Source-specific biomarkers as proxies for Arctic and Antarctic sea ice

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Abstract :

Over the last decade or so, certain source-specific C-25 highly branched isoprenoid (HBI) lipid biomarkers have emerged as useful proxies for Arctic and Antarctic sea ice. Thus, IP25 (Ice proxy with 25 carbon atoms) and IPSO25 (Ice proxy for the Southern Ocean with 25 carbon atoms) represent binary measures of past seasonal sea ice in the Arctic and Antarctic, respectively. A further tri-unsaturated HBI (generally referred to as HBI III) appears to provide proxy evidence for the region of open water found adjacent to sea ice (i.e. the marginal ice zone (MIZ)) in both polar regions. This review provides an update on current knowledge pertaining to each proxy. The first section focuses on describing those studies that have aimed to establish the underlying features of each proxy, including source identification and spatial distribution characteristics. The second section presents some important analytical considerations pertinent to the accurate identification and quantification of HBI biomarkers. The third section describes how each HBI proxy is normally interpreted within the sedimentary record for palaeo sea ice reconstruction purposes. This includes the interpretation of individual and combined biomarker profiles such as the PIP25 index and multivariate decision tree models. A summary of all previous palaeo sea ice reconstructions based on HBIs is also given, which includes examples that clarify or reinforce our understanding of the individual or combined biomarker signatures. Some knowledge gaps and areas for future research are also briefly described.

Highlights

Source-specific highly branched isoprenoid (HBI) biomarkers as sea ice proxies.
 IP₂₅ and IPSO₂₅ are proxies for Arctic and Antarctic sea ice, respectively.
 A tri-unsaturated HBI shows promise as a proxy for the Marginal Ice Zone (MIZ)
 Combined biomarker approaches provide more detailed sea ice descriptions.
 Overview of how HBI-based proxies are used for palaeo sea ice reconstructions.

Keywords : Biomarkers, HBIs, IP25, IPSO25, Sea ice, Proxies

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43 **1. Introduction**

44 1.1 Background to sea ice and sea ice proxies

Dramatic changes to climate in the Arctic and Antarctic, beginning towards the 45 46 end of the last century and continuing towards modern times, have stimulated a large array of research activity into the causes, consequences and contextualisation 47 of these transformations over the last decade or so (IPCC, 2013). Within the overall 48 climate structure of the polar regions, sea ice plays a central role (Thomas, 2017). 49 For example, due to its high albedo (reflectivity), sea ice acts as a highly efficient 50 51 regulator of incoming solar radiation to the surface oceans, and it also acts as a physical barrier to gas, heat and moisture exchange between the oceans and 52 53 atmosphere. During formation and melt, sea ice contributes brines and freshwater, 54 respectively, with important consequences for stratification, bottom-water formation 55 and ventilation, in particular (e.g. Dickson et al., 2007 and references therein). A further impact of ice melting during the spring is nutrient release which, when 56 57 combined with surface layer stratification and increasing light and temperature, often results in intense open water (pelagic) phytoplankton production, especially in the 58 region defined by the retreating ice edge – the so-called marginal ice zone (MIZ) 59 (Smith and Nelson 1986; Smith, 1987; Sakshaug et al., 2009; Perette et al., 2011). 60 61 Such primary production can exceed that of the permanently open ocean and is 62 often enhanced further through the seeding of the water column by microorganisms residing in bottom ice during the winter, which then proliferate prior to the main 63 bloom of the pelagic community (Michel et al., 1993; Lizotte, 2001). A further 64 65 community of sea ice-associated (sympagic) organisms undergo rapid growth within the host ice matrix itself, normally as light and nutrient availability increase during 66 67 spring (for an overview, see Arrigo, 2017).

68 With substantial changes in sea ice extent, particularly in the Arctic, during the 69 last half century or so (Stroeve et al., 2012; Fetterer et al., 2016, Serreze et al., 2016; Walsh et al., 2017), one area of recent research focus has centred on aiming to 70 71 better contextualise these modern changes through reconstruction of longer-term palaeo sea ice conditions. This has been achieved largely (although not exclusively) 72 73 by analysis of various proxies in marine sedimentary archives. A number of proxies for sea ice exist, and many of their relative merits and applications have already 74 75 been described elsewhere (e.g. de Vernal et al., 2013 and references therein). Sea 76 ice proxies possessing a biological origin are probably the most common, not least because of the influence that sea ice can have on marine-based ecological systems, 77 78 as described earlier. Indeed, the identification of certain ice-associated diatoms in 79 polar marine sediments has commonly been used as a proxy measure of sea ice 80 occurrence in the past, especially in the Antarctic (Armand et al., 2017). However, most of these represent species whose growth habitat is more closely associated 81 82 with the open waters of the MIZ rather than that of sea ice itself (Leventer et al., 2008; Leventer, 2013). In contrast, the strictly sympagic community, arguably a more 83 direct proxy measure of sea ice, is often under-represented in sedimentary records, 84 probably due to their generally lower abundance compared to their pelagic 85 86 counterparts, together with their often higher susceptibility towards degradation in 87 the water column and in sediments (Leventer, 2013).

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89 1.2 Biomarkers as sea ice proxies

90 The different ecological habitats of various classes, genera or species of 91 microorganisms in polar marine settings offers the potential to identify unique or 92 source-specific lipids that may serve as suitable biomarker proxies for discrete

93 oceanographic settings. Within the context of sea ice, such settings may be binary in 94 nature, such as its presence or absence. Alternatively, more nuanced scenarios including different ice types, ice thickness, extent or seasonality might also 95 96 potentially be deciphered. In practice, the main common algal lipid classes including fatty acids and sterols do not sufficiently satisfy the criterion of source-selectivity to 97 be useful, even for distinguishing sea ice cover from open water conditions. An 98 exception can be found, however, in a further lipid group, commonly referred to as 99 100 highly branched isoprenoids (HBIs), which are biosynthesised by a relatively small 101 number of diatom genera (Volkman et al., 1994; Belt et al., 2000; Grossi et al., 2004; 102 Sinninghe Damsté et al., 2004; Brown et al., 2014b). Despite the near-ubiquity of HBIs 103 in marine and lacustrine locations worldwide (Rowland and Robson, 1990), the 104 sources and distributions of some HBIs make them good candidates for proxies of 105 Arctic and Antarctic sea ice, and in a range of different sea ice settings. The first of 106 these HBIs – IP₂₅ (Ice Proxy with 25 carbon atoms; Belt et al., 2007) – is a mono-107 unsaturated C₂₅ HBI (I; Fig. 1) produced by certain Arctic sympagic diatoms (Brown 108 et al., 2014c), but has thus far not been identified in the Antarctic. The second 109 example is a close structural analogue of IP₂₅, but has an additional double bond in 110 its structure (II; Fig. 1). This di-unsaturated HBI co-occurs with IP₂₅ in Arctic sea ice 111 and associated sediments but, unlike IP₂₅, is also present in the Antarctic. A recent 112 study confirmed a sea ice diatom origin for HBI II and the term IPSO₂₅ (Ice Proxy for 113 the Southern Ocean with 25 carbon atoms) was given, at least when detected in the Antarctic (Belt et al., 2016). Finally, a third (at least) HBI has been linked with open-114 115 water (pelagic) conditions in both the Arctic and the Antarctic (Massé et al., 2011; Collins et al., 2013; Belt et al., 2015; Smik et al., 2016a,b). Although a common 116 117 constituent of marine settings (Belt et al., 2000), this tri-unsaturated HBI, sometimes

referred to as HBI III (III; Fig. 1), is also showing potential as a proxy for the MIZ in
both polar regions (Collins et al., 2013; Belt et al., 2015; Smik et al., 2016a,b;
Köseoğlu et al., 2018a,b).

121 Studies using HBI-based sea ice proxies for palaeo sea ice reconstruction purposes have largely paralleled those aimed at proxy development (see Tables 122 123 1,2). The majority of reconstructions carried out thus far span the time interval since the last glacial maximum (LGM) and the Holocene, in particular. However, some 124 125 recent studies have extended timeframes in the Arctic to recent glacial/interglacial 126 intervals (Stein and Fahl, 2012; Hoff et al., 2016; Stein et al., 2017a; Kremer et al., 127 2018a,b; Lo et al., 2018), the Mid-Pleistocene Transition (Detlef et al., 2018), the 128 Pliocene and Pliocene/Pleistocene boundary (Stein and Fahl, 2013; Knies et al., 129 2014; Clotten et al., 2018), and the late Miocene (Stein et al., 2016) (see Table 2 for 130 a summary). In the Antarctic, only one study has investigated HBI sea ice proxies in 131 older (last glacial) sediments (Collins et al., 2013).

132 An earlier review of the use of HBIs as sea ice proxies was published in 2013, with IP₂₅ as the focus (Belt and Müller, 2013). The purpose of the current review is to 133 134 provide an update on research activity carried out on IP₂₅, together with an overview of work carried out on other sea ice related HBIs (mainly IPSO₂₅ and HBI III). 135 136 Throughout, an emphasis is placed on describing the advances in our understanding 137 of how these biomarkers may be used as sea ice proxies, rather than in their application for individual case studies. Nonetheless, some brief illustrations of how 138 139 these proxies have been used in palaeo sea ice reconstructions are also provided, 140 especially when outcomes from these studies help illustrate the individual proxy

signatures of these organic geochemicals. Finally, clarification of current knowledge

should, hopefully, prevent incorrect or mis-leading descriptions and interpretations ofHBI-based sea ice proxy research in the future.

144

145 **2. Source-specific HBI sea ice biomarkers**

146 2.1 IP₂₅ – a binary measure of Arctic sea ice

The most frequently studied of the different HBI sea ice biomarkers is IP₂₅, 147 first identified in Arctic sea ice and sediments by Belt et al. (2007). IP₂₅ has since 148 been identified in numerous Arctic and subarctic surface sediments and downcore 149 150 records (Fig. 2a,b; Tables 1,2). In contrast, there have been perhaps surprisingly few studies on IP₂₅ in its native sea ice and these are restricted, spatially, to the 151 Canadian Arctic Archipelago and Hudson Bay regions (Fig. 2c; Table 1); however, it 152 153 is worthwhile highlighting some findings from these investigations. For example, 154 although several authors made early suggestions as to the likely origin(s) of IP₂₅ (see Belt and Müller, 2013 for a review), it was not until Brown et al. (2014c) carried out 155 analysis of individual sympagic diatom species that definitive source identifications 156 157 were made. Three (or four) individual sympagic diatom taxa have been identified as producers of IP₂₅ - Pleurosigma stuxbergii var. rhomboides (Cleve in Cleve & 158 Grunow) Cleve, Haslea kjellmanii (Cleve) Simonsen, H. crucigeroides (Hustedt) 159 160 Simonsen and/or *H. spicula* (Hickie) Lange-Bertalot. Further, Brown et al. (2014c) 161 also showed that, despite their relatively low contributions to sympagic diatom 162 communities (typically ca. 1-5%), these IP₂₅ producing species are, nevertheless, common across the Arctic and subarctic regions (Fig. 2c). Consistent with this, IP₂₅ 163 164 has been reported in (to date) more than 500 Arctic/subarctic surface sediment 165 samples (Fig. 2a; Table 1). On the other hand, IP₂₅ has not, thus far, been identified in any other diatoms, whether sympagic, pelagic or lacustrine. However, studies 166

167 dedicated to identifying IP₂₅ producers are still rare and other sources may 168 potentially be identified in the future. In two separate time series analyses of sea ice cores taken from Resolute Passage and the Amundsen Gulf (both in the Canadian 169 170 Arctic Archipelago (CAA)), temporal production of IP₂₅ coincided with the spring 171 sympagic bloom (Fig. 3) (Brown et al. 2011; Belt et al., 2013). As such, many 172 authors have subsequently interpreted the occurrence of IP₂₅ in the sedimentary record as proxy evidence of seasonal (spring) sea ice (see Belt and Müller, 2013). 173 174 Following its production in sea ice during spring, IP₂₅ is rapidly released into the 175 surface layer of the water column during ice melt. Indeed, analysis of IP₂₅ in the 176 water column during the late spring melting phase has demonstrated the dominance 177 of ice algal organic carbon (OC) input to surface waters at this time (Brown et al., 178 2016). Thus, a source-to-sink model for IP₂₅ might be considered as: production by 179 certain sympagic diatoms in the spring, release to the surface layer as a pulse of ice 180 algal organic carbon during early summer ice melt, and deposition in underlying 181 sediments thereafter. This description seems reasonable for regions experiencing annual cycles of first year sea ice formation in autumn/winter and melt in 182 183 spring/summer, and is supported further by the identification of higher amounts of IP₂₅ in some sediment trap studies during the late spring/summer months (Fig. 2d) 184 185 (Belt et al., 2008; Fahl and Stein, 2012). What is more challenging to rationalise 186 according to this model, and given current knowledge, is the occurrence of IP₂₅ in 187 sediments from some regions of the central Arctic Ocean (CAO) that experience 188 near-permanent ice cover with little/no ice melt (Xiao et al., 2015a), or some sub-189 arctic locations such as southeast Greenland and north Iceland, or the South-West Labrador Sea, where sea ice conditions reflect drift ice export from the Arctic Ocean 190 191 (Massé et al., 2008; Alonso-García et al., 2013; Sicre et al., 2013; Cabedo-Sanz et

al., 2016a; Darby et al., 2017) and (mainly) Baffin/Hudson Bay regions, respectively
(Weckström et al., 2013). Further work is therefore still needed to establish a more
comprehensive understanding of the conditions under which IP₂₅ is produced and
the mechanism(s) by which it is exported to underlying sediments.

The source-selective production of IP₂₅ by certain sympagic diatoms is further 196 evident from its somewhat enriched stable carbon isotopic composition ($\delta^{13}C$ = ca. -197 16 to -23%; summarised in Belt and Müller, 2013) and its general absence in marine 198 199 surface sediments from regions that experience little or no sea ice cover in modern times (Fig. 2a; Note that the locations of reported IP₂₅ absence only indicate those 200 201 studies where it was specifically analysed for, so likely under-reflects the broader 202 picture of absence). A few exceptions exist, however. For example, IP₂₅ has been 203 reported in a small number of surface sediments from locations slightly beyond the 204 modern maximum winter sea ice margin (Navarro-Rodriguez et al., 2013). This may reflect a deviation from strict vertical transport within the water column or re-205 suspension/advection subsequent to initial deposition in surface sediments (Navarro-206 207 Rodriguez et al., 2013). Alternatively, such anomalies may simply reflect the limited 208 resolution of satellite-based determinations of winter (i.e. maximum) ice margins or 209 the uncertainty of the temporal frameworks that surface sediments represent. 210 Further, IP₂₅ absence has been noted from some sea ice covered locations, although these are mainly in the CAO where near-perennial sea ice cover prevails (Fig. 2a; 211 212 Xiao et al., 2015a) and where surface sediments may not adequately reflect recent 213 accumulation. The significance of IP₂₅ absence, more generally, is discussed in more 214 detail in the next section.

215

216 2.2 Absent IP₂₅ – a more challenging scenario to interpret

217 While a reasonably clear (but not complete) picture for the interpretation of 218 IP_{25} presence is available (Section 2.1), it is less so for IP_{25} absence. In a number of 219 studies, two end-member scenarios for absent IP₂₅ have been described, especially 220 in downcore records. The first of these is the occurrence of ice-free conditions, and is reasonable to accept if the source-selectivity of IP₂₅ is as believed (i.e. 221 222 biosynthesis by certain sympagic diatoms only) and is supported by the general absence of IP₂₅ in surface sediments from regions of year-round ice-free conditions 223 224 (vide supra; Fig. 2a). The second scenario, of permanent or perennial sea ice cover, 225 requires more assumptions about the conditions by which IP₂₅ is (or is not) produced, together with the processes by which it is transferred from sea ice to the 226 227 sediments. For example, in the seminal work on IP₂₅ (Belt et al., 2007), absent IP₂₅ 228 in sediments from the northern regions of the Canadian Arctic experiencing near 229 year-round sea ice cover was interpreted as reflecting conditions unsuitable for ice 230 algal growth, release and deposition. However, although accepted at the time, and 231 re-iterated in many subsequent palaeo sea ice reconstructions and in the earlier 232 review by Belt and Müller (2013), this interpretation was, and continues to be, based 233 on supposition only. No targeted investigations aimed at clarifying the production/deposition of IP₂₅ under perennial sea ice cover have been carried out, 234 235 with the exception of the analysis of a suite of sediments from the CAO, which 236 yielded mixed (presence/absence) outcomes (Xiao et al., 2015a; Fig. 2a). As 237 described in the previous section, more work is needed to identify the IP₂₅ production 238 and deposition conditions before both presence and absence can be interpreted with 239 complete confidence.

240 One frequently adopted approach for distinguishing between the permanent 241 versus ice-free end-member scenarios, especially in downcore records, is the co242 measurement of certain other biomarkers, most commonly associated with pelagic 243 phytoplankton. First proposed by Müller et al. (2009), the co-measurement of certain algal sterols, in particular, potentially provides a means of distinguishing between 244 245 perennial sea ice cover from open water conditions on the basis of relatively low or high phytoplankton biomarker concentrations, respectively. This, of course, makes 246 247 various assumptions on factors controlling open water productivity and pelagicbenthic coupling, and is further complicated by the biosynthesis of many potential 248 249 open-water biomarkers from non-pelagic sources. Thus, many sterols can be derived 250 from marine, terrestrial and also sea ice algal sources (Huang and Meinschein, 1976; Volkman, 1986; Volkman et al., 1998; Belt et al., 2013,2018). Further 251 252 discussion of the role of open-water biomarkers for palaeo sea ice reconstruction 253 can be found in Sections 2.3 and 4.

254 More generally, IP₂₅ absence may reflect a range of sea ice conditions where the (IP₂₅-producing) diatoms are too low in abundance or even absent. Brown et al. 255 256 (2014c) described the common occurrence of IP₂₅-producers in previously reported taxonomic inventories of sea ice diatoms (Fig. 2c), but there are likely certain 257 258 scenarios where this is not the case. For example, the lower salinities associated with fjords or near-coastal settings influenced by large river discharges that are 259 260 common along the Arctic shelves may limit or preclude the colonisation of IP₂₅-261 producing diatoms in sea ice within such settings, a point made recently by Ribeiro 262 et al. (2017) when interpreting IP₂₅ distributions in surface sediments from a NE Greenland fjord, and by others following analysis of IP₂₅ in sediments from the Kara 263 264 and Laptev Seas (Xiao et al., 2013; Hörner et al., 2016). One could also speculate that sea ice with too low of a brine channel percentage or very low surface-to-bottom 265 266 light transmittance such as thick multi-year ice or ice with substantial snow cover,

267 could also sufficiently inhibit sympagic diatom growth to an extent that IP₂₅ 268 production fails to reach detection levels, as proposed previously (Belt and Müller, 2013); however, such hypotheses remain in need of further research. 269 270 Finally, IP₂₅ (sedimentary) absence may result from its degradation in sea ice, the water column, in sediments, or a combination of these, as described 271 272 previously (Belt and Müller, 2013). Alternatively, since ice algal organic carbon (OC) represents an important foodstock at the base of the polar food web, removal of IP₂₅ 273 274 through grazing and subsequent upward trophic transfer may also constrain 275 sedimentary accumulation. Indeed, analysis of IP₂₅ (and other HBIs) in primary 276 grazers and higher trophic level consumers has been used with some success to 277 trace the fate of ice algal OC into Arctic and Antarctic marine ecosystems (Brown et 278 al., 2014a, 2017a, b, 2018; Goutte et al., 2014, 2015; Schmidt et al., 2018). 279 Interestingly, amongst these studies, it was shown recently that the relative amounts 280 of IP₂₅ and other HBIs remained unaltered between food source, ingested material 281 and faecal pellets when mixed diatom sources were fed to certain Artemia sp. (brine shrimp) in laboratory experiments (Brown and Belt, 2017). These preliminary findings 282 283 suggest that source HBI distributions remain largely unaltered following grazing, which may have positive implications for the use of sedimentary HBI distributional 284 285 data for palaeo sea ice reconstruction (see Section 4). However, substantially more 286 work is needed before the impacts of grazing on the absolute and relative amounts of IP₂₅ and other HBIs in sediments can be fully understood. 287 288 In terms of degradative processes, relatively little attention has still been given 289 to this topic, although some laboratory studies have shown IP₂₅ to be relatively

stable, at least with respect to some other lipids (Rontani et al., 2011,2014b). On the

other hand, the susceptibility of IP₂₅ towards certain biotic and abiotic degradation

292 processes was demonstrated recently, following characterisation and detection of 293 various IP₂₅ oxidation products in some near surface sediments from the CAA (Rontani et al., 2018a,b). Interestingly, the same degradation processes did not 294 295 appear to be operating on IP₂₅ in the sea ice itself. In contrast, more unsaturated HBIs have been shown to undergo oxidation in Arctic sea ice (Rontani et al., 2014a). 296 297 However, according to Rontani et al. (2018a), determining the importance of degradation, more routinely, is likely to remain challenging due to the probable 298 299 secondary reactions of the initial degradation products, which limits their 300 accumulation in sediments.

In summary, I suggest that interpretations of absent IP_{25} , in particular, should be more circumspect, and certainly not limited to the extreme cases of ice-free versus perennial ice cover, which are themselves not sufficiently evidenced, at this point. An overview of how certain sea ice settings are currently believed to influence IP_{25} production is shown in Figure 4.

306 Finally, although IP₂₅ has received the most attention as an HBI sea ice proxy, 307 it is worth noting that its di-unsaturated structural homolog – HBI II (Fig. 1) – is also produced by certain Arctic sympagic diatoms (Brown et al., 2014c). Indeed, IP₂₅ and 308 309 HBI II concentrations are frequently well correlated in Arctic sedimentary records, 310 with the latter normally present in higher concentration. As a result, HBI II has been 311 used as a surrogate for IP₂₅ when concentrations of the latter have been close to (or 312 below) the limit of quantification (Andrews et al., 2018). In some reports, variations in the concentration ratio HBI II/IP₂₅ or DIP₂₅ index have been attributed to either 313 314 possible changes in temperature or sea ice dynamics (e.g. Vare et al., 2009; Fahl and Stein, 2012; Cabedo-Sanz et al., 2013; Müller and Stein, 2014; Hörner et al., 315 316 2016; Ruan et al., 2017); however, the former seems unlikely given the near-uniform 317 temperatures found at the base of seasonal sea ice where IP₂₅ and HBI II are 318 biosynthesised, and no in situ testing of the latter hypothesis has been reported. More fundamentally, apart from the study of Xiao et al. (2013), the relationship 319 320 between HBI II and sea ice conditions in the Arctic has not been investigated, which 321 is perhaps surprising, given its co-production with IP₂₅. It is thus plausible that HBI II 322 might, in fact, represent a 'better' sea ice proxy than IP₂₅, or at least an appropriate substitute in cases where IP₂₅ is absent (or below its detection limit). After all, HBI II 323 324 is proposed as a proxy for Antarctic sea ice (where it is referred to as IPSO₂₅), as 325 described in the following section (Section 2.3).

326

327 2.3 IPSO₂₅ – a proxy measure of Antarctic sea ice

328 As stated earlier (Section 1.2), IP₂₅ has not been identified in Antarctic sea ice 329 or sediments, probably due to the absence of the necessary diatom species. Indeed, none of the IP₂₅-producing species endemic to the Arctic (Section 2.1) have been 330 reported in the Antarctic. However, a di-unsaturated HBI (II; Fig. 1), which co-occurs 331 with IP₂₅ in the Arctic (Section 2.2), was first reported in Antarctic sea ice and 332 333 sediments more than 25 years ago (Nichols et al., 1988, 1989, 1993), although a definitive source remained elusive at that time and its structure also remained 334 335 uncertain. Following definitive structural characterisation of this HBI by Johns et al. 336 (1999), Massé et al. (2011) subsequently proposed the use of HBI II as a proxy for Antarctic sea ice and a number of palaeo Antarctic sea ice reconstructions have 337 since followed (Fig. 5b; Table 2). In a more recent study, Belt et al. (2016) identified 338 339 a source of HBI II as Berkeleya adeliensis (Medlin), a common constituent of 340 Antarctic sympagic diatom communities (Medlin, 1990). Consistent with this source, HBI II was also identified in a large number of sediments from near-coastal locations 341

342 around the Antarctic continent (Fig. 5a). Given its source identification and 343 widespread sedimentary occurrence, the term IPSO₂₅ – 'Ice Proxy for the Southern Ocean with 25 carbon atoms' was given to HBI II, by analogy with IP₂₅ for the Arctic. 344 345 It is worth noting, however, that the source-specificity of IPSO₂₅ is not as clear-cut as that for IP₂₅ since this HBI has also been identified in the benthic diatom Haslea 346 347 ostrearia (Johns et al., 1999; Rowland et al., 2001) and in sediments from some 348 temperate locations (Xu et al., 2006; He et al., 2016). However, a particularly notable characteristic of HBI II in the Antarctic is its distinctive stable carbon isotopic 349 composition, with δ^{13} C values ranging from ca. -5.7 to -8.5‰ in sea ice samples 350 (Massé et al., 2011). Importantly, ¹³C-enrichment has also been observed for this 351 352 HBI in sediments (Sinninghe Damsté et al., 2007, Massé et al., 2011; Belt et al., 353 2016) and in some near-surface waters proximal to melting sea ice (Schmidt et al., 354 2018), suggesting a sea ice origin in all cases. Thus, within the context of relatively modern sea ice-covered near-coastal environments around Antarctica, the use of the 355 term IPSO₂₅ appears appropriate, for now, at least. However, whether this is also 356 357 true for offshore locations spanning the entire Southern Ocean, or for older 358 sedimentary sequences where palaeoceanographic conditions may have differed 359 substantially from those of the modern era, remains to be verified. As such, further 360 isotopic measurements of this proxy should probably be carried out as routine, where possible, in order to confirm its origin. 361

More generally, the development of $IPSO_{25}$ as a proxy for Antarctic sea ice has not received as much attention as that for IP_{25} in the Arctic. Thus, apart from its recent source identification, establishment of its characteristic stable carbon isotopic composition, and its general presence in near-coastal surface sediments, the surface sedimentary distribution of $IPSO_{25}$ has not been calibrated against recent sea ice 367 conditions (e.g. seasonal sea ice concentrations) in the same way that IP₂₅ has been
368 investigated in the Arctic (Section 2.1), and a broader spatial assessment of its
369 distribution has also not been conducted. In fact, as stated earlier, even the
370 distribution of this biomarker in the Arctic has not been investigated in any detail,
371 something that might prove valuable in its development as an Antarctic sea ice
372 proxy.

Exceptionally, Massé et al. (2011) observed a general decline in sedimentary 373 374 IPSO₂₅ concentration in a short offshore transect from East Antarctica; a trend 375 shown subsequently to be quite general for various other Antarctic regions (Belt et 376 al., 2016). In the latter study, it was suggested that the origin of this trend might be 377 found in the preferred habitat of the known source of IPSO₂₅ (*B. adelienis*), which 378 has a tendency to proliferate in platelet ice, found most commonly in near-shore 379 locations covered by fast ice (Medlin, 1990). As such, it was hypothesised that 380 higher concentrations of IPSO₂₅ might be found in locations proximal to ice-shelves, 381 since their basal melt acts as the major driver for platelet ice formation (Jefferies et al., 1993). Re-examination of some palaeo sea ice records based on IPSO₂₅ added 382 383 further credibility to this suggestion (Fig. 6), and Smik et al. (2016a) also identified highest concentrations of IPSO₂₅ in near-shore surface waters soon after spring sea 384 385 ice melt. Nonetheless, there are still several aspects of proxy development that are 386 in need of attention before the sedimentary signature of IPSO₂₅ can be interpreted with greater confidence. These potentially include (but are not limited to): (i) 387 measurement of IPSO₂₅ in a larger range of Antarctic surface sediments and 388 389 comparison of findings with known sea ice conditions; (ii) combining IPSO₂₅ concentrations with those of other biomarkers (i.e. similar to the PIP₂₅ index used in 390 391 the Arctic; see Section 4.2); (iii) determination of additional sources (if any) of IPSO₂₅ whose habitat(s) may also influence the interpretation of the sedimentary signal; (iv)
determination of any diagenetic factors that may impact on the sedimentary profile.
For the latter, it is noted that IPSO₂₅ was shown to undergo relatively rapid (a few
hundred years) incorporation of sulphur in Ellis Fjord (East Antarctica) sediments
(Sinninghe Damsté et al., 2007), yet has been readily identified in Holocene and last
glacial sediments from other Antarctic regions (Table 2).

Regarding absent sedimentary $IPSO_{25}$, there are likely several potential explanations for this scenario, as described in more detail for absent IP_{25} (see Section 2.2).

401

402 2.4 Open water conditions and the marginal ice zone (MIZ)

403 The third setting for which source-specific biomarkers can potentially provide 404 useful proxy-based information pertinent to seasonal sea ice cover is the region 405 defined by the retreating ice edge or marginal ice zone (MIZ). A number of nuanced 406 definitions of the MIZ exist, and the challenge at arriving at a single description stems from its inherent dynamic behaviour, both spatially and temporally. For the 407 408 purposes of understanding how biomarker distributions might reflect the MIZ, I consider the definition of Wadhams (1986) to be as good as any. Thus, the MIZ is 409 410 defined as "that part of the ice cover, which is close enough to the open ocean 411 boundary to be affected by its presence". For some regions, this approximates to the 412 area bound by the positions of maximum winter and summer sea ice extent, although these are often variable on annual timeframes. For other locations, sea ice 413 414 dynamics can be far less pronounced or consistent, even on seasonal timeframes, with rapid fluctuations in extent from winter through to summer. These contrasting 415

scenarios provide important background context for interpretation of biomarkersignatures of the MIZ in palaeo records (Section 4).

With such dynamic behaviour, combined with surface ocean settings often 418 419 characterised by a melange of different sea ice types and open water conditions, the identification of any source-specific biomarkers that represent the MIZ uniquely is an 420 421 ambitious research objective, to say the least. However, it may be feasible to identify some potential candidates that at least partly align with the key attributes of source-422 423 selectivity. For example, a potentially useful starting set of criteria for identification of 424 MIZ biomarkers would be: (i) those that are not found in sea ice; (ii) those that are 425 produced by certain pelagic phytoplankton but do not have additional (e.g. terrestrial) 426 sources; (iii) those whose production is distinct from that found in permanently open 427 waters. The latter could potentially stem from an ecological preference for the 428 nutrient-rich MIZ surface waters or the lower salinities characteristic of the fresh 429 meltwater layer compared to the neighbouring open ocean, although, in practice, this 430 criterion likely represents the most challenging to be satisfied. In addition, the difficulty in identifying any such biomarker(s) is compounded further by the 431 432 challenges of carrying out representative in situ sampling of the MIZ, not least because of its highly dynamic and often heterogeneous nature. On the other hand, 433 434 identification of suitable MIZ biomarkers can potentially be deduced from the 435 analysis of surface sediments, even if their accumulation characteristics generally imply an integration of a number of different overlying surface or near-surface 436 437 conditions spanning several seasons, years, or longer.

In practice, many common algal biomarkers including fatty acids and
phytosterols do not satisfy the first two criteria. Indeed, in two recent studies – the
first based on fatty acid and sterol distributions in surface waters from East

441 Antarctica, the second based on variable sterol concentration in surface sediments 442 from the Barents Sea and Norwegian Sea in the Eurasian Arctic/subarctic - no significant differences in biomarker abundances or distributions were identified 443 444 between the respective MIZ and neighbouring open ocean locations (Navarro-Rodriguez et al., 2013; Belt et al., 2015; Smik et al., 2016a). On the other hand, in a 445 446 number of recent empirical studies, the elevated abundance of a tri-unsaturated HBI biomarker (often referred to as HBI III; Fig.1) in some near-surface waters and 447 surface sediments from the MIZ of certain Arctic and Antarctic regions, suggests that 448 449 this biomarker may at least part-satisfy several key criteria (Belt et al., 2015; Smik et al., 2016a; Schmidt et al., 2018) (see Fig. 7,8,9 and Tables 1,2 for summaries). 450 451 Initially, Collins et al. (2013) suggested that sedimentary HBI III might better 452 reflect phytoplankton production in the MIZ compared to the permanently open 453 ocean, based largely on its similar temporal profile to that of the sea ice proxy HBI II (now IPSO₂₅) in late glacial sediments from the Scotia Sea (Southern Ocean). In 454 455 support of this, relatively high concentrations of HBI III have been observed in the near-surface waters of the MIZ in the Scotia Sea (Schmidt et al., 2018) and also off 456 457 the Sabrina Coast (East Antarctica) (Fig. 8; Smik et al., 2016a). In the Arctic, HBI III concentration was shown to be significantly higher in Barents Sea surface sediments 458 459 from locations normally associated with the MIZ, at least compared to those settings 460 that experience ice-free or mainly year-round ice cover (Fig. 9; Belt et al., 2015). In addition, in a study of biomarker content in a small number of surface sediments 461 from a NE Greenland fjord, HBI III was most abundant for locations proximal to the 462 463 mid-July ice edge (Ribeiro et al., 2017).

464 Several *Rhizosolenia* spp. isolated from polar and sub-polar locations from 465 both hemispheres (Belt et al., 2017) have recently been identified as sources of HBI

III, whose isotopic composition, when detected in polar environments ($\delta^{13}C$ = ca. -35 466 467 to -40%; Massé et al., 2011; Smik et al., 2016a; Schmidt et al., 2018), is also consistent with production by pelagic, rather than sympagic, algae. Combined, these 468 469 background studies, albeit relatively small in number thus far, indicate that HBI III may prove to be a useful proxy measure for the MIZ in the Arctic and the Antarctic, 470 471 for some locations, at least. In terms of selection criteria, although the biosynthesis 472 of HBI III by certain pelagic diatoms is clear, the reason for its enhanced production 473 within the MIZ is not evident at this stage and is in need of further attention. Potentially, increased production might reflect an environment-specific response. For 474 475 example, the nutrient-rich conditions normally associated with the MIZ may 476 particularly favour the growth of *Rhizosolenia* spp., or at least the biosynthesis of HBI 477 III by such species. The possibility of HBI III biosynthesis by other polar pelagic diatoms should also be considered, although only certain *Pleurosigma* spp. have 478 previously been shown to be producers of this HBI, and such species are not 479 especially common or abundant in polar environments. For now, therefore, the use 480 481 of HBI III as a MIZ proxy is based largely on the aforementioned empirical 482 observations. As for absent HBI III, while it is tempting at this stage to interpret this 483 scenario in terms of permanent sea ice cover due to little or no pelagic algal 484 production, it may also result from an absence (or too low abundance) of the HBI IIIproducing diatoms in some settings/time intervals, or degradation in the water 485 column or sediments. The co-measurement of other phytoplanktic biomarkers is, 486 therefore, probably still useful in terms of elucidating productivity trends, more 487 488 generally. In the meantime, some suggestions for how the production of HBI III might be dictated by different Arctic sea ice settings is shown in Figure 4. 489

490

491 **3. Analytical considerations**

492 Central to the use of source-specific HBIs as sea ice proxies is the reliability of the analytical measurement, which includes both accurate identification and 493 494 quantification. The former should be straightforward given the availability of suitable laboratory standards, well-maintained GC–MS instrumentation and published 495 496 chromatographic and mass spectral data, but care should still be taken, not least 497 given the similar chromatographic and mass spectral properties of many HBIs. For example, Cabedo-Sanz and Belt (2015) identified a C₂₅ HBI monoene in ancient 498 499 Arctic sediments, which has a very similar GC retention index and mass spectrum to that of IP₂₅, but has not thus far been reported in sea ice. Further, for Arctic 500 501 sediments, which commonly contain both IP₂₅ and its di-unsaturated pseudo-502 homolog HBI II (Fig. 1), the near isobaric nature of their molecular (M⁺) and (M+2)⁺ 503 ions, respectively (both nominally m/z 350) (Fig. 10), together with their very similar 504 retention indices on non-polar stationary GC phases (e.g. RI_{HP5ms} 2081 and 2082 for IP₂₅ and HBI II, respectively; Belt and Cabedo-Sanz, 2015), provides an opportunity 505 for mis-identification, especially of IP₂₅. In fact, during an inter-laboratory 506 507 investigation of IP₂₅ and other HBIs (Belt et al., 2014), IP₂₅ was sometimes incorrectly identified in an Antarctic sediment (i.e. one known not to contain IP_{25}), 508 509 where HBI II was present in sufficient abundance for its (M+2)⁺ ion to be readily 510 detected and mis-assigned to the M⁺ ion of IP₂₅. Such mis-identification could 511 arguably be attributed to the blind nature of the sediments under study (the 512 participants were not aware of the origin of the sediments), but this cautionary tale is nonetheless useful for future analyses. 513

514 Ambiguity in HBI identification may potentially become more problematic for 515 more unsaturated HBIs, due to the larger number of isomeric forms biosynthesised 516 by diatoms (Belt et al., 1996,2000,2001; Grossi et al., 2004; Poulin et al., 2004; 517 Brown and Belt, 2016), the extremely similar mass spectra generally seen for isomeric HBIs (Belt et al., 2000; Brown and Belt, 2016), and the difficulties in often 518 519 obtaining high quality total ion current mass spectra from analysis of sediment 520 extracts, in any case, due to low abundances or spectrometric interferences. 521 Accurate identification is especially important, however, since only one of the structurally characterised HBI trienes (HBI III; Fig. 1) has been firmly associated with 522 523 the MIZ in the Arctic and Antarctic. A brief perusal of some reports of HBI III 524 suggests that it may have been mis-identified based on the literature cited when 525 describing it's characterisation.

526 The inter-laboratory study of sedimentary IP₂₅ (Belt et al., 2014) revealed 527 further analytical considerations important to its accurate identification and 528 quantification (and of other HBIs). For example, significant differences in 529 instrumental (GC–MS) response factors were observed between individual 530 laboratories (by up to a factor of 2–6), with further differences noted for the two internal standards employed (7-hexylnonadecane (7-HND) and 9-octylheptadec-8-531 532 ene (9-OHD)) and the specific biomarker ions selected for quantification. In the Plymouth laboratory, both of these IS are used for HBI quantification purposes, with 533 534 routine monitoring of biomarker-specific GC–MS response factors performed through 535 analysis of (i) a homogenised sediment with known HBI concentration and (ii) a series of standard solutions of variable HBI concentration. The first approach was 536 indeed a recommendation following the inter-laboratory investigation of IP₂₅ (Belt et 537 538 al., 2014), yet it is not always evident how such response factors are measured (if at all) in a number of published studies based on IP₂₅ and other HBIs, or how final 539 540 sedimentary concentrations using these are arrived at. While this may not be critical

541 when only interpreting relative changes to IP₂₅ (and other HBI) concentration in an 542 individual downcore sequence, or when converting individual biomarker data into PIP₂₅ indices (Section 4.2), it does have implications when making comparisons 543 544 between absolute biomarker concentrations obtained from different laboratories. For 545 example, in assessing some pan-Arctic IP₂₅ (and PIP₂₅) data compiled from new and 546 various published datasets, Xiao et al. (2015a) elected to omit some previously reported IP₂₅ data by Stoynova et al. (2013) on the basis of unusually high values, 547 which might have resulted from the employment of a different analytical method. As 548 549 such, it is recommended that all aspects of HBI identification and quantification (i.e. GC retention indices, mass spectral data, methods for calculating GC responses 550 551 factors, etc.) are reported in future studies, wherever possible.

552 The inter-laboratory study by Belt et al. (2014) also provided a brief 553 assessment of two different extraction methods commonly used in HBI and other biomarker analysis. In brief, while similar results were obtained for IP₂₅, IPSO₂₅ and 554 555 the internal standard 7-HND (Fig. 1) when using accelerated solvent extraction (ASE) or sonication (DCM/MeOH) methods, some degradation of more unsaturated 556 557 HBIs (e.g. HBI III) and the internal standard 9-OHD (Fig. 1) was observed using the former method, possibly due to the higher temperatures employed. In addition, the 558 559 effects of storage conditions on the stability of IP₂₅ and other HBIs in sediments and 560 sediment extracts has also been briefly investigated (Cabedo-Sanz et al., 2016b) following the recommendation of Belt and Müller (2013). In summary, over a two 561 year study period, tri-unsaturated HBIs such as HBI III were shown to be more 562 563 susceptible to degradation than IP₂₅, especially when sediments were stored in plastic bags and exposed to light at room temperature. In contrast, all HBIs were 564 565 relatively stable in sediments stored in glass vials and kept frozen in the dark. It was

also demonstrated that analysis of long-term stored sediment extracts could also
lead to anomalous results, even when kept at low temperature (-20°C) (CabedoSanz et al., 2016b).

569 A final point pertinent to the analytical measurement concerns the identification of the most appropriate threshold concentration of IP₂₅ or IPSO₂₅ for 570 571 sea ice inference, especially if primary interpretations, as described here, are based within a binary framework of sea ice presence/absence. To my knowledge, such a 572 573 threshold has yet to be identified and reported absences of IP₂₅ potentially reflect 574 limits of detection or quantification rather than strict absence. This point was already discussed in some detail by Belt and Müller (2013), but has received little or no 575 576 further attention since then. In the Plymouth laboratories, we define absence as 577 being below the limit of quantification using current GC–MS instrumentation 578 (equivalent to 0.05 ng/g dry weight sediment) following extraction from a maximum of 5 g dry sediment. However, this definition simply ensures in-house consistency 579 580 between investigations.

581

582 4. Reading the sedimentary record – converting biomarker profiles to 583 gualitative and semi-guantitative sea ice reconstructions

584

585 Having described the characteristics of various source-specific HBI sea ice 586 and MIZ biomarkers (Section 2), the following sections provide an overview of how 587 the individual and combined biomarker profiles recorded in various palaeo records 588 are routinely interpreted to provide qualitative and semi-quantitative estimates of 589 past sea ice conditions.

590

591 4.1 Individual biomarker profiles

592 In general, the starting point for palaeo sea ice reconstructions based on source-specific HBIs (and some other biomarkers) is analysis of their individual 593 594 concentration variability in well-dated downcore records. In the case of IP₂₅, the 595 principle of higher sedimentary concentrations being indicative of 'increased sea ice 596 concentration/extent/cover' as a gualitative outcome is widely applied, and has its foundation in the first downcore IP₂₅ record from North Iceland, where Massé et al. 597 598 (2008) identified excellent agreement between sedimentary IP₂₅ concentration and 599 historical (observational) sea ice records. Subsequent reports of surface sedimentary 600 distributions also mainly reflect this relationship (Section 2.1; Table 1), which is 601 sometimes supported further by data from other sea ice proxies (e.g. ice-rafted 602 debris; IRD) or those that reflect complementary oceanographic conditions such as sea surface temperature (SST). However, the relationship between sedimentary IP₂₅ 603 604 concentration and overlying sea ice conditions is not normally linear (or any other 605 simple function) and regional variability in IP₂₅ concentration for equivalent sea ice cover is significant (Stoynova et al., 2013; Xiao et al., 2015a). Some of this variability 606 607 may reflect differences in individual laboratory methodology as described earlier 608 (Section 3) and previously by Xiao et al. (2015a). Further, it has been suggested that 609 primary productivity (in sea ice) might be a more important factor than sea ice extent 610 in terms of determining sedimentary IP₂₅ concentration (Belt and Müller, 2013; 611 Cormier et al., 2016).

Nonetheless, the now quite extensive set of regional 'calibrations' spanning various Arctic and sub-Arctic regions provides some support to the general principle that directional changes in sedimentary IP₂₅ concentration likely reflect corresponding changes in sea ice extent, even if only qualitatively (Belt and Müller, 616 2013). The ambiguities associated with interpreting absent IP_{25} are potentially even 617 more problematic than with surface sediment analysis, which at least have known 618 modern conditions to serve as reference. On the other hand, distinguishing perennial 619 sea ice cover from ice-free settings (the most common interpretations of absent IP_{25}) 620 can potentially be resolved by consideration of other biomarkers indicative of the 621 open water setting (see Sections 2.2, 2.4 and 4.2).

For the Antarctic, palaeo sea ice reconstructions based on IPSO₂₅ (often 622 623 referred to as HBI II in previous publications) have mainly assumed a positive 624 relationship between biomarker concentration and sea ice extent, with 625 complementary proxy data (e.g. SST) provided in some cases (Table 2). However, 626 as described earlier (Section 2.3), no calibration studies comparing IPSO₂₅ 627 distributions with known sea ice cover have, as yet, been carried out, so the 628 assumption of increased IPSO₂₅ reflecting higher sea ice extent is based almost 629 entirely by analogy with IP₂₅ in the Arctic. Further, it has been suggested that the 630 ecology of *B* adeliensis (one of the sources of IPSO₂₅) might be the major influence over its sedimentary distribution (Belt et al., 2016). What is evident from the relatively 631 632 small number of previous investigations, however, is that considerably more work is required before the sedimentary signature of IPSO₂₅ can be fully understood, and at 633 634 least before any unequivocal comparisons with IP₂₅ for the Arctic can be made. 635 Determining the distributional pattern of this biomarker in Arctic sea ice and 636 sediments may also prove useful in this respect (Section 2.2).

Interpretations of HBI III profiles in palaeo records are probably most
meaningfully carried out alongside their IP₂₅ (and IPSO₂₅) counterparts, especially
given their respective signatures of the MIZ and sea ice. As background, relatively
high (low) IP₂₅ concentrations were identified in surface sediments from study sites in

641 the Barents Sea experiencing high (low) spring sea ice concentration, while the 642 opposite trend was observed for the abundance distribution of HBI III, consistent with its higher production in the MIZ following rapid ice margin retreat during the spring 643 644 (Fig. 9; Belt et al., 2015). This contrasting behaviour was also evident in some palaeo IP₂₅ and HBI III records from the region, with high IP₂₅ concentration 645 646 coincident with low HBI III over some sedimentary time intervals and vice versa in 647 others (Fig. 11). Such changes were interpreted as reflecting temporal shifts to the positions of the winter/summer ice margins within an otherwise annual cycle of sea 648 649 ice advance/retreat (Belt et al., 2015; Berben et al., 2017).

Although this out-of-phase behaviour of IP₂₅ and HBI III in some temporal 650 651 records is consistent with surface sediment distributions that reflect modern-day 652 regional sea ice dynamics, it is not always evident in some other downcore archives. 653 In fact, positively correlated or 'in-phase' IP₂₅ and HBI III profiles were reported in 654 some recent reconstructions (Fig. 11), including part of a recent century sea ice 655 record from western Svalbard (Cabedo-Sanz and Belt, 2016), two recent interglacial/glacial records from the Yermak Plateau/Barents Sea continental margin 656 657 (Stein et al., 2017a; Kremer et al., 2018b), and certain timeslices associated with the Mid-Pleistocene Transition in the Bering Sea (Detlef et al., 2018). In these cases, the 658 659 switch to in-phase biomarker behaviour was attributed to rapidly fluctuating sea ice 660 conditions or the presence of an offshore polynya; environments that likely had parallel influence over sea ice (IP₂₅) and ice-influenced (HBI III) biomarker production 661 662 (see Section 2.4). Prior to these relatively recent studies, in-phase temporal changes 663 between IP₂₅ and certain phytoplankton sterol concentrations in downcore records was also interpreted in terms of a rapidly advancing and retreating sea ice margin 664 (Müller et al., 2009,2011,2012). 665

666 To date, however, this interpretation has not been investigated further via in 667 situ measurements of sea ice and the surface waters of the MIZ, but analysis of surface sediments from western Svalbard – a region known to experience rapid 668 669 year-round fluctuations in sea ice conditions in modern times - revealed a similar positive relationship between IP₂₅ and HBI III (Smik and Belt, 2017). Otherwise, apart 670 671 from the analysis of IP₂₅ and HBI III in a relatively small number of surface sediments from two Greenland fjords (Ribeiro et al. 2017; Limoges et al., 2018), there have 672 673 been no additional investigations into their distributions in surface sediments from 674 other Arctic regions, and none in any detail. As such, it is not clear how representative the two contrasting observations and interpretations of Barents Sea 675 676 (and neighbouring regions) biomarker distributions are for other northern high-677 latitude locations. In the meantime, some further palaeo IP₂₅ and HBI III records from 678 North Iceland and the Sea of Okhotsk have been reported, although their temporal phase relationships were not interpreted in any detail (Cabedo-Sanz et al., 2016a; 679 680 Xiao et al., 2017; Lo et al., 2018).

In the Antarctic, Collins et al. (2013) discussed the contrasting temporal phase 681 682 relationships between IPSO₂₅ and HBI III in glacial sediments from the Scotia Sea, adding an element of seasonality to the interpretations. Thus, intervals where IPSO₂₅ 683 684 and HBI III were most positively correlated (i.e. strongly in-phase) were interpreted in 685 terms of semi-permanent or stationary sea-ice margins with low seasonality and coupled impact on the respective sea ice and MIZ biomarkers. Conversely, during 686 times of high sea ice seasonality, production of IPSO₂₅ and HBI III became more 687 688 decoupled. To some extent, these changes replicate the variable (relative) behaviour of IP₂₅ and HBI III in surface and downcore sedimentary records from the Barents 689 690 Sea, as described above. However, other downcore profiles of IPSO₂₅ and HBI III

from the Antarctic have been interpreted largely in terms of increases/decreases to sea ice extent with concomitant reverse trends in open water conditions (Table 2). Re-examination of some of those records might provide further insights into palaeo sea ice dynamics now that the relationship(s) between sea ice (IP₂₅ and IPSO₂₅) and HBI III are better understood.

696 Finally, an unresolved question, and one raised initially by Belt and Müller (2013) in an earlier review, concerns the most appropriate units for expressing IP_{25} 697 698 (and other HBI) sedimentary content in downcore records. The three most frequently 699 used are (i) mass (HBI)/mass dry sediment; (ii) mass (HBI)/total organic carbon 700 (TOC); (iii) flux (HBI). Each approach has been used in previous HBI-based 701 investigations, although a clear justification for their selection is not always evident. 702 Since each has different merits (Belt and Müller, 2013), obtaining similar outcomes 703 from each approach likely goes part way to resolving which is the most appropriate 704 for a given study. On the other hand, combining individual biomarker concentrations 705 using relatively simple ratio-based approaches, or more detailed distribution-based 706 methods, simplifies the debate considerably. This is addressed, in further detail, in 707 the next section.

708

4.2 Combining biomarkers – from the PIP₂₅ index to multivariate analysis

The second step normally taken when interpreting sea ice (and related) biomarker data is application of one or more combinative approach. Relatively simple biomarker ratio-based methods are common, of course, in organic geochemistry, most notably within palaeo-oceanographic investigations of surface and sub-surface SSTs via the U_{37}^{K} and TEX₈₆ indices (Brassell et al., 1986; for reviews, see Eglinton and Eglinton, 2008; Schouten et al., 2013). For biomarker-

716 based palaeo sea ice studies, such combinative approaches have thus far only been 717 employed for the Arctic and, until recently, have focussed entirely on the so-called 718 PIP₂₅ index. First introduced by Müller et al. (2011), the PIP₂₅ index combines the 719 relative concentrations of IP₂₅ and a selected phytoplankton biomarker (designated 720 P) according to Eqn. 1 (square brackets denote concentrations). The c factor is the 721 ratio of the mean concentrations of IP₂₅ and P for all sediments under study (i.e. Eqn. 2) and was introduced by Müller et al. (2011) to accommodate the normally much 722 723 higher concentrations of phytoplanktic lipids (P) compared to IP₂₅.

724

$$PIP_{25} = \frac{[IP_{25}]}{([IP_{25}] + c[P])} \#(1)$$

725

$$c = \frac{mean[IP_{25}]}{mean[P]} \#(2)$$

726

$$P_{III}IP_{25} = \frac{[IP_{25}]}{([IP_{25}] + 0.63[III])} \#(3)$$

727

$$SpSIC (\%) = \frac{(P_{III}IP_{25} - 0.0692)}{0.0107} \#(4)$$

728

As a result, all PIP₂₅ indices fall within the range 0–1, which potentially addresses some of the difficulty in interpreting larger-scale variability in absolute biomarker concentrations as described earlier (Section 4.1). In general, higher PIP₂₅ values are interpreted in terms of higher sea ice concentration or extent, on the assumption that primary production is biased towards IP₂₅ under such conditions. At the upper limit, 734 $PIP_{25} = 1$ implies biosynthesis of IP_{25} but no phytoplankton (or selected biomarker) production, which is rarely, if ever, the case. Conversely, the lower limit (i.e. PIP_{25} = 735 0) is arrived at for absent (or below the detection limit) IP₂₅, which has been 736 737 frequently been interpreted as representing either ice-free conditions or permanent 738 ice cover. However, the latter interpretation, at least, likely needs re-consideration 739 given the occurrence of IP₂₅ in some sediments from regions of permanent sea ice cover (Xiao et al., 2015a) and for other reasons outlined earlier (Section 2.2). It 740 741 should also be noted that, if the assumption of absent IP₂₅ for ice-free or perennial 742 ice cover is correct, then the PIP₂₅ index cannot be used to distinguish between these two end-members, since PIP₂₅ is equal to zero in each case. However, on 743 744 some occasions where IP₂₅ and phytoplankton markers have been found to be 745 extremely low/absent (presumed to reflect heavy/perennial sea ice conditions), PIP₂₅ 746 has sometimes been set to 1, which is potentially mis-leading. Under such 747 circumstances, interpretations based on the individual biomarkers are probably more 748 robust.

The reliability of the PIP₂₅ index as a semi-quantitative measure of Arctic sea 749 750 ice conditions remains a topic of debate for all of the reasons described by Belt and 751 Müller (2013) and a further detailed account is not warranted here. In brief, the 752 accuracy of the PIP₂₅ index for semi-quantitative sea ice prediction depends on (i) 753 the region of study; (ii) the choice of phytoplanktic marker (and whether it has a strict 754 pelagic origin); (iii) the algorithmic relationship between PIP₂₅ and sea ice conditions (e.g. linear, logarithmic, etc.); (iv) the c factor; (v) the temporal interval in downcore 755 756 records (which impacts on the c factor).

Despite the general lack of progress in the development of the PIP₂₅ index
 since it was first reviewed by Belt and Müller (2013), some positive features can

759 nonetheless be identified. For example, although in the majority of studies PIP₂₅ 760 profiles simply resemble the corresponding IP₂₅ trends (or at least do not reverse them), the conversion of univariate IP₂₅ and P concentration data to a uniform scale 761 762 is probably useful for consistency and comparison purposes. The ratio-based method also removes any need to identify the most appropriate units for the 763 764 individual biomarker concentrations or fluxes, since any denominator used in such terms is eliminated, algebraically, a point unfortunately missed in a recent 765 766 assessment of the impacts of different units on PIP₂₅ indices (Pieńkowski et al., 767 2017). Further, for one particular region (the Barents Sea), the use of HBI III as the phytoplanktic counterpart to IP_{25} when calculating PIP_{25} indices (hereafter $P_{III}IP_{25}$) 768 769 has been shown to alleviate, to a large extent, most of the frequent drawbacks 770 associated with points (i)-(v) above. In particular, the more closely matched sedimentary IP₂₅ and HBI III concentrations, at least in sediments from the Barents 771 Sea, somewhat limits the variability in the *c* factor, and a fixed value for *c* was 772 773 proposed based on a regional calibration (Smik et al., 2016b). The benefit of a fixed c factor, in particular, ensures that $P_{III}IP_{25}$ indices at individual sedimentary 774 775 timepoints remain fixed, and are independent of the overall time interval under study, something that is not the case when *c* is calculated on a piecemeal basis, as 776 777 discussed previously (Belt and Müller, 2013). Xiao et al. (2015a) also proposed the 778 possible use of a pan-Arctic c factor derived from analysis of surface sediments from 779 different Arctic/sub-arctic regions; however, this value is not especially representative for any particular region and has not been used in more recent palaeo 780 781 sea ice reconstructions.

In addition, the only known sources of HBI III are marine diatoms, thus making
it a more selective phytoplanktic contributor to PIP₂₅ index calculations, while its

apparently higher production within the MIZ (Section 2.4) also aligns well with the 784 785 underlying principles of the PIP₂₅ index, with a switch-over in biomarker responses between the two end members of sea ice cover and open water settings (Fig. 4). In 786 787 fact, the switch from higher IP₂₅ (sea ice) to increased HBI III (MIZ) is exemplified further from the good linear relationship between P_{III}IP₂₅ and spring sea ice 788 789 concentration (SpSIC) (Eqn. 4) for the Barents Sea (Smik et al., 2016b). A minimum threshold for summer sea ice occurrence ($P_{III}IP_{25} > 0.8$) was also proposed (Smik et 790 791 al. 2016b). Semi-quantitative estimates of SpSIC (and changes thereof) in early to 792 late Holocene records from the region have subsequently been reported (Cabedo-793 Sanz and Belt, 2016; Berben et al., 2017). However, although some further records 794 of HBI III have been reported from other Arctic and subarctic regions (Stein et al., 795 2017a; Kremer et al., 2018b; Lo et al., 2018), none have so far been used to calculate P_{III}IP₂₅ indices using a fixed *c* factor derived from a regional calibration, or 796 797 for more quantitative SpSIC estimates. Before this is carried out, it is recommended 798 that further regional scale calibrations are conducted in order to establish the 799 generality (or otherwise) of the approach.

Despite the success of using HBI III as a phytoplankton biomarker for the 800 PIP₂₅ index, as described above, uncertainties regarding selection of the most 801 802 appropriate phytoplanktic biomarker, more generally, remain. Further, it is still not 803 clear whether the PIP₂₅ method is even applicable in some regions, and the 804 problems associated with biomarker co-variance, as discussed previously (Müller et al., 2011,2012; Belt and Müller, 2013), also persist. Under such circumstances, PIP₂₅ 805 806 indices remain largely invariant, despite potentially significant changes to sea ice 807 conditions.

To take a different approach, Köseoğlu et al. (2018b) recently investigated the 808 809 potential of multivariate non-parametric methods for calibrating biomarker 810 distributions against sea ice conditions. Such approaches make no a priori 811 assumptions about the 'best' biomarker for individual settings (sea ice, MIZ, open water, etc), although some pre-selection of potential candidates is judicious. In the 812 813 current context, only HBIs with known sympagic and pelagic sources were selected, with exclusion of other lipid classes potentially derived from other (e.g. terrestrial) 814 815 environments. In the classification tree (CT) approach adopted by Köseoğlu et al. 816 (2018), a suite of HBI distributional data obtained from surface sediment analysis 817 (the so-called descriptive or independent variable) was first used to create a model 818 from which the target (or dependant) variable could be predicted; in this case, semi-819 quantitative categorical descriptions of sea ice extent (Fig. 12a). The output from this 820 calibration consists of a relatively simple threshold criteria tree structure (Fig. 12b) 821 from which any new distribution of biomarkers can be readily interpreted. In fact, a 822 further feature of the CT model approach is the visually intuitive nature of the data 823 output. Using surface sediment biomarker data from ca. 200 locations across the 824 Barents Sea and neighbouring regions, Köseoğlu et al. (2018b) showed that the 825 variable distributions of relatively simple assemblages of HBI lipids (typically 4-6 826 HBIs) could provide consistent predictions of three different classes of sea ice 827 conditions, with high accuracy. Indeed, model performance data are standard 828 outputs from CT methods. Perhaps not surprisingly, given previous investigations, IP₂₅ was found to be a primary predictor of sea ice cover in the Barents Sea, with 829 830 HBI II (co-produced with IP₂₅ in the Arctic) as a surrogate variable in cases where IP₂₅ might be absent (or below the detection limit). Interestingly, for the MIZ or open 831 832 water settings, the geometric isomer of HBI III (i.e. IV; Fig. 1) was identified as the

main predicting variable (with HBI III as a surrogate), even though it was normally
present in higher concentration. Further, based on analysis of a suite of HBIs in
some relatively short cores spanning recent centuries from different regions of the
Barents Sea (Fig. 12c), CT model predictions of sea ice conditions showed good
agreement with those recorded in historical records, and also with P_{III}IP₂₅-based
estimates of SpSIC (Fig. 12d).

Some potential disadvantages of the CT approach are discussed in more detail by Köseoğlu et al. (2018a,b) so only a few are described in brief here. First, as with the PIP₂₅ index, it is almost certainly a requirement that individual CT models are created (and tested) for different regions, not least, because the precise distributions of biomarker sets may depend on factors other than sea ice, depending on location.

Second, distributional variations observed in surface sediments reflecting 845 modern sea ice conditions may not always be replicated in downcore records. 846 847 especially if sea ice conditions in the past do not have a parallel for the region in modern times. For example, this might be important in the case of permanent sea ice 848 849 cover in the Barents Sea (e.g. during glacial intervals), for which there is no 850 contemporary analogue. A further mis-match between modern and palaeo 851 distributions might also result if differential biomarker degradation is significant. 852 Thus, although the relative sedimentary stability of IP₂₅ and HBI III has not been 853 investigated, the latter has been shown to be more susceptible to oxidative degradation in laboratory experiments (Rontani et al., 2011, 2014b) and probably 854 855 also in the water column (Rontani et al., 2016). Of course, differential biomarker degradation will also likely impact on other biomarker-based approaches. Although 856 857 these factors are in need of detailed investigation in the future, it is interesting to note

that, in a recent study, Köseoğlu et al. (2018a) showed that CT model-based
reconstructions of sea ice conditions for three sub-regions of the Barents Sea over
the last ca. 16 cal. kyr BP were, in fact, in good agreement with those obtained from
other proxy data, suggesting that this multivariate approach does, indeed, have
potential within the palaeo record.

863 Third, the employment of unique threshold values for distinguishing individual sea ice classifications (see Fig. 12b) necessitates the accurate quantification of all 864 865 biomarkers under study. In this sense, the routine determination of GC-MS response 866 factors (see Section 3) is paramount and it cannot be assumed that these will be 867 equivalent (or even similar) for all HBIs, despite their similar structures (Belt et al., 868 2014). This is less of a concern when calculating PIP₂₅ indices according to Eqn. 1 869 and 2, since the *c* factor will automatically accommodate any differences. However, 870 accurate biomarker quantification is essential if a fixed c factor is used (see Section 871 4.2). Some specific examples of the impacts of inaccurate biomarker quantification 872 on CT model output can be found in Köseoğlu et al. (2018a).

Finally, using biomarker distributions to predict broader classifications of sea ice extent (e.g. 0–10%,10–50%, 50–100%; Fig. 12) is arguably a more realistic or reliable target than integer-resolution SpSIC estimates from PIP₂₅ index calibrations.

877 5 Knowledge gaps and areas for future research

Since the first review of IP_{25} and other HBIs by Belt and Müller (2013), some clear progress has been made towards their development as sea ice proxies, but some knowledge gaps remain or have since emerged. Thus, specific diatom sources for IP_{25} , $IPSO_{25}$ and HBI III have been identified (Sections 2.1, 2.3, 2.4), some regional calibrations of single and combined biomarker distributions versus sea ice 883 conditions have been completed, and a suite of palaeo sea ice reconstructions based on these biomarkers have been reported spanning different regions and 884 timeframes (Tables 1 and 2). On the other hand, as alluded to at various points 885 886 within this review, some further work is needed before the full potential of sourcespecific HBIs can be realised. These likely represent ab initio investigations such as 887 888 determination of the factors that control production, deposition and preservation of HBIs, while others are more empirical in nature, like the further regional calibration of 889 890 HBI distributions in surface and downcore records, both of which also make 891 assumptions about the nature of the reference data (e.g. accuracy of satellite-based sea ice extent data, surface sediment timeframes, etc). In writing this review, a 892 893 number of such future research areas came to mind, but only a few are described in 894 brief here.

First, there is the need for a larger spatial assessment of IP₂₅ and IPSO₂₅ 895 production by Arctic and Antarctic sea ice diatoms, respectively. Currently, this has 896 897 been confined to an extremely small number of locations (Fig. 2c,5c), yet palaeo records based on these HBIs are emerging rapidly from both polar regions. In similar 898 vein, the analysis of IP₂₅ and IPSO₂₅ in different ice types (e.g. first-year ice, multi-899 900 year ice, landfast ice, drift ice, platelet ice, etc) will likely provide further insights into 901 how sedimentary distributions might be better interpreted. Second, further regional 902 calibrations of combined biomarker datasets (e.g. the PIP₂₅ index or CT models) against known sea ice conditions would add further confidence in their application for 903 palaeo reconstruction purposes. In this sense, as demonstrated quite recently for 904 905 HBI III in certain Arctic and Antarctic regions, there may be further (better) pelagic biomarkers that act as suitable counterparts to IP₂₅ and IPSO₂₅ for characterisation 906 907 of the MIZ, or open waters in the polar regions, more generally. The measurement of
908 a range of biomarkers under in situ conditions (e.g. in the water column and in 909 sediment traps) would certainly promote the development of this area and potentially 910 help clarify the significance of their contrasting spatial and temporal phase 911 relationships as described here (Sections 2,4). There may also be further statistical approaches that help decipher the origins of certain biomarkers on a case-by case 912 913 basis rather than extrapolation of findings from previous studies, which might not be relevant, environmentally. Third, greater efforts should be made to ensure the 914 915 accurate identification and quantification of all HBIs (and other biomarkers for that 916 matter), which includes the subsequent reporting of these in research outputs - this 917 is also true for output from my own laboratory. Fourth, it would be valuable for more 918 comparison studies of different sea ice proxies to be carried out. Thus far, these 919 have been relatively few (Table 1) and interpretations have largely centred around 920 trying to establish which is the 'best' proxy, rather than aiming to understand the 921 potential nuances between them; however, this is not a trivial task.

922

923 6. Concluding remarks

924 The source-selectivity of IP₂₅ and IPSO₂₅, in particular, represents an important characteristic in terms of their suitability as sea ice proxies. Of course, one 925 926 might argue that these biomarkers more accurately represent proxy measures of 927 their sympagic diatom sources than of sea ice per se, and some previous 928 descriptions of IP₂₅ and IPSO₂₅ as 'direct' proxies of sea ice are possibly over-stated, 929 especially given the various unresolved caveats governing their production and fate 930 described herein. On the other hand, gaining a better understanding of the environmental conditions that influence IP₂₅ and IPSO₂₅ production could potentially 931 932 enhance their value as sea ice proxies, as described in more detail by Belt et al.

933 (2016). It is also worth noting that biosynthesis of IP₂₅ and IPSO₂₅ by sympagic 934 diatoms does not unequivocally enhance their usefulness as sea ice proxies, and 935 other 'less direct' methods may be more robust in some settings. On the other hand, 936 their source-selectivity appears to provide a reasonably secure positive (seasonal) sea ice signature, even if only qualitatively. In any case, the identification of the 937 938 boundary conditions for the formation and sedimentary deposition of IP₂₅ and IPSO₂₅ represent important next-stage objectives. The extent to which qualitative outcomes 939 can be routinely and reliably translated into more quantitative or nuanced 940 941 descriptions of sea ice conditions also constitutes an interesting but challenging research area. 942

943

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1497 Figures

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Figure 1. Structures of HBI biomarkers discussed in this review. The structures of
two internal standards often used in the quantification of HBIs are also shown.

Figure 2. Summary maps of locations where IP₂₅ has been investigated for proxy development and palaeo Arctic sea ice reconstruction purposes: (a) surface sediments; (b) palaeo sea ice studies (c) sea ice, sea ice algae and taxonomic studies where the IP₂₅-producing diatoms have been reported; (d) sediment trap (sinking particulate matter) and water column (suspended particulate matter)

1507 samples. See Tables 1,2 for more details.

1508

1509 Figure 3. Temporal changes in IP₂₅ concentration in Arctic sea ice from the 1510 Amundsen Gulf (2008; red symbols, dotted line) and Resolute Passage (2011: green 1511 symbols, solid line; 2012: blue symbols, dashed line) showing peak production in spring (May–June). The outer ordinate scale corresponds to data from the 1512 1513 Amundsen Gulf and Resolute Passage (2011); the inner scale refers to data from 1514 Resolute Passage (2012). Note the parallel trends between IP₂₅ and Chl a, a bulk measure of ice algal primary production. A map showing the approximate sampling 1515 1516 locations is also shown. Adapted from Belt et al. (2013). 1517

1518 Figure 4. Schematic representation summarising the proposed relative

abundance production of IP₂₅ and HBI III in different near-surface oceanographic

1520 settings within the Arctic. Note that some scenarios (e.g. a constantly fluctuating

1521 sea ice margin) are not shown. In brief, IP₂₅ production is known to take place in

1522 seasonal sea ice prior to melting and ice margin retreat in spring (see also Fig. 3; Brown et al., 2011; Belt et al., 2013). According to sedimentary distributions, 1523 highest IP₂₅ concentration is normally associated with more frequent or long-1524 1525 lasting seasonal sea ice, with moderate/high levels also found for regions 1526 proximal to the sea ice edge or the marginal ice zone (MIZ), including polynyas. 1527 In contrast, IP₂₅ production in multi-year ice, thick snow-covered ice, etc, is likely very low (or absent) but is in need of further investigation. IP₂₅ is not believed to 1528 be produced in open waters. Production of HBI III is thought to be limited to ice 1529 1530 free conditions, with highest concentrations associated with the open waters of the MIZ (Belt et al., 2015). Please refer to Sections 2.1, 2.2 and 2.4 of the main 1531 1532 text for more detailed descriptions.

1533

Figure 5. Summary maps of locations where IPSO₂₅ has been investigated for proxy development and palaeo Antarctic sea ice reconstruction purposes: (a) surface sediments; (b) palaeo sea ice studies; (c) sea ice and taxonomic reports of *Berkeleya adeliensis* (a source of IPSO₂₅); (d) water column (phytoplankton) samples. See Tables 1,2 for more details.

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Figure 6. Examples where analysis of IPSO₂₅ (HBI II) has been used to reconstruct palaeo Antarctic sea ice conditions for the West Antarctic Peninsula spanning different timeframes. The blue shaded areas correspond to intervals of elevated IPSO₂₅ concentration that also coincide with periods of glacial meltwater or ice shelf influence as derived from other proxy records. Figure adapted from Belt et al. (2016); data taken from Barbara et al. (2013,2016) and Etourneau et al., 2013. 1547

Figure 7. Summary maps showing locations where HBI III has been investigated
for proxy development and palaeo sea ice (Marginal Ice Zone) purposes: (a)
Arctic surface sediments; (b) Arctic palaeo records and water column studies; (c)
Antarctic surface sediments; (d) Antarctic palaeo records and water column
studies. All studies were carried out on sediment material unless otherwise
indicated. See Tables 1,2 for more details.

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Figure 8. Distributions of IPSO₂₅ and HBI III in near surface waters from East 1555 Antarctica. Symbol sizes reflect the relative concentration ranges in each case. 1556 1557 Note the absence of IPSO₂₅ in the Permanently Open Ocean Zone (POOZ). The 1558 highest relative abundances of IPSO₂₅ and HBI III are found in the Seasonal Sea 1559 Ice (SSI) zone and the Marginal Ice Zone (MIZ), respectively, according to the definitions of sea ice conditions used by Smik et al. (2016a). ACC: Antarctic 1560 1561 Circumpolar Current: ACoC: Antarctic Coastal Current. Figure adapted from Smik 1562 et al. (2016a).

1563

Figure 9. Distributions of IP₂₅ and HBI III in surface sediments from the Barents 1564 1565 Sea. Symbol sizes reflect the relative concentration ranges in each case. The 1566 regions with highest biomarker concentration are also highlighted (red ovals). The 1567 white lines indicate the position of the winter (April) sea ice extent: Minimum extent: April 2006; maximum extent: April 1981; median extent: April 1981–2010. 1568 1569 The region between the April 1981 and 2006 extent approximates to the MIZ during the spring. Note the highest concentrations of HBI III in the MIZ during 1570 1571 spring. In contrast, IP₂₅ concentrations are generally highest for locations found

1572 further north where spring sea ice extent is greater; such locations also
1573 experience MIZ conditions during the summer months. Figure adapted from Belt
1574 et al. (2015).

1575

Figure 10. Mass spectra of source-specific HBIs described in the text. Retention indices are those obtained using an HP5ms GC column. The ion at m/z 350 for IPSO₂₅ corresponds to the (M+2)⁺ ion (see Section 3).

1579

Figure 11: Representative downcore records of IP₂₅ and HBI from different regions of the Barents Sea spanning different timeframes. (a) out-of-phase profiles reflecting changes in the position of the winter ice margin for annual advance/retreat cycles; (b) in-phase profiles likely resulting from more rapid seasonal fluctuations in sea ice dynamics. See the main text (Section 4.1) for a more detailed discussion. Data taken from Belt et al. (2015), Cabedo-Sanz and Belt (2016), Stein et al. (2017a) and Kremer et al. (2018b).

1587

1588 Figure 12. Development and application of HBI-based Classification Tree (CT) models for palaeo Arctic sea ice reconstruction. (a) location of surface sediments 1589 1590 from which HBI distributions were used for CT model construction by Köseoğlu et al. (2018b). Modern sea ice classifications for each location are also shown; (b) 1591 1592 Outcome of CT model showing the two main predicative variables of sea ice 1593 conditions (i.e. IP₂₅ and HBI IV) together with the corresponding threshold criteria for each sea ice classification; (c) Locations of short cores used to test the CT 1594 1595 model. The four cores represent regions of contrasting modern sea ice extent 1596 (see (a) for colour coding); (d) CT model and PIP₂₅-based estimates of sea ice

- 1597 conditions for each of the four cores in (c) spanning the last few centuries. Note
- 1598 the agreement between the SpSIC estimates obtained by the PIP₂₅ (left-hand
- 1599 axis) and CT model (right-hand axis) approaches. Figures adapted from those in
- 1600 Köseoğlu et al. (2018b). See Section 4.2 and Köseoğlu et al. (2018b) for more
- 1601 detailed discussions.







Ellesmer

sland

80°W

Greenland

60°W













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Figure








Figure Fig. 11





Study region	Sample(s)	Study type	Reference(s)
Arctic			
Arctic Ocean	Sediment traps	IP ₂₅ (sterols)–seasonal deposition	Fahl and Stein, 2012
	Surface sediments	IP ₂₅ (PIP ₂₅)–sea ice calibration	Xiao et al., 2015a
Kara/Laptev Seas	Surface sediments	IP ₂₅ (PIP ₂₅)–sea ice calibration	Xiao et al., 2013
			Stoynova et al., 2013
Fram Strait/Svalbard	Sea ice algae	IP ₂₅ identification	Brown et al., 2017a
	Phytoplankton	Source identification (HBI III)	Belt et al., 2017
	Sediment traps	IP ₂₅ –seasonal deposition	Lalande et al., 2016
	Surface sediments	IP ₂₅ (HBI III)–sea ice calibration	Smik and Belt, 2017
		IP_{25} (PIP ₂₅)-sea ice calibration	Müller et al., 2011
Barents Sea	Surface sediments	CT model development	Köseoğlu et al., 2018b
		P _{III} IP ₂₅ development	Smik et al., 2016b
		IP ₂₅ (HBI III)–sea ice calibration	Belt et al., 2015
		$IP_{25}(PIP_{25})$ – sea ice calibration	Navarro-Rodriguez et al., 2013
Norway	Surface sediments	CT model development	Köseoğlu et al., 2018b
Iceland	Surface sediments	IP ₂₅ (HBI III)–sea ice comparison	Cabedo-Sanz et al., 2016a
	Sediment core	IP ₂₅ -historical sea ice comparison	Massé et al., 2008
NE/E Greenland	Surface sediments	HBI-sea ice comparison	Ribeiro et al. 2017
		·····	Limoges et al., 2018
		IP_{25} (PIP ₂₅)-sea ice calibration	Müller et al., 2011
SW Labrador Sea	Sediment cores	IP_{25} (PIP ₂₅) vs. other sea ice proxies	Weckström et al., 2013
Baffin Bay	Sediment core	IP_{25} vs. other sea ice proxies	Cormier et al., 2016
,	Surface sediments	IP_{25} (PIP ₂₅)-sea ice calibration	Stovnova et al., 2013
Canadian Arctic Archipelago	Sea ice	IP ₂₅ identification	Belt et al 2007
••••••••••••••••••••••••••••••••••••••		Sterol identification	Belt et al 2018
		IP ₂₅ (sterols)–temporal changes	Belt et al. 2013
		n 25 (eterele) temperar enangee	Brown et al 2011
		IP ₂₅ (HBI) degradation	Rontani et al 2014a
	Sea ice algae	IP _{or} source identification	Brown et al. 2014c
	Sea ice/sediment tran/sediments	IP_{22} and HBI II isotopes (δ^{13} C)	Belt et al. 2008
	Water column DOM	IP_{25} and $IDI II ISO(0) = (0 C)$	Brown at al. 2016
		rr ₂₅ transfer following ice meit	DIUWITEL al., 2010

Summary of study locations where source-specific HBIs and other biomarkers have been used in sea ice proxy development studies.

Study region	Sample(s)	Study type	Reference(s)
		IP ₂₅ (HBI) degradation/reactivity	Rontani et al., 2016
	Surface sediments	IP ₂₅ distribution	Belt et al., 2007,2013
			Tolosa et al., 2013
			Pieńkowski et al., 2017
Hudson Bay	Sea ice	IP ₂₅ identification	Belt et al., 2007
	Surface sediments	IP ₂₅ (PIP ₂₅)–sea ice calibration	Stoynova et al., 2013
		IP ₂₅ identification	Belt et al., 2007
Bering Sea/Gulf of Alaska	Surface sediments	IP ₂₅ -sea ice calibration	Sharko, 2010
		IP ₂₅ (PIP ₂₅)–sea ice calibration	Stoynova et al., 2013
		IP ₂₅ (sterols) distribution	Méheust et al., 2013
Sea of Okhotsk	Surface sediments	IP ₂₅ (PIP ₂₅)–sea ice calibration	Stoynova et al., 2013
			Lo et al., 2018
Chukchi/E Siberian Seas	Water column POM	IP ₂₅ distribution	Tesi et al., 2017
	Surface sediments	IP ₂₅ –sea ice calibration	Sharko, 2010
		IP ₂₅ (PIP ₂₅)–sea ice calibration	Stoynova et al., 2013
			Xiao et al., 2015a
Antarctica			
Antarctic Peninsula	Sea ice	Sterol identification	Belt et al., 2018
		IPSO ₂₅ source identification	Belt et al., 2016
		HBI II (IPSO ₂₅) identification	Massé et al., 2011
McMurdo Sound	Sealice	HBI II (IPSO ₂₅) identification	Nichols et al., 1988,1989,1993
			Johns et al., 1999
E Antarctica	Sealce	HBI II (IPSO ₂₅) identification	Massé et al., 2011
	Phytoplankton	HBI II (IPSO ₂₅) & HBI III distributions*	Smik et al., 2016a
			Masse et al., 2011
	Surface sediments/short cores	HBI II (IPSO ₂₅) & HBI III distributions [*]	Masse et al., 2011
	Sediment core	HBI II (IPSO ₂₅) reactivity [*]	Sinninghe Damste et al., 2007
	Phytoplankton	Source identification (HBI III)	Belt et al., 2017
Scotla Sea	Water column	IPSO ₂₅ and HBI III distributions	Schmidt et al., 2018
	Sediment cores	IPSO ₂₅ and HBI III distributions	Collins et al., 2013
Various locations	Surface sediments	IPSO ₂₅ and HBI III distributions	Belt et al., 2016
Other	Cadina anta	An ab the all meather all fam ID	SMIK, 2010 Dalt at al. 2010
Uther	Seaiments	Analytical method for IP ₂₅	Belt et al., 2012D
		Inter-laboration study of IP_{25} (HBIS)	Beit et al., 2014

Study region	Sample(s)	Study type	Reference(s)
		Confirmed structure - sedimentary IP ₂₅	Belt et al., 2012a
	Sediments/extracts	IP ₂₅ (HBI) degradation/reactivity	Rontani et al., 2018a,b
			Cabedo-Sanz et al., 2016b
			Belt and Cabedo-Sanz, 2015

* includes some stable isotope ($\delta^{13}\text{C}$) data

Summary of study locations and timeframes where source-specific HBIs and other biomarkers have been used for palaeo sea ice reconstructions. For further detail of individual sterols and PIP₂₅ indices, please refer to the cited publication(s). *Denotes more than one core.

Study region	Core	Timeframe	Biomarkers	Reference(s)
Arctic				
Arctic Ocean	PS2767-4	Last 60 ka	IP _{ar} HBLII sterol	Stein and Fabl 2012
Arelie Geean	PS2446-4*	MIS 3-1	IPor sterol	Xiao et al. 2015b
	PS2138-2	MIS 6-5	IPor HBLIII sterol PIPor	Stein et al. 2017a
	PS87/106	Late Miocene	IPor sterol PIPor	Stein et al. 2016
Kara Sea	BP00-07/7	Holocene (last 8 ka)	IPor sterol PIPor	Hörner et al. 2017
	BP00-36/4*	Last 12 ka	IPor sterol PIPor	Hörner et al. 2018
Lantev Sea	PS2458-4	Last 16 ka	IPor HBLII sterol PIPor	Fahl and Stein 2012
Edptor ood	PS51/154-11*	Last 17 ka	IPor HBI II sterol PIPor	Hörner et al 2016
Yermak Plateau-Fram Strait	PS92/039-2	Last 160 ka	IP ₂₅ HBI III sterol PIP ₂₅	Kremer et al 2018b
	ODP Hole 910C	Pliocene/Pleistocene (5.3-2.6 Ma)	IP ₂₅ , sterol, PIP ₂₅	Knies et al., 2014
	ODP Hole 912A*	Quaternary (last 2.2 Ma)	IP ₂₅ , HBI II–III, sterol, PIP ₂₅	Stein and Fahl, 2013
N Svalbard	GeoB10817-4	Ca. 16-8 ka: 2-0 ka	IP ₂₅ , sterol. PIP ₂₅	Bartels et al., 2017
E Fram Strait	MSM5/5-712-1	Holocene (last 2 ka)	IP ₂₅ , HBI III, sterol, PIP ₂₅	Cabedo-Sanz and Belt. 2016
	MSM5/5-723-2*	Holocene (last 9 ka)	IP ₂₅ , sterol. PIP ₂₅	Müller et al., 2012
	MSM5/5-712-2	LGM-Early Holocene (30-9 ka)	IP ₂₅ , HBI II, sterol, PIP ₂₅	Müller and Stein, 2014
	PS2837-5	Last 30 ka	IP ₂₅ , sterol	Müller et al., 2009
	PS93/006-1	Last 190 ka	IP ₂₅ , sterol, PIP ₂₅	Kremer et al., 2018a
Barents Sea	BASICC 1*	Recent centuries	IP ₂₅ , HBIs II–VI, PIP ₂₅	Köseoğlu et al., 2018b
			IP ₂₅	Vare et al., 2010
	JM10-10GC	Mid-late Holocene (last 6.5 ka)	IP ₂₅ , sterol	Knies et al., 2016
	NP05-11-70GC	Holocene (last 10 ka)	IP ₂₅ , HBI III, sterol, PIP ₂₅	Berben et al., 2017
			IP ₂₅ , HBIs II–VI, PIP ₂₅	Köseoğlu et al., 2018a
	JM09-KA11-GC	Holocene (last 12 ka)	IP ₂₅ , sterol	Berben et al., 2014
		YD-Holocene (last 13 ka)	IP ₂₅ , HBI III, sterol, PIP ₂₅	Belt et al., 2015
			IP ₂₅ , HBIs II–VI, PIP ₂₅	Köseoğlu et al., 2018a
		LGM (ca. 30-16 ka)	IP ₂₅	Knies et al., 2018
N Norway	JM99-1200	YD-early Holocene (13-7 ka)	IP ₂₅ , HBI III, sterol, PIP ₂₅	Belt et al., 2015
			IP ₂₅ , HBI II, sterol, PIP ₂₅	Cabedo-Sanz et al., 2013
			IP ₂₅ , HBIs II–VI, PIP ₂₅	Köseoğlu et al., 2018a
SE Norwegian Sea	JM11-FI-19PC	Last 90 ka	IP ₂₅ , sterol, PIP ₂₅	Hoff et al., 2016
Iceland Sea	ODP 907	Pliocene (3.5–2.4 Ma)	IP ₂₅ , sterol	Clotten et al., 2018
SW/NE/N Iceland	MD99-2275	Recent millenia	IP ₂₅	Massé et al., 2008

Study region	Core	Timeframe	Biomarkers	Reference(s)
			IP ₂₅	Axford et al., 2011
	MD99-2263		IP ₂₅	Andrews et al., 2009
	MD99-2273		IP_{25}^{-1}	Sicre et al., 2013
	MD99-2269*	Holocene (last 8 ka)	IP ₂₅ , HBI III	Cabedo-Sanz et al., 2016a
	MD99-2272	Last 15 ka	IP ₂₅ , HBI III, sterol, PIP ₂₅	Xiao et al., 2017
	B997-326PC1*	Ca. 16-12 ka BP	IP ₂₅ , HBI II	Andrews et al., 2018
E Greenland	PO175GKC#7*	Recent centuries	IP ₂₅ , HBI II, sterol	Alonso-García et al., 2013
	PS2641-4	Mid-late Holocene (last 5 ka)	IP ₂₅ , sterol, PIP ₂₅	Kolling et al., 2017
	MD99-2322	Holocene (last 8-9 ka)	IP ₂₅	Darby et al., 2017
	PS2641-4		IP ₂₅ , sterol, PIP ₂₅	Müller et al., 2012
W Greenland	HU2008029-12PC	Ca. 17-12 ka BP	IP ₂₅	Jennings et al., 2017
		Ca. 26-12 ka BP	IP ₂₅ , sterol	Jennings et al., 2018
		Last 2.2 ka	IP ₂₅ , HBI III, sterol, PIP ₂₅	Kolling et al., 2018
SW Labrador Sea	A107-04BC*	Recent centuries	IP ₂₅ , sterol, PIP ₂₅	Weckström et al., 2013
	A107-14G	YD-early Holocene (ca. 13-10 ka)	IP ₂₅	Pearce et al., 2013,2014
Baffin Bay	2008-029-040BC	Recent centuries	IP ₂₅ , sterol, PIP ₂₅	Cormier et al., 2016
Canadian Arctic Archipelago	99LSSL-001	Recent centuries	IP ₂₅ , sterol, PIP ₂₅	Pieńkowski et al., 2016
	ARC-4*	Holocene (last 7 ka)	IP ₂₅	Belt et al., 2010
	ARC-3	Holocene (last 10 ka)	IP ₂₅ , HBI II	Vare et al., 2009
Bering Sea	BR07	Holocene (ca. 11–2 ka)	IP ₂₅ , HBI II, sterol, PIP ₂₅	Ruan et al., 2017
	SO201-2-12KL*	Last 18 ka	IP ₂₅	Méheust et al., 2016
	SO202-07-6*	LGM-Holocene (ca. 25–5 ka)	IP ₂₅ , sterol, PIP ₂₅	Méheust et al., 2018
	LV29-114-3*	Ca. 138–70 ka BP	IP ₂₅	Max et al., 2014
	U1343	MPT (ca. 1.53–0.34 Ma)	IP ₂₅ , HBI III	Detlef et al., 2018
Sea of Okhotsk	MD01-2414	Last 130 ka	IP ₂₅ , HBI III	Lo et al., 2018
Chukchi-Alaskan Margin	HLY0501-05TC/JPC*	Holocene (last 11 ka)	IP ₂₅ , sterol, PIP ₂₅	Polyak et al., 2016
Chukchi/E Siberian Seas	ARA2B-1A*	Holocene (last 10 ka)	IP ₂₅ , sterol, PIP ₂₅	Stein et al., 2017b
Antarctica				
Western Antarctic Peninsula	JPC-10	Holocene (last 9 ka)	HBI II (IPSO25). HBI III	Etourneau et al., 2013
Antarctic Peninsula	MTC-38C*	Recent centuries	HBI II (IPSO ₂₅), HBI III	Barbara et al., 2013
	JPC-38	Holocene (last 9 ka)	HBI II (IPSO ₂₅), HBI III	Barbara et al., 2016
E Antarctica	MD130-MC02	Recent seasons	HBI II (IPSO ₂₅), HBI III	Massé et al., 2011
	DTCI2010	Recent decades	HBI II (IPSO ₂₅), HBI III	Campagne et al., 2016
	CB2010	Recent centuries	HBI II (IPSO ₂₅), HBI III	Campagne et al., 2015
	SMB-Ellis Fjord		HBI II (IPSO ₂₅)	Sinninghe Damsté et al 2007
	MD03-2601 [*]	Holocene (last 9 ka)	HBI II (IPSO ₂₅), HBI III	Denis et al., 2010
	NBP0101-JPC24	Deglaciation (11–9 ka)	HBI II (IPSO ₂₅), HBI III	Barbara et al., 2010

Study region	Core	Timeframe	Biomarkers	Reference(s)
Scotia Sea	TPC286*	Last 60 ka	HBI II (IPSO ₂₅), HBI III	Collins et al., 2013
McMurdo Sound (Ross Sea)	83-3a	Unspecified (short core)	HBI II	Venkatasen, 1988
Lützow-Holm Bay	Core A*	Unspecified (short core)	HBI II	Matsumoto et al., 1992