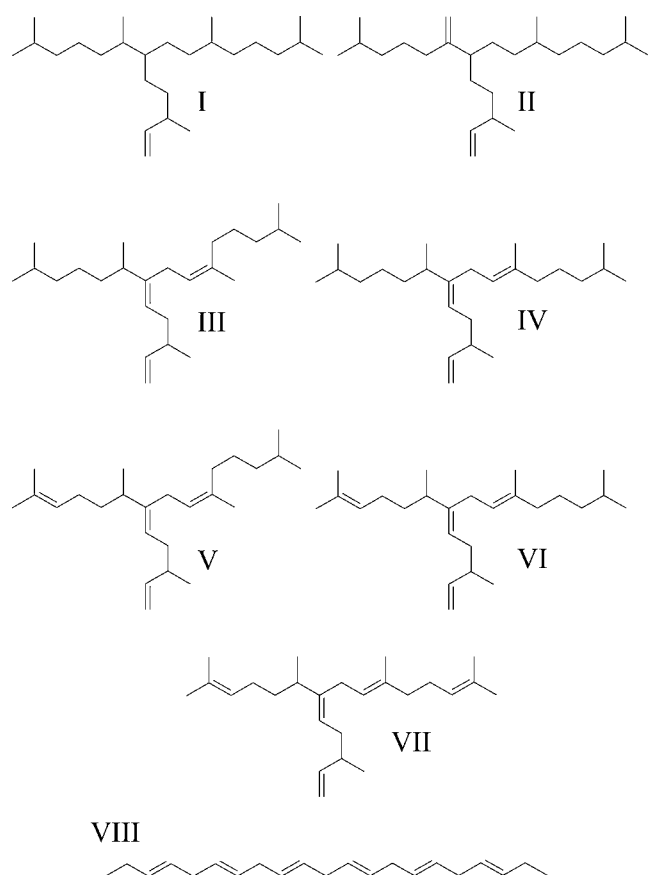


Fig. 1. Structures of the HBI isomers described in the current study. I, IP₂₅; II, di-unsaturated HBI; III-IV, tri-unsaturated HBIs; V-VI, tetra-unsaturated HBIs; VII, penta-unsaturated HBI; VIII, *n*-C_{21:6} (hencosaehaene).

history of the north-west passage in the Canadian Arctic Archipelago using measurements of IP₂₅ in sections of dated sediments, whilst Müller *et al.* (2009) demonstrated that the use of IP₂₅ could be extended to longer timescales (> 30 ky BP) and examined sections of a sediment core collected from northern Fram Strait. They determined that in the early part of the sedimentary record of their core, sea ice was permanently present in the area, whilst during the Holocene, the sea ice regime over the coring site was seasonal and similar to present-day conditions. These studies confirm the usefulness of IP₂₅ as a proxy for Arctic sea ice in addition to other proxies which are already well used and accepted (e.g. Armand & Leventer 2010, Polyak *et al.* 2010).

Although IP₂₅ has a widespread occurrence in Arctic sea ice (Brown *et al.* 2010 and references therein), it has never been reported in Antarctic sea ice and sediments. However, a number of studies have reported the presence of a di-unsaturated HBI in samples from the Antarctic. Nichols *et al.* (1988) reported a HBI diene in mixed sea ice diatom samples, and Venkatesan (1988) showed that this diene was present in sediment horizons dated as over 2.5 ky old. Later

Johns *et al.* (1999) identified the diene as (II) (Fig. 1) by comparing the mass spectrum and gas chromatographic retention index of the diene with samples authenticated by nuclear magnetic resonance spectroscopy after isolation from cultures of the temperate diatom *Haslea ostrearia* (Gaillon) Simonsen. A HBI diene other than (II) and unidentified HBI trienes were reported from water column particulate material from the Bellinghousen Sea, as well as from a coastal site close to Signy Island (South Orkney Islands) (Cripps 1995, Cripps & Clarke 1998). In the samples collected from Signy Island, Cripps & Clarke (1998) reported the presence of unidentified di- and tri-unsaturated HBIs in the material trapped during the summer (January and February). Cripps (1995) also reported the presence of a tri-unsaturated HBI isomer in particulate matter and sediments collected during spring under the pack ice in the Bellinghousen Sea area. Matsumoto *et al.* (1992) identified a HBI diene in sections of sediment cores from Lützw-Holm Bay and suggested that it originated from sea ice diatoms. More recently, Damsté *et al.* (2007) reported the presence of (II) in anoxic sediments from Ellis Fjord in East Antarctica. This fjord is a small meromictic basin where the water stratification favours the development of anoxic conditions. These authors interpreted the co-occurrence of (II) and a structurally-related thiane as evidence for the rapid diagenetic incorporation of sulphur into (II). Damsté *et al.* (2007) also determined the ¹³C isotopic composition of (II) and suggested that δ¹³C values of -9.1 to -9.4‰ were consistent with a sea ice diatom origin for the alkene.

In the present study, we extend reports of numerous HBI alkenes in Antarctic sediment samples, and notably we also report the presence of (II) in sea ice and other HBIs in phytoplankton together with the δ¹³C composition of individual HBIs in both sea ice and sediments. Differences in the structures and isotopic compositions allowed us to assign the origins of HBI isomers present in recent sediments collected from the Adélie Land area in the East Antarctic continental shelf area, representing 13 months of sedimentation. We propose the presence of isotopically ¹³C enriched HBI diene (II) as a proxy indicator for contributions of sea ice diatom organic matter to recent Antarctic sediments. In addition, subject to limitations placed by diagenetic effects, a ratio of the concentrations of diene/triene concentrations might reflect the relative contributions of sea ice organic matter and phytoplankton derived organic matter to Antarctic sediments. Two recent studies, comparing diene/triene ratios to diatom counts, have suggested that such a ratio is applicable to Holocene sediments, in which diagenetic effects have not been extensive (Barbara *et al.* 2010, Denis *et al.* 2010).

Methods

Sea ice and phytoplankton samples

Sea ice sampling was performed in 2006 during the biogeochemical sea ice sampling of the Winter Weddell

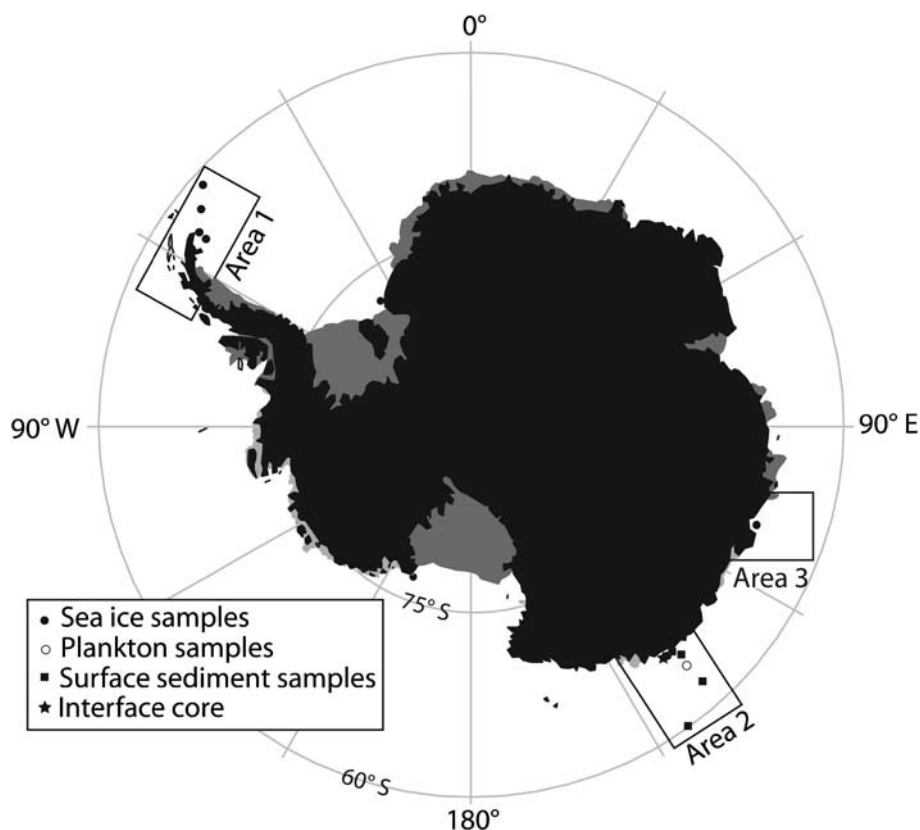


Fig. 2. Map of Antarctica showing approximate sample locations.

Outflow Study (WWOS) with the RV *Polarstern* (September–October 2006; Fig. 2, area 1) and at Casey research station (November 2006; Fig. 2, area 2). Samples were collected during the spring–summer period when sea ice algal growth is at a maximum. The biology-rich bottom ice horizons (5 cm) were used from the Weddell Sea ice and chlorophyll *a* concentrations ranged from 19 to $>2000 \mu\text{g l}^{-1}$. The ice samples from the Weddell Sea were collected using a Kovacs Mark II ice corer from predominantly first year ice. Ice cores were sectioned immediately into 10 cm sections in order to avoid brine drainage. Sectioned cores were then melted in the dark at 4°C and the particulate material collected onto GF/F filters by vacuum filtration. The samples were kept frozen until later analyses. For area 2 samples, the bottom ice flora was scraped by divers. In the laboratory, these were allowed to melt in the dark at 4°C in $0.2 \mu\text{m}$ filtered seawater. After complete melting, algal cells were concentrated via centrifugation and freeze-dried prior to analysis. Phytoplankton samples were obtained during the MD130-Image X CADO cruise (January 2003, area 3) using a $150 \mu\text{m}$ phytoplankton net. No identification of species composition was made. All samples were kept frozen prior to their analysis. A sample of the diatom *Navicula glaciei* Van Heurck (strain 2743) was obtained from the Provasoli-Guillard collection (National Center for Culture of Marine Phytoplankton, ME, USA).

Sediment samples

Surface sediments and core MD130-MC02 ($66^\circ24.74'\text{S}$, $140^\circ25.26'\text{E}$, 982 m water depth) were retrieved during the MD130-Images X-CADO cruise in 2003 on board the RV *Marion Dufresne II* (Denis *et al.* 2009).

Hydrocarbon analyses, compound specific isotope analysis

Lipids were extracted from samples using a $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (2/1) mixture and purified using open column chromatography (after Belt *et al.* 2007). Hydrocarbon fractions were analysed using a Hewlett-Packard 5890 Series II gas chromatograph (GC) fitted with a 30 m fused silica HP-1 column (0.25 mm i.d. , $0.25 \mu\text{m}$ film) and coupled to a 5970 Series mass selective detector (MSD). Spectra (m/z 40–550) were collected using Hewlett-Packard MS-Chemstation software. Individual HBIs were identified on the basis of comparison between their GC retention indices and mass spectra with those of previously authenticated HBIs (e.g. Johns *et al.* 1999).

Determination of the relative ^{13}C isotopic composition of individual HBIs was performed by gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS) at the NERC Life Science Mass Spectrometry Facility (University of Bristol, UK, application LSMSFBRISTOL007; Belt *et al.* 2008).

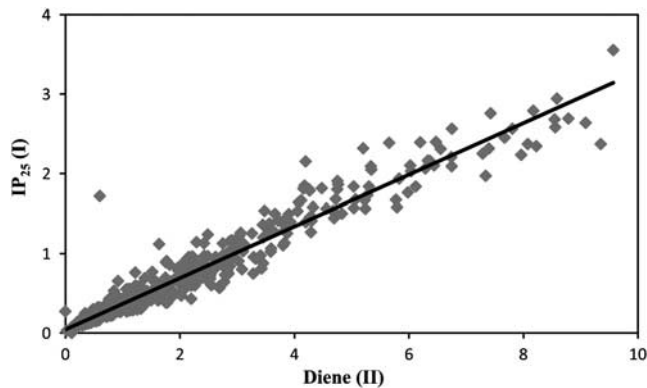


Fig. 3. Concentrations of IP₂₅ HBI monoene vs concentrations of HBI diene (II) in 214 sediments from the north Icelandic shelf (Massé *et al.* 2008). Concentrations are given in ng g⁻¹ of dry sediments.

Diatom analysis

Sediments were prepared as outlined in Crosta *et al.* (2005). Diatom identification was performed to species level and the relative abundance of each species was expressed as a percentage of the total diatom abundance.

Sediment geochemistry

Carbon isotopic composition ($\delta^{13}\text{C}$, 0.1‰ reproducibility) of the sediments from multi-core MD130-MC02 retrieved at CADO site 2 was determined using a Carlo Erba 2500 elemental analyser in line with a VG Isoprime IR-MS (Crosta *et al.* 2005). Biogenic silica (BSi) was determined (2% reproducibility, Crosta *et al.* 2005).

Results and discussion

Sea ice

In studies of numerous sediment samples from the Arctic (e.g. Massé *et al.* 2008, Andrews *et al.* 2009, Belt *et al.* 2010, Vare *et al.* 2010), we noted the co-occurrence of HBI monoene IP₂₅ and HBI diene (II). Here we show the correlation between the relative concentrations of IP₂₅ and (II) in 214 Holocene sediment samples collected in the north Icelandic shelf (Fig. 3). A linear algorithm describes 94% of the variance of this correlation. Despite the absence of IP₂₅, the distributions of HBI (II) in Antarctic sediments might reflect the contributions of sea ice diatom derived organic matter, as suggested previously for (II) and an unidentified HBI diene based on their identification in a

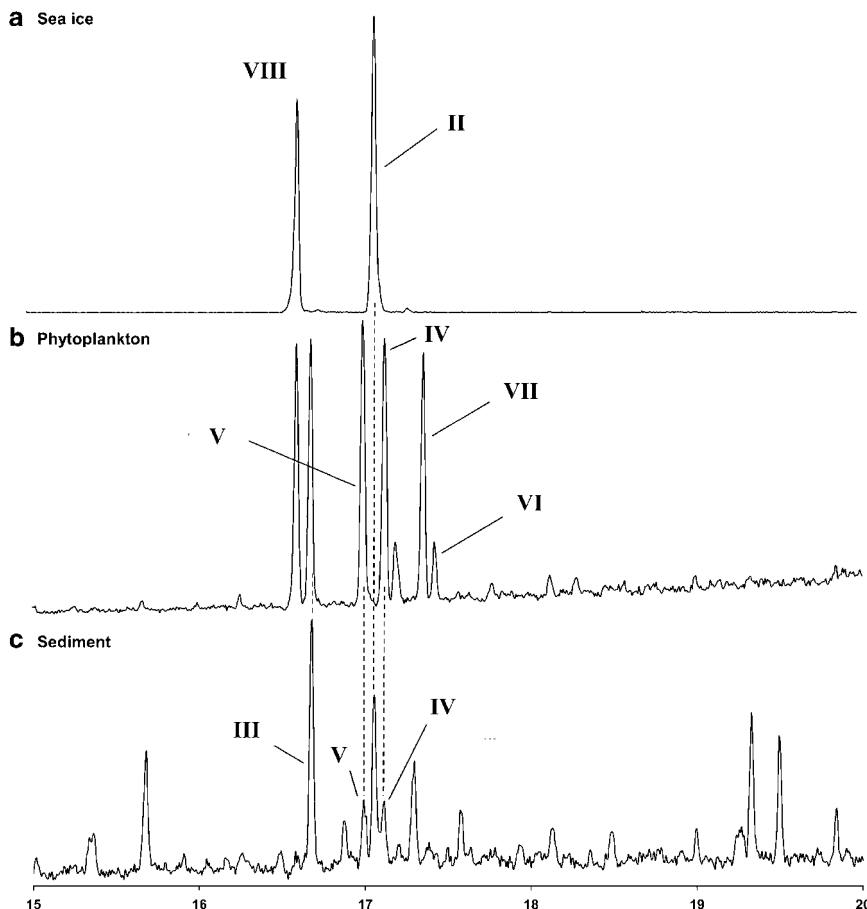


Fig. 4. Gas chromatography-mass spectrometry (GC-MS) total ion current chromatograms of hydrocarbon extracts of samples from the Antarctic. **a.** Sea ice (O'Brien Bay 1), **b.** mixed phytoplankton (MD130-PN07), **c.** sediment (MD130-MC02 0–0.5 cm).

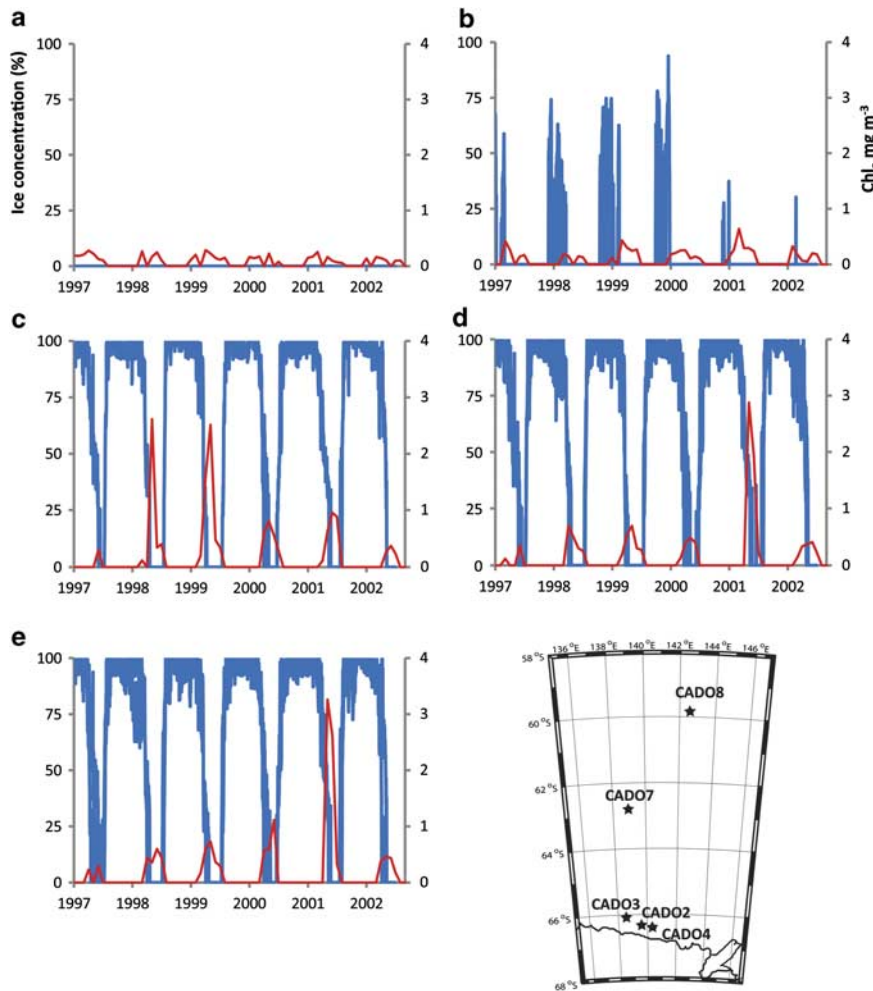


Fig. 5. September 1997–September 2002 satellite derived sea ice (blue line, SSM/I, 25 km resolution) and chlorophyll *a* (red line, SEAWIFS, 9 km) concentrations. **a.** CADO 8, **b.** CADO 7, **c.** CADO 4, **d.** CADO 3, and **e.** CADO 2.

sample of mixed sea ice diatoms (II); Nichols *et al.* 1988, Johns *et al.* 1999) and sediments from Ellis Fjord and Lützow-Holm Bay (Matsumoto *et al.* 1992 (unidentified

HBI diene), Damsté *et al.* 2007 (II)). In order to test this hypothesis further, we obtained nine sea ice samples from two well separated regions of the Antarctic (Fig. 2) and

Table I. Summary of sea ice, phytoplankton and sediment samples.

Sample name	Sample type	Ice thickness/water depth (m)	Latitude	Longitude	HBI
Weddell Sea 1	Ice	0.61/2910	61°11.07'S	48°54.11'W	II
Weddell Sea 2	Ice	1.27/346	63°39.71'S	53°51.89'W	II
Weddell Sea 3	Ice	1.55/338	64°43.55'S	57°19.87'W	II
Weddell Sea 4	Ice	1.21/356	65°3.13'S	57°20.63'W	II
O'Brien Bay 1	Ice	1.40/-	66°17.62'S	110°32.23'E	II
O'Brien Bay 2	Ice	1.30/-	66°17.62'S	110°32.23'E	II
Honkala Island	Ice	1.40/-	66°13.40'S	110°36.22'E	II
Stevenson Cove	Ice	1.30/-	66°14.28'S	110°35.42'E	II
MD130-PN07	Plankton	NA/250	66°24.71'S	140°25.81'E	III, IV, V, VI, VII
MD130-PN11	Plankton	NA/250	64°16.76'S	139°22.38'E	III, IV, V, VI, VII
MD130-MC02 (CADO 02)	Interface core	NA/982	66°24'S	140°25'E	II, III, IV, VI
CADO 02	Surface sediments	NA/982	66°24'S	140°25'E	II, III, IV
CADO 03	Surface sediments	NA/750	66°20'S	139°33'E	II, III, IV, VI
CADO 04	Surface sediments	NA/750	66°04'S	138°33'E	II, III, IV, VI
CADO 07	Surface sediments	NA/3325	62°47'S	138°57'E	II, III, IV, V
CADO 08	Surface sediments	NA/4110	59°50'S	142°32'E	III, IV, VI

examined the hydrocarbon fractions of extracts using GC–MS (gas chromatography–mass spectrometry) (e.g. Fig. 4a). These revealed the occurrence of C₂₅ HBI diene (II) together with *n*-C_{21:6} (hencosaheptaene) in all of the samples (Table I). The diene was identified by comparison of its retention index and mass spectrum with those reported previously for (II) identified in Antarctic sea ice diatoms and sediments (Nichols *et al.* 1988, Johns *et al.* 1999) and in Arctic sea ice (Belt *et al.* 2007, 2008). Diene (II) was also reported previously in cultures of the diatom *Haslea ostrearia* a benthic diatom commonly observed in temperate areas, when cultured in the laboratory at 5°C (Rowland *et al.* 2001). Although *H. ostrearia* has never been reported in polar environments, some *Haslea* spp. are commonly reported in the sympagic flora both in the Arctic and the Antarctic (Belt *et al.* 2007 and references therein). To date, every attempt to grow these sympagic species in our laboratories under the exacting conditions prevailing in sea ice has failed. However, every *Haslea* species investigated to date, as well as numerous members of the related genera *Navicula*, *Pleurosigma* and *Gryosigma* have been shown to biosynthesize HBIs (Damsté *et al.* 2004). These observations further support the suggestion (Damsté *et al.* 2007, Matsumoto *et al.* 1992) that the source of (II) in Antarctic sea ice could be one or more of these diatom genera. Coolen *et al.* (2006), using specific primers to amplify fossil DNA from recent Antarctic sediments, restricted the list of potential sources for this sea ice derived isomer to members of closely related *Navicula*/*Haslea* genera. Examination of an extract of a single sample of the diatom *Navicula glaciei* (Strain CCMP2743) from the Provasoli-Guillard culture collection herein, however, failed to reveal any HBIs.

Determination of the stable carbon isotopic compositions ($\delta^{13}\text{C}$) of HBI II in the sea ice produced average values of -8.5 and -5.7‰ for the samples collected in the Weddell Sea and Stevenson Cove in East Antarctica (Table II). These values are similar to those reported by Damsté *et al.* (2007) for (II) in sediments from Ellis Fjord, Antarctica (-9.1 and -9.4‰) and are entirely consistent with an origin from diatoms growing within the sea ice where CO₂ concentrations are sometimes depleted, depending on the physical condition of the ice (Gibson *et al.* 1999, Kennedy *et al.* 2002, Belt *et al.* 2008).

Phytoplankton

Highly branched isoprenoid (II) was not detected in the hydrocarbon fractions obtained from phytoplankton samples collected in Antarctic open waters during a summer algal bloom (Fig. 4b) but GC-MS analysis did reveal a suite of tri-, tetra- and penta-unsaturated HBI isomers (III–VII, Fig. 1). Comparison of their mass spectra and retention times with authenticated standards revealed that these isomers were identical to those previously observed in some temperate *Pleurosigma* spp. (Belt *et al.* 2000).

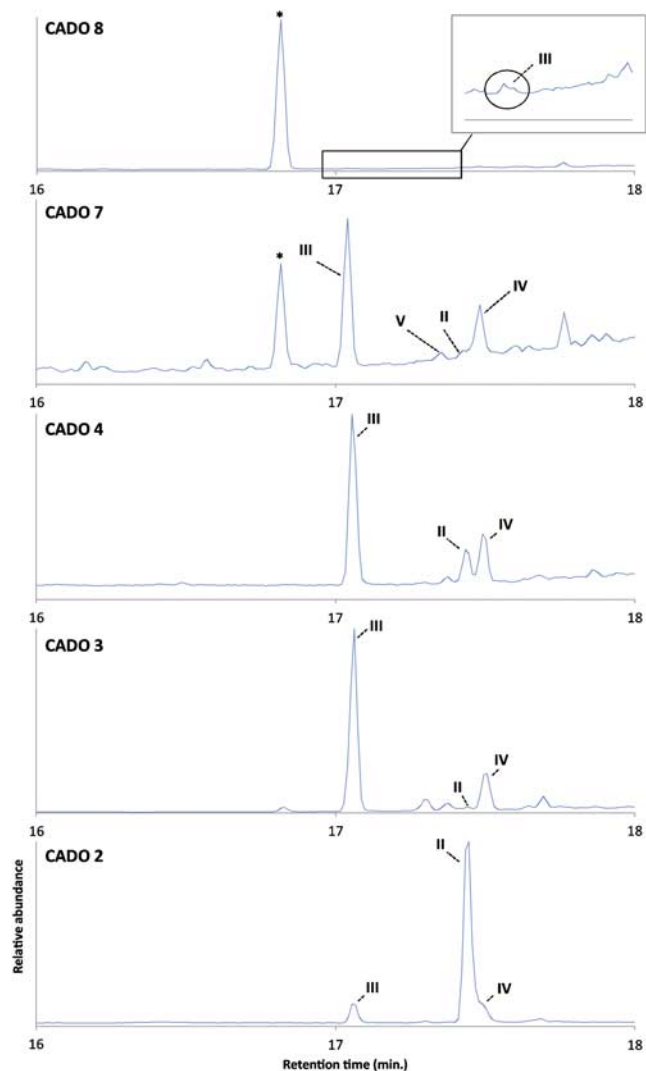


Fig. 6. Gas chromatography-mass spectrometry (GC-MS) total ion current chromatograms of hydrocarbon extracts of surface sediments collected in CADO 2, 3, 4, 7 and 8 sites. * = unidentified hydrocarbon.

The $\delta^{13}\text{C}$ composition of the HBIs in the phytoplankton samples ranged from -38 to -41‰ (Table II). Belt *et al.* (2008) measured $\delta^{13}\text{C}$ values from -35 to -40‰ for HBI (III) associated with a suite of HBI isomers not detected in our phytoplankton samples, in marine sediments collected in the Canadian Arctic Archipelago, although they were unable to conclude on the specific origin of the latter HBIs. Given the values obtained for our phytoplankton derived HBIs, it seems probable that the polyunsaturated HBI isomers observed in Arctic sediments were also of phytoplankton origin.

Surface sediments

We next carried out analyses of hydrocarbon fractions of extracts from core tops of sediment cores from six locations in the Adélie Land area of Antarctica. Briefly, the surface

Table II. ^{13}C isotopic data for selected HBI alkenes in samples of Antarctic sea ice, phytoplankton and sediment.

Sample	HBI	$\delta^{13}\text{C}$ (‰)
Weddell Sea 3	II	-8.5 ± 0.6
O'Brien Bay 1	II	-5.7 ± 0.3
MD130-PN07	III, IV, V, VI	-40.2 ± 0.5 (III); -38.3 ± 0.6 (IV)
MD130-PN11	III, IV, V, VI	$-35.35 \pm \text{n.d.}^*$ (IV)
MD130-MC02	II, III, IV, VI	-17.8 ± 1.0 (II); -41.6 ± 1.1 (III); -36.1 ± 4.2 (IV); -39.1 ± 3.0 (VI)

*only one replicate

sediment samples (CADO 2-4, 6-8), were obtained from an area between $138^{\circ}33'$ – $144^{\circ}46'$ E and $59^{\circ}50'$ – $66^{\circ}25'$ S (Figs 2 & 5, Table I). Except for the northernmost station (CADO 8), all the sites experience sea ice cover during at least one to two months per year (Fig. 5). For the more coastal stations (e.g. CADO 2, 3 & 4), a landfast ice buttress extending between 135° and 142° E is present over the sites during

seven to ten months per year (Giles *et al.* 2008, Fraser *et al.* 2010). Although landfast ice is a recurrent feature in the area, it does not usually reach latitudes lower than 65° S, so stations 6 and 7 are usually covered by the drifting pack ice which is usually observed up to 60° S (Fraser *et al.* 2010). This pack ice results from the interception by fast ice and icebergs grounded on the 'd'Urville bank' of the sea ice formed in the

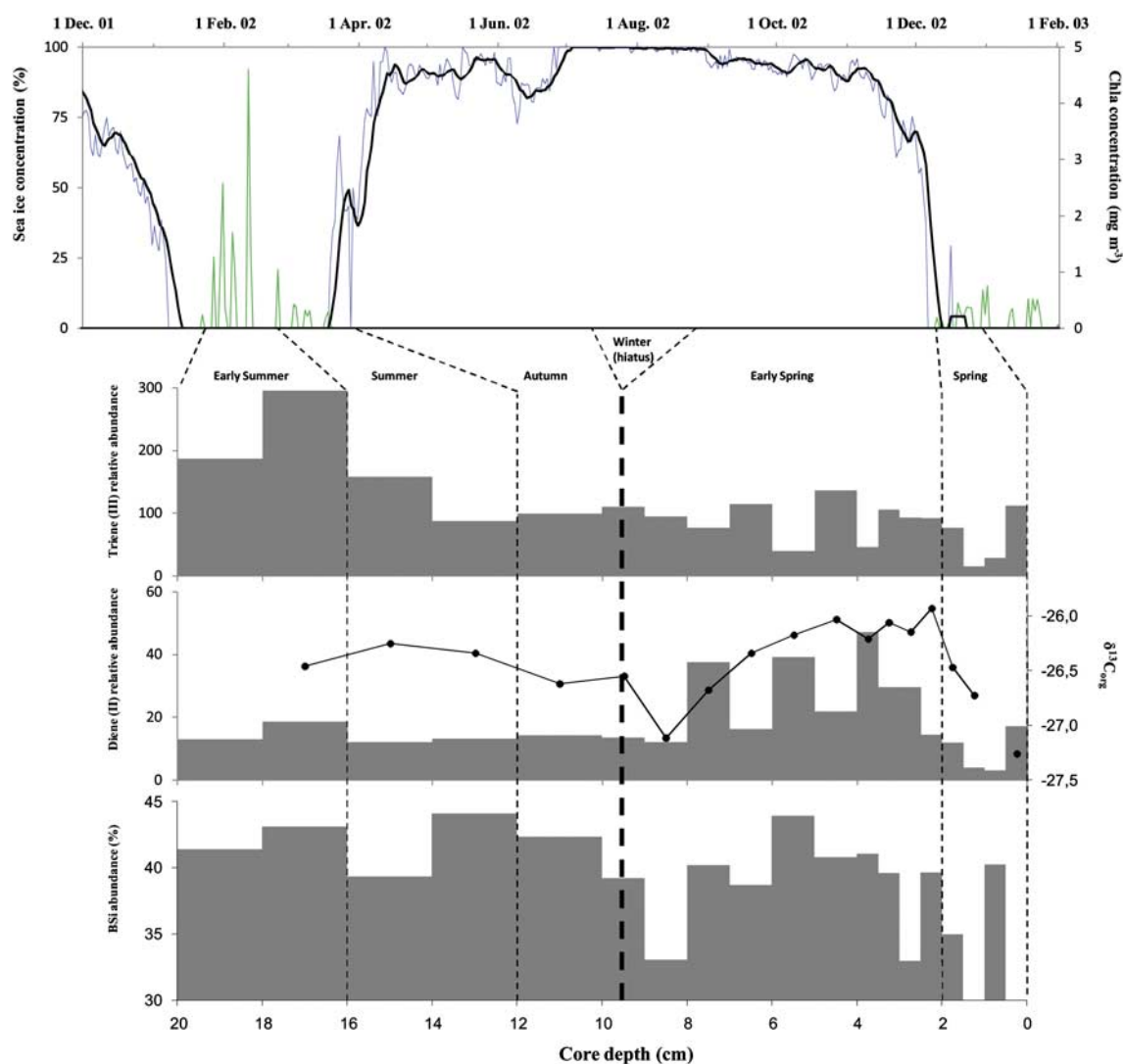


Fig. 7. 2001–03 satellite derived sea ice (SSM/I, 25 km resolution) and chlorophyll *a* (SEAWIFS, 9 km) concentrations at CADO 2 coring site. Highly branched isoprenoid, $\delta^{13}\text{C}$ and BSi concentration along core MD130-MC02.

Mertz Glacier polynya and swept westward by both katabatic and synoptic winds. When examined by GC–MS, nearly all the hydrocarbon fractions from the CADO surface sediments were found to contain (II), co-occurring with the HBIs (III–VII) which were those observed in the phytoplankton samples (Figs 4c & 6). The only sediment samples that did not contain (II) were those collected at the CADO 8 site, where only trace amounts of the tri-unsaturated HBI isomer (III) were observed. Satellite observations indicate that sea ice does not occur at this site, even during winter (Fig. 5). At the CADO 7 site, tri-unsaturated isomers dominated the HBI distribution, with tetra-unsaturated isomers (V & VI) also present, whilst only trace amounts of the sea ice derived isomer (II) could be detected. The low abundance of (II), in particular, probably reflects the ice conditions in the area, which only occurs for one to two months per year. In contrast, a relatively high abundance of the tri-unsaturated isomers reflects the high primary productivity and enhanced export efficiency associated with the marginal ice zone (Buesseler *et al.* 2003). Gas chromatography-mass spectrometry analysis of the hydrocarbons extracted from the surface sediments obtained from the more coastal sites (CADO 2, 3 & 4) revealed the presence of di-, tri-, tetra- and penta-unsaturated HBI isomers. For CADO 3 and 4, although the sea ice derived isomer (II) was more abundant, the tri- and tetra-unsaturated HBIs (III–VI) remained the dominant isomers with (III) approximately 50 and 5 times more abundant than (II) in CADO 3 and CADO 4 samples, respectively. In contrast, for CADO 2 sediments, although the same HBI isomers were present, diene (II) dominated the HBI distributions, being approximately ten times more abundant than triene (III).

The hydrocarbons of sediment sections of an additional 20 cm long core collected at the CADO 2 site (core MD130-MC02), were also analysed (Fig. 4c) and the ^{13}C isotopic compositions of HBIs in the uppermost 0–0.5 cm interval were determined (Table II). Thus, $\delta^{13}\text{C}$ values were obtained for the diene (II), trienes (III, IV) and one of the tetraenes (VI). The $\delta^{13}\text{C}$ value of diene (II) was $-17.8 \pm 1.0\text{‰}$. This is somewhat different to that of (II) in the sea ice samples (-8.5 and -5.7‰ , Table II), similar to that of IP₂₅ in Arctic sea ice and sediments ($-22.3 \pm 0.4\text{‰}$ (sea ice), $-19.6 \pm 1.1\text{‰}$ (sediment traps) and $-19.3 \pm 2.3\text{‰}$ (sediments); Belt *et al.* 2008) and to both IP₂₅ and (II) in Arctic macrofauna (-17 to -18‰ , Brown 2011). Further, this value was different to those found for the polyunsaturated HBIs (III–VII) in phytoplankton (-38 to -41‰ , Table II). We interpret these findings to indicate that (II) in the Antarctic sediments originated from sea ice diatoms, and that the sedimentary isotopic signature (*c.* -18‰) reflects inputs of (II) biosynthesized both during periods of ice melt (when the ice is more permeable to CO₂ and nutrient replenishment is possible, Kennedy *et al.* 2002 and references therein) and during earlier phases, when maximum algal growth occurs and CO₂ supply becomes limited (Gibson *et al.* 1999). In contrast to (II), HBIs (III, IV and V) were significantly

Table III. $^{210}\text{Pb}_{\text{excess}}$ data for core MD130-MC02.

Core depth (cm)	^{210}Pb excess (mBq g ⁻¹)
0–0.5	281 ± 32
1–1.5	263 ± 26
4.5–5	252 ± 19
10–11	275 ± 21
20–21	269 ± 25

depleted in ^{13}C with $\delta^{13}\text{C}$ values of -41.6‰ , -36.1‰ and -39.1‰ , respectively (Table II), in excellent agreement with the corresponding values obtained from the phytoplankton samples.

We next examined the concentrations of HBIs in further, deeper, sections of the interface core MD130-MC02 collected in February 2003 (Fig. 7). Activities of ^{210}Pb excess presents a mean value of about 265 mBq g⁻¹ from 0–21 cm, revealing virtually no decrease down core (Table III). This indicates that either the sediments were heavily bioturbated, or that the sedimentation rate was extremely high. Exceptionally high sedimentation rates with an average of 2.3 cm yr⁻¹ over the entire Holocene have been measured previously at this site (Costa *et al.* 2007). Visual examination of the sediments revealed a succession of multi-centimetre dark and light seasonal laminations, indicating that the sediments were not bioturbated. It is probable, therefore, that the sediments from this 20 cm long interface core represent only a few months of sedimentation, although in the absence of a confirmed age model, interpretations of temporal changes can only be speculative. Since the core was collected in February 2003 during the summer, we suggest that sediments from the 0–2.5 cm interval correspond mainly to particles that were sedimenting during December 2002–January 2003 when ice was largely absent. Gas chromatography-mass spectrometry analysis of the hydrocarbon fractions revealed low concentrations of (II) and (III) in this period (although sufficient amounts were present for $\delta^{13}\text{C}$ determinations), suggesting that most of the organic matter produced during the spring bloom of phytoplankton had not reached the seafloor at the time of collection of the core (explaining also the low excess of the short-lived ^{234}Th at the interface of MD130-MC02). In the 2.5–8 cm interval, (II) was two to three times more abundant than in the other sections. We suggest that these elevated relative concentrations of (II) reflect the inputs of organic matter from the melting sea ice in September–December 2002. The proposed increased contribution of the ice derived organic matter (OM) is also reflected in the slightly higher $\delta^{13}\text{C}$ values of the total OM during this period (Fig. 7).

Using sediment traps deployed in shallow waters near Davis Station (East Antarctica), Gibson *et al.* (1999) also observed a similar increase in the ^{13}C content of OM sedimenting during springtime and attributed this to the same phenomenon. They observed a 5‰ difference between the OM collected in traps during the spring months

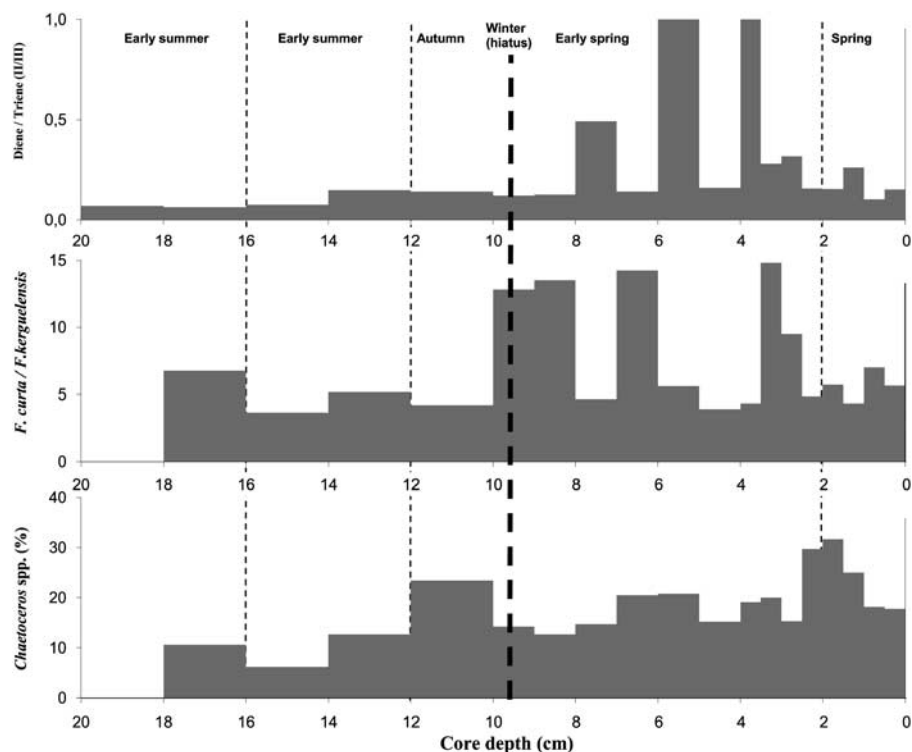


Fig. 8. Relative concentrations of Diene (II) vs Triene (III), *Fragilariopsis curta* vs *Fragilariopsis kerguelensis* and relative abundances of *Chaetoceros* spp. along core MD130-MC02.

(October–December) compared to that of OM collected from April–September. The OM from core MD130-MC02 sediments exhibited much more depleted ^{13}C values ($-26.4 \pm 0.4\%$) than those observed in the surface sediments examined by Gibson *et al.* (1999; $-19.4 \pm 0.6\%$) but these large differences can probably be explained by a more pronounced influence of sea ice OM in the shallow coastal area sampled by Gibson *et al.* (1999). These authors also observed a pronounced depletion of ^{13}C in the trapped OM (September) concomitant with near zero sedimentation during the preceding winter months (August–September). We suggest that the depletion of the $\delta^{13}\text{C}_{\text{org}}$ in the 8–9 cm interval in the MD130-MC02 core also reflects limited winter sedimentation. Significantly lower biogenic silica is observed during this interval, probably as a consequence of reduced biological productivity during winter when the ice coverage was at a maximum. The highest concentrations of biogenic silica were observed in the 14–20 cm core interval along with a corresponding increase of the concentration of triene (III). We suggest that this interval corresponds to a period where the particles from the 2002 phytoplankton bloom reached the seafloor.

The distributions and ^{13}C isotopic compositions of HBI alkenes in the Antarctic sediments we have examined here, suggest that in the uppermost sediments at least, they reflect the relative inputs of sea ice diatoms (II) and water column phytoplankton (III–VII), respectively. Thus, a ratio of (II)/(III), for example, might reflect these relative contributions in Antarctic sediments and be a useful additional proxy for the duration of certain sea ice conditions. Whether such

a signature is generally preserved during diagenesis is yet to be more fully established.

Clearly, unlike IP_{25} which, to date at least, has not been reported in environments other than the Arctic, diene (II) cannot be claimed to be unique to the Antarctic, especially as it has been reported from a wide range of environments (e.g. Johns *et al.* 1999 and references therein). However, in the Polar Regions the presence of ^{13}C isotopically enriched (II) can be taken as more characteristic of a sea ice origin (cf. Brown 2011).

Our results, therefore, suggest that HBIs have the potential to become useful proxies for the relative contributions of organic matter derived from sea ice diatoms (II) and phytoplankton (III). Although there are already well-established proxy methods for sea ice or productivity reconstruction (Armand & Leventer 2010), HBIs can be detected in extremely small sediment samples (< 1 g) and therefore permit high-resolution studies to be achieved routinely. Our analysis of the laminated sediments from core MD130-MC02 provides evidence for the potential of HBIs to provide information about the oceanic conditions (in particular sea ice) at an unprecedented sub-seasonal resolution.

Based on suggestions we made earlier (Massé *et al.* 2007), Barbara *et al.* (2010) and Denis *et al.* (2010) examined variations in the ratio (II)/(III), in sections of dated sediment cores from the Prydz Bay and Adélie Land areas and observed a strong correlation with the relative abundances of the diatom species *Fragilariopsis curta* (Van Heurck) and *Fragilariopsis kerguelensis* (O'Meara)

Hustedt. They proposed the use of the ratio of (II)/(III) as a complementary proxy to diatom counts. Although *F. curta* occurs in open waters, it is commonly considered as representative of the sea ice environment (Armand *et al.* 2005), while *F. kerguelensis* blooms around Antarctica during summer in open waters (Crosta *et al.* 2005). In order to test this hypothesis further, we performed diatom counts on sediments from core MD130-MC02. The diatom population was found to be relatively diverse with over 50 species identified in the samples. Amongst the major groups, *Fragilariopsis* species were found to dominate the assemblage, representing on average over 55% of the total diatom population. *Fragilariopsis curta* was found to be most abundant, representing between 26 and 51% of the total diatom population, while *F. kerguelensis* represented between 2 and 10%. *Chaetoceros* species (vegetative cells and spores) were also abundant, accounting for between 6 and 32% of the total diatom population. Figure 8 shows the (II)/(III) and *F. curta*/*F. kerguelensis* ratios in the sediment core. The HBI ratio is highest in the 2.5–8 cm interval, corresponding to spring, when the ice derived OM was reaching the seafloor. In contrast, the (II)/(III) ratio is at a minimum in the 14–20 cm interval when the ice cover in the area was minimal and phytoplankton were blooming. A somewhat similar trend is observed in the *F. curta* vs *F. kerguelensis* ratio, with the highest relative abundance of *F. curta* in the 2.5–10 cm interval. However, the maximum in *F. curta* cell numbers occurred somewhat earlier than the maximum in the (II)/(III) ratio. These differences in the timing of the maxima in the two ratios are probably attributable to differences in the ecology of the *Fragilariopsis* spp. compared to HBI producing diatom species. Although, so far as we are aware, neither *F. curta* or *F. kerguelensis* have been examined for HBI hydrocarbons, investigation of *Fragilariopsis cylindrus* (Grunow) Krieger (strain CCMP11022), which is a sea ice diatom species, as well as other species from the *Bacillariales*, failed to reveal any HBI producers (Damsté *et al.* 2004). It is probable, therefore, that *F. curta* and *F. kerguelensis* are not the diatom species responsible for the presence of HBIs in the Antarctic environment. It has been observed previously, in temperate environments, that maxima in HBI concentrations do not correlate exactly with those of other diatom biomarkers. Thus, in sediments of the Tamar Estuary, UK, seasonal maxima in the ubiquitous diatom biomarkers fucoxanthin and hencosaehaene, slightly post dated maxima in HBI concentrations over two year periods (Hird & Rowland 1995, Cooke *et al.* 1998). Although *F. kerguelensis* blooms around Antarctica during summer in open waters, maximum abundances of *F. curta* were observed in both fast and pack ice of regions experiencing nine to eleven months of sea ice per year but also in waters near the ice edge (Armand *et al.* 2005). In our MD130-MC02 sediments, relative abundances of *F. kerguelensis* are at a maximum in the sediments corresponding to the summer–autumn interval (10–18 cm).

This species is then rapidly replaced by more cryophilic species (e.g. *F. curta*) during the winter–early spring interval (2.5–10 cm). Relatively low abundances of *Chaetoceros* spp. are also observed in the 12–18 cm and 2.5–10 cm intervals while a sharp increase in both vegetative cells and spores are observed in the 10–12 and 0–2.5 cm intervals (Fig. 8). *Chaetoceros* (CRS) blooms usually result from enhanced water stratification following the ice melt (e.g. spring) or reflect the degradation of the growth conditions when sea ice starts to form in autumn (Armand *et al.* 2005). In our MD130-MC02 sediments, the high CRS abundances in the 10–12 cm interval reflect the late autumn export with the formation of sea ice in the area promoting spore formation and settling. In contrast, the large abundance of CRS in the early spring interval (0–2.5 cm) reflects the enhanced water stratification induced by the ice melt.

Although there are some differences in the profiles of the two ratios (*F. curta*/*F. kerguelensis* and HBI ((II)/(III))), there appears to be a general agreement between the two. The small temporal differences might be induced by differences in the ecology of the two *Fragilariopsis* spp. and sea ice (II) and phytoplanktonic (III) HBI producing diatoms.

Conclusions

We have extended previous reports of HBI alkenes in sediment samples from the Antarctic and report an HBI diene (II) in sea ice and other HBIs in phytoplankton. We determined the $\delta^{13}\text{C}$ composition of individual HBIs in both sea ice and sediments and used the differences in the structures and isotopic compositions to assign HBI isomers present in sediments from the East Antarctic continental shelf to specific origins. We propose that the presence of isotopically ^{13}C enriched HBI diene (II) might be a useful proxy for contributions of organic matter derived from sea ice diatoms to recent Antarctic sediments. Although limitations due to diagenetic effects need to be considered, a ratio of the concentrations of (II)/(III) might reflect the relative contributions of sea ice organic matter and phytoplankton derived organic matter to Antarctic sediments.

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