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**Distinctive ^{13}C isotopic signature distinguishes a novel sea ice biomarker in
Arctic sediments and sediment traps**

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Abstract

A C₂₅ highly branched isoprenoid (HBI) monoene hydrocarbon, designated IP₂₅, has been proposed previously to originate from diatoms living in Arctic sea ice, while the presence of IP₂₅ in sediments has been suggested to be a proxy for the occurrence of former Arctic sea ice. Here, we show that the ¹³C isotopic composition of IP₂₅ in sea ice, in sediment trap material collected under sea ice, and in high latitude northern sediments, is distinctive (isotopically ‘heavy’) and distinguishable from that of organic matter of planktonic or terrigenous origin. Mean δ¹³C values for IP₂₅ were -22.3 ± 0.4‰ (sea ice), -19.6 ± 1.1‰ (sediment traps) and -19.3 ± 2.3‰ (sediments). These measurements, therefore, support further the proposed use of IP₂₅ as an Arctic sea ice proxy.

Keywords: Arctic, Isotopes, Biomarker, IP₂₅, δ¹³C, Sea Ice, Sediment.

1. Introduction

An overview of IP₂₅ – an organic geochemical sea ice proxy

Highly branched isoprenoid (HBI) alkenes are ubiquitous biomarkers found in a wide range of marine sediments (e.g. Robson and Rowland, 1986; Rowland and Robson, 1990; Belt et al., 2000a; Sinninghe Damsté et al., 2004). HBIs occur mainly as sester- (C₂₅) and triterpenoids (C₃₀) with between 1-6 double bonds (Volkman et al., 1994; Belt et al., 1996, 2000a, 2001a; Wraige et al., 1997; Grossi et al., 2004). In recent years, structures and source organisms (diatoms) of many HBIs have been reported (Volkman et al., 1994; Belt et al., 2001b,c; Grossi et al., 2004), along with studies of their biosynthesis (Massé et al., 2004), reactivity (Robson and Rowland, 1988; Belt et al., 2000b) and factors affecting the distribution of individual isomers in microalgae (Wraige et al., 1998; Rowland et al., 2001; Belt et al., 2002). In the latter case, a strong dependence of C₂₅ HBI unsaturation on growth temperature was noted for one of the source diatoms *Haslea ostrearia* (Gaillon) Simonsen, with less unsaturation with decreasing temperature (Rowland et al., 2001). Since other *Haslea* species have been reported to inhabit Arctic sea ice (Poulin, 1990; Booth and Horner, 1998), it was postulated that less unsaturated isomers may therefore be produced by sea ice diatoms and, if these isomers were then also present in sediments below sea ice, it was hypothesized further that they could be used as proxies for the former presence of sea ice (Belt et al., 2007). Consistent with this hypothesis, we reported recently on the presence of a mono-unsaturated HBI alkene in Arctic sea ice and in Arctic sediments, the oldest of which was dated to be at least 9,000 years old (Belt et al., 2007). The structure of the alkene was determined using NMR spectroscopy and by independent

synthesis. We proposed the term IP₂₅ (Ice Proxy with 25 carbon atoms) for this compound (Fig. 1; compound **1**) to distinguish it from other HBI isomers. Since IP₂₅ has thus far not been reported in sediments from more temperate environments, or indeed from northern high latitude open-water or ice-free phytoplankton, we suggested its presence in high latitude sediments to be specific to a sea ice origin (Belt et al., 2007). Indeed, we used the abundance of IP₂₅ occurrence in a marine sediment core from the North Icelandic Shelf to reconstruct a palaeo sea ice record for much of the last 1,000 years. The IP₂₅ data were remarkably consistent with historical sea ice records and with other palaeoclimatic parameters (Massé et al., 2008).

Stable isotope ($\delta^{13}\text{C}$) composition as a measure of sea ice origin

In a number of empirical studies, analysis of the stable isotope ($\delta^{13}\text{C}$) composition of organic matter (OM) extracted from polar sea ice has revealed an enrichment in ^{13}C relative to ^{12}C (Gibson et al., 1999; McMinin et al., 1999; Thomas et al., 2001; Kennedy et al., 2002; Stein and Macdonald, 2004; Drenzek et al., 2007). Typically, the resultant $\delta^{13}\text{C}$ values for sea ice-derived OM have been found to lie within the range of -5‰ to -20‰, whereas the related values for open-water, or phytoplankton-derived OM typically lie within the range of -22‰ to -30‰ (Kennedy et al., 2002; Drenzek et al., 2007). Although outliers probably exist, the separation of these ranges suggests that distinguishing OM of sea ice origin from that biosynthesized by open-water phytoplankton should be straightforward and, furthermore, should be useful when attempting to determine the origins of organic geochemicals found in sediments. To date, the majority of stable isotope analyses have been carried out on sea ice-derived OM from the Antarctic, and these studies have been conducted on bulk OM rather than on individual compounds. For example, McMinin et al. (1999) analyzed

the lower 5 cm of fast ice from McMurdo Sound, Antarctica and found the OM to be relatively enriched in ^{13}C ($\delta^{13}\text{C} = -12\text{‰}$ to -18‰). ^{13}C -enrichment has also been observed by Kennedy et al. (2002) for OM in sea ice from the Weddell Sea, and by Thomas et al. (2001) and Gibson et al. (1999) for particulate OM obtained from sediment traps from the eastern Weddell Sea and Prydz Bay, Antarctica, respectively. The relative enrichment of ^{13}C has often been attributed to the restricted access of sea ice photosynthetic organisms to CO_2 . Reductions in CO_2 concentrations are thought to occur in sea ice due to limited exchange between the sea ice and the underlying seawater. This hypothesis is certainly consistent with the $\delta^{13}\text{C}$ values of algal-derived OM when microalgae are grown under CO_2 -limiting conditions (Wada et al., 1987; Fischer 1991; Rau et al., 1991). However, the relationship between $\delta^{13}\text{C}$ and ‘available’ CO_2 is probably not straightforward since some of the most ^{13}C -enriched OM in sea ice has been found in relatively exposed ice conditions where CO_2 exchange would be expected to be relatively facile (Kennedy et al., 2002). It is likely, therefore, that there are also phenotypic controls governing the $\delta^{13}\text{C}$ values that are currently not well understood. In addition, the extent of stable isotope fractionation is also associated with cell growth rates (e.g. Pancost et al., 1997; Popp et al., 1998); this too needs to be considered when interpreting $\delta^{13}\text{C}$ data. Nonetheless, the clear empirical relationship between the ranges of $\delta^{13}\text{C}$ values and the origins of marine OM (sea ice versus open-water phytoplankton) remains, for the Antarctic, at least. Similar to the studies of Antarctic samples, in the Arctic region, analysis of the carbon isotopic composition of sedimentary material has been limited largely to the analysis of bulk OM (reviewed by Stein and Macdonald, 2004) although a few more compound specific studies have appeared recently for both polar regions (Drenzek et al., 2007; Sinninghe Damsté et al., 2007). On the basis of an albeit small number of

previous measurements, $\delta^{13}\text{C}$ values for Arctic sea ice-derived OM (e.g. -15‰ to -21‰) appears to have a somewhat different isotopic range to that commonly reported for biomass in Southern Hemisphere sea ice (e.g. -5‰ to -20‰). However, whether these few measurements are representative of ^{13}C values of sea ice OM from northern high latitudes in general, is questionable, and in need of further investigation. In the present study, we therefore determined the isotopic composition of a known sea ice specific biomarker (IP₂₅) in samples of sea ice, in OM from sediment traps below sea ice and in northern high latitude sediments. We made comparisons with the $\delta^{13}\text{C}$ values of other co-occurring hydrocarbons (e.g. *n*-alkanes) and bulk OM in order to better understand the contributions that sea ice-derived OM might make to Arctic sediments. We propose that the distinctive isotopic signature of IP₂₅ produced in sea ice and found in sediment traps and in sediments, is further evidence of the utility of this compound as a sea ice proxy (c.f. Belt et al., 2007).

2. Experimental

2.1 Sea ice, sediment trap and sediment sampling

Sea ice sampling was conducted in May 2004 on first-year land-fast ice in Franklin Bay (Fig. 2). Cores were collected with a Mark II ice corer (9 cm internal diameter, Kovacs Enterprises). The bottom 5 cm of each core was immediately cut with a stainless steel saw and stored in isothermal metallic containers which were then transferred and stored at -80°C. Subsequently, sea ice samples were analyzed for HBI content as described previously (Belt et al., 2007). Surface sediment material (NOW-1 and NOW-2) was obtained from the Geological Survey of Canada (Atlantic Division, Bedford Institute of Oceanography, Dartmouth, Nova Scotia). Combinations of

surface sediment (box core), trigger weight cores (TWC) and piston cores (PC) were obtained from six locations (ARC-1 – ARC-6; Fig. 2, Table 1) during the August-September 2005 ArcticNet expedition of the CCGS *Amundsen* across the Canadian High Arctic. Further details on the core locations are given elsewhere (Belt et al., 2007). Sediment traps, deployed in Franklin Bay (July 2004) during the 2003-2004 Canadian Arctic Shelf Exchange Study (CASES) were retrieved during the 2005 ArcticNet expedition. A 26-cup time-programmed (1-4 week intervals) sediment trap was deployed at ca. 200 m from mid-July 2004 to mid-August 2005 at a mooring site (ca. 250 m bottom depth) in Franklin Bay. A more detailed account of the sediment trap sample collection procedure can be found in Forest et al. (2008). Stable isotope ($\delta^{13}\text{C}$) measurements on the bulk OM in the sediment trap material were performed according to the methods of Fernandes and Sicre (2000).

2.2 Lipid analysis

Extraction of hydrocarbon lipids from sea ice, sediments and sediment trap material together with quantification of individual compounds by gas chromatography – mass spectrometry (GC/MS) was carried out as described previously (Belt et al., 2007). For selected samples that contained sufficient abundances of IP₂₅, other HBIs and *n*-alkanes, extracts were further analyzed in triplicate by gas chromatography-combustion-isotope ratio mass spectrometry (GC/C/IRMS) using the Natural Environment Research Council (NERC, UK) Life Sciences Mass Spectrometry Facility at the University of Bristol (Application LSMSFBRISTOL007). $\delta^{13}\text{C}$ determinations (‰) are reported here as referenced to the Vienna Pee-Dee Belemnite (VPDB) standard.

3. Results

3.1 Sea ice samples

We previously reported the occurrence of the sea ice biomarker IP₂₅ (1; Fig.1) in sea ice samples from Hudson Bay, McDougall Sound (near Resolute) and Franklin Bay (Fig. 2; Belt et al., 2007). For the current study, GC/MS analysis of the hydrocarbon extract obtained from a sea ice sample from Franklin Bay showed the presence of IP₂₅ as a major component (Fig. 3). Subsequent analysis of this extract by GC/C/IRMS gave a $\delta^{13}\text{C}$ value of -22.3‰ for IP₂₅ (Fig. 4). Chromatographic overlap with other compounds prevented us from carrying out similar measurements for extracts obtained from Hudson Bay or McDougall Sound. The hydrocarbon fraction from the Franklin Bay sea ice sample extract also contained a suite of *n*-alkanes whose $\delta^{13}\text{C}$ values ranged from about -26‰ to -30‰ (Fig. 4).

3.2 Sediment trap samples

Sediment trap samples from Franklin Bay (Fig. 2) were analyzed in two ways. Firstly, $\delta^{13}\text{C}$ values were determined for bulk OM from sediment trap samples collected from August 2004 to mid-July 2005 at one-, two- or four-weekly intervals (Fig. 5). These $\delta^{13}\text{C}$ values ranged from ca. -25.0‰ to -26.5‰ for the majority of the sampling periods, with the exception of mid-late May, where the $\delta^{13}\text{C}$ value increased to about -23.5‰. In a second set of measurements, we determined the abundances and $\delta^{13}\text{C}$ values of IP₂₅ in some of the trap samples (November 2004 – June 2005) as a potentially more reliable indicator of the isotopic composition of sea ice-derived OM than bulk OM values. When analyzed by GC/MS, IP₂₅ was found to be present in all of these sediment trap samples (Fig. 3), with an elevated abundance during May (Fig.

5). Where abundance and chromatographic separation permitted, $\delta^{13}\text{C}$ values for IP₂₅ were measured and found to be higher than the bulk OM in all cases, with a mean value of $-19.6 \pm 1.1\text{‰}$ (n=11; Fig.5). The sediment trap samples also contained *n*-alkanes. Of those samples that were sufficiently abundant for $\delta^{13}\text{C}$ measurement (C₁₉ – C₃₁; Fig. 4; Table 1), the *n*-alkanes were all found to be relatively depleted in ^{13}C compared to either the bulk OM, IP₂₅ or the *n*-alkanes found in the sea ice sample from the same location, with $\delta^{13}\text{C}$ values ranging from -29.7‰ to -32.3‰ . Finally, the sediment trap OM obtained from July 2005 (after the major ice melt) also contained *n*-C_{21:6} from planktonic diatoms (Blumer et al., 1971; Yunker et al., 1995) and this compound was also depleted in ^{13}C ($\delta^{13}\text{C} = -28.3 \pm 0.7\text{‰}$) relative to the bulk OM and sea ice-derived IP₂₅.

3.3 Sediment samples

Carbon isotope analysis was carried out on a number of individual biomarkers identified in hydrocarbon extracts obtained from surface sediments (box cores) collected from across the Canadian High Arctic (Fig. 2). A limited number of downcore analyses were also performed on sediments where trigger weight and/or piston cores were available (e.g. ARC-3 to ARC-5). The $\delta^{13}\text{C}$ values for individual HBIs and *n*-alkanes are summarized in Table 1. In all cases, the sea ice biomarker, IP₂₅, was the most abundant of the HBI isomers as previously reported (Belt et al., 2007), and GC/MS chromatograms of the hydrocarbon fractions were dominated by this biomarker and a series of *n*-alkanes (typically C₁₆-C₃₁; Fig.3). For the surface sediments, the $\delta^{13}\text{C}$ values for IP₂₅ ranged from -16.3‰ (NOW-2) to -23.2‰ (ARC-6) with a mean value of $-19.3 \pm 2.3\text{‰}$ for all samples analyzed (n=56). Individual

downcore $\delta^{13}\text{C}$ values for IP₂₅ from ARC-3 showed little variation from the mean value of $-18.5 \pm 0.7\text{‰}$, which was the same as in the surface sample obtained from a box core. Similarly, the mean $\delta^{13}\text{C}$ values for IP₂₅ in downcore samples from ARC-4 (-18.6‰) and ARC-5 (-18.8‰) were found to be similar to the mean $\delta^{13}\text{C}$ value found for ARC-3, although a somewhat greater spread in individual values was observed (Table 1). Some variation in $\delta^{13}\text{C}$ values was noted, however, for IP₂₅ extracted from sediments from the North Water (NOW) region and other locations in northern Baffin Bay and west Greenland. IP₂₅ was found to be lighter in both ARC-1 ($\delta^{13}\text{C} = -20.7\text{‰}$) and ARC-2 ($\delta^{13}\text{C} = -20.5\text{‰}$) sediments compared to ARC-3 ($\delta^{13}\text{C} = -18.5\text{‰}$), but heavier in NOW-1 (-16.9‰) and NOW-2 (-16.3‰) sediments. IP₂₅ was found to be lightest of all in the ARC-6 sediment, with a $\delta^{13}\text{C}$ value (-23.2‰) similar to that found for IP₂₅ isolated from sea ice in Franklin Bay ($\delta^{13}\text{C} = -22.3\text{‰}$) which is a nearby location (Fig. 2).

For all sediments analyzed, HBI isomers other than the sea ice biomarker IP₂₅ were also found in the hydrocarbon fractions as detected by GC/MS, although they were always present in lower abundances than IP₂₅. For ARC-3 and ARC-4, sufficient quantities of an HBI diene and/or two trienes were present to allow determination of their $\delta^{13}\text{C}$ values and comparison with those of co-occurring IP₂₅. For ARC-3, the diene **2** (Fig.1) had a $\delta^{13}\text{C}$ value of -18.2‰ , virtually identical to that found for IP₂₅ in the same sediment. In contrast, $\delta^{13}\text{C}$ values for diene **2** and two trienes (**3** and **4**) in ARC-4 sediments were respectively heavier (-17.0‰) and lighter (-20.4‰ , -23.7‰) than IP₂₅ (-18.7‰).

In contrast to these relatively ^{13}C -enriched isomers, three other HBI isomers, that are significantly isotopically 'lighter' than IP₂₅, were detected. Triene **5** (Fig. 1) was present in sediments from ARC-1,2,3 with a mean $\delta^{13}\text{C}$ value of $-37.9 \pm 2.2\text{‰}$, while

tetraene **6** was found in ARC-1,2,5 with a mean $\delta^{13}\text{C}$ value of $-36.4 \pm 1.3\text{‰}$. A further diene isomer, previously unreported and postulated here to have structure **7** (which is pseudo-homologous to triene **5** and tetraene **6**), was detected in ARC-2 and found to be heavily ^{13}C -depleted ($\delta^{13}\text{C} = -42.2\text{‰}$) relative to IP₂₅.

In addition to these HBI biomarkers, a suite of *n*-alkanes was present in each of the sediments analyzed and their $\delta^{13}\text{C}$ values are summarized in Table 1. Although a full range (C₁₆-C₃₁) of hydrocarbons was detectable in each sediment extract by GC/MS, some individual compounds were too low in concentration for accurate $\delta^{13}\text{C}$ determination. For the lower molecular weight compounds (C₂₁-C₂₇), the mean $\delta^{13}\text{C}$ values for the *n*-alkanes fell in the approximate range of $-30.0 \pm 1.2\text{‰}$ to $-32.0 \pm 1.5\text{‰}$, while the C₂₉ and C₃₁ analogues were slightly ‘lighter’, with mean $\delta^{13}\text{C}$ values of $-33.4 \pm 2.3\text{‰}$ and $-34.1 \pm 1.5\text{‰}$ respectively.

4. Discussion

4.1 Isotopic composition of biomarkers versus bulk organic matter

Historically, $\delta^{13}\text{C}$ values of bulk OM have been used to evaluate sources of organic carbon in Arctic sediments (e.g. Fernandes and Sicre, 2000). Typically, these data have been used in conjunction with carbon to nitrogen ratios and biomarker (e.g. *n*-alkanoic acids, *n*-alkanes, sterols) distributions to evaluate relative inputs of terrigenous and marine OM to Arctic sediments (reviewed by Stein and MacDonald, 2004). Amongst the recognized challenges faced when using $\delta^{13}\text{C}$ values of bulk OM for elucidating the relative contributions of individually sourced OM, are the difficulties in identifying unique end member values for the various sources (Stein and Macdonald, 2004), along with the limitations of assigning individual compound

classes to specific sources. The issue of end member determination is particularly problematic for marine OM. End members ($\delta^{13}\text{C}$) for marine derived OM in the Arctic typically lie within the range of -19‰ to -24‰ (e.g. Goñi et al., 2000, 2005) although a more extended range of about -17‰ to -30‰ has also been reported (Stein and MacDonald, 2004). Terrigenous organic matter is better defined, with an accepted range ($\delta^{13}\text{C}$) of -26‰ to -28‰ (Stein and MacDonald, 2004). Previously, these end members have been used to interpret $\delta^{13}\text{C}$ measurements carried out on bulk sedimentary OM. For example, Schubert and Calvert (2001) measured $\delta^{13}\text{C}$ values for bulk OM obtained from box cores from the central Arctic region ranging from -21‰ to -23‰. Isotopically lighter (-23‰ to -24‰) profiles were recorded for locations closer to Svalbard, consistent with a higher abundance of terrestrial plant biomarkers (Schubert and Stein, 1997). Similarly, $\delta^{13}\text{C}$ values for OM from the Mackenzie Shelf area and the Bering Strait/Chukchi Sea in the western Arctic have been found to increase with distance offshore, reflecting a higher proportion of marine derived OM (Naidu et al., 2000; Stein and MacDonald, 2004). Goñi et al. (2005) have also determined $\delta^{13}\text{C}$ values for Mackenzie River (-26‰ to -27‰) and Beaufort Shelf sediments (-25‰ to -26‰) and showed these to be characteristic of their source materials with an enhanced marine contribution to the shelf sediments, as expected. Forest et al. (2007) reported $\delta^{13}\text{C}$ values for OM obtained from sediment traps deployed on the Mackenzie Shelf. Their data showed little deviation in $\delta^{13}\text{C}$ values from ca. -26‰, even with variations in the relative contributions of marine and terrigenous inputs, indicating that the corresponding end member values were similar. An exception to this uniformity in $\delta^{13}\text{C}$ values was coincident with the spring ice melt, at which point they increased sharply to between -20‰ and -21‰. This was attributed to a significant input of isotopically 'heavy' OM originating from the sea

ice, consistent with Southern Ocean sea ice observations (Gibson et al., 1999; Thomas et al., 2001; Kennedy et al., 2002). Similar values for $\delta^{13}\text{C}$ (ca. -25‰), with ^{13}C -enrichment during the late spring ($\delta^{13}\text{C}$ = ca. -21‰), were also noted for OM isolated from sediment traps from the Beaufort Shelf (O'Brien et al., 2006). As such, the $\delta^{13}\text{C}$ data presented here for OM isolated from sediment traps in Franklin Bay are entirely consistent with previous findings reported for other western Canadian Arctic locations. However, in addition, the increases in $\delta^{13}\text{C}$ values for bulk OM obtained from sediment traps observed during the spring ice melt are accompanied by higher abundances of the sea ice biomarker IP₂₅ (Fig. 5) as expected following autochthonous input. At other times, lower abundances of IP₂₅ are likely due to smaller year-round deposition, consistent with additional input of OM from allochthonous sources (Forest et al., 2008). Indeed, there is also greater variation in the baseline $\delta^{13}\text{C}$ values for the Franklin Bay sediment trap OM given here (Fig. 5) compared with those reported previously for the Mackenzie River or Beaufort Shelf samples. This is to be expected since the isotopic composition of bulk OM will be strongly influenced by allochthonous processes such as continental erosion and resuspension of previously deposited OM that are known to occur in Franklin Bay (Forest et al., 2008).

The magnitude of the increase in $\delta^{13}\text{C}$ attributed to sea ice-derived OM noted by Forest et al. (2007), O'Brien et al. (2006) and now in this study, is somewhat smaller than that observed for the related phenomenon in the Southern Ocean (Gibson et al., 1999). This is presumably due to either a lower flux of relatively ^{13}C -enriched OM from the sea ice in the Arctic and/or indicates that the Arctic sea ice OM is less ^{13}C -enriched than Antarctic OM. Direct measures of isotopic signatures of OM from Arctic sea ice have been reported only rarely. When studying distributions in $\delta^{13}\text{C}$

values of OM in the central Arctic, Schubert and Calvert (2001) made measurements on sea ice, meltwater ponds and surface waters. The ice core samples had $\delta^{13}\text{C}$ values of -18.3‰ to -20.6‰ with values in nearby sediment-free meltwater ponds of -15.3‰. In contrast, filtered surface seawater had values of -23‰ to -27.6‰, although it was noted that these may have been influenced by some contributions from isotopically ‘lighter’ terrestrial inputs. This highlights further, one of the difficulties in interpreting $\delta^{13}\text{C}$ values from bulk OM. One approach used to address this limitation when investigating the relative inputs to sedimentary OM, is to analyze for source specific biomarkers and, where possible, combine these analyses with compound specific isotopic determinations. For the Arctic, a limited number of studies have adopted this combined approach. For example, Goñi et al. (2005) determined the stable isotopic composition of low molecular weight fatty acids in Mackenzie River sediments and showed them to be substantially ^{13}C -depleted ($\delta^{13}\text{C} = -36\text{‰}$ to -40‰) compared to the corresponding compounds identified in the Beaufort Shelf sediments ($\delta^{13}\text{C} = -25\text{‰}$ to -29‰), consistent with contrasting sources. In a further study, Drenzek et al. (2007) measured the ^{13}C composition of a wider range of fatty acids ($\text{C}_{14}\text{-C}_{30}$) and co-occurring *n*-alkanes ($\text{C}_{14}\text{-C}_{35}$) from Beaufort Sea sediments. Both the fatty acids ($\delta^{13}\text{C} = -25\text{‰}$ to -33‰) and the *n*-alkanes ($\delta^{13}\text{C} = -28\text{‰}$ to -32‰) became isotopically ‘lighter’ with increasing molecular weight, consistent with increased terrestrial plant input. For the Antarctic, Sinninghe Damsté et al. (2007) reported the occurrence and isotopic composition of an HBI diene and a related thiane in sediments from Ellis Fjord. The ^{13}C -enrichment of the diene ($\delta^{13}\text{C} = \text{ca. } -9\text{‰}$) and the thiane ($\delta^{13}\text{C} = \text{ca. } -10\text{‰}$ to -15‰) supported an origin from sea ice diatoms for the diene with subsequent formation of the thiane within the sulfidic sediments (Sinninghe Damsté et al., 2007). The same diene had been reported

previously in mixed sea ice diatom populations from the Antarctic (Nichols et al., 1988; Johns et al., 1999). The co-occurrence of both ‘heavy’ (e.g. ^{13}C -enriched HBI alkene) and ‘light’ (e.g. ^{13}C -depleted sterols) biomarkers within the Ellis Fjord sediments illustrated the additional benefit that analysis by GC/C/IRMS offers when assessing sedimentary inputs of organic chemicals from different sources. Our current study, therefore, utilized this approach with a particular focus on the sea ice biomarker, IP₂₅.

The mean $\delta^{13}\text{C}$ values for IP₂₅ for all our sediment ($\delta^{13}\text{C} = -19.3\text{‰}$) and sediment trap ($\delta^{13}\text{C} = -19.6\text{‰}$) samples lie at the ‘heavy’ end of the range cited by Goñi et al. (2005) for marine OM, while the values of -16.9‰ and -16.3‰ found for IP₂₅ from NOW-1 and NOW-2 sediments respectively, correspond to the most heavily ^{13}C -enriched marine end member for Arctic OM according to Stein and Macdonald (2004). For the *n*-alkanes, our ^{13}C isotope data are comparable to those reported by Drenzek et al. (2007) who measured very similar $\delta^{13}\text{C}$ values for *n*-alkanes extracted from surface sediments from the Beaufort Sea. These authors assigned a predominantly terrigenous source (higher plant waxes and weathering of organic-rich sedimentary rocks) for the *n*-alkanes, and the same origins seem likely here. In any case, whatever the relative terrigenous inputs to these ubiquitous chemicals are, the isotopic signatures of the *n*-alkanes in sediments ($\delta^{13}\text{C} = \text{ca. } -29\text{‰}$ to -34‰ ; Table 1) are substantially different from the HBIs described here, especially the sea ice-derived IP₂₅ (ca. -19‰ to -22‰).

4.2 Major outcomes of the present study

The principal aim of this paper is to report the isotopic signatures of HBI biomarkers (especially IP₂₅), *n*-alkanes and bulk OM in Arctic sea ice, sediment traps and sediments from seasonally ice-covered locations from the Canadian High Arctic. A

summary of these isotopic signatures together with related data obtained from literature cited in this paper is shown in Figure 6. The specificity of IP₂₅ to a sea ice origin means that, wherever detected, its isotopic signature should ideally reflect its formation from within this isolated environment. The similarity between the single $\delta^{13}\text{C}$ value for IP₂₅ in sea ice ($\delta^{13}\text{C} = -22.3\text{‰}$) and the mean $\delta^{13}\text{C}$ values for IP₂₅ analyzed in all sediments ($\delta^{13}\text{C} = -19.3\text{‰}$) and sediment trap samples ($\delta^{13}\text{C} = -19.6\text{‰}$) endorses the proposed uniformity of origin for IP₂₅, and these mean values are consistent with previously reported $\delta^{13}\text{C}$ values for Arctic sea ice OM which range from -18.3‰ to -20.6‰ (Schubert and Calvert, 2001). The small variations in isotopic composition of IP₂₅ likely reflect the localized sea ice conditions and the influences that these have on diatom growth and isotopic composition of individual lipids. Indeed, we acknowledge that, as presented, there appears a notable difference between the individual $\delta^{13}\text{C}$ value for IP₂₅ in sea ice and its mean value in sediments or sediment trap material. However, the latter are influenced by spatial and time averaging and therefore, such a difference is not too surprising, with the sea ice value reported here representing the ‘light’ end of the full range for IP₂₅. We also note that the $\delta^{13}\text{C}$ value for IP₂₅ in sea ice ($\delta^{13}\text{C} = -22.3\text{‰}$), although ‘lighter’ than the mean sediment and sediment trap values, compares well with the corresponding value ($\delta^{13}\text{C} = -23.2\text{‰}$) obtained for sedimentary material from a similar location. Confirmation of whether, for example, CO₂ concentrations, temperature, diatom growth rates or a combination of these contribute to determining the isotopic compositions of individual lipids and of bulk sea ice OM will require analysis of a greater number of sea ice samples from different locations in the future, with parallel measurements of such parameters.

What is also clear from this study, is that the mean $\delta^{13}\text{C}$ signature of IP₂₅ (ca. -20‰), whilst substantially ‘heavier’ than that of Arctic planktonic marine OM (e.g. *n*-C_{21:6}; $\delta^{13}\text{C} = -28.3 \pm 0.7\text{‰}$), is ‘lighter’ than the majority of the $\delta^{13}\text{C}$ values reported previously for sea ice OM in the Antarctic (Gibson et al., 1999; Thomas et al., 2001; Kennedy et al., 2002). However, McMinn et al. (1999) showed that the ^{13}C -enrichment in sea ice OM was lowest at the ice-water interface ($\delta^{13}\text{C} = -18.0\text{‰}$), while Thomas et al. (2001) noted that $\delta^{13}\text{C}$ values for sediment trap OM collected below platelet ice did not show the same ^{13}C -enrichment as that found for trap OM below sheet sea ice (Gibson et al., 1999), possibly due to a less ‘closed’ environment for the former. The same effect may be responsible for the observed relatively ‘light’ values described here for Arctic sea ice OM. The magnitude of the $\delta^{13}\text{C}$ values for IP₂₅ are consistent, however, with our measurements on bulk OM in sediment traps, with an increase in $\delta^{13}\text{C}$ values observed during the spring ice melt to ca. -23.5‰. The benefit of carrying out compound specific isotopic analysis using GC/C/IRMS is further illustrated by consideration of our data for the various HBI isomers. Specifically, diene **2** and triene **3**, which are pseudohomologous with IP₂₅ (**1**), were found to have similar isotopic compositions to IP₂₅ and are likely derived from a common source for the samples studied here, even though these isomers are not restricted to a sea ice origin in all environments. Indeed, the small differences observed between $\delta^{13}\text{C}$ values for diene **2**, triene **3** and IP₂₅ may, in part, be due to some allochthonous input from e.g. open-water planktonic diatom species. In contrast to these relatively ^{13}C -enriched HBIs, the isomeric diene **7**, triene **5** and tetraene **6** were all substantially depleted in ^{13}C ($\delta^{13}\text{C} = -35.0\text{‰}$ to -42.2‰), suggesting they result from an entirely different origin, possibly from freshwater diatoms. These highly depleted $\delta^{13}\text{C}$ signatures are more typical of the lipids of freshwater algae as

previously reported for long chain fatty acids (Goñi et al., 2005). Previously, we have reported on the presence of both triene **5** and tetraene **6** in the benthic diatom *Pleurosigma intermedium* W. Smith (Belt et al., 2000a) and **6** in a planktonic species within the *Pleurosigma* genus (Belt et al., 2001c). A geometric isomer, **8**, of triene **5** has been reported in the planktonic diatom *Rhizosolenia setigera* Brightwell (Belt et al., 2002; Massé et al., 2004) and in sea ice (Belt et al., 2007), and the corresponding tetraene isomer (**9**) has been found in *R. setigera* (Belt et al., 2002; Massé et al., 2004) and the freshwater species *Navicula sclesvicensis* Grunow (Belt et al., 2001b), but both of these isomers were absent from the sediments described here. Thus, while the exact sources of triene **5** and tetraene **6** remain uncertain at this point, their absence from sea ice samples and their isotopically very ‘light’ $\delta^{13}\text{C}$ values presented here, certainly argue against a sea ice origin.

Our $\delta^{13}\text{C}$ data for the *n*-alkanes agree with those reported by Drenzek et al. (2007) who measured $\delta^{13}\text{C}$ values for these hydrocarbons from Beaufort Sea sediments, with a general trend towards greater ^{13}C -depletion with increasing chain length. Of course, the ubiquity of these *n*-alkanes somewhat limits the interpretation of either abundances or of isotopic composition, but it is interesting to note the clear trends in $\delta^{13}\text{C}$ values observed for these biomarkers between the sea ice, sediment traps and sediments (Fig. 4). The relatively ‘light’ sedimentary $\delta^{13}\text{C}$ values likely arise from a significant terrigenous input as concluded previously for Beaufort Sea sediments (Drenzek et al., 2007), with a trend towards ‘heavier’ or more marine-like values from sediments to sediment traps to sea ice (Fig. 4). Given the ubiquity of the *n*-alkanes and the potential for the sea ice to receive some allochthonous inputs from the water column, $\delta^{13}\text{C}$ values for these chemicals in the sea ice samples are unlikely to be truly representative of an autochthonous origin from sea ice biota. As such, extrapolating

$\delta^{13}\text{C}$ values of specific sea ice biomarkers such as IP_{25} to represent a ‘bulk sea ice’ isotopic signature may be more reliable than carrying out isotopic measurements on bulk OM from sea ice directly, since the latter may be influenced by allochthonous inputs. Therefore, the distinctive isotopic signature of IP_{25} is not only further evidence of its validity as a sea ice proxy but, given the uncertainties in firmly identifying end members for $\delta^{13}\text{C}$ values for Arctic OM from different sources and their subsequent use in calculating percentage source contributions, the identification of a specific sea ice isotopic signature should prove valuable for the interpretation of $\delta^{13}\text{C}$ data from bulk sedimentary OM which are more routinely available.

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Figure and Table Legends

Figure 1. Chemical structures of highly branched isoprenoid (HBI) alkenes described in the current study. IP₂₅: **1**; Dienes: **2,7**; Trienes: **3,4,5,8**; Tetraenes: **6,9**.

Figure 2. Map of sampling locations for sea ice, sediment trap and sediment samples. Individual numbering corresponds to specific locations cited in the text.

Figure 3. Representative partial GC/MS chromatograms of extracts obtained from sea ice, sediment trap material (May 2005) and box core sediment from Franklin Bay. Selected *n*-alkanes (C₁₉-C₂₄) are denoted by solid circles. The peak labeled * is due to IP₂₅.

Figure 4. $\delta^{13}\text{C}$ values for *n*-alkanes (C₁₉-C₃₁) and IP₂₅ from sea ice, sediment traps and sediments from the Canadian High Arctic. The magnitudes of the standard deviations for each dataset (*n*-alkanes) are indicated by the $\pm\sigma$ entries.

Figure 5. Seasonal variations in the IP₂₅ abundances (open circles) and $\delta^{13}\text{C}$ profiles for bulk organic material (triangles) and IP₂₅ (solid circles) in sediment trap material from Franklin Bay (August 2004 – July 2005).

Figure 6. Summary of $\delta^{13}\text{C}$ values for bulk organic matter and individual biomarkers described in the text: (a) experimental data obtained in the current study; (b) literature data cited in the text. Ranges in $\delta^{13}\text{C}$ values correspond to high/low limits rather than statistical variations from a mean in order to enable comparison with literature ranges.

Table 1. Summary of $\delta^{13}\text{C}$ values for individual biomarkers described in the current study. For sediments, individual core horizons are designated by depth and core type (BC: Box Core; TWC: Trigger Weight Core; PC: Piston Core).