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Abstract: Over the last decade or so, certain source-specific C₂₅ 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.

- Source-specific highly branched isoprenoid (HBI) biomarkers as sea ice proxies
- IP_{25} and $IPSO_{25}$ 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

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

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20

21 Abstract

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40 biomarker signatures. Some knowledge gaps and areas for future research are also
41 briefly described.

42

43 **1. Introduction**

44 *1.1 Background to sea ice and sea ice proxies*

45 Dramatic changes to climate in the Arctic and Antarctic, beginning towards the
46 end of the last century and continuing towards modern times, have stimulated a
47 large array of research activity into the causes, consequences and contextualisation
48 of these transformations over the last decade or so (IPCC, 2013). Within the overall
49 climate structure of the polar regions, sea ice plays a central role (Thomas, 2017).
50 For example, due to its high albedo (reflectivity), sea ice acts as a highly efficient
51 regulator of incoming solar radiation to the surface oceans, and it also acts as a
52 physical barrier to gas, heat and moisture exchange between the oceans and
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
56 further impact of ice melting during the spring is nutrient release which, when
57 combined with surface layer stratification and increasing light and temperature, often
58 results in intense open water (pelagic) phytoplankton production, especially in the
59 region defined by the retreating ice edge – the so-called marginal ice zone (MIZ)
60 (Smith and Nelson 1986; Smith, 1987; Sakshaug et al., 2009; Perette et al., 2011).
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
63 residing in bottom ice during the winter, which then proliferate prior to the main
64 bloom of the pelagic community (Michel et al., 1993; Lizotte, 2001). A further
65 community of sea ice-associated (sympagic) organisms undergo rapid growth within
66 the host ice matrix itself, normally as light and nutrient availability increase during
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;
70 Walsh et al., 2017), one area of recent research focus has centred on aiming to
71 better contextualise these modern changes through reconstruction of longer-term
72 palaeo sea ice conditions. This has been achieved largely (although not exclusively)
73 by analysis of various proxies in marine sedimentary archives. A number of proxies
74 for sea ice exist, and many of their relative merits and applications have already
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
77 because of the influence that sea ice can have on marine-based ecological systems,
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,
81 most of these represent species whose growth habitat is more closely associated
82 with the open waters of the MIZ rather than that of sea ice itself (Leventer et al.,
83 2008; Leventer, 2013). In contrast, the strictly sympagic community, arguably a more
84 direct proxy measure of sea ice, is often under-represented in sedimentary records,
85 probably due to their generally lower abundance compared to their pelagic
86 counterparts, together with their often higher susceptibility towards degradation in
87 the water column and in sediments (Leventer, 2013).

88

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
95 including different ice types, ice thickness, extent or seasonality might also
96 potentially be deciphered. In practice, the main common algal lipid classes including
97 fatty acids and sterols do not sufficiently satisfy the criterion of source-selectivity to
98 be useful, even for distinguishing sea ice cover from open water conditions. An
99 exception can be found, however, in a further lipid group, commonly referred to as
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
114 Antarctic (Belt et al., 2016). Finally, a third (at least) HBI has been linked with open-
115 water (pelagic) conditions in both the Arctic and the Antarctic (Massé et al., 2011;
116 Collins et al., 2013; Belt et al., 2015; Smik et al., 2016a,b). Although a common
117 constituent of marine settings (Belt et al., 2000), this tri-unsaturated HBI, sometimes

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

121 Studies using HBI-based sea ice proxies for palaeo sea ice reconstruction
122 purposes have largely paralleled those aimed at proxy development (see Tables
123 1,2). The majority of reconstructions carried out thus far span the time interval since
124 the last glacial maximum (LGM) and the Holocene, in particular. However, some
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,
133 with IP₂₅ as the focus (Belt and Müller, 2013). The purpose of the current review is to
134 provide an update on research activity carried out on IP₂₅, together with an overview
135 of work carried out on other sea ice related HBIs (mainly IPSO₂₅ and HBI III).
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
138 application for individual case studies. Nonetheless, some brief illustrations of how
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
141 signatures of these organic geochemicals. Finally, clarification of current knowledge

142 should, hopefully, prevent incorrect or mis-leading descriptions and interpretations of
143 HBI-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*

147 The most frequently studied of the different HBI sea ice biomarkers is IP₂₅,
148 first identified in Arctic sea ice and sediments by Belt et al. (2007). IP₂₅ has since
149 been identified in numerous Arctic and subarctic surface sediments and downcore
150 records (Fig. 2a,b; Tables 1,2). In contrast, there have been perhaps surprisingly few
151 studies on IP₂₅ in its native sea ice and these are restricted, spatially, to the
152 Canadian Arctic Archipelago and Hudson Bay regions (Fig. 2c; Table 1); however, it
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
155 Belt and Müller, 2013 for a review), it was not until Brown et al. (2014c) carried out
156 analysis of individual sympagic diatom species that definitive source identifications
157 were made. Three (or four) individual sympagic diatom taxa have been identified as
158 producers of IP₂₅ - *Pleurosigma stuxbergii* var. *rhomboides* (Cleve in Cleve &
159 Grunow) Cleve, *Haslea kjellmanii* (Cleve) Simonsen, *H. crucigeroides* (Hustedt)
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,
163 common across the Arctic and subarctic regions (Fig. 2c). Consistent with this, IP₂₅
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
166 in any other diatoms, whether sympagic, pelagic or lacustrine. However, studies

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
169 cores taken from Resolute Passage and the Amundsen Gulf (both in the Canadian
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
173 record as proxy evidence of seasonal (spring) sea ice (see Belt and Müller, 2013).
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
182 annual cycles of first year sea ice formation in autumn/winter and melt in
183 spring/summer, and is supported further by the identification of higher amounts of
184 IP₂₅ in some sediment trap studies during the late spring/summer months (Fig. 2d)
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
190 Labrador Sea, where sea ice conditions reflect drift ice export from the Arctic Ocean
191 (Massé et al., 2008; Alonso-García et al., 2013; Sicre et al., 2013; Cabedo-Sanz et

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

196 The source-selective production of IP₂₅ by certain sympagic diatoms is further
197 evident from its somewhat enriched stable carbon isotopic composition ($\delta^{13}\text{C} = \text{ca. } -$
198 16 to -23‰ ; summarised in Belt and Müller, 2013) and its general absence in marine
199 surface sediments from regions that experience little or no sea ice cover in modern
200 times (Fig. 2a; Note that the locations of reported IP₂₅ absence only indicate those
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
205 reflect a deviation from strict vertical transport within the water column or re-
206 suspension/advection subsequent to initial deposition in surface sediments (Navarro-
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
211 these are mainly in the CAO where near-perennial sea ice cover prevails (Fig. 2a;
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 IP₂₅ presence is available (Section 2.1), it is less so for IP₂₅ 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
221 is reasonable to accept if the source-selectivity of IP₂₅ is as believed (i.e.
222 biosynthesis by certain sympagic diatoms only) and is supported by the general
223 absence of IP₂₅ in surface sediments from regions of year-round ice-free conditions
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)
226 produced, together with the processes by which it is transferred from sea ice to the
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
234 production/deposition of IP₂₅ under perennial sea ice cover have been carried out,
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 co-

242 measurement of certain other biomarkers, most commonly associated with pelagic
243 phytoplankton. First proposed by Müller et al. (2009), the co-measurement of certain
244 algal sterols, in particular, potentially provides a means of distinguishing between
245 perennial sea ice cover from open water conditions on the basis of relatively low or
246 high phytoplankton biomarker concentrations, respectively. This, of course, makes
247 various assumptions on factors controlling open water productivity and pelagic-
248 benthic coupling, and is further complicated by the biosynthesis of many potential
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,
251 1976; Volkman, 1986; Volkman et al., 1998; Belt et al., 2013,2018). Further
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
255 the (IP₂₅-producing) diatoms are too low in abundance or even absent. Brown et al.
256 (2014c) described the common occurrence of IP₂₅-producers in previously reported
257 taxonomic inventories of sea ice diatoms (Fig. 2c), but there are likely certain
258 scenarios where this is not the case. For example, the lower salinities associated
259 with fjords or near-coastal settings influenced by large river discharges that are
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
263 Greenland fjord, and by others following analysis of IP₂₅ in sediments from the Kara
264 and Laptev Seas (Xiao et al., 2013; Hörner et al., 2016). One could also speculate
265 that sea ice with too low of a brine channel percentage or very low surface-to-bottom
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,
269 2013); however, such hypotheses remain in need of further research.

270 Finally, IP₂₅ (sedimentary) absence may result from its degradation in sea
271 ice, the water column, in sediments, or a combination of these, as described
272 previously (Belt and Müller, 2013). Alternatively, since ice algal organic carbon (OC)
273 represents an important foodstock at the base of the polar food web, removal of IP₂₅
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
282 shrimp) in laboratory experiments (Brown and Belt, 2017). These preliminary findings
283 suggest that source HBI distributions remain largely unaltered following grazing,
284 which may have positive implications for the use of sedimentary HBI distributional
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
287 of IP₂₅ and other HBIs in sediments can be fully understood.

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
290 stable, at least with respect to some other lipids (Rontani et al., 2011,2014b). On the
291 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
294 (Rontani et al., 2018a,b). Interestingly, the same degradation processes did not
295 appear to be operating on IP₂₅ in the sea ice itself. In contrast, more unsaturated
296 HBIs have been shown to undergo oxidation in Arctic sea ice (Rontani et al., 2014a).
297 However, according to Rontani et al. (2018a), determining the importance of
298 degradation, more routinely, is likely to remain challenging due to the probable
299 secondary reactions of the initial degradation products, which limits their
300 accumulation in sediments.

301 In summary, I suggest that interpretations of absent IP₂₅, in particular, should
302 be more circumspect, and certainly not limited to the extreme cases of ice-free
303 versus perennial ice cover, which are themselves not sufficiently evidenced, at this
304 point. An overview of how certain sea ice settings are currently believed to influence
305 IP₂₅ 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
308 produced by certain Arctic sympagic diatoms (Brown et al., 2014c). Indeed, IP₂₅ and
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
313 the concentration ratio HBI II/IP₂₅ or DIP₂₅ index have been attributed to either
314 possible changes in temperature or sea ice dynamics (e.g. Vare et al., 2009; Fahl
315 and Stein, 2012; Cabedo-Sanz et al., 2013; Müller and Stein, 2014; Hörner et al.,
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.
319 More fundamentally, apart from the study of Xiao et al. (2013), the relationship
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
323 substitute in cases where IP₂₅ is absent (or below its detection limit). After all, HBI II
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,
330 none of the IP₂₅-producing species endemic to the Arctic (Section 2.1) have been
331 reported in the Antarctic. However, a di-unsaturated HBI (II; Fig. 1), which co-occurs
332 with IP₂₅ in the Arctic (Section 2.2), was first reported in Antarctic sea ice and
333 sediments more than 25 years ago (Nichols et al., 1988, 1989, 1993), although a
334 definitive source remained elusive at that time and its structure also remained
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
337 Antarctic sea ice and a number of palaeo Antarctic sea ice reconstructions have
338 since followed (Fig. 5b; Table 2). In a more recent study, Belt et al. (2016) identified
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,
341 HBI II was also identified in a large number of sediments from near-coastal locations

342 around the Antarctic continent (Fig. 5a). Given its source identification and
343 widespread sedimentary occurrence, the term IPSO₂₅ – ‘Ice Proxy for the Southern
344 Ocean with 25 carbon atoms’ was given to HBI II, by analogy with IP₂₅ for the Arctic.
345 It is worth noting, however, that the source-specificity of IPSO₂₅ is not as clear-cut as
346 that for IP₂₅ since this HBI has also been identified in the benthic diatom *Haslea*
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
349 characteristic of HBI II in the Antarctic is its distinctive stable carbon isotopic
350 composition, with $\delta^{13}\text{C}$ values ranging from ca. -5.7 to -8.5‰ in sea ice samples
351 (Massé et al., 2011). Importantly, ^{13}C -enrichment has also been observed for this
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
355 modern sea ice-covered near-coastal environments around Antarctica, the use of the
356 term IPSO₂₅ appears appropriate, for now, at least. However, whether this is also
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,
361 where possible, in order to confirm its origin.

362 More generally, the development of IPSO₂₅ as a proxy for Antarctic sea ice
363 has not received as much attention as that for IP₂₅ in the Arctic. Thus, apart from its
364 recent source identification, establishment of its characteristic stable carbon isotopic
365 composition, and its general presence in near-coastal surface sediments, the surface
366 sedimentary distribution of IPSO₂₅ 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.

373 Exceptionally, Massé et al. (2011) observed a general decline in sedimentary
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. adeliensis*), 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
382 al., 1993). Re-examination of some palaeo sea ice records based on IPSO₂₅ added
383 further credibility to this suggestion (Fig. 6), and Smik et al. (2016a) also identified
384 highest concentrations of IPSO₂₅ in near-shore surface waters soon after spring sea
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
387 with greater confidence. These potentially include (but are not limited to): (i)
388 measurement of IPSO₂₅ in a larger range of Antarctic surface sediments and
389 comparison of findings with known sea ice conditions; (ii) combining IPSO₂₅
390 concentrations with those of other biomarkers (i.e. similar to the PIP₂₅ index used in
391 the Arctic; see Section 4.2); (iii) determination of additional sources (if any) of IPSO₂₅

392 whose habitat(s) may also influence the interpretation of the sedimentary signal; (iv)
393 determination of any diagenetic factors that may impact on the sedimentary profile.
394 For the latter, it is noted that IPSO₂₅ was shown to undergo relatively rapid (a few
395 hundred years) incorporation of sulphur in Ellis Fjord (East Antarctica) sediments
396 (Sinninghe Damsté et al., 2007), yet has been readily identified in Holocene and last
397 glacial sediments from other Antarctic regions (Table 2).

398 Regarding absent sedimentary IPSO₂₅, there are likely several potential
399 explanations for this scenario, as described in more detail for absent IP₂₅ (see
400 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
407 stems from its inherent dynamic behaviour, both spatially and temporally. For the
408 purposes of understanding how biomarker distributions might reflect the MIZ, I
409 consider the definition of Wadhams (1986) to be as good as any. Thus, the MIZ is
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,
413 although these are often variable on annual timeframes. For other locations, sea ice
414 dynamics can be far less pronounced or consistent, even on seasonal timeframes,
415 with rapid fluctuations in extent from winter through to summer. These contrasting

416 scenarios provide important background context for interpretation of biomarker
417 signatures of the MIZ in palaeo records (Section 4).

418 With such dynamic behaviour, combined with surface ocean settings often
419 characterised by a melange of different sea ice types and open water conditions, the
420 identification of any source-specific biomarkers that represent the MIZ uniquely is an
421 ambitious research objective, to say the least. However, it may be feasible to identify
422 some potential candidates that at least partly align with the key attributes of source-
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
431 difficulty in identifying any such biomarker(s) is compounded further by the
432 challenges of carrying out representative in situ sampling of the MIZ, not least
433 because of its highly dynamic and often heterogeneous nature. On the other hand,
434 identification of suitable MIZ biomarkers can potentially be deduced from the
435 analysis of surface sediments, even if their accumulation characteristics generally
436 imply an integration of a number of different overlying surface or near-surface
437 conditions spanning several seasons, years, or longer.

438 In practice, many common algal biomarkers including fatty acids and
439 phytosterols do not satisfy the first two criteria. Indeed, in two recent studies – the
440 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
443 significant differences in biomarker abundances or distributions were identified
444 between the respective MIZ and neighbouring open ocean locations (Navarro-
445 Rodriguez et al., 2013; Belt et al., 2015; Smik et al., 2016a). On the other hand, in a
446 number of recent empirical studies, the elevated abundance of a tri-unsaturated HBI
447 biomarker (often referred to as HBI III; Fig.1) in some near-surface waters and
448 surface sediments from the MIZ of certain Arctic and Antarctic regions, suggests that
449 this biomarker may at least part-satisfy several key criteria (Belt et al., 2015; Smik et
450 al., 2016a; Schmidt et al., 2018) (see Fig. 7,8,9 and Tables 1,2 for summaries).

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
454 (now IPSO₂₅) in late glacial sediments from the Scotia Sea (Southern Ocean). In
455 support of this, relatively high concentrations of HBI III have been observed in the
456 near-surface waters of the MIZ in the Scotia Sea (Schmidt et al., 2018) and also off
457 the Sabrina Coast (East Antarctica) (Fig. 8; Smik et al., 2016a). In the Arctic, HBI III
458 concentration was shown to be significantly higher in Barents Sea surface sediments
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
461 addition, in a study of biomarker content in a small number of surface sediments
462 from a NE Greenland fjord, HBI III was most abundant for locations proximal to the
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

466 III, whose isotopic composition, when detected in polar environments ($\delta^{13}\text{C} = \text{ca. } -35$
467 to -40‰ ; Massé et al., 2011; Smik et al., 2016a; Schmidt et al., 2018), is also
468 consistent with production by pelagic, rather than sympagic, algae. Combined, these
469 background studies, albeit relatively small in number thus far, indicate that HBI III
470 may prove to be a useful proxy measure for the MIZ in the Arctic and the Antarctic,
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.
474 Potentially, increased production might reflect an environment-specific response. For
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
478 diatoms should also be considered, although only certain *Pleurosigma* spp. have
479 previously been shown to be producers of this HBI, and such species are not
480 especially common or abundant in polar environments. For now, therefore, the use
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 III-
485 producing diatoms in some settings/time intervals, or degradation in the water
486 column or sediments. The co-measurement of other phytoplanktic biomarkers is,
487 therefore, probably still useful in terms of elucidating productivity trends, more
488 generally. In the meantime, some suggestions for how the production of HBI III might
489 be dictated by different Arctic sea ice settings is shown in Figure 4.

490

491 3. Analytical considerations

492 Central to the use of source-specific HBIs as sea ice proxies is the reliability
493 of the analytical measurement, which includes both accurate identification and
494 quantification. The former should be straightforward given the availability of suitable
495 laboratory standards, well-maintained GC–MS instrumentation and published
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
498 example, Cabedo-Sanz and Belt (2015) identified a C₂₅ HBI monoene in ancient
499 Arctic sediments, which has a very similar GC retention index and mass spectrum to
500 that of IP₂₅, but has not thus far been reported in sea ice. Further, for Arctic
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
505 IP₂₅ and HBI II, respectively; Belt and Cabedo-Sanz, 2015), provides an opportunity
506 for mis-identification, especially of IP₂₅. In fact, during an inter-laboratory
507 investigation of IP₂₅ and other HBIs (Belt et al., 2014), IP₂₅ was sometimes
508 incorrectly identified in an Antarctic sediment (i.e. one known not to contain IP₂₅),
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
513 nonetheless useful for future analyses.

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
518 isomeric HBIs (Belt et al., 2000; Brown and Belt, 2016), and the difficulties in often
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
522 structurally characterised HBI trienes (HBI III; Fig. 1) has been firmly associated with
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
531 internal standards employed (7-hexylnonadecane (7-HND) and 9-octylheptadec-8-
532 ene (9-OHD)) and the specific biomarker ions selected for quantification. In the
533 Plymouth laboratory, both of these IS are used for HBI quantification purposes, with
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
536 series of standard solutions of variable HBI concentration. The first approach was
537 indeed a recommendation following the inter-laboratory investigation of IP₂₅ (Belt et
538 al., 2014), yet it is not always evident how such response factors are measured (if at
539 all) in a number of published studies based on IP₂₅ and other HBIs, or how final
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
543 PIP₂₅ indices (Section 4.2), it does have implications when making comparisons
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
547 reported IP₂₅ data by Stoyanova et al. (2013) on the basis of unusually high values,
548 which might have resulted from the employment of a different analytical method. As
549 such, it is recommended that all aspects of HBI identification and quantification (i.e.
550 GC retention indices, mass spectral data, methods for calculating GC responses
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
554 biomarker analysis. In brief, while similar results were obtained for IP₂₅, IPSO₂₅ and
555 the internal standard 7-HND (Fig. 1) when using accelerated solvent extraction
556 (ASE) or sonication (DCM/MeOH) methods, some degradation of more unsaturated
557 HBIs (e.g. HBI III) and the internal standard 9-OHD (Fig. 1) was observed using the
558 former method, possibly due to the higher temperatures employed. In addition, the
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)
561 following the recommendation of Belt and Müller (2013). In summary, over a two
562 year study period, tri-unsaturated HBIs such as HBI III were shown to be more
563 susceptible to degradation than IP₂₅, especially when sediments were stored in
564 plastic bags and exposed to light at room temperature. In contrast, all HBIs were
565 relatively stable in sediments stored in glass vials and kept frozen in the dark. It was

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

569 A final point pertinent to the analytical measurement concerns the
570 identification of the most appropriate threshold concentration of IP₂₅ or IPSO₂₅ for
571 sea ice inference, especially if primary interpretations, as described here, are based
572 within a binary framework of sea ice presence/absence. To my knowledge, such a
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
575 discussed in some detail by Belt and Müller (2013), but has received little or no
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
579 5 g dry sediment. However, this definition simply ensures in-house consistency
580 between investigations.

581

582 **4. Reading the sedimentary record – converting biomarker profiles to** 583 **qualitative and semi-quantitative 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
593 source-specific HBIs (and some other biomarkers) is analysis of their individual
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 qualitative outcome is widely applied, and has its
597 foundation in the first downcore IP₂₅ record from North Iceland, where Massé et al.
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
603 sea surface temperature (SST). However, the relationship between sedimentary IP₂₅
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
606 cover is significant (Stoyanova et al., 2013; Xiao et al., 2015a). Some of this variability
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).

612 Nonetheless, the now quite extensive set of regional ‘calibrations’ spanning
613 various Arctic and sub-Arctic regions provides some support to the general principle
614 that directional changes in sedimentary IP₂₅ concentration likely reflect
615 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).

622 For the Antarctic, palaeo sea ice reconstructions based on $IPSO_{25}$ (often
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 $IPSO_{25}$
627 distributions with known sea ice cover have, as yet, been carried out, so the
628 assumption of increased $IPSO_{25}$ reflecting higher sea ice extent is based almost
629 entirely by analogy with IP_{25} in the Arctic. Further, it has been suggested that the
630 ecology of *B adeliensis* (one of the sources of $IPSO_{25}$) might be the major influence
631 over its sedimentary distribution (Belt et al., 2016). What is evident from the relatively
632 small number of previous investigations, however, is that considerably more work is
633 required before the sedimentary signature of $IPSO_{25}$ can be fully understood, and at
634 least before any unequivocal comparisons with IP_{25} 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).

637 Interpretations of HBI III profiles in palaeo records are probably most
638 meaningfully carried out alongside their IP_{25} (and $IPSO_{25}$) counterparts, especially
639 given their respective signatures of the MIZ and sea ice. As background, relatively
640 high (low) IP_{25} 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
643 its higher production in the MIZ following rapid ice margin retreat during the spring
644 (Fig. 9; Belt et al., 2015). This contrasting behaviour was also evident in some
645 palaeo IP₂₅ and HBI III records from the region, with high IP₂₅ concentration
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
648 positions of the winter/summer ice margins within an otherwise annual cycle of sea
649 ice advance/retreat (Belt et al., 2015; Berben et al., 2017).

650 Although this out-of-phase behaviour of IP₂₅ and HBI III in some temporal
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
656 interglacial/glacial records from the Yermak Plateau/Barents Sea continental margin
657 (Stein et al., 2017a; Kremer et al., 2018b), and certain timeslices associated with the
658 Mid-Pleistocene Transition in the Bering Sea (Detlef et al., 2018). In these cases, the
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
661 parallel influence over sea ice (IP₂₅) and ice-influenced (HBI III) biomarker production
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
664 was also interpreted in terms of a rapidly advancing and retreating sea ice margin
665 (Müller et al., 2009,2011,2012).

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
668 surface sediments from western Svalbard – a region known to experience rapid
669 year-round fluctuations in sea ice conditions in modern times – revealed a similar
670 positive relationship between IP₂₅ and HBI III (Smik and Belt, 2017). Otherwise, apart
671 from the analysis of IP₂₅ and HBI III in a relatively small number of surface sediments
672 from two Greenland fjords (Ribeiro et al. 2017; Limoges et al., 2018), there have
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
675 representative the two contrasting observations and interpretations of Barents Sea
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
679 phase relationships were not interpreted in any detail (Cabedo-Sanz et al., 2016a;
680 Xiao et al., 2017; Lo et al., 2018).

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

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

696 Finally, an unresolved question, and one raised initially by Belt and Müller
697 (2013) in an earlier review, concerns the most appropriate units for expressing IP₂₅
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

709 *4.2 Combining biomarkers – from the PIP₂₅ index to multivariate analysis*

710 The second step normally taken when interpreting sea ice (and related)
711 biomarker data is application of one or more combinative approach. Relatively
712 simple biomarker ratio-based methods are common, of course, in organic
713 geochemistry, most notably within palaeo-oceanographic investigations of surface
714 and sub-surface SSTs via the U^K₃₇ and TEX₈₆ indices (Brassell et al., 1986; for
715 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 PIP_{25} index. First introduced by Müller et al. (2011), the PIP_{25} index combines the
719 relative concentrations of IP_{25} 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 IP_{25} and P for all sediments under study (i.e. Eqn.
722 2) and was introduced by Müller et al. (2011) to accommodate the normally much
723 higher concentrations of phytoplanktic lipids (P) compared to IP_{25} .

724

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

725

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

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

729 As a result, all PIP_{25} indices fall within the range 0–1, which potentially addresses
730 some of the difficulty in interpreting larger-scale variability in absolute biomarker
731 concentrations as described earlier (Section 4.1). In general, higher PIP_{25} values are
732 interpreted in terms of higher sea ice concentration or extent, on the assumption that
733 primary production is biased towards IP_{25} under such conditions. At the upper limit,

734 $PIP_{25} = 1$ implies biosynthesis of IP_{25} but no phytoplankton (or selected biomarker)
735 production, which is rarely, if ever, the case. Conversely, the lower limit (i.e. $PIP_{25} =$
736 0) is arrived at for absent (or below the detection limit) IP_{25} , which has been
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 IP_{25} in some sediments from regions of permanent sea ice
740 cover (Xiao et al., 2015a) and for other reasons outlined earlier (Section 2.2). It
741 should also be noted that, if the assumption of absent IP_{25} for ice-free or perennial
742 ice cover is correct, then the PIP_{25} index cannot be used to distinguish between
743 these two end-members, since PIP_{25} is equal to zero in each case. However, on
744 some occasions where IP_{25} and phytoplankton markers have been found to be
745 extremely low/absent (presumed to reflect heavy/perennial sea ice conditions), PIP_{25}
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.

749 The reliability of the PIP_{25} index as a semi-quantitative measure of Arctic sea
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 PIP_{25} 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 PIP_{25} and sea ice conditions
755 (e.g. linear, logarithmic, etc.); (iv) the c factor; (v) the temporal interval in downcore
756 records (which impacts on the c factor).

757 Despite the general lack of progress in the development of the PIP_{25} index
758 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 PIP_{25}
760 profiles simply resemble the corresponding IP_{25} trends (or at least do not reverse
761 them), the conversion of univariate IP_{25} and P concentration data to a uniform scale
762 is probably useful for consistency and comparison purposes. The ratio-based
763 method also removes any need to identify the most appropriate units for the
764 individual biomarker concentrations or fluxes, since any denominator used in such
765 terms is eliminated, algebraically, a point unfortunately missed in a recent
766 assessment of the impacts of different units on PIP_{25} indices (Pieńkowski et al.,
767 2017). Further, for one particular region (the Barents Sea), the use of HBI III as the
768 phytoplanktic counterpart to IP_{25} when calculating PIP_{25} indices (hereafter $P_{III}IP_{25}$)
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
771 sedimentary IP_{25} and HBI III concentrations, at least in sediments from the Barents
772 Sea, somewhat limits the variability in the c factor, and a fixed value for c was
773 proposed based on a regional calibration (Smik et al., 2016b). The benefit of a fixed
774 c factor, in particular, ensures that $P_{III}IP_{25}$ indices at individual sedimentary
775 timepoints remain fixed, and are independent of the overall time interval under study,
776 something that is not the case when c is calculated on a piecemeal basis, as
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
780 representative for any particular region and has not been used in more recent palaeo
781 sea ice reconstructions.

782 In addition, the only known sources of HBI III are marine diatoms, thus making
783 it a more selective phytoplanktic contributor to PIP_{25} index calculations, while its

784 apparently higher production within the MIZ (Section 2.4) also aligns well with the
785 underlying principles of the PIP_{25} index, with a switch-over in biomarker responses
786 between the two end members of sea ice cover and open water settings (Fig. 4). In
787 fact, the switch from higher IP_{25} (sea ice) to increased HBI III (MIZ) is exemplified
788 further from the good linear relationship between $P_{III}IP_{25}$ and spring sea ice
789 concentration (SpSIC) (Eqn. 4) for the Barents Sea (Smik et al., 2016b). A minimum
790 threshold for summer sea ice occurrence ($P_{III}IP_{25} > 0.8$) was also proposed (Smik et
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
796 calculate $P_{III}IP_{25}$ indices using a fixed c factor derived from a regional calibration, or
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.

800 Despite the success of using HBI III as a phytoplankton biomarker for the
801 PIP_{25} index, as described above, uncertainties regarding selection of the most
802 appropriate phytoplanktic biomarker, more generally, remain. Further, it is still not
803 clear whether the PIP_{25} method is even applicable in some regions, and the
804 problems associated with biomarker co-variance, as discussed previously (Müller et
805 al., 2011,2012; Belt and Müller, 2013), also persist. Under such circumstances, PIP_{25}
806 indices remain largely invariant, despite potentially significant changes to sea ice
807 conditions.

808 To take a different approach, Köseoğlu et al. (2018b) recently investigated the
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
812 water, etc), although some pre-selection of potential candidates is judicious. In the
813 current context, only HBIs with known sympagic and pelagic sources were selected,
814 with exclusion of other lipid classes potentially derived from other (e.g. terrestrial)
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,
829 IP₂₅ was found to be a primary predictor of sea ice cover in the Barents Sea, with
830 HBI II (co-produced with IP₂₅ in the Arctic) as a surrogate variable in cases where
831 IP₂₅ might be absent (or below the detection limit). Interestingly, for the MIZ or open
832 water settings, the geometric isomer of HBI III (i.e. IV; Fig. 1) was identified as the

833 main predicting variable (with HBI III as a surrogate), even though it was normally
834 present in higher concentration. Further, based on analysis of a suite of HBIs in
835 some relatively short cores spanning recent centuries from different regions of the
836 Barents Sea (Fig. 12c), CT model predictions of sea ice conditions showed good
837 agreement with those recorded in historical records, and also with $P_{III}IP_{25}$ -based
838 estimates of SpSIC (Fig. 12d).

839 Some potential disadvantages of the CT approach are discussed in more
840 detail by Köseoğlu et al. (2018a,b) so only a few are described in brief here. First, as
841 with the PIP_{25} index, it is almost certainly a requirement that individual CT models
842 are created (and tested) for different regions, not least, because the precise
843 distributions of biomarker sets may depend on factors other than sea ice, depending
844 on location.

845 Second, distributional variations observed in surface sediments reflecting
846 modern sea ice conditions may not always be replicated in downcore records,
847 especially if sea ice conditions in the past do not have a parallel for the region in
848 modern times. For example, this might be important in the case of permanent sea ice
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 IP_{25} and HBI III has not been
853 investigated, the latter has been shown to be more susceptible to oxidative
854 degradation in laboratory experiments (Rontani et al., 2011, 2014b) and probably
855 also in the water column (Rontani et al., 2016). Of course, differential biomarker
856 degradation will also likely impact on other biomarker-based approaches. Although
857 these factors are in need of detailed investigation in the future, it is interesting to note

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

863 Third, the employment of unique threshold values for distinguishing individual
864 sea ice classifications (see Fig. 12b) necessitates the accurate quantification of all
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 PIP_{25} 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).

873 Finally, using biomarker distributions to predict broader classifications of sea
874 ice extent (e.g. 0–10%, 10–50%, 50–100%; Fig. 12) is arguably a more realistic or
875 reliable target than integer-resolution SpSIC estimates from PIP_{25} index calibrations.

876

877 **5 Knowledge gaps and areas for future research**

878 Since the first review of IP_{25} and other HBIs by Belt and Müller (2013), some
879 clear progress has been made towards their development as sea ice proxies, but
880 some knowledge gaps remain or have since emerged. Thus, specific diatom sources
881 for IP_{25} , $IPSO_{25}$ and HBI III have been identified (Sections 2.1, 2.3, 2.4), some
882 regional calibrations of single and combined biomarker distributions versus sea ice

883 conditions have been completed, and a suite of palaeo sea ice reconstructions
884 based on these biomarkers have been reported spanning different regions and
885 timeframes (Tables 1 and 2). On the other hand, as alluded to at various points
886 within this review, some further work is needed before the full potential of source-
887 specific HBIs can be realised. These likely represent ab initio investigations such as
888 determination of the factors that control production, deposition and preservation of
889 HBIs, while others are more empirical in nature, like the further regional calibration of
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
892 sea ice extent data, surface sediment timeframes, etc). In writing this review, a
893 number of such future research areas came to mind, but only a few are described in
894 brief here.

895 First, there is the need for a larger spatial assessment of IP_{25} and $IPSO_{25}$
896 production by Arctic and Antarctic sea ice diatoms, respectively. Currently, this has
897 been confined to an extremely small number of locations (Fig. 2c,5c), yet palaeo
898 records based on these HBIs are emerging rapidly from both polar regions. In similar
899 vein, the analysis of IP_{25} and $IPSO_{25}$ in different ice types (e.g. first-year ice, multi-
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 PIP_{25} index or CT models)
903 against known sea ice conditions would add further confidence in their application for
904 palaeo reconstruction purposes. In this sense, as demonstrated quite recently for
905 HBI III in certain Arctic and Antarctic regions, there may be further (better) pelagic
906 biomarkers that act as suitable counterparts to IP_{25} and $IPSO_{25}$ for characterisation
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
912 approaches that help decipher the origins of certain biomarkers on a case-by case
913 basis rather than extrapolation of findings from previous studies, which might not be
914 relevant, environmentally. Third, greater efforts should be made to ensure the
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 IP_{25} and $IPSO_{25}$, in particular, represents an
925 important characteristic in terms of their suitability as sea ice proxies. Of course, one
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 IP_{25} and $IPSO_{25}$ 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
931 environmental conditions that influence IP_{25} and $IPSO_{25}$ production could potentially
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)
937 sea ice signature, even if only qualitatively. In any case, the identification of the
938 boundary conditions for the formation and sedimentary deposition of IP₂₅ and IPSO₂₅
939 represent important next-stage objectives. The extent to which qualitative outcomes
940 can be routinely and reliably translated into more quantitative or nuanced
941 descriptions of sea ice conditions also constitutes an interesting but challenging
942 research area.

943

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- 1496

1497 **Figures**

1498

1499 Figure 1. Structures of HBI biomarkers discussed in this review. The structures of
1500 two internal standards often used in the quantification of HBIs are also shown.

1501

1502 Figure 2. Summary maps of locations where IP₂₅ has been investigated for proxy
1503 development and palaeo Arctic sea ice reconstruction purposes: (a) surface
1504 sediments; (b) palaeo sea ice studies (c) sea ice, sea ice algae and taxonomic
1505 studies where the IP₂₅-producing diatoms have been reported; (d) sediment trap
1506 (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
1512 spring (May–June). The outer ordinate scale corresponds to data from the
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
1515 measure of ice algal primary production. A map showing the approximate sampling
1516 locations is also shown. Adapted from Belt et al. (2013).

1517

1518 Figure 4. Schematic representation summarising the proposed relative
1519 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;
1523 Brown et al., 2011; Belt et al., 2013). According to sedimentary distributions,
1524 highest IP₂₅ concentration is normally associated with more frequent or long-
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
1528 very low (or absent) but is in need of further investigation. IP₂₅ is not believed to
1529 be produced in open waters. Production of HBI III is thought to be limited to ice
1530 free conditions, with highest concentrations associated with the open waters of
1531 the MIZ (Belt et al., 2015). Please refer to Sections 2.1, 2.2 and 2.4 of the main
1532 text for more detailed descriptions.

1533

1534 Figure 5. Summary maps of locations where IPSO₂₅ has been investigated for
1535 proxy development and palaeo Antarctic sea ice reconstruction purposes: (a)
1536 surface sediments; (b) palaeo sea ice studies; (c) sea ice and taxonomic reports
1537 of *Berkeleya adeliensis* (a source of IPSO₂₅); (d) water column (phytoplankton)
1538 samples. See Tables 1,2 for more details.

1539

1540 Figure 6. Examples where analysis of IPSO₂₅ (HBI II) has been used to
1541 reconstruct palaeo Antarctic sea ice conditions for the West Antarctic Peninsula
1542 spanning different timeframes. The blue shaded areas correspond to intervals of
1543 elevated IPSO₂₅ concentration that also coincide with periods of glacial meltwater
1544 or ice shelf influence as derived from other proxy records. Figure adapted from
1545 Belt et al. (2016); data taken from Barbara et al. (2013,2016) and Etourneau et
1546 al., 2013.

1547

1548 Figure 7. Summary maps showing locations where HBI III has been investigated
1549 for proxy development and palaeo sea ice (Marginal Ice Zone) purposes: (a)
1550 Arctic surface sediments; (b) Arctic palaeo records and water column studies; (c)
1551 Antarctic surface sediments; (d) Antarctic palaeo records and water column
1552 studies. All studies were carried out on sediment material unless otherwise
1553 indicated. See Tables 1,2 for more details.

1554

1555 Figure 8. Distributions of IPSO₂₅ and HBI III in near surface waters from East
1556 Antarctica. Symbol sizes reflect the relative concentration ranges in each case.
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
1560 definitions of sea ice conditions used by Smik et al. (2016a). ACC: Antarctic
1561 Circumpolar Current; ACoC: Antarctic Coastal Current. Figure adapted from Smik
1562 et al. (2016a).

1563

1564 Figure 9. Distributions of IP₂₅ and HBI III in surface sediments from the Barents
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
1568 extent: April 2006; maximum extent: April 1981; median extent: April 1981–2010.
1569 The region between the April 1981 and 2006 extent approximates to the MIZ
1570 during the spring. Note the highest concentrations of HBI III in the MIZ during
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

1576 Figure 10. Mass spectra of source-specific HBIs described in the text. Retention
1577 indices are those obtained using an HP5ms GC column. The ion at m/z 350 for
1578 IPSO₂₅ corresponds to the (M+2)⁺ ion (see Section 3).

1579

1580 Figure 11: Representative downcore records of IP₂₅ and HBI from different
1581 regions of the Barents Sea spanning different timeframes. (a) out-of-phase
1582 profiles reflecting changes in the position of the winter ice margin for annual
1583 advance/retreat cycles; (b) in-phase profiles likely resulting from more rapid
1584 seasonal fluctuations in sea ice dynamics. See the main text (Section 4.1) for a
1585 more detailed discussion. Data taken from Belt et al. (2015), Cabedo-Sanz and
1586 Belt (2016), Stein et al. (2017a) and Kremer et al. (2018b).

1587

1588 Figure 12. Development and application of HBI-based Classification Tree (CT)
1589 models for palaeo Arctic sea ice reconstruction. (a) location of surface sediments
1590 from which HBI distributions were used for CT model construction by Köseoğlu et
1591 al. (2018b). Modern sea ice classifications for each location are also shown; (b)
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
1594 for each sea ice classification; (c) Locations of short cores used to test the CT
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.

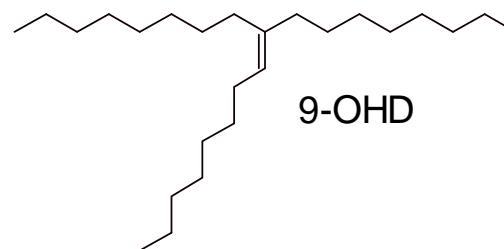
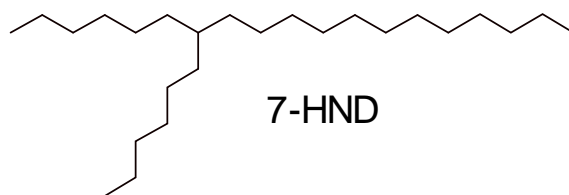
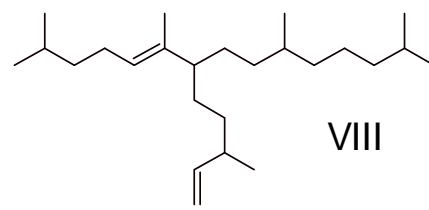
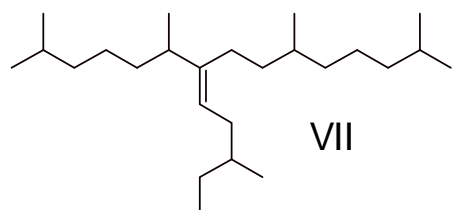
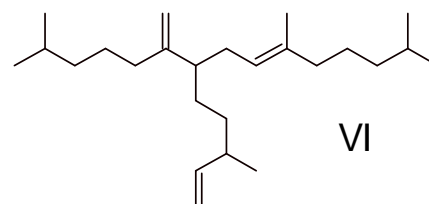
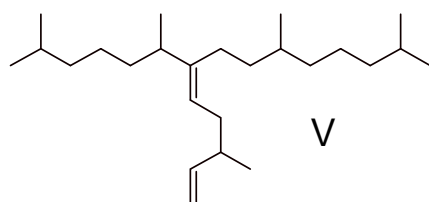
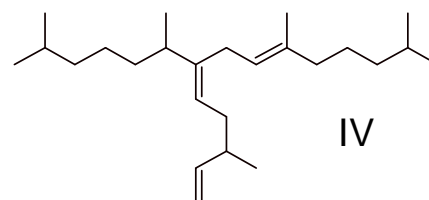
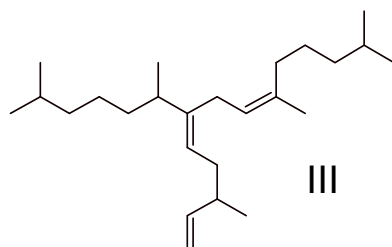
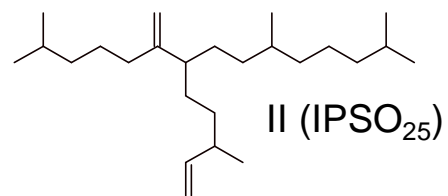
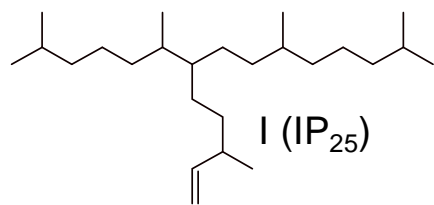


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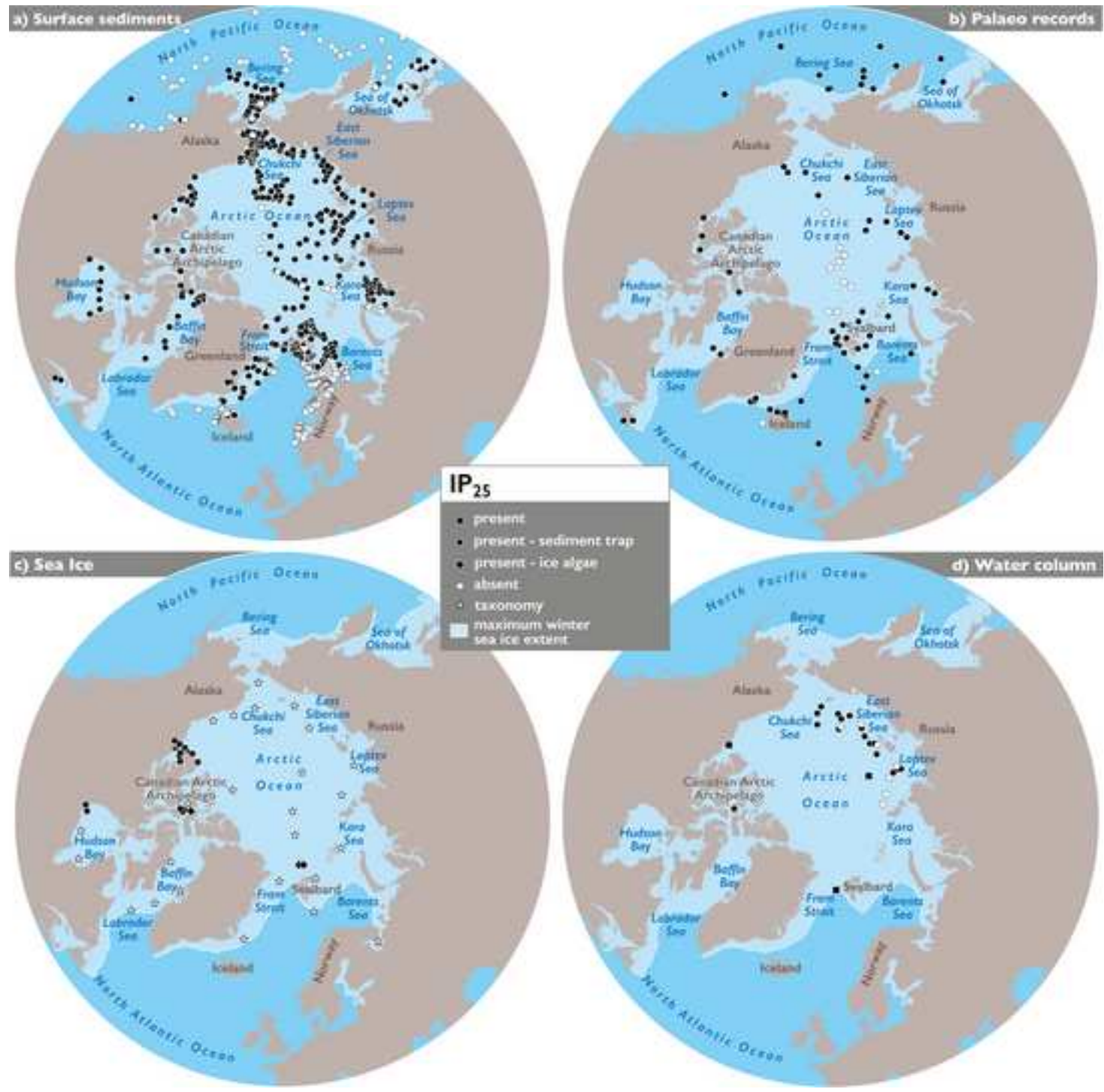
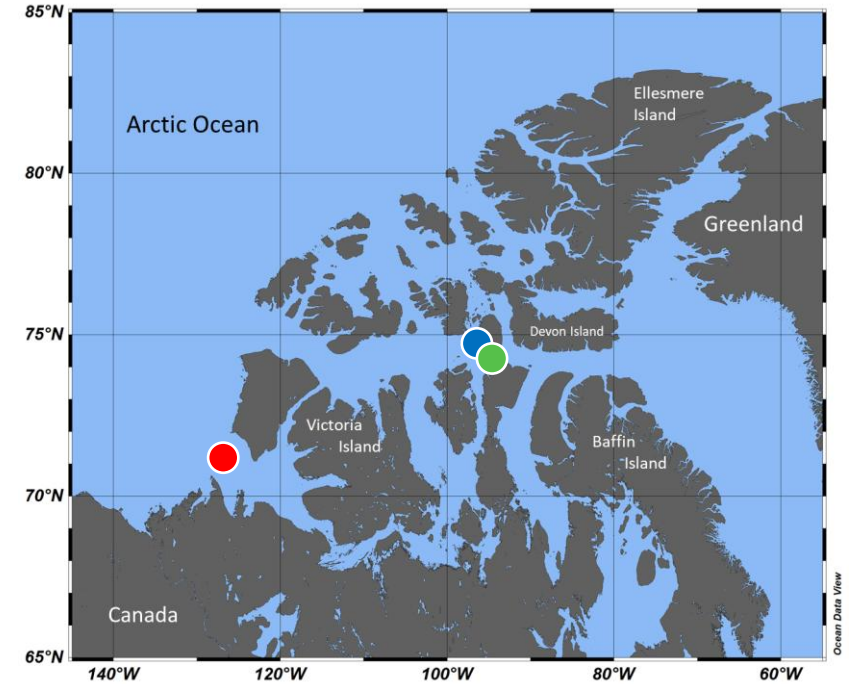
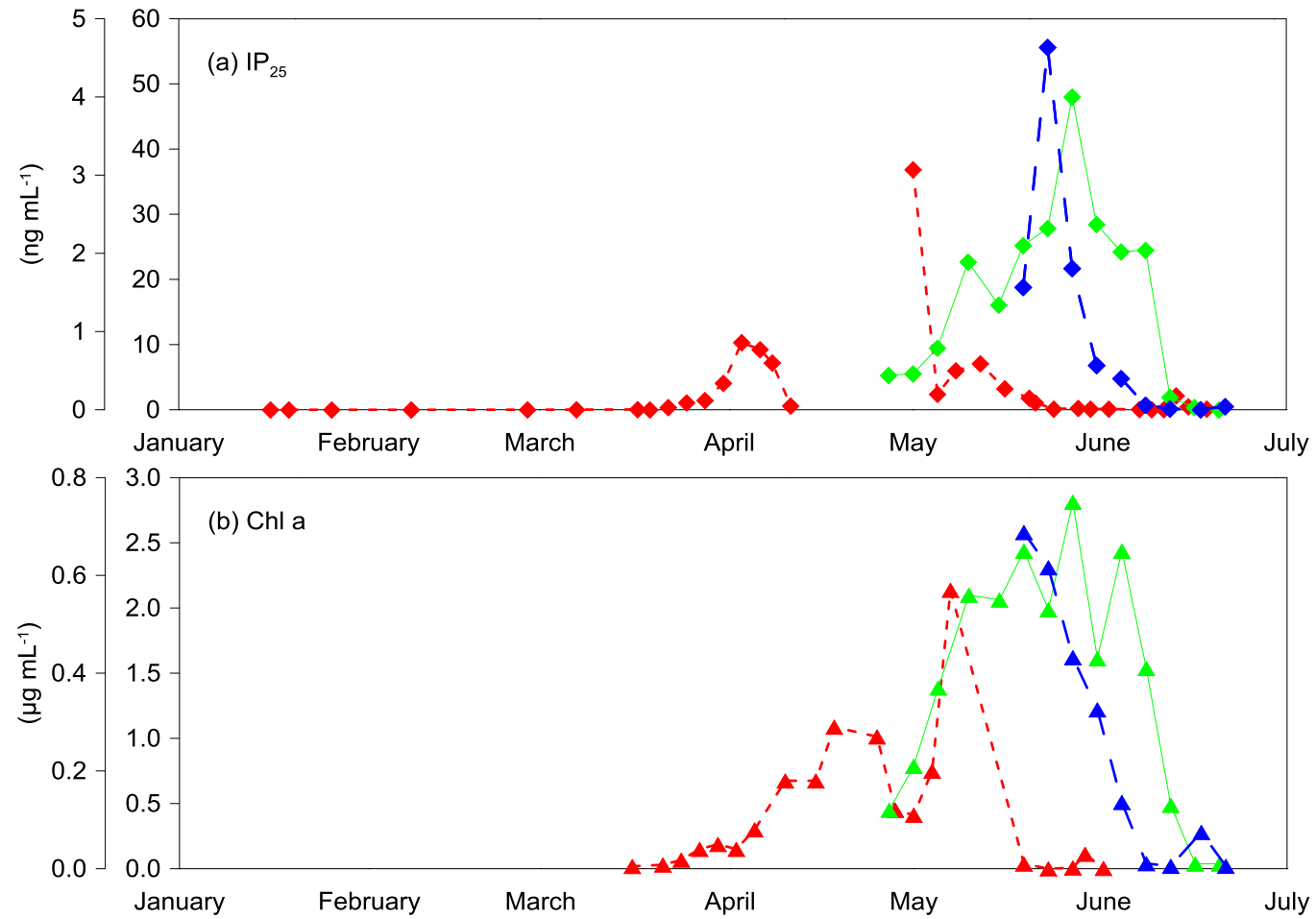


Figure
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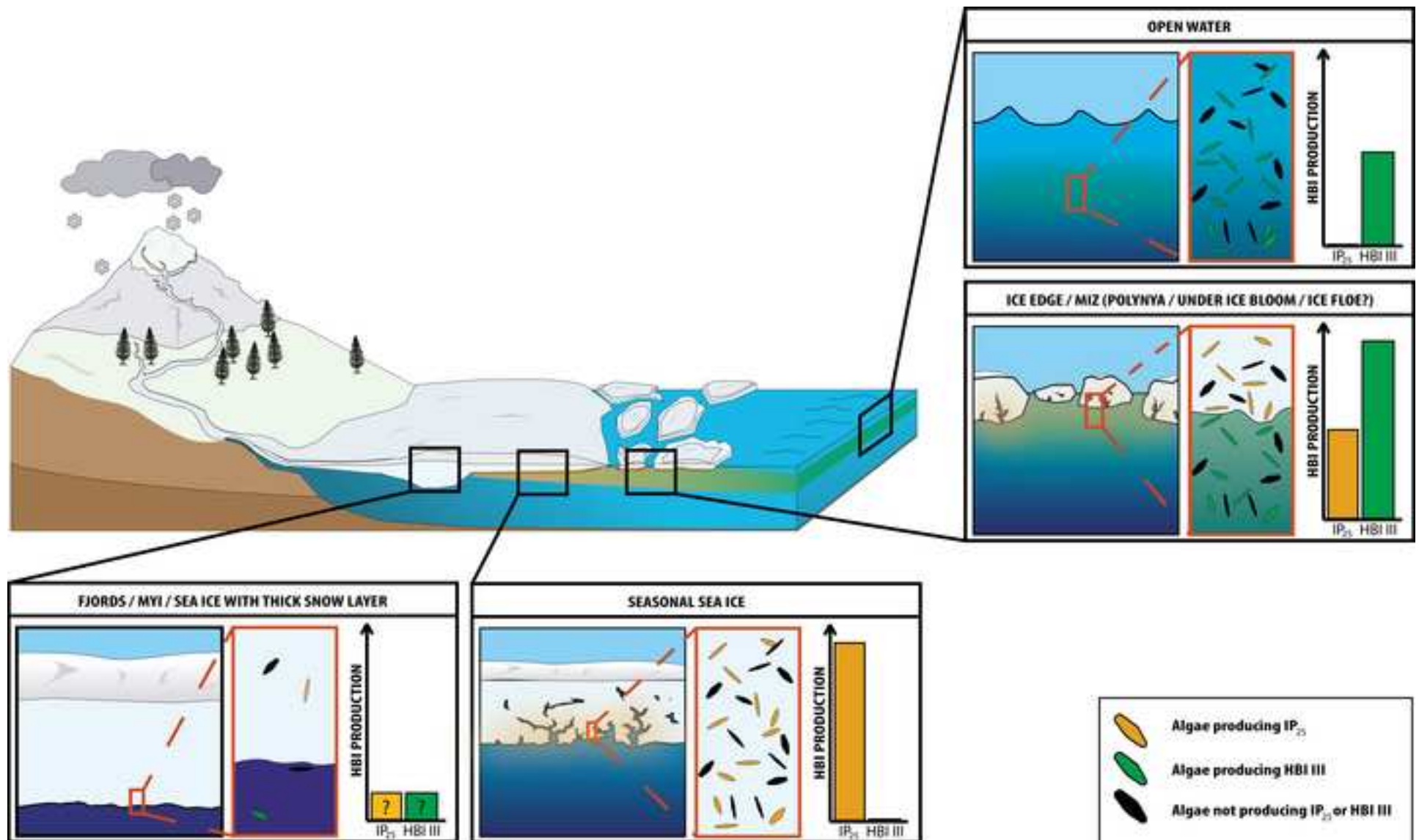
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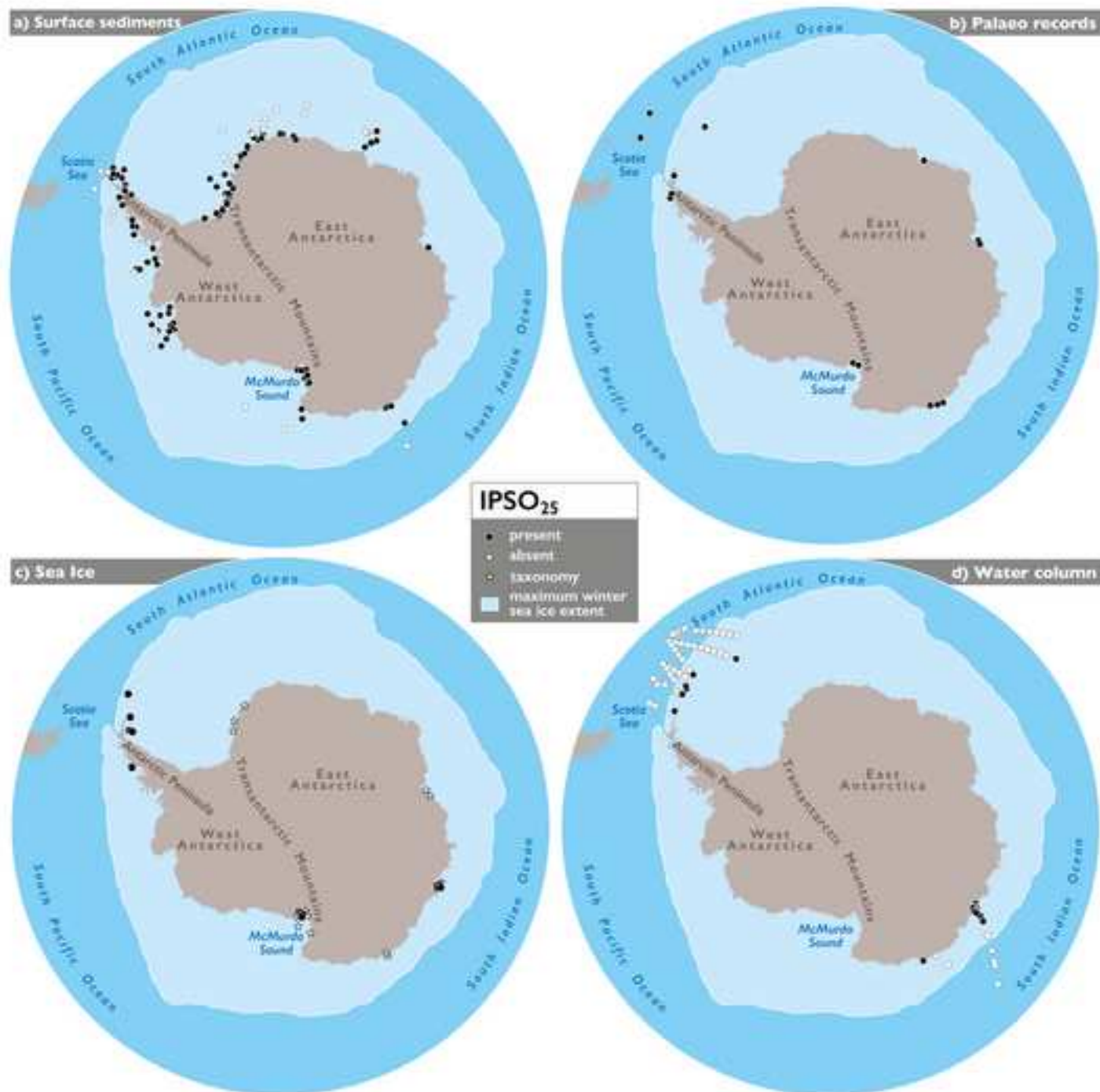
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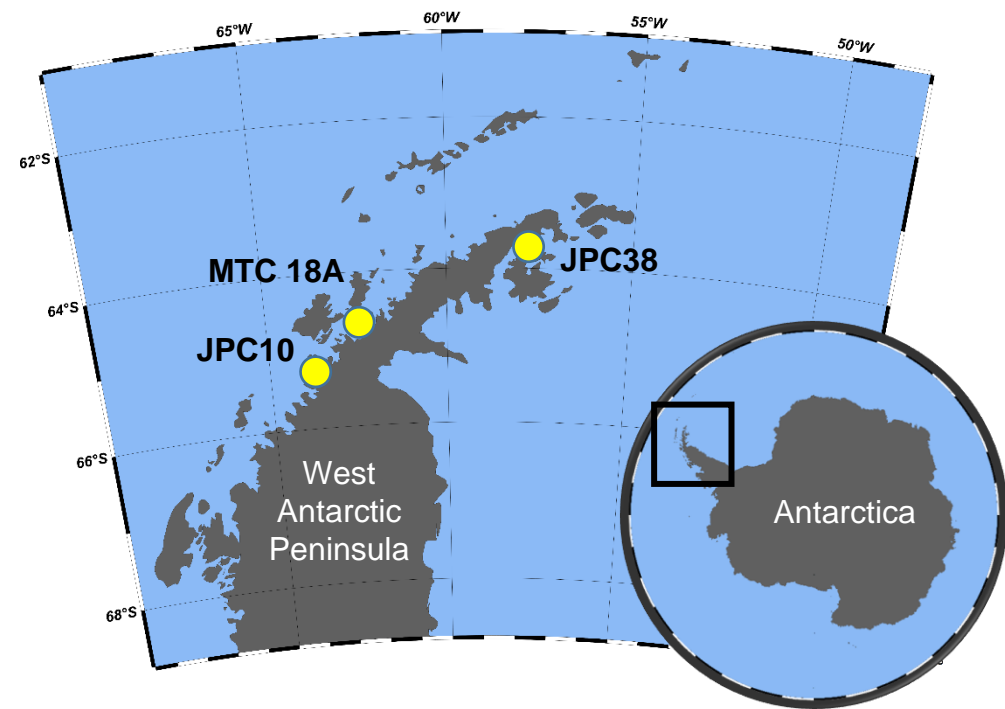
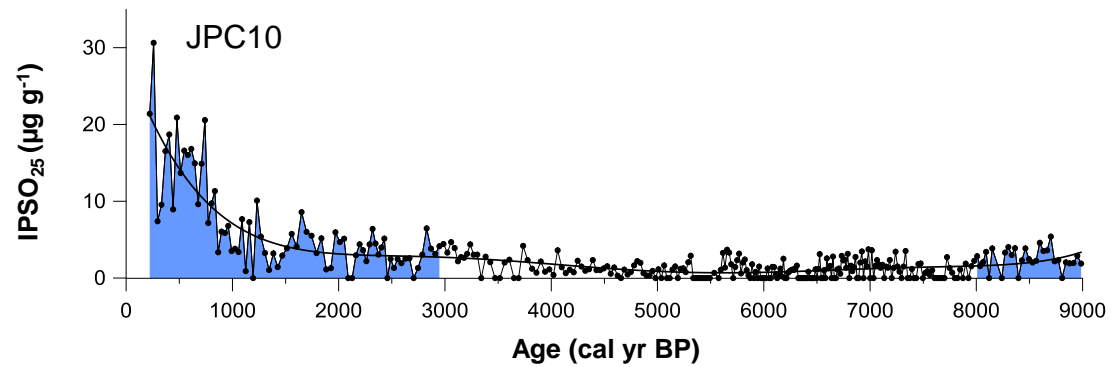
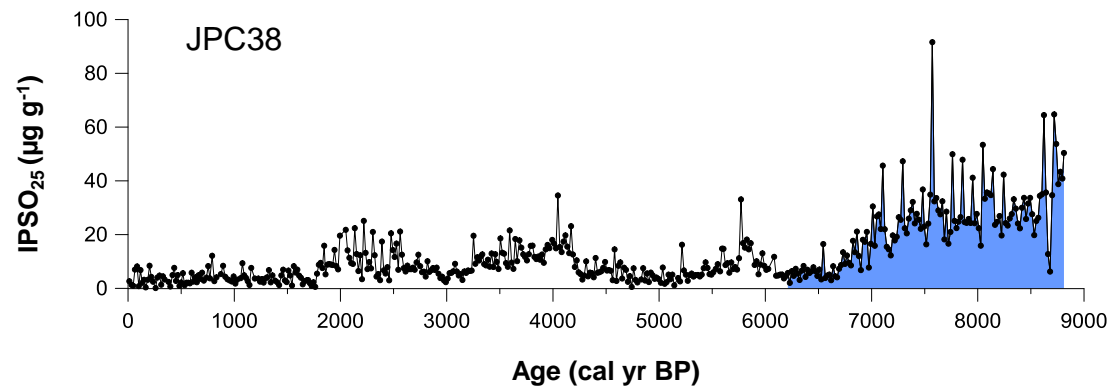
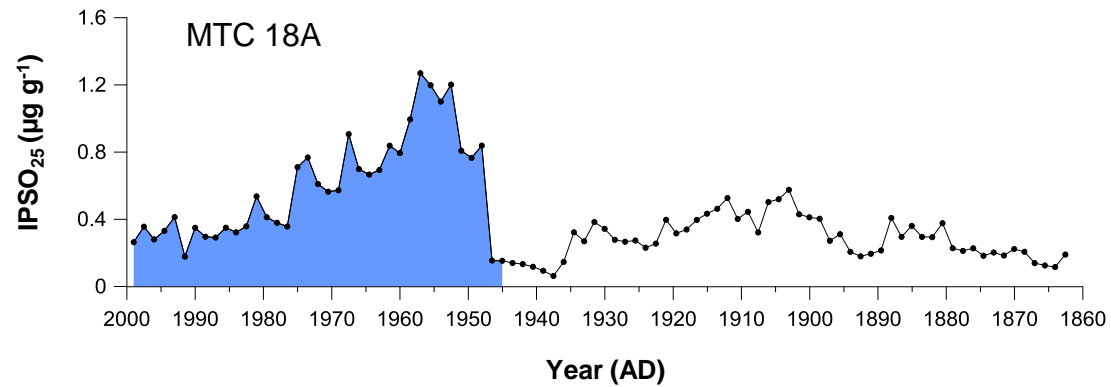


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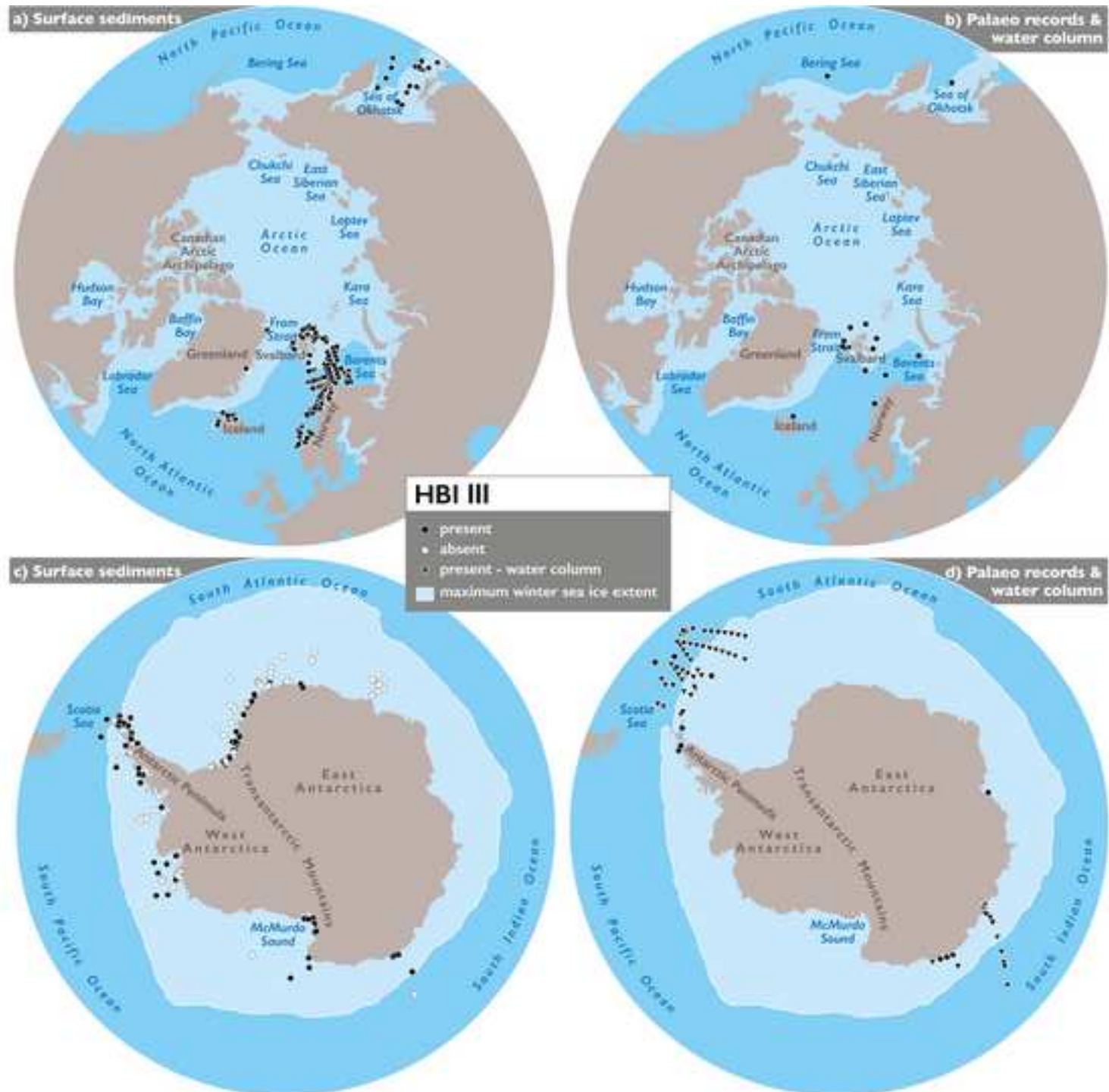
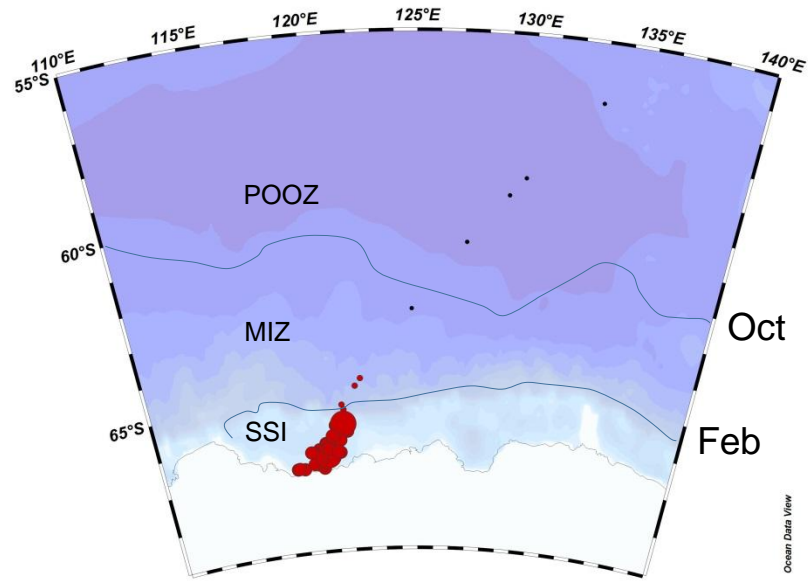


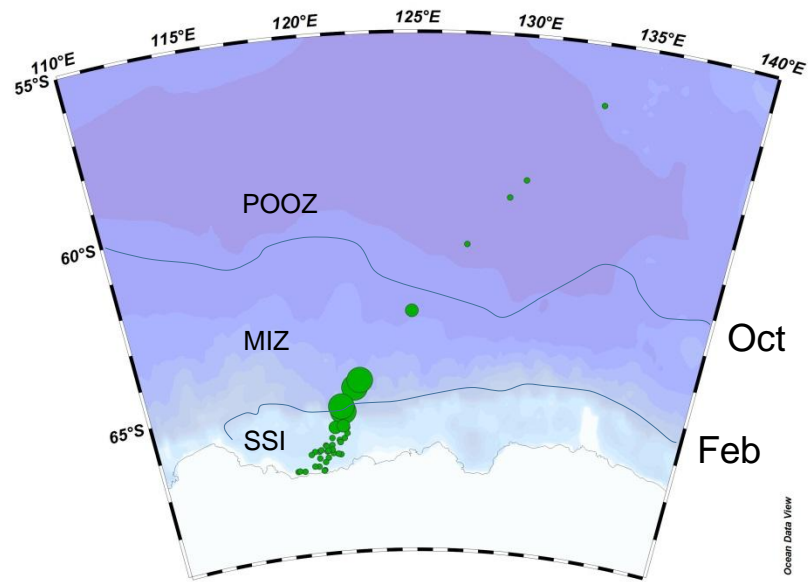
Figure
Fig. 8

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IPSO₂₅

| | |
|------|--------|
| POOZ | Absent |
| MIZ | Low |
| SSI | High |



HBI III

| | |
|------|--------|
| POOZ | Low |
| MIZ | High |
| SSI | Medium |

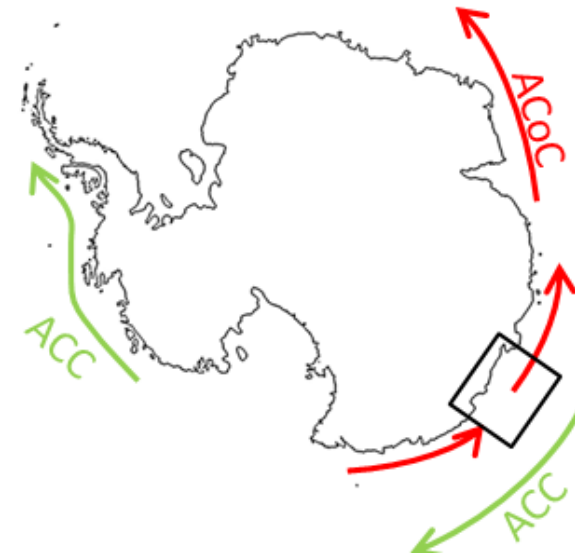


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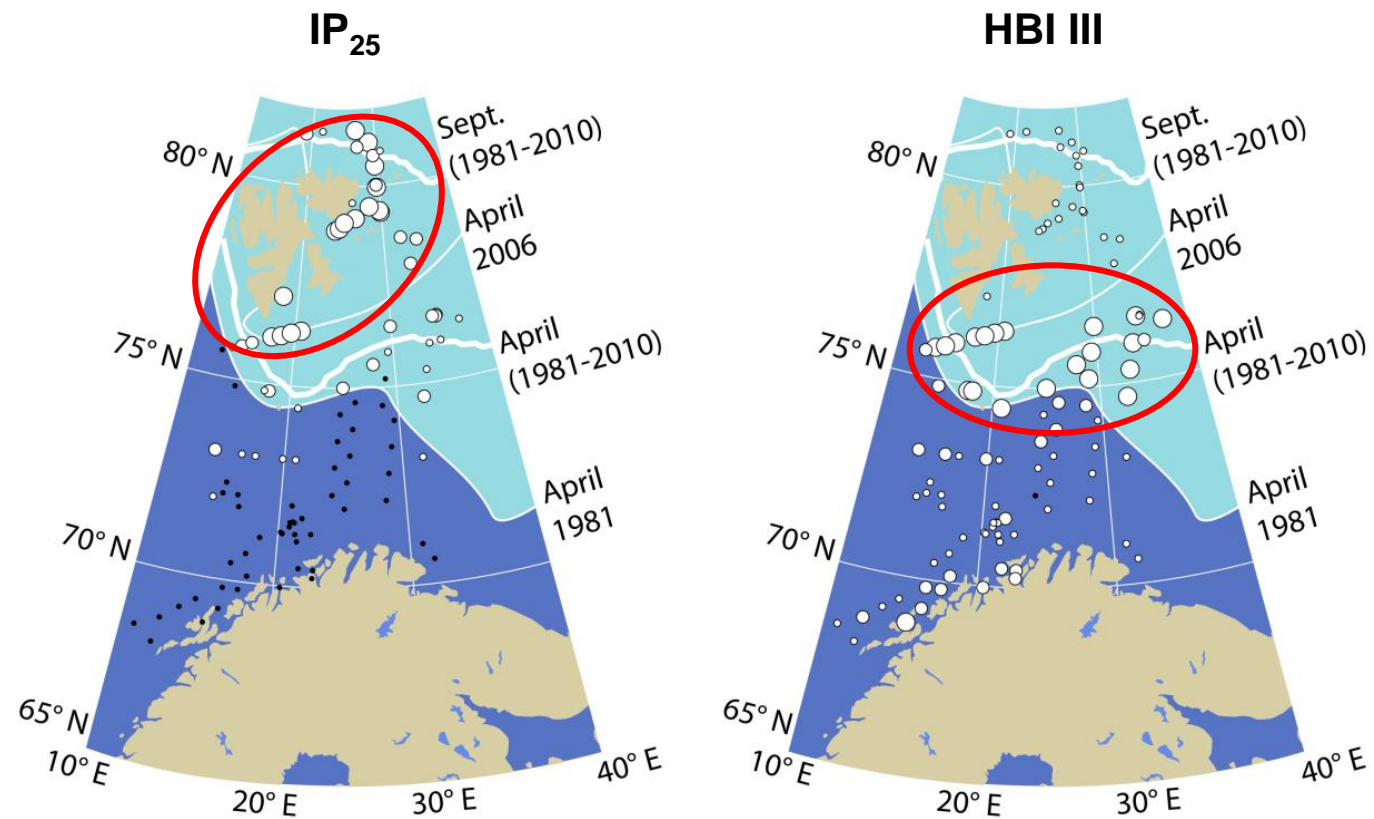


Figure 10

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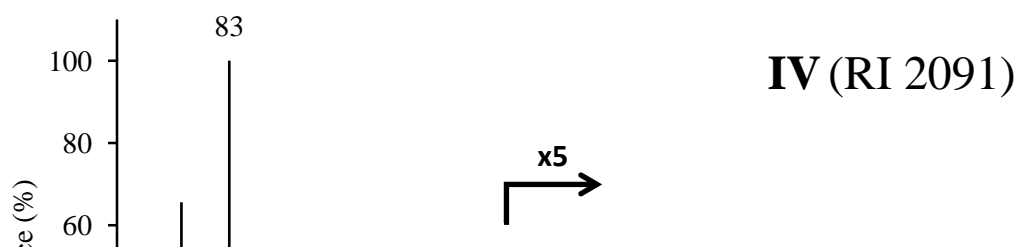
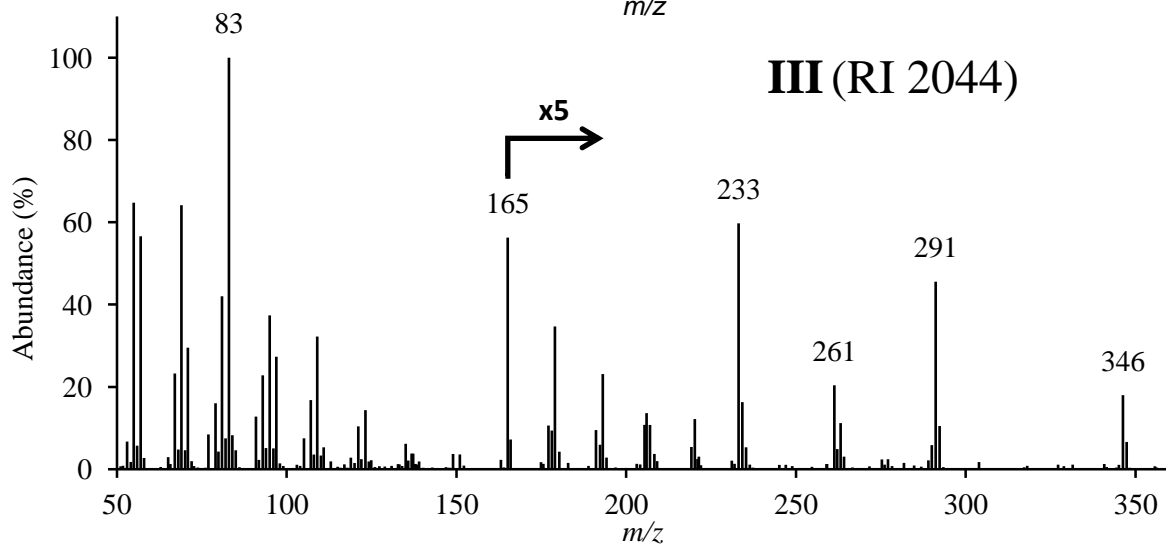
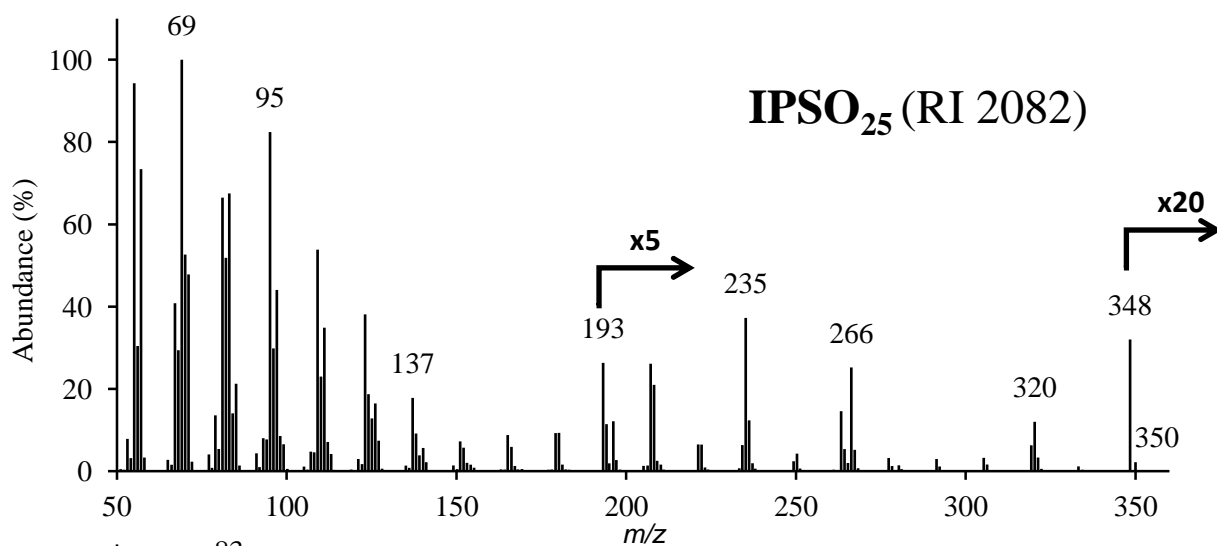
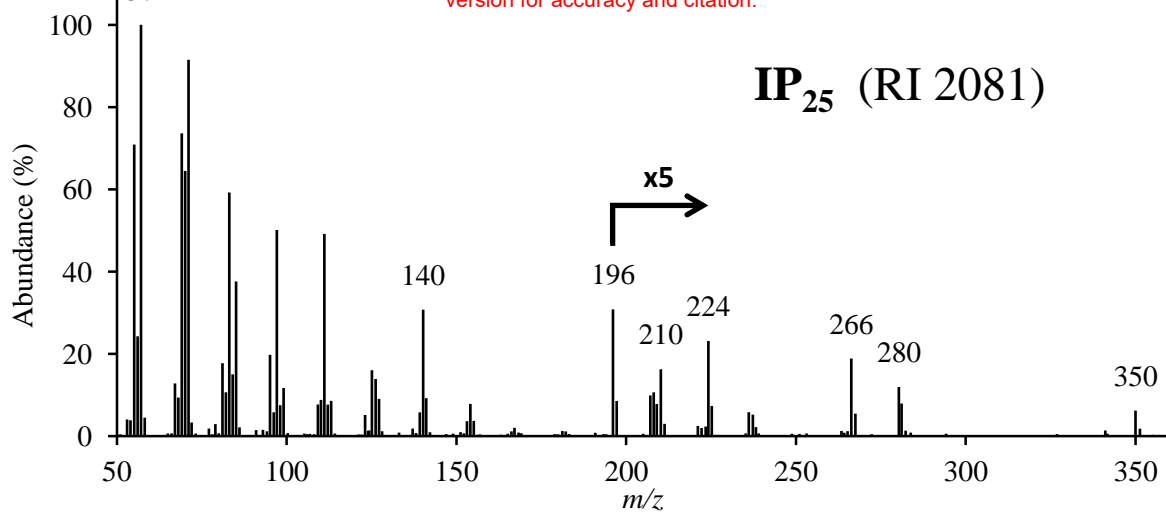
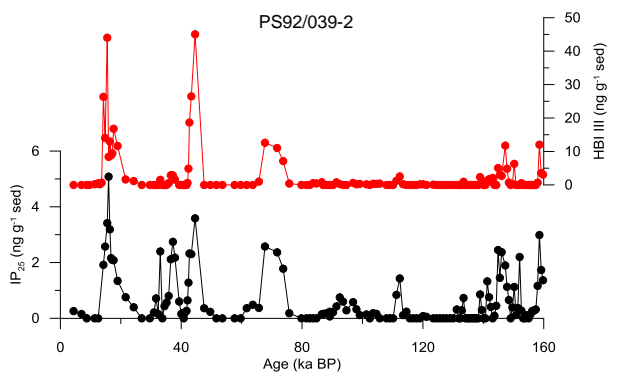
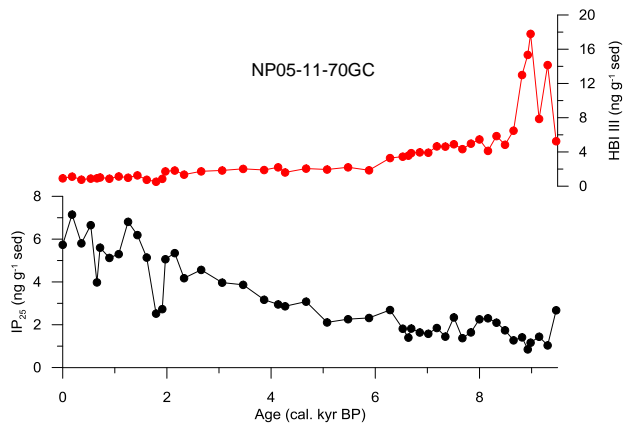
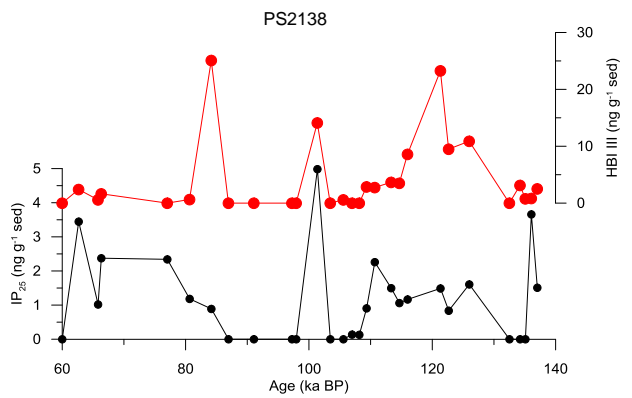
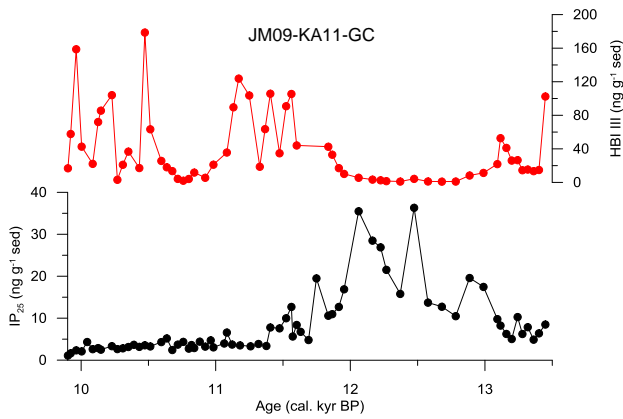
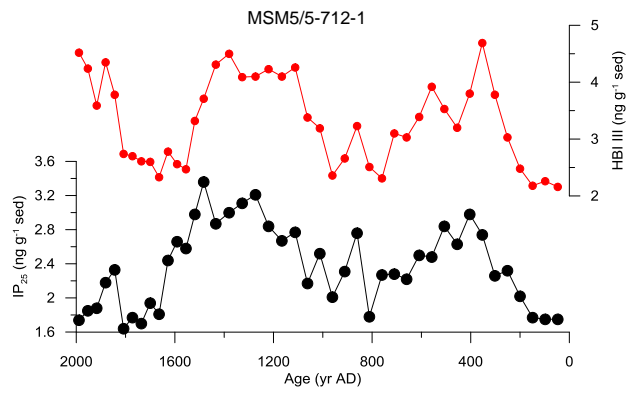
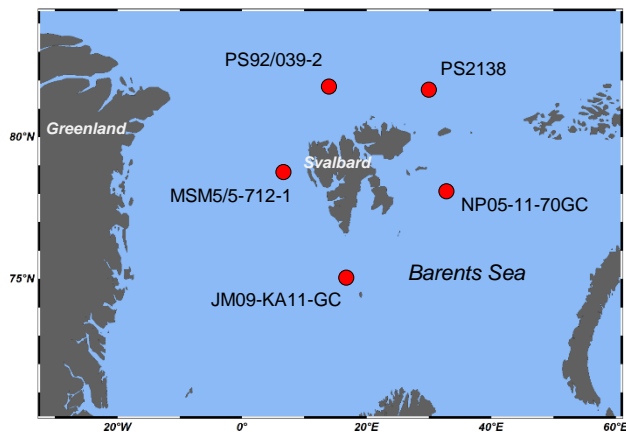


Fig. 11

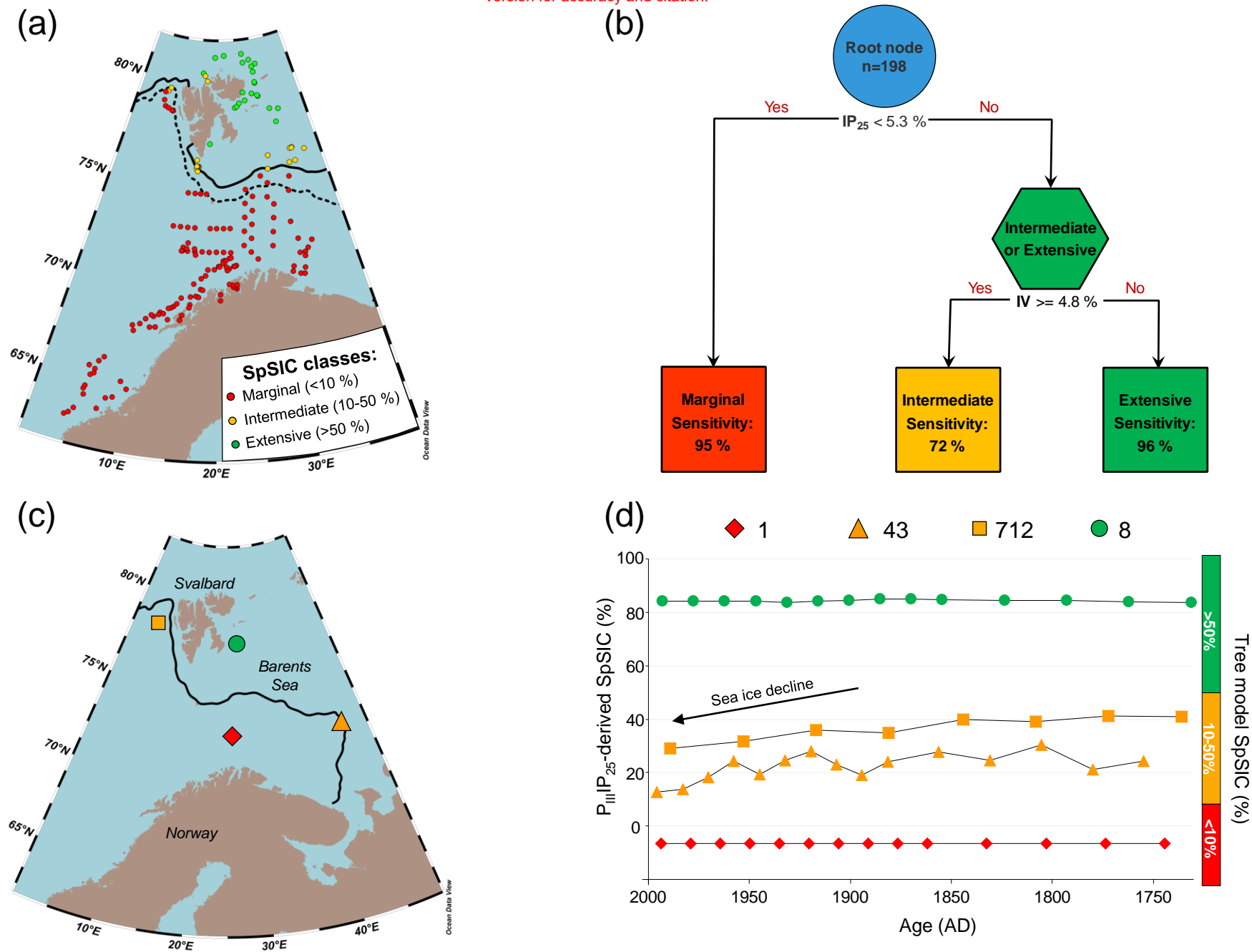


(a) Out-of-phase

(b) In-phase

Figure 12

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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) |
|-----------------------------|--|---|--|
| Arctic | | | |
| Arctic Ocean | Sediment traps | IP ₂₅ (sterols)–seasonal deposition | Fahl and Stein, 2012 |
| Kara/Laptev Seas | Surface sediments | IP ₂₅ (PIP ₂₅)–sea ice calibration | Xiao et al., 2015a |
| | 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 |
| Barents Sea | Surface sediments | IP ₂₅ (PIP ₂₅)-sea ice calibration | Müller et al., 2011 |
| | | 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 |
| Norway | Surface sediments | IP ₂₅ (PIP ₂₅)–sea ice calibration | Navarro-Rodriguez et al., 2013 |
| Iceland | Surface sediments | CT model development | Köseoğlu et al., 2018b |
| | Sediment core | IP ₂₅ (HBI III)–sea ice comparison | Cabedo-Sanz et al., 2016a |
| NE/E Greenland | Surface sediments | IP ₂₅ -historical sea ice comparison | Massé et al., 2008 |
| | | HBI-sea ice comparison | Ribeiro et al., 2017 Limoges et al., 2018 |
| SW Labrador Sea | Sediment cores | IP ₂₅ (PIP ₂₅)–sea ice calibration | Müller et al., 2011 |
| | | 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 | Stoynova 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 Brown et al., 2011 |
| | Sea ice algae | IP ₂₅ (HBI) degradation | Rontani et al., 2014a |
| | | IP ₂₅ source identification | Brown et al., 2014c |
| | | IP ₂₅ and HBI II isotopes ($\delta^{13}\text{C}$) | Belt et al., 2008 |
| Water column POM | IP ₂₅ transfer following ice melt | Brown et al., 2016 | |

| Study region | Sample(s) | Study type | Reference(s) |
|--------------------------------|--|---|--|
| | Surface sediments | IP ₂₅ (HBI) degradation/reactivity IP ₂₅ distribution | Rontani et al., 2016 Belt et al., 2007,2013 Tolosa et al., 2013 Pieńkowski et al., 2017 |
| Hudson Bay | Sea ice Surface sediments | IP ₂₅ identification IP ₂₅ (PIP ₂₅)–sea ice calibration IP ₂₅ identification | Belt et al., 2007 Stoynova et al., 2013 Belt et al., 2007 |
| Bering Sea/Gulf of Alaska | Surface sediments | IP ₂₅ –sea ice calibration IP ₂₅ (PIP ₂₅)–sea ice calibration IP ₂₅ (sterols) distribution | Sharko, 2010 Stoynova et al., 2013 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 Surface sediments | IP ₂₅ distribution IP ₂₅ –sea ice calibration IP ₂₅ (PIP ₂₅)–sea ice calibration | Tesi et al., 2017 Sharko, 2010 Stoynova et al., 2013 Xiao et al., 2015a |
| Antarctica | | | |
| Antarctic Peninsula | Sea ice | Sterol identification IPSO ₂₅ source identification HBI II (IPSO ₂₅) identification | Belt et al., 2018 Belt et al., 2016 Massé et al., 2011 |
| McMurdo Sound | Sea ice | HBI II (IPSO ₂₅) identification | Nichols et al., 1988,1989,1993 Johns et al., 1999 |
| E Antarctica | Sea ice Phytoplankton | HBI II (IPSO ₂₅) identification HBI II (IPSO ₂₅) & HBI III distributions* | Massé et al., 2011 Smik et al., 2016a Massé et al., 2011 |
| South Atlantic (sub-Antarctic) | Surface sediments/short cores Sediment core | HBI II (IPSO ₂₅) & HBI III distributions* HBI II (IPSO ₂₅) reactivity* | Massé et al., 2011 Sinninghe Damsté et al., 2007 |
| Scotia Sea | Phytoplankton Water column | Source identification (HBI III) IPSO ₂₅ and HBI III distributions | Belt et al., 2017 Schmidt et al., 2018 |
| Various locations | Sediment cores Surface sediments | IPSO ₂₅ and HBI III distributions IPSO ₂₅ and HBI III distributions | Collins et al., 2013 Belt et al., 2016 Smik, 2016 |
| Other | Sediments | Analytical method for IP ₂₅ Inter-laboratory study of IP ₂₅ (HBIs) | Belt et al., 2012b Belt et al., 2014 |

| Study region | Sample(s) | Study type | Reference(s) |
|--------------|--------------------|---|--|
| | Sediments/extracts | Confirmed structure - sedimentary IP ₂₅ IP ₂₅ (HBI) degradation/reactivity | Belt et al., 2012a 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 ₂₅ , HBI II, sterol | Stein and Fahl, 2012 | |
| | PS2446-4* | MIS 3-1 | IP ₂₅ , sterol | Xiao et al., 2015b | |
| | PS2138-2 | MIS 6-5 | IP ₂₅ , HBI III, sterol, PIP ₂₅ | Stein et al., 2017a | |
| | PS87/106 | Late Miocene | IP ₂₅ , sterol, PIP ₂₅ | Stein et al., 2016 | |
| Kara Sea | BP00-07/7 | Holocene (last 8 ka) | IP ₂₅ , sterol, PIP ₂₅ | Hörner et al., 2017 | |
| | BP00-36/4* | Last 12 ka | IP ₂₅ , sterol, PIP ₂₅ | Hörner et al., 2018 | |
| Laptev Sea | PS2458-4 | Last 16 ka | IP ₂₅ , HBI II, sterol, PIP ₂₅ | Fahl and Stein, 2012 | |
| Yermak Plateau-Fram Strait | PS51/154-11* | Last 17 ka | IP ₂₅ , HBI II, sterol, PIP ₂₅ | Hörner et al., 2016 | |
| | 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 | |
| Barents Sea | PS93/006-1 | Last 190 ka | IP ₂₅ , sterol, PIP ₂₅ | Kremer et al., 2018a | |
| | BASICC 1* | Recent centuries | IP ₂₅ , HBIs II–VI, PIP ₂₅ | Köseoğlu et al., 2018b | |
| | JM10-10GC | Mid-late Holocene (last 6.5 ka) | IP ₂₅ | Vare et al., 2010 | |
| | NP05-11-70GC | Holocene (last 10 ka) | IP ₂₅ , sterol | Knies et al., 2016 | |
| N Norway | JM09-KA11-GC | Holocene (last 12 ka) | IP ₂₅ , HBI III, sterol, PIP ₂₅ | Berben et al., 2017 | |
| | | YD-Holocene (last 13 ka) | IP ₂₅ , HBIs II–VI, PIP ₂₅ | Köseoğlu et al., 2018a | |
| | JM99-1200 | LGM (ca. 30-16 ka) | IP ₂₅ , sterol | Berben et al., 2014 | |
| | | YD-early Holocene (13-7 ka) | IP ₂₅ , HBI III, sterol, PIP ₂₅ | Belt et al., 2015 | |
| | SE Norwegian Sea | JM11-FI-19PC | | IP ₂₅ , HBIs II–VI, PIP ₂₅ | Köseoğlu et al., 2018a |
| | | | | IP ₂₅ , HBI II, sterol, PIP ₂₅ | Knies et al., 2018 |
| Iceland Sea | ODP 907 | Pliocene (3.5–2.4 Ma) | IP ₂₅ , HBI III, sterol, PIP ₂₅ | Belt et al., 2015 | |
| SW/NE/N Iceland | MD99-2275 | | IP ₂₅ , HBI II, sterol, PIP ₂₅ | Cabedo-Sanz et al., 2013 | |
| | | | IP ₂₅ , sterol, PIP ₂₅ | Köseoğlu et al., 2018a | |
| | | Recent millenia | IP ₂₅ , sterol | Hoff et al., 2016 | |
| | | | IP ₂₅ | Clotten et al., 2018 | |
| | | | | Massé et al., 2008 | |

| Study region | Core | Timeframe | Biomarkers | Reference(s) |
|-----------------------------|------------------------|--|---|---|
| E Greenland | MD99-2263 | Holocene (last 8 ka) Last 15 ka Ca. 16-12 ka BP Recent centuries Mid-late Holocene (last 5 ka) Holocene (last 8-9 ka) | IP ₂₅ | Axford et al., 2011 |
| | MD99-2273 | | IP ₂₅ | Andrews et al., 2009 |
| | MD99-2269* | | IP ₂₅ | Sicre et al., 2013 |
| | MD99-2272 | | IP ₂₅ , HBI III | Cabedo-Sanz et al., 2016a |
| | B997-326PC1* | | IP ₂₅ , HBI III, sterol, PIP ₂₅ | Xiao et al., 2017 |
| | PO175GKC#7* | | IP ₂₅ , HBI II | Andrews et al., 2018 |
| | PS2641-4 | | IP ₂₅ , HBI II, sterol | Alonso-García et al., 2013 |
| | MD99-2322 | | IP ₂₅ , sterol, PIP ₂₅ | Kolling et al., 2017 |
| | PS2641-4 | | IP ₂₅ | Darby et al., 2017 |
| | W Greenland | | HU2008029-12PC | Ca. 17-12 ka BP Ca. 26-12 ka BP Last 2.2 ka |
| SW Labrador Sea | A107-04BC* | Recent centuries | IP ₂₅ , HBI III, sterol, PIP ₂₅ IP ₂₅ , sterol, PIP ₂₅ | Kolling et al., 2018 Weckström et al., 2013 |
| Baffin Bay | A107-14G | YD-early Holocene (ca. 13-10 ka) | IP ₂₅ | Pearce et al., 2013,2014 |
| Canadian Arctic Archipelago | 2008-029-040BC | Recent centuries | IP ₂₅ , sterol, PIP ₂₅ | Cormier et al., 2016 |
| | 99LSSL-001 | Recent centuries | IP ₂₅ , sterol, PIP ₂₅ | Pieńkowski et al., 2016 |
| Bering Sea | 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 |
| | 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 |
| Sea of Okhotsk | 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 |
| | 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 |
| 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 (IPSO ₂₅), 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 |
