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The Arctic sea ice biomarker IP_{25}: a review of current understanding, recommendations for future research and applications in palaeo sea ice reconstructions

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ABSTRACT

In recent years, a novel proxy for the past occurrence of Arctic sea ice has been proposed that is based on the variable marine sedimentary abundance of an organic geochemical lipid derived from sea ice diatoms in the spring. This lipid, termed IP_{25} (Ice Proxy with 25 carbon atoms), is a highly branched isoprenoid mono-unsaturated alkene that appears to be sufficiently stable in sediments to permit meaningful palaeo sea ice reconstructions to be carried out over short- to long-term timescales. Since the first proposed use of IP_{25} as a proxy for palaeo sea ice by Belt et al. (2007), a number of laboratories have measured this biomarker in Arctic sediments and it is anticipated that research activity in this area will increase further in the future. The content of this review is divided into a number of sections. Firstly, we describe the scientific basis for the IP_{25} proxy and its initial discovery in Arctic sea ice, sedimenting particles and sediments. Secondly, we summarise the relatively few studies that have, to date, concentrated on examining the factors that influence the production and fate of IP_{25} and we identify some areas of future research that need to be addressed in order to improve our understanding of IP_{25} data obtained from sedimentary analyses. What is clear at this stage, however, it that the presence of IP_{25} in Arctic marine sediments appears to represent a proxy measure of past seasonal sea ice rather than permanent or multi-year ice conditions. Thirdly, we highlight the importance of rigorous analytical identification and quantification of IP_{25}, especially if measurements of this biomarker are going to be used for quantitative sea ice reconstructions, rather than qualitative analyses alone (presence/absence). Fourthly, we review some recent attempts to make the interpretations of IP_{25} biomarker data more detailed and quantitative by combining sedimentary abundances with those of phytoplankton- and other sea ice-derived biomarkers. Thus, the bases for the so-called PIP_{25} and DIP_{25} indices are described, together with an overview of potential limitations, concluding that investigations into the use of these indices needs further research before their full potential can be realised. In the final section, we provide a summary of IP_{25}-based palaeo sea ice reconstruction case studies performed to date. These case studies cover different Arctic regions and timescales spanning decades to tens of thousands of years.

1. Introduction

The purpose of this paper is to provide a review of current knowledge regarding the Arctic sea ice proxy biomarker IP_{25}. In the first section of the paper, we describe the scientific basis behind, and the subsequent discovery of, IP_{25}, while in the second section, we provide an overview of areas that we have identified as needing further attention before the full potential of the IP_{25} proxy can be realized. In the third section, we describe how sedimentary IP_{25} abundances may be coupled with those of other biomarkers to potentially obtain either quantitative or more detailed information about past sea ice conditions and, finally, we summarise how the analysis of IP_{25} and other biomarkers in Arctic marine sediments has been used as the basis for several palaeo sea ice reconstruction studies in recent years. In this respect, some comparisons are also made with other proxy data, although the emphasis in this review is placed on the analysis of IP_{25} and other biomarkers.

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1.1. Background to biomarkers and applications in palaeoclimatology

Molecular biomarkers are chemical signatures or fingerprints of the biota from which they are produced (e.g. Peters et al., 2005; Killops and Killops, 2009). They occur across all taxonomic levels and can be classified into general classes (e.g. lipids), smaller groupings (e.g. fatty acids, sterols) or individual representatives of these (e.g. cholesterol is a specific and commonly occurring example of a sterol). In addition, biomarkers may be either primary or secondary metabolites and their occurrence can either represent general indicators of origin (e.g. long-chain *n*-alkanes from terrestrial plants) or be of a more source-specific nature (e.g. alkenones from unicellular eukaryotic haptophytes – coccolithophores). In recent decades, an increasing appreciation of the structures and sources of individual and groups of such chemicals has resulted in several biomarker-based applications in palaeoclimatology across the geosphere (for a recent review, see Eglinton and Eglinton, 2008) and the development of these methods has been further aided by an understanding of the environmental factors that influence the production and distributions of individual chemicals. For example, the influence of temperature on the distribution of alkenones from the coccolithophore *Emiliana Huxleyi* (Brassell et al., 1986) and glycerol dialkyl glycerol tetraethers (GDGTs) from Archaea (Schouten et al., 2002; Kim et al., 2008) have provided the basis for the $U^{K'}_{37}$ and TEX_{86} indices, used commonly for reconstructing past sea surface temperatures. A further attribute of the alkenones and the GDGTs is their source-specific nature, which enables their occurrence and distributions to be interpreted with greater certainty. Indeed, it is through an understanding of source specificity and the influences of environmental factors on biomarker distributions that molecular biomarker-based proxies are developed, so studies on both of these aspects remain key research areas for organic geochemists/palaeoclimatologists.

1.2. Highly branched isoprenoid (HBI) alkenes as source-specific biomarkers from diatoms

Highly branched isoprenoid (HBI) alkenes are unusual (structurally) secondary metabolites produced by a relatively small number of marine and freshwater diatoms belonging to the *Haslea*, *Navicula*, *Pleurosigma* and *Rhizosolenia* genera (Volkman et al., 1994; Belt et al., 1996, 2000a, 2001a,b,c; Sinninghe Damsté et al., 1999, 2004). HBIs occur with C_{20}, C_{25} and C_{30} carbon skeletons and are widely distributed in marine sediments worldwide, although the C_{25} alkenes are the most commonly reported (Rowland and Robson, 1990; Belt et al., 2000a). Over the past two decades, the sources and structures of ca 20 individual HBI lipid biomarkers have been reported, mainly following large-scale culturing of individual diatom taxa and subsequent analysis of purified extracts using a combination of mass spectrometric (MS) and nuclear magnetic resonance (NMR) spectrometric methods (e.g. Belt et al., 1996, 2000a, 2001a,b,c; Sinninghe Damsté et al., 1999, 2004). In particular, these investigations have enabled the number, position and stereochemistries of the double bonds to be determined (e.g. Fig. 1). The majority of C_{25} HBIs reported in sediments contain 2–5 double bonds (e.g. Rowland and Robson, 1990; Belt et al., 2000a), although mono- and more poly-unsaturated isomers have also been reported (Dunlop and Jefferies, 1985; Wraige et al., 1997; Xu et al., 2006). Some relationships between the positions of the double bonds and the source diatoms have been identified; for example, HBIs biosynthesized by *Haslea* spp. generally possess a double bond in the C6–C17 or C5–C6 positions (e.g. 2; Fig. 1), while counterparts from *Pleurosigma* spp. usually contain double bonds between C7 and C20 (e.g. 3; Fig. 1). A further difference between HBIs from *Haslea* spp. with those from *Pleurosigma* spp. is that both *E* and *Z* stereoisomers (see C9–C10 positions for 3 and 4; Fig. 1) are usually observed with HBIs from the latter genera. This unusual structural feature is also exhibited by C_{25} and C_{30} HBIs made by *R. setigera* (e.g. Belt et al., 2002). The biosynthesis of HBIs by a limited number of diatom genera has also been demonstrated using molecular phylogeny techniques (Sinninghe Damsté et al., 2004). Despite these advances in source identifications and structural determinations, the functions or role(s) of HBIs in diatoms remains unknown, although the biosynthetic mechanisms responsible for their formation have been established (Massé et al., 2004). What is clear, however, is that the source-specific nature of HBIs makes them potentially useful biomarkers for palaeoenvironment studies.

1.3. Influence of temperature on HBIs and the development of the IP_{25} sea ice diatom proxy

Relatively few studies have investigated the physiological or phenotypic variables that influence or control the distributions of individual HBI alkenes in diatoms and the majority of those

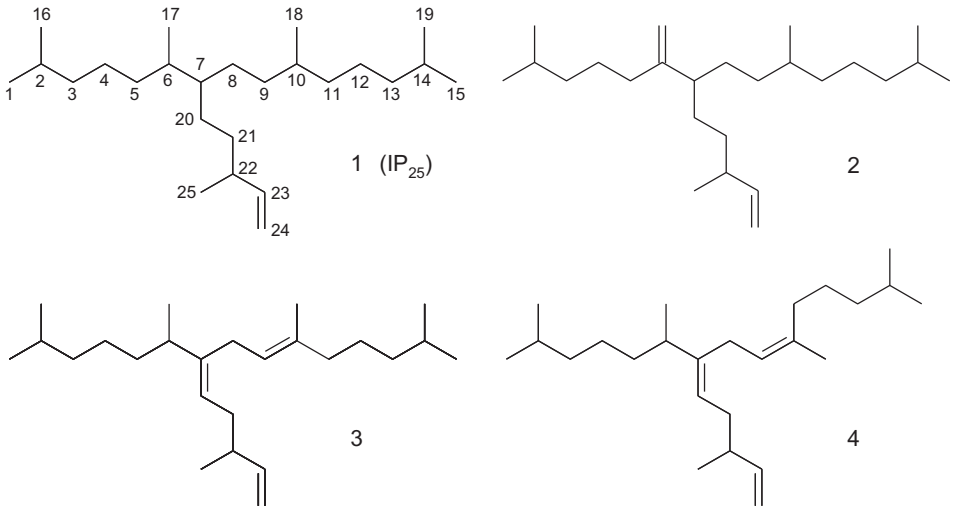

Fig. 1. Structures of C_{25} highly branched isoprenoid alkenes described in the text. (1) IP_{25}; (2) $C_{25:2}$; (3) and (4) HBI trienes.

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investigations that have been conducted have not resulted in particularly conclusive findings (e.g. Wraige et al., 1998; Massé, 2003). The most definitive relationship between growth conditions and HBI distributions was first identified by Rowland et al. (2001), who showed that, in *Haslea ostrearia* (Gaillon) Simonsen, the degree of unsaturation (number of double bonds) varied inversely with culture growth temperature. Since *H. ostrearia* produced (predominantly) HBI tetraenes (4 double bonds), trienes (3 double bonds) and dienes (2 double bonds) at 25 °C, 15 °C and 5 °C, respectively, it was hypothesized that HBI monoenes (1 double bond) might be biosynthesized by Arctic sea ice-dwelling *Haslea* spp. at ca 0 °C or colder (Belt et al., 2007). Further, if such HBI monoenes were subsequently deposited in underlying Arctic sediments, then their presence therein, could provide the basis for a novel proxy for the past occurrence of Arctic sea ice. Although this hypothesis could not be tested in the laboratory, since *H. ostrearia* failed to grow below 5 °C (Rowland et al., 2001; Massé, 2003), a mono-unsaturated C_{25} HBI alkene was identified amongst a suite of HBIs in hydrocarbon extracts obtained from sea ice samples collected from 3 different regions of the Canadian Arctic Archipelago (CAA) and Hudson Bay (Canadian sub-Arctic) during the spring algal bloom (Belt et al., 2007). The structure of this HBI monoene (1; Fig. 1), including the position of the double bond, was determined by independent synthesis and characterization using NMR spectroscopy (Belt et al., 2007).

Significantly, the gas chromatographic (GC retention index) and mass spectrometric properties of this synthetic standard were identical to that of the C_{25} HBI monoene identified in Arctic sea ice extracts. As such, the first component of the original hypothesis, that certain diatoms (probably *Haslea* spp.) in Arctic sea ice could biosynthesize a mono-unsaturated HBI alkene, was confirmed. Since the chromatographic and mass spectral properties of the sea ice-derived biomarker were different to those found for C_{25} monoenes reported previously (Dunlop and Jefferies, 1985; Xu et al., 2006), and this chemical was absent in numerous open-water phytoplankton samples collected from an East–West transect of the CAA, Belt et al. (2007) also concluded that this particular HBI isomer was produced selectively by some Arctic sea ice diatoms and thus possessed a key attribute required for palaeo sea ice reconstruction. As a result, this particular HBI was named IP_{25} (Ice Proxy with 25 carbon atoms).

2. Production and fate of IP_{25}

2.1. IP_{25} in sea ice

Since IP_{25} biosynthesis is related to the diatoms that occupy the interstitial channels at the base of Arctic sea ice, it will be important, in the future, to gain a more detailed account of the factors that control this biosynthetic pathway, in order that the sedimentary record can be interpreted more comprehensively. As such, some key questions that relate to aspects of production are: Which Arctic sea ice diatom species are responsible for biosynthesizing IP_{25} and are these species pan-Arctic? What are the sea ice conditions under which IP_{25} is produced? What are the influences of environmental controls (e.g. ice thickness, snow cover, irradiance, nutrients, etc.) on IP_{25} production?

Apart from the outcomes of the recent study by Brown et al. (2011) described below, the current understanding of IP_{25} production by Arctic sea ice diatoms is rather incomplete due, in part, to the challenges offered by either *in situ* sampling of sea ice, or laboratory culturing of diatoms under realistic model conditions. For example, to date, the individual species responsible for biosynthesising IP_{25} have not been identified, although it is likely that either *Haslea* spp. or *Navicula* spp. (or both) are the probable sources, since these diatom genera are known to produce C_{25} HBIs in culture and both have been found in sea ice samples containing IP_{25} (Belt et al., 2007; Brown et al., 2011). Further, *Haslea* spp. and *Navicula* spp. are common in Arctic sea ice diatom populations (Poulin, 1990; Różańska et al., 2009). Unfortunately, laboratory culturing of individual *Haslea* spp. obtained from the Canadian Arctic yielded $C_{25:3}$ and $C_{25:4}$ HBIs, but not IP_{25} (Massé, personal communication), suggesting that the latter may only be biosynthesized under strict sea ice conditions which makes modelling the environmental controls over IP_{25} production additionally challenging. Identification of IP_{25}-producing diatoms and their pan-Arctic distribution should help determine whether there are any regional limitations to the application of the IP_{25} proxy and the use of molecular ecology methods (e.g. Coolen et al., 2004) may help in the identification of IP_{25} producers in the future. What is clear, however, is that IP_{25}-producing diatom species likely represent the minority taxa.

In general, the growth, production and biomass of sea ice algal communities are controlled by a number of factors including rapid bottom ice melt (Lavoie et al., 2005), the availability of nutrients present in the underlying surface waters (e.g. Gradinger, 2009; Różańska et al., 2009; Arrigo et al., 2010) and by sea ice thickness and snow cover (e.g. Mundy et al., 2005), which influence the amount of transmitted light through the ice matrix (Arrigo et al., 2010). Short-term reductions to biomass production due to snow cover may be somewhat compensated for by a lengthening of the algal growth period in the Canadian Arctic (Mundy et al., 2005). In terms of specific biomarker lipids, increased snow cover and irradiance have been shown to influence both the quantity and the quality of fatty acids in some sea ice algae (Leu et al., 2011), while nutrients and light intensity are known to affect unsaturation in alkenones (e.g. Laws et al., 2001; Versteegh et al., 2001). The extent to which snow cover, irradiance or nutrient levels also influence IP_{25} biosynthesis will require further analysis of sea ice samples from different regions of the Arctic. Clearly, however, there are a number of parameters that may potentially influence the production of IP_{25} in Arctic sea ice and thus, the abundances in underlying sediments from which the palaeo record is derived. Such influences should be considered alongside the sedimentary fate of IP_{25} discussed later.

Only a small number of sea ice sampling studies have thus far provided useful information regarding IP_{25} production. Other than the initial identification of IP_{25} in Arctic sea ice (Belt et al., 2007), Brown et al. (2011) investigated IP_{25} accumulation in Arctic sea ice cores collected from the southeast Beaufort Sea from late winter through to the ice melt in late spring/early summer 2008. The main outcomes of this study were that the IP_{25} was absent (or below the limit of detection) during the winter, increased in abundance during the early spring, and reached maximum concentrations coincident with the spring algal bloom (April–May). The strong seasonal influence on IP_{25} production was clear, with more than 90% accumulation occurring during a relatively short (4–6 weeks) interval during the spring (Brown et al., 2011). Further, by analysing the composition of sectioned sea ice cores, Brown et al. (2011) also demonstrated that IP_{25} accumulation was largely restricted to regions of the sea ice cores that had brine volume fractions suitable for supporting colonisation and growth of diatoms (>5%; Golden et al., 2007) and that the highest IP_{25} concentrations were found in sections distal to the ice–seawater interface; both outcomes being consistent with production by sea ice-associated diatoms. The wider implication of the study by Brown et al. (2011) with respect to palaeo sea ice reconstructions is that if the requisite (and subtle) structural sea ice conditions are not met, then IP_{25} production would be prevented (or significantly reduced) due to a failure in diatom growth; however, this hypothesis needs testing

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through further field collection of sea ice cores and lipid analysis. Under more extreme conditions, like other photosynthetic organisms, the growth of sea ice diatoms is subject to light availability, which is significantly reduced under thick and dense ice cover. Consequently, perennial ice cover almost certainly limits the accumulation and release of IP_{25}-producing diatoms to the water column and towards the seafloor. Since IP_{25} has also been shown to be absent from open water phytoplankton assemblages in the Arctic (Belt et al., 2007), the absence of IP_{25} in Arctic sediments likely indicates the absence of sea ice or, alternatively, severe sea ice conditions characterized by permanent ice coverage throughout the year (Belt et al., 2007).

Further confirmation of the sea ice origin of IP_{25} was provided through measurement of its stable isotopic composition in Arctic sea ice, sedimenting particles and in sediments (Belt et al., 2008; Brown, 2011). In all cases reported to date, IP_{25} has been relatively enriched in ^{13}C, consistent with a sea ice origin (e.g. Gradinger, 2009 and references therein) and, although there is a noticeable range in $\delta^{13}C$ values, this has also been observed for other organic matter (OM) derived from within Arctic sea ice (Gradinger, 2009). Thus, reported $\delta^{13}C$ values for IP_{25} range from −16.9‰ to −22.7‰ in sea ice (Belt et al., 2008; Brown, 2011) and −16.3‰ to −23.2‰ in sediments (Belt et al., 2008). It is not clear, at present, why there is such a large range in $\delta^{13}C$ values for IP_{25} in sea ice and sediments or why the relative isotopic enrichment in ^{13}C is generally lower than for HBIs and other organic matter produced by Antarctic sea ice flora (e.g. Gibson et al., 1999; Thomas et al., 2001; Kennedy et al., 2002), although both may potentially be explained by a more variable and open brine channel network in Arctic sea ice, with greater replenishment of CO_2 from sub-surface waters. Such a hypothesis is consistent with lighter $\delta^{13}C$ values for OM obtained from the ice–water interface (McMinn et al., 1999) and from under platelet ice in the Antarctic (Thomas et al., 2001). A larger study, however, is required before a more comprehensive explanation can be offered to account for the Arctic-based observations. What is clear, however, is that IP_{25} has a stable isotopic composition that is significantly heavier than the majority of phytoplanktic OM from the Arctic (see Belt et al., 2008 and references therein) and this can be attributed, in part, to the specific origin of this biomarker.

Interestingly, IP_{25} has not been reported in sea ice flora or sediments from the Antarctic, despite the occurrence of the structurally related HBI diene (Structure 2; Fig. 1) (Nichols et al., 1988; Johns et al., 1999; Sinninghe Damsté et al., 2007; Massé et al., 2011), which has recently been proposed as a proxy for Antarctic sea ice (Massé et al., 2011). The reason for the absence of IP_{25} in Antarctic sea ice diatoms or sediments is not known but may reflect different diatom species in the Southern Hemisphere compared to the Arctic; alternatively, there may be (as yet) unidentified environmental controls over the biosynthetic mechanism responsible for IP_{25} production that do not exist in the Antarctic.

Finally, by gaining a greater understanding of the factors that influence IP_{25} production and abundance, it should be possible to gain additional insights into how the interpretations of IP_{25}-based sea ice proxy data may differ from those derived from other sea ice proxy records. In this respect, the already established seasonal (spring) production of IP_{25} during the spring sea ice diatom bloom helpfully focuses the interpretation of its sedimentary occurrence.

While some general areas of future research work pertinent to IP_{25}-based palaeo sea ice reconstruction can be readily identified, there are also clear resource and logistical constraints associated with the sampling and analysis of sea ice and sea ice algae that may limit, in particular, the detailed assessment of those factors that influence the production of IP_{25} and its transfer and subsequent fate in sediments. In contrast, given the plethora of archived sediment cores and the prevalence of on-going cruise campaigns, it is likely that the majority of biomarker-based palaeo sea ice research activity in the near future will consist of sedimentary analysis of IP_{25} and other organic geochemicals, together with the application of empirical studies described herein. Some areas of future research pertinent to these aspects are identified in the following sections.

2.2. Vertical transport and deposition of IP_{25}

Since palaeo sea ice reconstructions using IP_{25} are (and are likely to continue to be) based on sedimentary analyses of this biomarker, it will also be important to identify factors that influence the fate of IP_{25} following production in Arctic sea ice. These factors exist both pre- and post-deposition in sediments, so it will be necessary to consider a range of environments and influences that potentially exist within each of these. As such, some pertinent questions related to the fate of IP_{25} might be: What is the rate of transfer of IP_{25} from melting sea ice to sediments (pelagic-benthic coupling)? How is pelagic-benthic coupling of IP_{25} influenced by chemical and biological processes occurring in the water column such as heterotrophic grazing of sea ice diatoms? How stable is IP_{25} in sea ice, the pelagic system and the sedimentary environment? To what extent can surface calibrations of IP_{25} be extrapolated down-core? What are the degradation processes in sediments (if any) and can rates of IP_{25} modification be identified? Can stability information be extrapolated between different regions?

With respect to the transfer of IP_{25} from sea ice to the pelagic system, Belt et al. (2008) initially showed that IP_{25} could be identified in sediment traps deployed under seasonal sea ice in Franklin Bay in the Canadian Arctic. Further, peak abundances of IP_{25} in the sediment traps were coeval with the period of ice melt at the end of spring, consistent with production by sea ice diatoms and subsequent release into the pelagic system. In a more recent and detailed study, Fahl and Stein (2012) presented IP_{25} concentration data derived from sediment trap experiments in the Arctic Ocean, thus providing an important contribution to the understanding of how IP_{25}-producing sea ice diatoms (and phytoplankton) are influenced by the seasonal variability of sea ice coverage. Analyses of ice-algal communities and the biomarker inventory of two sediment traps (deployed at the same position but at different water depths) from the southern Lomonosov Ridge (Fig. 2) demonstrated the seasonal variability of the production of IP_{25} and its downward transport through the water column. Significantly, almost no IP_{25} reached the traps during permanently ice covered conditions (i.e. during winter), whereas maximum IP_{25} and phytoplankton biomarker content occurred during summer, almost certainly following break-up of the ice at the end of spring with formation of ice-edge conditions beneficial for primary production (Fahl and Stein, 2012). Regarding the observed decreasing biomarker concentrations with increasing water depths (possibly due to biogeochemical degradation and/or organic matter incorporation into the marine food web), Fahl and Stein (2012) identified the importance of considering concentration changes during water column transfer for the interpretation of IP_{25} and phytoplankton biomarker data in sedimentary records.

More generally, the deposition of IP_{25} in Arctic sediments depends on efficient pelagic-benthic coupling, regardless of how direct, or otherwise, this overall process is. Vertical transport has been suggested to be responsible for significant (e.g. >50%; Legendre et al., 1992; Arrigo et al., 2010) transfer of carbon flux to the sedimentary regime in ice covered waters and sinking rates of diatoms can be rapid (up to 100 m day^{-1}; Smetacek, 1985), in part, as a result of aggregation (Riebesell et al., 1991). In addition, there can be an overall acceleration in the rate of transport of ice algal OM through the water column following heterotrophic grazing (e.g. by zooplankton). Ice algae constitute the main food source for ice-associated and pelagic herbivorous protists (Michel et al., 2002)

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Fig. 2. Locations where IP_{25} has been studied in Arctic sediments. Core sites of palaeo (downcore) studies are indicated with red dots. Coloured boxes refer to regions where analyses of surface sediments have been carried out. The red triangle refers to a study involving the analysis of sediment trap material. The boxes with a red border refer to studies described in this issue.

and metazoans (Nozais et al., 2001) and individual sea ice algal-derived lipids have been identified as being important for both reproduction and growth (e.g. Falk-Petersen et al., 2008; Søreide et al., 2008, 2010; Leu et al., 2011). Once ingested, algal-derived OM may be utilized directly, remineralised or reconstituted as part of faecal material that can be rapidly transferred to underlying sediments. Alternatively, material of sea ice origin may be assimilated by benthic filter and suspension feeders (e.g. McMahon et al., 2006). Interestingly, IP_{25} has been identified in both zooplankton and benthic macrofauna from the Canadian Arctic and its presence has provided direct evidence for the involvement of sea ice algae in the diets of such constituents within Arctic food webs (Brown and Belt, 2012; Brown et al., 2012). Whether these trophic transfer processes represent a significant removal mechanism for IP_{25} or a potential increase in transport efficiency to the sedimentary environment following incorporation into rapidly sinking faecal material, will require further investigation.

A further potential removal mechanism for IP_{25} (and other biomarkers) is photo-degradation during transfer to sediments. However, Rontani et al. (2011) showed that IP_{25} was significantly less prone to visible light induced photo-degradation than more unsaturated HBIs and other biomarkers and suggested that this may explain (in part) the consistency in occurrence of IP_{25} in Arctic sediments, while other, polyunsaturated counterparts are often only present in much lower abundances or absent.

Within the marine sedimentary environment, there are a large number of chemical, physical and biological processes that contribute to the preservation or degradation of organic matter (for recent reviews of this topic, see Wakeham and Canuel, 2006; Zonneveld et al., 2010). In general, chemical degradation can arise due to a combination of the intrinsic instability of some chemicals, reactions with other chemicals present in the sediments (e.g. sulphur) or as a result of other physico-chemical properties of the sediment (e.g. pH). Degradation due to physical processes results from, amongst other things, the varying influences of particle sizes, mineralogical composition and surface properties, while biologically-driven modifications are probably the most complex or, at least, large in number. In general, effective and direct degradation of OM through biologically mediated processes results from a combination of action by aerobic/anaerobic organisms, consumption and metabolism. More indirect degradation can occur through processes such as bioturbation, where increased biological activity can promote aerobic degradation due to increased oxygen exposure. In practice, OM degradation occurs as a result of

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a combination of chemical, physical and biological processes and it can be difficult to separate out individual contributions, and the identification of definitive experimental protocols for measuring degradation processes quantitatively, can be additionally challenging. Stratigraphic variations in some lipid ratios have been used to assess changes in redox conditions (e.g. Sinninghe Damsté et al., 2003) but it does not necessarily follow that there is an associated degradation of other biomarkers. Further, it is not clear how knowledge relating to degradation pathways gained from one study may be extrapolated to sediments from other locations. As such, the extent of OM degradation probably needs to be made on a case-by-case basis, which is likely to be time-consuming and, potentially, not always achievable. However, some relatively straightforward measures can be adopted to assess for significant degradation such as measuring stratigraphic variations in TOC, quantification of biomarkers with well-defined diagenetic properties, or by reducing the magnitude of changes to absolute sedimentary concentrations through measurement of biomarker ratios. All of these approaches, however, have their limitations, not least because of the individual properties and behaviours of individual biomarkers which, in any case, typically represent less than 0.1% of the TOC and are often much less. More qualitative assessments might include whether higher abundances of biomarkers occur in lower sedimentary horizons compared to upper and younger sections to provide evidence against significant down-core degradation, although this, like that of other approaches, does not remove the possibility of diagenetic overprinting.

It is beyond the scope of the current article to detail all possible degradation pathways, but it is worth highlighting some key general outcomes from previous biomarker-based palaeoenvironment studies that may provide some future direction for palaeo sea ice reconstructions based on IP_{25}. Specifically, a number of SST reconstructions based on alkenones and GDGTs have shown that: (i) sedimentary signals may indicate environmental conditions that contrast those of known sea surface characteristics (e.g. SST) (e.g. Prahl et al., 2000); (ii) Sub-surface profiles of lipid biomarkers may be reduced significantly compared to surface concentrations implying a substantial degree of post-depositional degradation (e.g. Wakeham and Canuel, 2006) and this can also be true for oxidising intervals in deeper sediments (e.g. Huguet et al., 2008); (iii) degradation rates for individual lipids are not necessarily uniform (e.g. Sinninghe Damsté et al., 2002; Huguet et al., 2009; Kim et al., 2009), which has clear consequences for proxies based on quantitative ratios (or other functions) like the $U^{K'}_{37}$ or TEX_{86} indices and especially so for those that rely on individual abundances like IP_{25}.

With respect to analysis of IP_{25} in Arctic marine sediments, the question of potential degradation is crucial if concentrations of IP_{25} (and those of phytoplankton biomarkers for that matter) are to be used to assess for changes in past sea ice occurrence and consideration of the three main points (i)–(iii) above provides a useful framework for future work.

Previously, it has been noted that IP_{25} concentrations and fluxes are quite variable across different Arctic regions. For example, in the studies by Vare et al. (2009) and Belt et al. (2010), fluxes in the northern part of the CAA (Barrow Strait) were at least one order of magnitude higher than for the two study locations further south. Similar magnitude variations in IP_{25} abundances were also found in relatively recent (last few hundred years) sediments from three regions of the Barents Sea (Fig. 2; Vare et al., 2010) and IP_{25} abundances in surface sediments from other regions of the Arctic have also been shown to exhibit a large degree of variability. These differences may, potentially be attributed to significantly greater preservation or degradation of IP_{25} in some locations. Alternatively, the significantly enhanced IP_{25} concentrations in sediments from some regions (e.g. Barrow Strait, northern Barents Sea) may simply result from increased sea ice algal biomass in the first place, especially in regions of high productivity. A similar suggestion has been offered to explain the changes in alkenone concentrations in surface sediments from different regions (Zonneveld et al., 2010 and references therein). Relatively little is still known about those factors that influence IP_{25} production (see previous section) but these clearly need to be considered alongside the potential diagenetic removal of IP_{25} and other biomarkers if quantitative concentration data are going to be used reliably for past sea ice reconstructions and this may prove to be especially important when making comparisons between different regions.

As far as we are aware, there have been no field- or laboratory-based studies to investigate the degradation of IP_{25} in sediments or how any such processes can be accounted for when carrying out palaeo sea ice reconstructions based on this biomarker. A small number of reactivity studies of more unsaturated HBIs in sediments have been carried out, however, and the outcomes of these investigations illustrate the challenges of determining degradation pathways in a consistent and transferable manner. Thus, studies carried out on some Antarctic and Black Sea sediments (Kohnen et al., 1990; Sinninghe Damsté et al., 2007) have revealed the rapid (near surface) transformation of certain HBIs, while other studies have shown that the same HBIs may be stable for thousands of years. For example, in the specific case of the di-unsaturated HBI 2 (Fig. 1), Sinninghe Damsté et al. (2007) showed that this isomer underwent rapid and complete sedimentary transformation in less than ca 500 yr by reaction with inorganic sulphur in a sulfidic Antarctic lake, yet the same isomer has been identified in other Antarctic sediments throughout the Holocene (Barbara et al., 2010; Denis et al., 2010). Significantly, reactions of this type are likely made possible by the presence of at least two degrees of unsaturation within the carbon skeleton of the HBI biomarker and increasing unsaturation probably leads to further reactivity, as indicated through laboratory modelling experiments (Belt et al., 2000b). In contrast, IP_{25} might be expected to be less reactive towards chemical transformation due to the presence of a single and less reactive double bond to those found in more unsaturated HBIs (Belt et al., 2000b), and this likely contributes to its apparent stability in sediments. This does not preclude, however, the possibility of significant (and variable) degradation of IP_{25} in some sediments and further attention should be given to this in the future.

Finally, with further reference to the potential degradation of biomarker lipids, we highlight the potential importance of proper storage of sediment samples. Previously, it has been suggested that sediment material should be stored in clean glass vials and kept frozen until further chemical treatment (e.g. Reuss and Conley, 2005; Weller, 2007). Prior to extraction, freeze-drying is an important means to remove water and therewith the basis of microbial activity. In terms of specific degradation of biomarkers, Grimalt et al. (1988) observed alteration and degradation processes that affected the hydrocarbon composition of some sediments following a 1-month storage period at room temperature. Comparative studies of sediments that were stored in brown glass vials and those that were stored in plastic bags revealed that the latter were contaminated following the release of alcohols, fatty acids and, in particular, short-chain *n*-alkanes from the container material (Weller, 2007). The extent to which the abundances of IP_{25} and related biomarkers described here are influenced by storage procedures has yet to be investigated, but represents a further important area for future work.

2.3. IP_{25} in surface sediments – relationships to known sea ice conditions

A number of the IP_{25} and other biomarker-based sediment studies that have been carried out to date have focused on the

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analysis of surface material and the relationships of the biomarker data with known recent sea ice conditions. For example, Belt et al. (2007) first analysed surface sediments from across the Canadian Arctic (Fig. 2) for the presence of IP_{25} and other HBI alkenes and identified IP_{25} in sediments from all locations of seasonal sea ice cover, often as the most abundant HBI alkene (Belt et al., 2007). In contrast, IP_{25} was absent in sediments from regions of permanent ice cover, reflecting unsuitable conditions for sea ice diatom growth.

Subsequently, Müller et al. (2011) analysed the biomarker composition of surface sediments from different regions of the continental margins of East Greenland and West Spitsbergen and compared the biomarker data with sea ice concentrations derived from satellite observations and numerical modelling experiments. Encouragingly, IP_{25} content in these surface sediments, presumed to represent recent decades of accumulation, showed a positive correlation with mean (spring) sea ice concentrations derived from satellite data. In addition, reduced IP_{25} content was also determined at core sites of highest (near permanent) sea ice coverage consistent with the early findings for the Canadian Arctic (Belt et al., 2007). A clearer (linear) correlation was noted between the PIP_{25} values (see Section 4.2) of these sediments and sea ice concentrations, which supported the principle of coupling IP_{25} abundances with those from phytoplankton biomarkers (e.g. brassicasterol or dinosterol) to provide more detailed assessments of sea ice conditions. A further comparison of these proxy-based sea ice estimates with modelled (NAOSIM) sea ice concentration and thickness data helped to address the growing demand for cross-evaluations of proxy and model data for palaeoclimate studies (Müller et al., 2011). Interestingly, and with respect to the efficiency of organic matter transport towards the seafloor, it was noted that the biomarker concentrations determined for the various core sites showed no correlation with water depth (see Müller et al., 2011 for details and discussion).

A further spatial account of the recent (decades) sea ice cover across the Barents Sea has been carried out by Navarro-Rodriguez et al. (in this issue) who demonstrated a clear relationship between regions of known seasonal sea ice cover and the occurrence of IP_{25}, although the linear correlations between IP_{25} (and PIP_{25}) data and sea ice concentrations were poorer than those reported previously following analysis of sediments from the continental margins of East Greenland and West Spitsbergen (Müller et al., 2011). In contrast, IP_{25} was absent from the majority of locations that have experienced ice-free conditions in recent decades although, exceptionally, IP_{25} was present in a small number of sediments representing locations beyond the position of maximum sea ice extent. For these latter sediments, it was hypothesized that the presence of IP_{25} represented allochthonous input, likely as a result of sediment advection following initial deposition of IP_{25} in ice covered locations.

With their analysis of surface sediments from the Kara and Laptev Sea (Fig. 2), Xiao et al. (in this issue) have provided a valuable extension of the IP_{25} database of Arctic Ocean surface samples. The study area covers sites from the Ob, Lena and Yenisei estuaries, coastal and shelf areas, continental margins and regions of the central Arctic Ocean. Thus, the investigation by Xiao et al. (in this issue) focused on Arctic environments characterised by severe sea ice coverage and enormous riverine freshwater supply and, therefore, provided a valuable inventory of information about the distribution of IP_{25} and other biomarkers related to complex sea surface conditions. The distribution patterns of IP_{25} and other marine and terrigenous biomarkers provided an essential insight into the impact that a significant river discharge and highly diverse sea ice settings (permanent to seasonally ice-free conditions, fast-ice, ice massifs, polynya conditions) can have on the primary productivity of ice algae and phytoplankton in such environmental systems. Interestingly, neither IP_{25} nor PIP_{25} (see Section 4.4) data correlated well with sea ice concentrations (recent decades) and this was suggested to be related to the complex sea ice settings and the strong river discharge (Xiao et al., in this issue).

An expanded data set of IP_{25} and phytoplankton biomarker abundances in surface sediments from the East Siberian Sea, the Chukchi and Bering Seas, the NE and NW subpolar Pacific, and the NW Atlantic Ocean (Fig. 2) has been generated by Stoynova et al. (in this issue). Despite the occurrence of similar sea ice conditions for parts of these regions (derived from satellite data), Stoynova et al. (in this issue) identified (generally) higher IP_{25} concentrations in the Atlantic sector compared to the Pacific. These large-scale basin-specific differences between IP_{25} and sea ice concentrations appeared to be somewhat reduced following calculation of the PIP_{25} index (see Section 4.2), which showed a significantly higher correlation with satellite-derived sea ice concentrations than with IP_{25} alone. With regard to different PIP_{25} values for the same ice cover, however, and further regional heterogeneities in biomarker abundances, Stoynova et al. (in this issue) further highlighted the need to consider the potential impacts of different environmental settings and sea ice properties that govern IP_{25} and phytoplankton productivity.

3. Identification and quantification of IP_{25}

As the number of laboratories performing IP_{25}-based analyses continues to increase and efforts are also being made to make palaeo sea ice reconstructions based on IP_{25} more quantitative, we believe that some discussion of the identification and quantification of this biomarker is worthwhile, especially as accuracy in each of these is likely to be critical when considering the reliability of modelled (proxy-based) outcomes. In addition, some areas of future work related to the quantification of IP_{25}, in particular, are also identified.

3.1. *Identification of IP_{25}*

The unambiguous identification of IP_{25} in Arctic marine sediments lies at the heart of all IP_{25}-based sea ice reconstructions. Of course, accurate identification represents a key component of all proxy measurements, but the complexity of the composition of organic matter found in marine sediments, coupled with the relatively low abundances of the majority of individual components compared to the bulk extract, means that routine identification of individual biomarkers such as IP_{25} is not necessarily straightforward and quality procedures should be implemented routinely, if the presence of IP_{25} and any abundance data are to be interpreted with confidence.

Importantly, the structure of IP_{25} in sediments has been confirmed recently following large-scale extraction and purification from combined sediment material from the Canadian Arctic and the NMR spectroscopic and mass spectrometric characteristics of this sediment-extracted chemical were identical to those reported for synthetic IP_{25} reported previously (Belt et al., 2007, 2012a).

More routinely, identification of IP_{25} in sediments is carried out by the examination of hydrocarbon (or non-polar lipid) extracts using gas chromatography–mass spectrometry (GC–MS) and, in particular, by comparison of the retention index and mass spectrum of IP_{25} in sediment extracts with those obtained from an authentic standard (Belt et al., 2007, 2012a); however, obtaining the mass spectrum, which is the more definitive of the two measures in terms of identification, can often be problematic due to co-elution of other analytes, especially when IP_{25} abundances are relatively low. Under such circumstances, IP_{25} may, alternatively, be identified using

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selective ion monitoring (SIM) methods (e.g. analysis of the molecular ion; *m/z* 350), although this approach also suffers limitations and it is recommended that analysis is made of multiple characteristic ions before identification of IP_{25} is confirmed using SIM methods. Further detailed discussions on the identification of IP_{25} can be found elsewhere (Belt et al., 2007, 2012a, 2012b).

3.2. Quantification of IP_{25}

The topic of IP_{25} quantification can be sub-divided further into two main categories; firstly, there is the analytical quantification of IP_{25} in sediments (e.g. concentrations and fluxes) and, secondly, there is the interpretation of IP_{25} data in terms of reconstructing quantitative sea ice conditions (e.g. percentage sea ice cover, proportion of ice-present versus ice-free years, etc.). Some pertinent questions relevant to this particular theme are, therefore: How accurate are the analytical measurements and how consistent are these between different laboratories? What are the most meaningful representations of sedimentary abundance data (These could include unit mass-based concentrations (μg/g), normalized concentrations relative to other indicators of productivity such as total organic carbon (TOC) or more specific and representative biomarkers such as other HBIs, or fluxes, where abundance data factor in the temporal changes associated with variable sedimentation rates)? Is it possible to conduct realistic calibrations of IP_{25} data with respect to sea ice conditions based on empirical measurements (e.g. through comparison of surface data with satellite-derived sea ice records from recent decades) or is a greater systematic measurement of the production and fate of IP_{25} pre- and post-deposition required (or a combination of both)?

Some previous IP_{25}-based sea ice investigations have focused on the presence/absence of this biomarker and semi-quantitative interpretations of variations in abundance (e.g. Massé et al., 2008; Vare et al., 2009, 2010; Belt et al., 2010; Max et al., 2012). Thus, identification of IP_{25} has indicated the presence of seasonal sea ice and relative increases/decreases in temporal profiles have been interpreted as reflecting corresponding changes in sea ice occurrence or frequency. Such semi-quantitative interpretations contrast those derived from other proxies, such as dinocyst assemblages, where the application of transfer functions has yielded more quantitative estimates of sea ice cover (e.g. months/year; de Vernal et al., 2001, 2005; Ledu et al., 2008; McKay et al., 2008; Bonnet et al., 2010). As the potential to use IP_{25} content to reconstruct past Arctic sea ice conditions has become more widely recognized, more recent research has aimed to calibrate abundances with known sea ice conditions, with the overall objective of making the interpretations of IP_{25} abundance data more quantitative (e.g. Müller et al., 2011). As such, the importance of establishing rigorous quantification methods for IP_{25} becomes increasingly significant.

The accurate quantification of IP_{25} requires use of a validated extraction method, employment of a suitable internal standard (at least one) and determination of instrumental (GC–MS) response factors. Collectively, the importance of these factors has been discussed elsewhere (Belt et al., 2012b) and a Standard Operating Procedure (SOP) for the extraction, identification and quantification of IP_{25} in marine sediments has recently been published (Belt et al., 2012b). Given the increasing number of laboratories engaged in the analysis of IP_{25} and the importance of obtaining accurate identification and quantification as outlined here, it is recommended that one priority area for future research is an inter-laboratory study of IP_{25} analyses using 'blind' sediment material from different Arctic regions. Such an approach has previously been carried out for the analysis of other organic geochemical biomarkers including alkenones (Rosell-Melé et al., 2001) and GDGTs (Schouten et al., 2009) used for determining sea surface temperatures.

It is also recommended that further attention is placed on how best to express IP_{25} concentrations (see questions at the beginning of this section) including various normalization procedures that may account for, amongst other things, regional differences in production and any degradation in sediments.

4. Recent advances in IP_{25} research

4.1. Coupling IP_{25} with phytoplankton biomarkers

As stated previously (Section 2.1), the intuitive interpretation of the IP_{25} biomarker as a presence/absence indicator of past Arctic sea ice becomes complicated when the study site experienced permanent or non-seasonal sea ice conditions, both of which result in an absence of IP_{25} (Fig. 3).

In order to distinguish between these two extreme scenarios, initially, Müller et al. (2009) analysed a sediment core from the Yermak Plateau and compared IP_{25} data to those of brassicasterol (24-methylcholesta-5,22E-dien-3β-ol; Kanazawa et al., 1971; Volkman, 1986), a phytoplankton-derived biomarker considered to be an indicator of ice-free sea surface conditions. In particular, by analysing brassicasterol data during periods when IP_{25} was absent, different climatic extremes could be distinguished, with the (additional) absence or low abundance of brassicasterol reflecting permanent sea ice coverage and elevated brassicasterol content indicating predominantly ice-free conditions. Furthermore, the nature of intermediate palaeo sea ice conditions (e.g. seasonal ice margin) could be determined from high (but variable) abundances of both IP_{25} and brassicasterol, reflecting beneficial environments for the growth of sea ice diatoms and phytoplankton (Fig. 3; Smith et al., 1985, 1987; Sakshaug, 2004). Hence, by considering both IP_{25} and phytoplankton biomarkers, there is the potential to distinguish between ice-free and permanent sea ice cover scenarios and also to provide additional information about primary productivity and the sea ice conditions that strongly influence it (e.g. the presence of a marginal ice zone; Fig. 3). The possibility to identify palaeo sea ice margins is additionally significant since they denote areas of contrasting sea surface conditions that control atmospheric and oceanic interactions which, for example, influence continental ice-sheet dynamics. Application of this combinatory biomarker approach may, therefore, enable sea ice margins to be located and this may inform large-scale climate modelling studies.

4.2. Towards quantitative sea ice reconstructions: PIP_{25}

In an attempt to make the combinatory biomarker approach to sea ice reconstruction more quantitative, Müller et al. (2011) combined IP_{25} and phytoplankton biomarker data obtained from surface sediments from the continental margins of East Greenland and West Spitsbergen (Section 2.3) to establish a novel index (PIP_{25}; Eq. (1)) that could potentially provide a more detailed assessment of sea ice conditions that would be useful, in particular, for climate modellers.

$$PIP_{25} = IP_{25}/(IP_{25} + (\text{phytoplankton biomarker} \times c)) \quad (1)$$

By calculating the ratio of IP_{25} to the combined IP_{25} and phytoplankton biomarker abundances, the PIP_{25} index integrates environmental information pertinent to both sea ice diatoms and open water phytoplankton (Fig. 3); however, Müller et al. (2011) noted the need to include a balance factor (c; Eq. (1)) to compensate for the distinctly higher phytoplankton biomarker content compared to the relatively low IP_{25} concentrations within sediments from East Greenland and West Spitsbergen (Müller et al., 2011). It was also suggested that this term would likely have to

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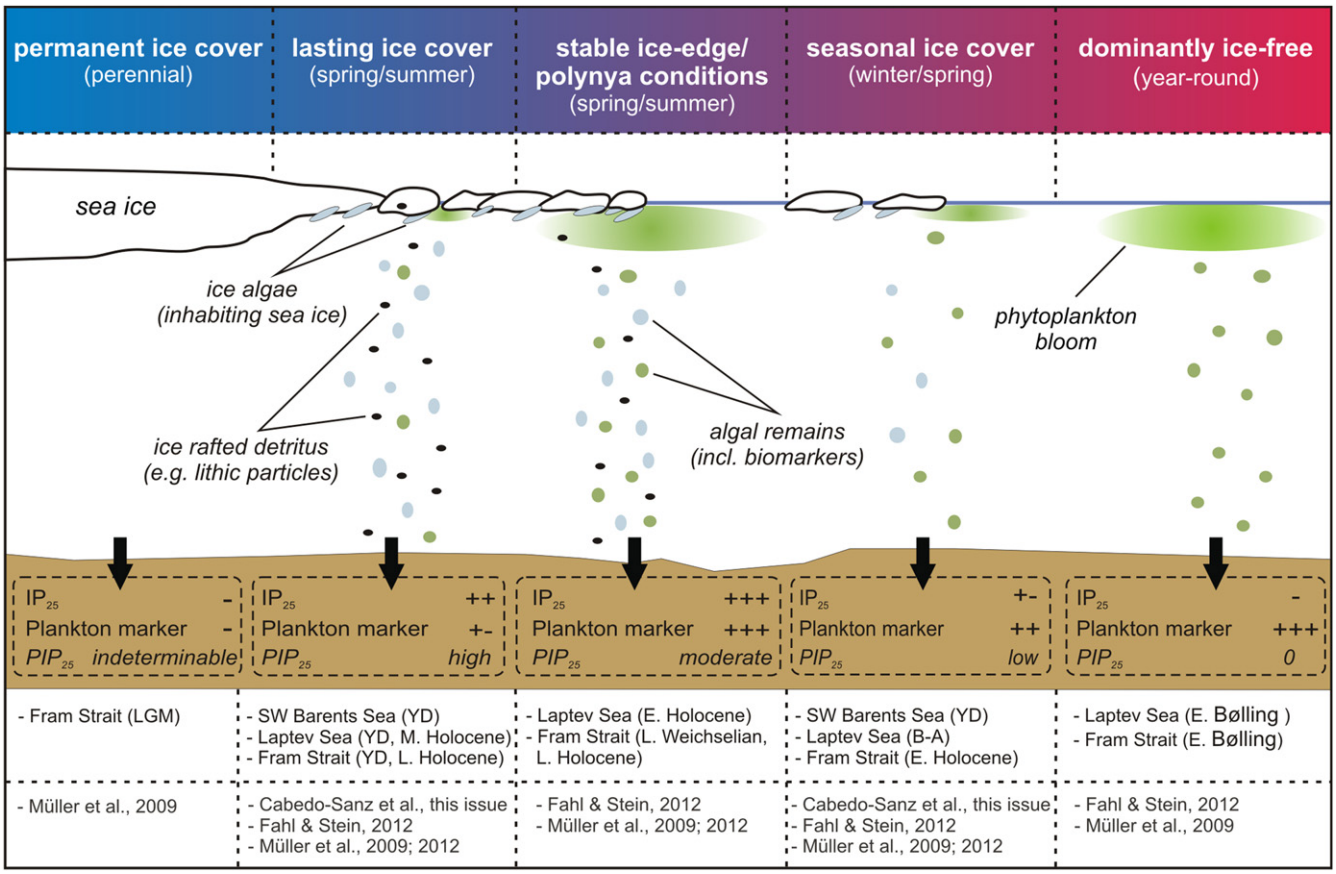

Fig. 3. Schematic representation of different sea ice conditions and respective IP_{25} and phytoplankton biomarker contents within sediments together with the resulting PIP_{25} indices (modified from Müller et al., 2011). Release of ice rafted detritus is also indicated as this represents an important mechanism to accelerate the vertical transport of organic matter towards the seafloor. Examples of recent palaeo application studies where the combinatory biomarker approach has been used for sea ice reconstructions in the Arctic Ocean are also listed.

be re-calculated for different regions of the Arctic Ocean. In addition, although the emphasis of the initial study was placed on using brassicasterol as a phytoplanktic indicator, Müller et al. (2011) stated that it should also be feasible to determine related PIP_{25} indices using other marine biomarkers derived from organisms living at the (ice-free) sea surface.

In essence, relatively high IP_{25} and low phytoplankton biomarker abundances yield high PIP_{25} values consistent with frequent or extensive sea ice cover (Fig. 3), low IP_{25} content and relatively high phytoplankton biomarker concentrations result in low PIP_{25} values indicative of minimum sea ice coverage (Fig. 3), while intermediate PIP_{25} values imply marginal sea ice or ice-edge conditions (Fig. 3; Müller et al., 2011). In support of this model, Müller et al. (2011) found good linear correlations between satellite-derived spring sea ice concentrations and PIP_{25} values obtained from analysis of surface sediments from the continental margins of East Greenland and West Svalbard, and suggested that this approach may be adopted for other study areas and for palaeo sea ice reconstructions. Indeed, Stoynova et al. (in this issue) adopted this method to show that PIP_{25} values derived from analysis of biomarkers in surface sediments from regions of the arctic and subarctic Atlantic and Pacific also correlated well with satellite-derived sea ice concentrations, although the correlations were better defined by logarithmic (PIP_{25}) relationships. In contrast, poor correlations between near-surface PIP_{25} data and sea ice concentrations have been observed for the Barents Sea (Navarro-Rodriguez et al., in this issue) and the Kara & Laptev Seas (Xiao et al., in this issue).

4.3. Limitations of the PIP_{25} index

Although the rationale behind coupling IP_{25} and phytoplankton biomarker data is clear, it is also apparent that this approach to obtaining more detailed and quantitative assessments of past sea ice conditions is relatively new and requires further validation (e.g. Müller et al., 2011, 2012). In the first instance, an evaluation of the approach would benefit from a larger number of sediments from different regions, especially for those where good satellite records of recent sea ice conditions exist.

A potentially limiting aspect of the PIP_{25} method is that most phytoplankton biomarkers are not specific to single source organisms or environments. For example, brassicasterol may be derived from diatoms, dinoflagellates or certain haptophytes, and dinosterol or short-chain *n*-alkanes are also produced by various types of algae (see Blumer et al., 1971; Volkman et al., 1993, 1998; Volkman, 2006 and references therein). In contrast, IP_{25} is believed to be limited to production by certain Arctic sea ice diatoms (Belt et al., 2007). Further, some phytoplankton species may tolerate colder, polar waters and even sea ice cover, while others may be restricted to warmer sea surface temperatures so, ideally, the environmental conditions and dominant phytoplankton assemblages (if known) should be considered when choosing phytoplankton biomarkers when combining with IP_{25} to generate PIP_{25} indices. In this regard, it is noted that the PIP_{25}-sea ice concentration relationships investigated for East Greenland/West Spitsbergen (Müller et al., 2011) and the Atlantic/Pacific (Stoynova et al., in this issue) were strongest when different sterols were employed as the

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phytoplankton biomarkers (*viz.* brassicasterol and dinosterol, respectively).

Furthermore, the employment of the balance factor (c), that is used to account for any significant concentration differences between phytoplankton biomarkers and IP_{25}, may prove problematic for some PIP_{25}-based palaeo sea ice reconstructions. Following the description in Müller et al. (2011) this "palaeo c-factor" hitherto has been calculated as the ratio of mean IP_{25} and phytoplankton biomarker concentrations of the studied sediment interval (Cabedo-Sanz et al., in this issue; Fahl and Stein, 2012; Müller et al., 2012; Stein et al., 2012). One potential problem that may arise using this approach is if the PIP_{25} index is to be calculated for a limited section of a sediment core, since a c-factor determined for the past 10 ka may differ substantially from that calculated for the last 100 ka. Consequently, different c-factors may cause significant shifts in the PIP_{25} record and these could impact on interpretations of sea ice conditions, particularly in terms of absolute sea ice concentrations. This potential limitation may be alleviated to some extent through determination of a c-factor derived from surface sediments from the study area, although this may not reliably take into account any significant palaeo variability or the likely differential degradation of IP_{25} and the phytoplankton biomarker within the sediments (see Section 2.2).

An additional limitation of the PIP_{25} approach arises when there are in-phase fluctuations of IP_{25} and phytoplankton biomarkers. For example, Müller et al. (2011) noted that coevally low (due to a permanent-like sea ice cover) or high (due to marginal ice zone conditions) changes to individual biomarker content would result in similar PIP_{25} values, despite clear differences in sea ice conditions. Indeed, this outcome has been observed for the PIP_{25} record of a sediment core from the West Spitsbergen slope, where the Late Holocene was characterized by short-term biomarker fluctuations caused by a rapidly advancing and retreating sea ice margin (see Section 5.3; Müller et al., 2012). In this instance, Müller et al. (2012) suggested basing environmental (i.e. sea ice) reconstructions on the individual IP_{25} and phytoplankton biomarker records, instead of focusing on PIP_{25} values alone. Indeed, a recommendation when using the PIP_{25} index for carrying out palaeo sea ice reconstructions in the future is to interpret such data alongside those of the individual biomarker records in order to obtain a more balanced assessment.

Some further limitations associated with the employment of the c-factor are discussed by Navarro-Rodriguez et al. (in this issue) and it is clear, at this stage, that some caution should be taken when interpreting PIP_{25} data until further validations/calibrations have been carried out.

4.4. Using HBI ratios to further characterize sea ice conditions

There exist a number of reasons for measuring ratios of biomarkers as proxy measures of past climate conditions, but one is that the influences of substantial changes to absolute concentrations can be reduced (not eliminated). This is certainly the case for the calculation of SSTs using $U^{K'}_{37}$ and GDGT indices and the same is true, to some extent for the PIP_{25} index described here, although it is also possible that, in certain instances, IP_{25} and phytoplankton biomarkers are influenced by sufficiently independent environmental controls that coupling them together is of little benefit. Reduction or removal of the influence of absolute abundances works best, therefore, when the biomarkers under consideration are derived from sources that are closely coupled or even from the same organism(s). In the case of IP_{25}, it has been noted previously that co-occurrence of a structurally related HBI diene 2 (Fig. 1) is usually found in sea ice and in sedimenting particles and sediments under sea ice (e.g. Belt et al., 2007, 2008; Vare et al., 2009) and that the isotopic composition of HBI diene 2 is also consistent with production by sea ice diatoms (Belt et al., 2008). Despite these observations, relatively little has been done to investigate any potential significance between the relative abundances of IP_{25} and HBI diene 2. Exceptionally, Vare et al. (2009) suggested that slightly enhanced abundances of HBI diene 2 compared to IP_{25} in the early Holocene for a core from Barrow Strait (CAA), was possibly consistent with warmer conditions during this time, since HBI unsaturation in *Haslea* spp. had previously been shown to follow growth temperature (Rowland et al., 2001), but this was not examined in any further detail and this explanation seems unlikely given the reasonably constant temperatures that exist in bottom ice during ice algal growth. More recently, the previously reported co-occurrence of IP_{25} and HBI diene 2 prompted Fahl and Stein (2012), Cabedo-Sanz et al. (in this issue) and Xiao et al. (in this issue) to examine this relationship in more detail to see if any environmental significance could be derived. Fahl and Stein (2012) suggested the use of a diene/IP_{25} ratio, which they calculated for a sediment core from the Laptev Sea (see Section 5.4), as a further tool to estimate palaeo sea ice conditions alongside IP_{25} and PIP_{25} data and found relatively higher diene/IP_{25} values during warmer or low sea ice intervals. In a separate study, Cabedo-Sanz et al. (in this issue) measured the diene/IP_{25} ratio in over 1000 sediment samples from three cores from the CAA and North Icelandic Shelf covering thousands of years throughout the Holocene and demonstrated a strong linear relationship between these two biomarkers and coined the term DIP_{25} to indicate a diene-IP_{25} index (c.f. PIP_{25} for the phytoplankton-IP_{25} index; Müller et al., 2011). It was also noted that the magnitude of the DIP_{25} ratio, although extremely consistent for each of the 3 cores studied, varied according to the study location and, thus, the DIP_{25} ratio could potentially be used to 'fingerprint' the location of sea ice formation, although this would need testing further with cores from a greater number of Arctic locations. Finally, it was hypothesized that the regularity in DIP_{25} values likely represented consistent sea ice conditions for a given location and that variability in DIP_{25} may, in contrast, indicate more variable or unstable sea ice conditions, at least within the temporal sampling resolution. With their analysis of the distribution of IP_{25} and the HBI diene in surface sediments from the Kara and Laptev Seas, Xiao et al. (in this issue) also suggest a common origin for IP_{25} and the HBI diene and demonstrate a positive correlation between the diene/IP_{25} ratios (i.e. DIP_{25}) and SSTs in the study area. In contrast, a negative correlation was observed between diene/IP_{25} values and salinity (Xiao et al., in this issue). Although the DIP_{25} index is in need of further investigation, the initial case studies by Vare et al. (2009), Fahl and Stein (2012), Cabedo-Sanz et al. (in this issue) and Xiao et al. (in this issue) suggest that the use of this combined HBI biomarker approach has the potential to provide additional and valuable information about seasonal sea ice conditions that will likely complement the qualitative and quantitative estimates of sea ice available from analysis of IP_{25} and PIP_{25} data.

5. Applications of IP_{25}, PIP_{25} and DIP_{25} for palaeo sea ice reconstructions

Since the initial identification of IP_{25} in Arctic sea ice and a small number of sediment cores from the Canadian Arctic (Belt et al., 2007), a series of IP_{25}-based palaeo sea ice reconstructions have been reported for a number of regions of the Arctic covering different timescales and temporal resolutions. To date, two main types of interpretation of IP_{25} abundance data have been carried out. Firstly, changes to absolute stratigraphic concentrations of IP_{25} have been interpreted in terms of corresponding directional changes to seasonal sea ice. In some cases, IP_{25} concentrations have been converted to annual fluxes by combining abundance data with

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accumulation rates derived from age models (e.g. Müller et al., 2009; Vare et al., 2009; Belt et al., 2010). Belt et al. (2010) suggested that flux data may be a more reliable representation from which to propose changes to sea ice on the basis that IP_{25} production and subsequent release during ice melt likely occurs on a consistent temporal timescale (annual in the case of first year ice), although this approach also relies on the availability of a suitably accurate age model. Secondly, IP_{25} concentrations have been combined with those of other biomarkers, including those derived from open-water phytoplankton (Sections 4.1 and 4.2), with the objective of providing more detailed or contextualized accounts of past sea conditions and variations, thereof (e.g. Müller et al., 2009, 2012; Fahl and Stein, 2012; Cabedo-Sanz et al., in this issue). Both approaches have been applied to reconstructions of sea ice for different Arctic regions covering variable timescales, with the success of these reconstructions estimated through comparison with known sea ice conditions, data derived from other sea ice proxy-based methods, other palaeoclimate information, or a combination of these. The following section provides a summary of IP_{25}-based palaeo sea ice reconstructions that have been carried out to date, and is arranged according to well-known geographical regions within the Arctic (see Fig. 2 for locations of core sites).

5.1. Northern shelf of Iceland

The first detailed IP_{25}-based palaeo sea ice reconstruction was carried out by Massé et al. (2008) who examined the IP_{25} content in a marine sediment core (MD99-2275) from the North Icelandic Shelf (Fig. 2). This core location was selected as a suitable 'ground truthing' case study for the application of IP_{25} due to its proximity to the Polar Front and known fluctuations in sea ice documented in historical records. IP_{25} was detected in all sediment horizons covering the last ca 1200 yr (Fig. 4). Abundances of IP_{25}, however, were highly variable and these variations corresponded well to known changes in sea ice conditions over decadal to centennial timescales. For example, average centennial IP_{25} abundances were highest during the 17th and 19th centuries, consistent with these being the coldest intervals during the last millennium in the Northern Hemisphere (e.g. Mann et al., 1998; Crowley, 2000). Conversely, IP_{25} concentrations were lower during warmer periods (e.g. 16th and 18th centuries). This study also revealed a number of strong correlations between IP_{25} abundances and previously documented sea ice conditions at decadal resolution, enabling short-term changes to be identified. Finally, the IP_{25} record provided insights into sea ice or climate conditions during periods for which there was an absence of historical records (e.g. ca 800–1300 AD and 1430–1560 AD).

In a follow-up study, IP_{25} concentrations were measured in a marine core from NW Iceland (MD99-2263; Djupall Trough) and the temporal abundance profile compared well with that from MD99-2275 and with other sea ice proxies (e.g. ice rafted detritus, IRD; Andrews et al., 2009). Thus, for both locations, enhanced IP_{25} abundances were found after ca 1200 AD, interpreted as more pervasive sea ice conditions. In contrast, lower than median IP_{25} abundances prior to ca 1200 AD and in recent decades indicated a warmer climate and less severe ice conditions. Greater differences, however, were noted between the IP_{25} abundance profile for MD99-2263 and that of allochthonous quartz and potassium and sodium feldspars, which are considered as 'foreign' to the region and are interpreted as proxies for drift ice around Iceland (Andrews and Eberl, 2007; Andrews, 2009). Although the overall pattern of enhanced sea ice since ca 1200 AD was also seen in the IRD profile, greater fluctuations were also seen at higher resolution compared with the IP_{25} record, likely due to differences in the exact nature of the individual proxies (Andrews et al., 2009).

More detailed comparisons between IP_{25}, quartz and other sedimentary proxies for Iceland were made by Axford et al. (2011) in a study designed to test the relationships between a suite of 19 marine and lacustrine proxy records from seven sites covering the

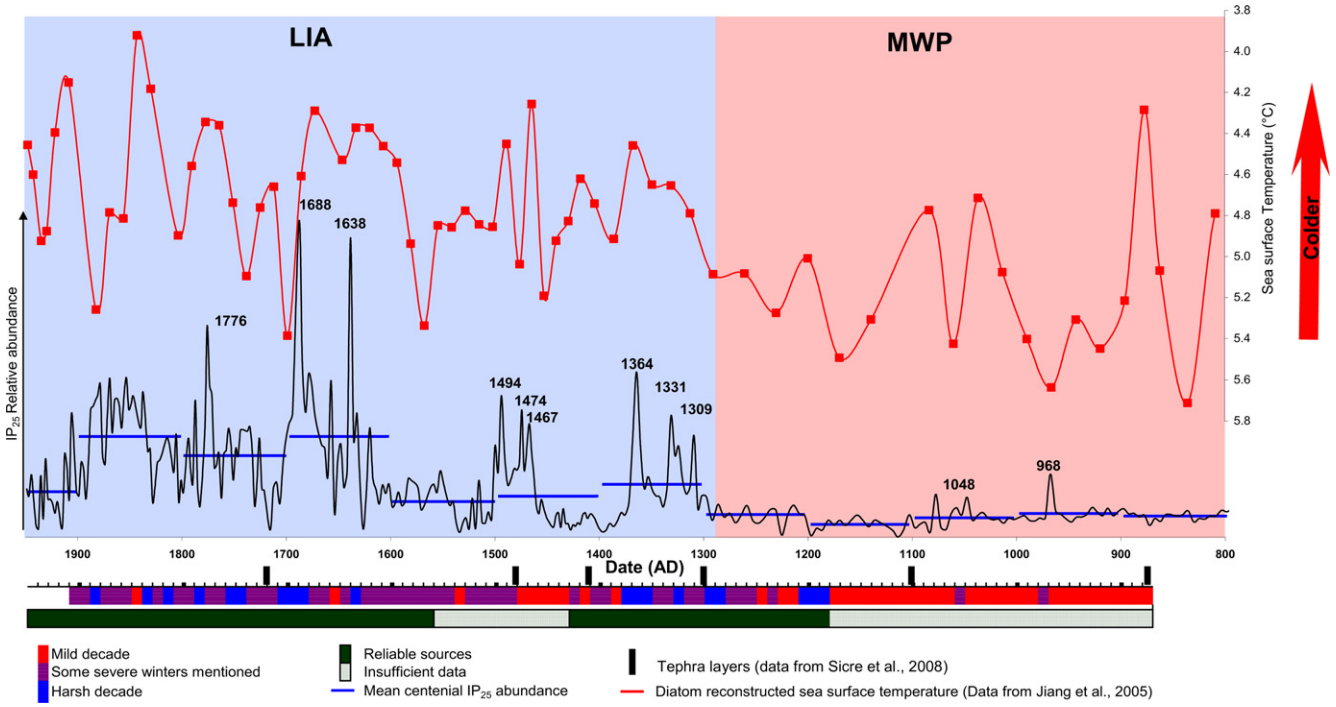

Fig. 4. Relative abundances of IP_{25} found in the core MD99-2275 for the period 800–1950 AD plotted against historical records of Icelandic sea ice interpreted from Ogilvie (1992) and Ogilvie and Jónsson (2001) (bottom scales) and diatom-based reconstructed sea surface temperature (Jiang et al., 2005) (Reproduced from Massé et al., 2008).

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last ca 2 ka. Overall, strong positive correlations were observed between the sea ice (IP_{25} and quartz) proxy data obtained from marine sediments and these were mainly inversely correlated with temperature records inferred from a combination of geochemical and biological indicators (e.g. benthic and planktic foraminifera, TOC, carbonate, chironomids, biogenic silica). Significantly, as part of this study, IP_{25} was shown to be absent (or, at least, below the analytical limit of detection) for a marine core from SW Iceland (MD99-2258), for which observational records failed to reveal the occurrence of sea ice during the study period. Quartz content was also very low compared to N and NW Iceland (Axford et al., 2011).

5.2. Canadian Arctic Archipelago (CAA)

The first IP_{25}-based sea ice reconstruction covering the Holocene was carried out by Vare et al. (2009) who examined the IP_{25} content of a core from Barrow Strait which is located at the western end of Lancaster Sound in the Canadian Arctic and is covered with landfast ice for much of the year (e.g. Stein and Macdonald, 2004; Lavoie et al., 2005). The presence of IP_{25} in more than 600 sediment horizons (Fig. 5) indicated continuous seasonal sea ice cover for this location throughout the Holocene (Vare et al., 2009) and the stable isotope composition ($\delta^{13}C$) of IP_{25} in selected horizons confirmed a sea ice origin for this biomarker (Belt et al., 2008). Consistent with previous studies for N and NW Iceland, IP_{25} abundances were variable down-core and these variations were interpreted in terms of providing evidence for four distinct intervals in the sea ice record. Firstly, in the early part of the record (ca 10–6 cal. ka BP), IP_{25} abundances were consistently below the median Holocene value, and this was interpreted by Vare et al. (2009) as representing relatively low, but consistent spring sea ice occurrence. Between ca 6 and 4 cal. ka BP, IP_{25} abundances increased slightly, signifying somewhat increased sea ice cover, although they remained below the median Holocene value. Between ca 4.0 and 3.0 cal. ka BP, IP_{25} abundances increased more rapidly compared to any previous interval and remained above the median between ca 3.0 and 0.4 cal. ka BP (core top). Abundances were also much more variable in this last interval than for the earlier parts of the record, indicative of shorter-term variations in sea ice conditions. Finally, the increase in IP_{25} fluxes around ca 4.0 to 3.0 cal. ka BP was further interpreted as representing the termination of the Holocene Thermal Maximum (Kaufman et al., 2004; Vare et al., 2009).

In a second study, Belt et al. (2010) quantified IP_{25} (and other proxies) in two further cores from the CAA from Victoria Strait and Dease Strait (Figs. 2 and 5). Consistent with the findings from Barrow Strait, IP_{25} was again identified in all horizons, with lowest fluxes occurring during the early part of the records (ca 7.0–3.5 cal. ka BP), before increasing around 3.0 cal. ka BP. The overall agreement in IP_{25} profiles for the three cores from the CAA was further evidenced by re-calculating temporal fluxes over a fixed (100-yr) timescale, which illustrated more quantitative correlations between the records (Fig. 5; Belt et al., 2010). The major difference in the two lower latitude sites compared with Barrow Strait was a pronounced reduction in IP_{25} fluxes starting around 2.0–1.8 cal. ka BP before reaching minima (and below median values) at ca 1.0 cal. ka BP. These reduced IP_{25} abundances were interpreted as reflecting a period of reduced sea ice occurrence, consistent with previous palaeoclimate records for the region, derived mainly from bowhead whale remains (e.g. Dyke et al., 1996) and from lacustrine records (e.g. Podritske and Gajewski, 2007; Zabenskie and Gajewski, 2007; Porinchu et al., 2009). For all three locations, IP_{25} fluxes increased in the most recent parts of the records, beginning ca 700–500 cal. yr BP (Belt et al., 2010).

5.3. Fram Strait and the sub-polar North Atlantic

The third major Arctic region that has attracted attention in terms of IP_{25}-based palaeo sea ice reconstructions is Fram Strait and its adjacent sub-polar seas.

Vare et al. (2010) produced an IP_{25}-derived sea ice record covering the last few hundred years for three areas of the Barents Sea (Fig. 2) which demonstrated the potential to conduct reconstructions over longer-term timescales in the future for this region. Briefly, IP_{25} was identified in sediment horizons covering the last ca 300 yr for locations in the NW and SE parts of the Barents Sea consistent with known sea ice occurrence from historical records. Variability was greatest for the SE location, as expected given the proximity of the core site to the Polar Front, while both records showed reduced IP_{25} abundances in recent decades, consistent with observational records (Divine and Dick, 2006). In contrast, the SW Barents Sea has remained free of sea ice in recent centuries and IP_{25} was absent from all horizons from this core location, as expected (c.f. related observation from SW Iceland; MD99-2258 (Section 5.1)).

More recently, Müller et al. (2012) studied the IP_{25}, phytoplankton biomarker and IRD composition of sediment cores from the Fram Strait and the continental shelf of East Greenland (Fig. 2) to reconstruct the sea ice conditions during the past 9 ka. A general increase in IP_{25} concentrations (and PIP_{25} values) during the Holocene was observed in three sediment cores from northern and eastern Fram Strait, indicating an increase in sea ice coverage at these sites, which was also consistent with a continuous enhancement in the IRD content determined in one of the cores. These sea ice advances within Fram Strait have been related to a weakening of the West Spitsbergen Current carrying warm Atlantic Water to the Arctic Ocean and likely correspond to a general decline in insolation (Laskar et al., 2004) and lowered high latitude atmospheric temperatures (NGRIP-Members, 2004). Furthermore, coeval short-term fluctuations in IP_{25} and phytoplankton biomarker content coincided with Late Holocene glacier fluctuations on Svalbard (Svendsen and Mangerud, 1997), thus pointing to rapid advances and retreats of the sea ice margin in eastern Fram Strait due to variations in the North Atlantic oceanic-atmospheric circulation regime. In contrast, relatively constant IP_{25} concentrations and PIP_{25} values in a core from the inner East Greenland Shelf were interpreted as reflecting more stable sea ice conditions at this location, which was largely unaffected by the Holocene long-term cooling (Müller et al., 2012).

Cabedo-Sanz et al. (in this issue) produced a sea ice record for northern Norway (Fig. 2) following the deglaciation. In contrast to other IP_{25}-based studies, the IP_{25} record exhibited alternating intervals of presence/absence and provided evidence for the occurrence of seasonal sea ice occurrence during the Younger Dryas only. Further, through the analysis of combined biomarker data (PIP_{25} and DIP_{25}), Cabedo-Sanz et al. (in this issue) also demonstrated that this stadial could be divided into two discrete intervals corresponding to the early-mid (ca 12.9–11. 9 cal. ka BP) and late (ca 11.9–11.5 cal. ka BP) Younger Dryas, with ca 60–90% and 0–60% (estimated) seasonal sea ice cover, respectively. The combined biomarker analyses (DIP_{25}) also provided evidence for the occurrence of much more stable sea ice conditions during the early-mid Younger Dryas.

A detailed IP_{25} biomarker investigation of palaeo sea ice conditions in the northern North Atlantic was carried out by Müller et al. (2009) who reconstructed a 30 ka record for northern Fram Strait (core PS2837-5; Fig. 2), the major gateway between the Arctic and Atlantic Ocean. This study also represented the first example of comparing IP_{25} data with those obtained from an open-water phytoplankton biomarker (brassicasterol). Through consideration of both biomarkers, Müller et al. (2009) proposed a model whereby

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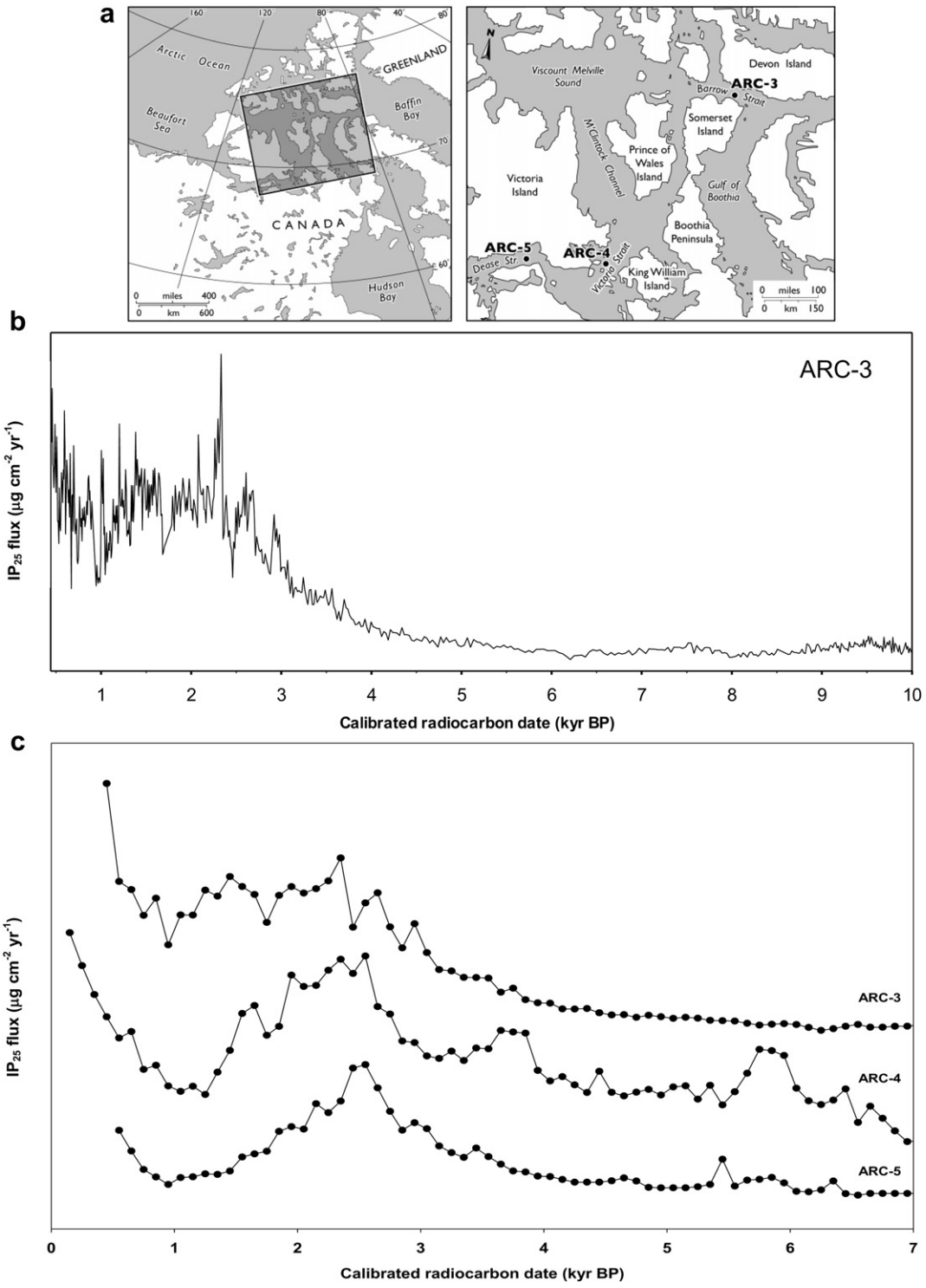

Fig. 5. IP_{25} profiles for sediment cores from the CAA: (a) map of sampling locations; (b) high resolution study from ARC-3; (c) 100-yr averaged IP_{25} flux datasets for ARC-3, ARC-4 and ARC-5. The individual datasets have been offset for illustrative purposes only (Adapted from Vare et al., 2009; Belt et al., 2010).

different sea ice conditions could be distinguished and these were categorized as perennial sea ice cover, stationary ice margin, seasonal sea ice cover and (predominantly) ice-free conditions. Müller et al. (2009) were able to associate these Last Glacial and deglacial sea ice fluctuations with the waxing and waning of the Svalbard-Barents Sea ice sheet and show how the reconstructed sea ice distribution aligned with previous estimates of the sub-polar North Atlantic sea ice coverage at that time. For example, accumulation rates of both biomarkers were at their lowest during the majority of the Late Weichselian glacial period and the Last Glacial Maximum (ca 30–17 cal. ka BP) due to extremely low primary production of sea ice diatoms and phytoplankton during this time. In contrast, high fluxes of IP_{25} and brassicasterol were observed during periods of a stationary ice margin between 27

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and 24 cal. ka BP, which favours the productivity of both sea ice diatoms (IP_{25}) and phytoplankton (brassicasterol) during the spring and early summer blooms, while more intermediate fluxes of both biomarkers were interpreted as more variable spring sea ice conditions (e.g. during the Holocene). Finally, near ice-free conditions during the Early Bølling were characterized by the occurrence of high brassicasterol fluxes from efficient phytoplankton production yet very low IP_{25} fluxes due to the limited opportunities for sea ice diatom growth. Investigation of the sediment sections covering the Last Glacial Maximum or the Early Bølling warm period, both of which had zero or near-zero IP_{25} abundances, highlighted the need to consider further climate (environmental) information to distinguish between a permanently ice-covered and an ice-free sea surface, so the value of considering phytoplankton biomarkers alongside IP_{25} was further demonstrated (see Section 4.1).

In a subsequent study, Stein et al. (2012) presented the corresponding PIP_{25} record (core PS2837-5, Fig. 6) in their recent review of the long- and short-term history of Arctic Ocean sea ice coverage and showed that the PIP_{25} record was a particularly helpful addition to the individual biomarker data especially as the parallel nature of the underlying IP_{25} and brassicasterol records (Müller et al., 2009) for most of the time intervals meant that climate-related deviations were less obvious. Importantly, Stein et al. (2012) also identified IP_{25} in sediments as old as 150 ka BP. As part of a pilot study, IP_{25} was detected in the sediment core PS2138-1 collected from the northern Barents Sea continental slope (Fig. 2) which covers the time period from MIS 6 to MIS 1 (i.e., the past 150 ka BP; for details see Knies et al., 1999; Matthiessen and Knies, 2001). Stein et al. (2012) associated the occurrence of IP_{25} in sediments from glacial periods with minima in the palaeo productivity at the core site (deduced from foraminifera data of this core; Wollenburg et al., 2001, 2004), thus inferring a recurrent sea ice coverage at ca 150 ka BP and 130 ka BP, at least. This identification of IP_{25} in sediments from MIS 6 strengthens the utility of this proxy for sea ice reconstructions covering time intervals prior to 30 ka BP (Müller et al., 2009) and suggests efficient preservation of IP_{25} in ancient sediments (Stein et al., 2012).

By studying sediments from ODP Hole 912 in the Fram Strait, Stein and Fahl (in press) identified IP_{25} and more unsaturated C_{25} HBIs dating back to the Plio-Pleistocene transition at about 2 Ma. By considering the IP_{25} concentrations together with those of other biomarkers (including brassicasterol) and IRD data, Stein and Fahl (in press) demonstrated an interval of reduced sea ice cover during the Late Pliocene and Early Pleistocene (2.2–1.2 Ma) and a general increase in sea ice coverage in the Mid and Late Pleistocene (past 1.2 Ma). Further, the PIP_{25} data supported the sea ice reconstructions, which were also in good agreement with known glacial and interglacial climate fluctuations.

5.4. The eastern and central Arctic Ocean

Alongside the sediment trap data for IP_{25} described previously (see Section 2.2) Fahl and Stein (2012) also reported on the occurrence of IP_{25} in a sediment core (PS2458) from the northern Laptev Sea continental margin (Fig. 2). IP_{25} data was presented along with those from the related HBI diene (Fig. 1; structure 2) and the phytoplankton-derived brassicasterol to assess the extent of sea ice coverage (Fahl and Stein, 2012). Consistent with the findings of Müller et al. (2009), the individual, as well as the combined (i.e. PIP_{25} and diene/IP_{25} ratio) biomarker records for this core, indicated reduced sea ice coverage (even ice-free conditions) during the relatively warm Bølling–Allerød interval and a maximum sea ice cover during the Younger Dryas (Fahl and Stein, 2012). The authors also suggested that the sudden increase in sea ice at the onset of the Younger Dryas may have been triggered by an enormous freshwater outburst from the glacial Lake Agassiz towards the Arctic Ocean - possibly via the Mackenzie River (Murton et al., 2010). Finally, maximum PIP_{25} values during the mid and late Holocene suggested increased sea ice cover at the core site during these intervals (Fahl and Stein, 2012).

5.5. The subpolar northwest Pacific

In their recent study regarding sea surface temperature and sea ice variability in the NW Pacific during the last deglacial, Max et al. (2012) combined alkenone-based temperature records, diatom abundances and qualitative IP_{25} data determined for 6 sediment cores from the Bering Sea and the Sea of Okhotsk (Fig. 2). IP_{25} measurements were carried out for selected time slices only and served as a presence/absence indication of sea ice at the various core sites. IP_{25} was found to be absent during the Bølling–Allerød and the Early Holocene which coincided with maximum SSTs and maximum abundances of certain diatom species indicative of open-water conditions. In contrast, IP_{25} was detected during the Heinrich 1 event and the Younger Dryas which were further characterized by minimum SSTs and maximum abundances of the sea ice-associated diatom *Fragilariopsis oceanica* (Max et al., 2012). The authors' conclusions about the rapidly varying sea ice extent in the Bering Sea during the deglacial were in good agreement with other findings for the Arctic Ocean (Fahl and Stein, 2012) and the subpolar North Atlantic (Cabedo-Sanz et al., in this issue; Müller et al., 2009), thus pointing to a common cause and similar impacts of these climate fluctuations on different (and distant) areas in northern high latitude regions.

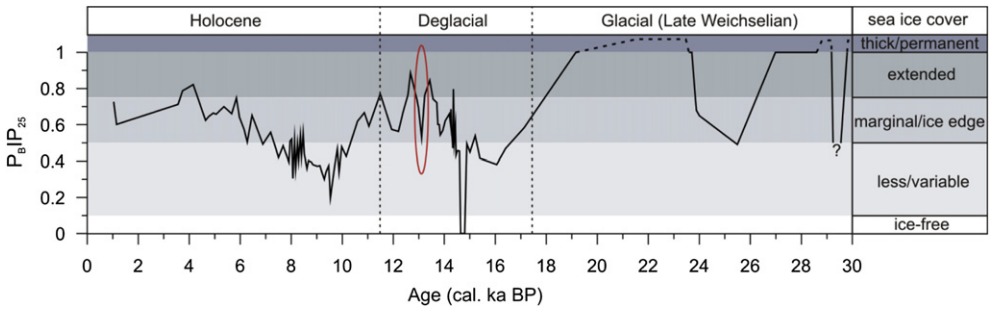

Fig. 6. P_BIP_{25} values for core PS2837-5 (western Yermak Plateau; after Stein et al., 2012) calculated from IP_{25} and brassicasterol data. Light to dark blue shadings indicate different degrees of sea ice cover (right). Dashed lines depict permanently ice covered intervals causing a lack of IP_{25} and brassicasterol, which hinders a calculation of the P_BIP_{25} index. Red ellipse refers to the Intra-Allerød or Younger Dryas cooling, which is not properly displayed by the P_BIP_{25} index. (Adapted from Stein et al., 2012).

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6. Summary of key attributes of IP_{25} as a proxy for Arctic sea ice

Since the initial discovery of IP_{25} in Arctic sea ice and sediments (Belt et al., 2007), analysis of this biomarker in sediments has formed the basis of a proxy measure for the past occurrence of Arctic sea ice and a number of palaeo sea ice reconstructions have appeared (Section 5). Importantly, the success of these studies has relied on the combined attributes of the IP_{25} biomarker proxy and these are summarised as follows:

(1) The detailed characterization of the *structure* of IP_{25}, both by independent synthesis (Belt et al., 2007) and following extraction and purification from Arctic sediments (Belt et al., 2012a), ensures that its identification using analytical methods (GC–MS) can be achieved unambiguously and with confidence.
(2) Since the structure of IP_{25} is known, it has been confirmed as being different from that of other mono-unsaturated HBIs found in temperate regions and the source of IP_{25} appears to be restricted to some (not all) Arctic sea ice diatoms. As such, its detection in the palaeo record represents a *selective* indicator of organic matter derived from Arctic sea ice. Despite the limited number of likely diatom sources, IP_{25} has been detected in sediments from diverse regions of the Arctic.
(3) Consistent with a sea ice diatom source, the majority of IP_{25} accumulation in Arctic sea ice coincides with the spring sea ice diatom bloom and production is largely limited to interstitial brine channels with sufficient networks for diatom growth (Brown et al., 2011). As such, the occurrence of IP_{25} in sediments is believed to reflect *seasonal* sea ice cover rather than ice-free, multi-year or permanent sea ice conditions.
(4) The analytical protocol for the identification and quantification of IP_{25} in sediments (see e.g. Belt et al., 2012b) means that, depending on sedimentary concentrations, IP_{25} can normally be detected and quantified using less than 1 g sediment, facilitating the production of high resolution records (sub-decadal in some cases). Further, the rapidity of the analytical measurement ensures that large numbers of analyses can be carried out over reasonable timescales. As such, a further attribute of IP_{25} is that it represents a *sensitive* proxy measure of Arctic sea ice.
(5) To date, IP_{25} has been detected in marine sediments to (at least) 150 ka BP (Stein et al., 2012) and, most recently, in a 2 Ma year old sediment section of ODP core 912 in central Fram Strait (Stein and Fahl, in press). As such, IP_{25} appears to be relatively *stable* in the geological record. Further work is required, however, to investigate this attribute more quantitatively.

7. Summary

The presence of the sea ice diatom biomarker IP_{25} in Arctic sediments provides the basis for a proxy measure of the occurrence of seasonal Arctic sea ice in the past. In contrast, the absence of IP_{25} from Arctic sediments suggests either ice-free or permanent sea ice cover conditions, and these extreme scenarios can potentially be distinguished on the basis of the abundances of other (phytoplankton) biomarkers. A greater understanding of the factors that influence the production of IP_{25} in sea ice and its fate within the pelagic and sedimentary environments is required before more detailed and quantitative assessments can be made; however, empirically-derived correlations between surface concentrations of IP_{25} and known sea ice conditions are showing great promise for calibration purposes, and the combined measurement of IP_{25} and other organic geochemicals, including other sea ice-derived biomarkers and those derived from open water phytoplankton, provides further potential to carry out more quantitative or well defined sea ice reconstructions in the future.

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