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1 An assessment of biomarker-based multivariate classification methods versus the PIP<sub>25</sub> index  
2 for paleo Arctic sea ice reconstruction

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4 Denizcan Köseoğlu<sup>a</sup>, Simon T Belt<sup>a\*</sup>, Katrine Husum<sup>b</sup>, Jochen Knies<sup>c,d</sup>

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6 <sup>a</sup> Biogeochemistry Research Centre, School of Geography, Earth and Environmental  
7 Sciences, Plymouth University, Plymouth, PL4 8AA, UK.

8 <sup>b</sup> Norwegian Polar Institute, Fram Centre, NO-9296 Tromsø, Norway.

9 <sup>c</sup> CAGE – Centre for Arctic Gas Hydrate, Environment and Climate, Department of  
10 Geosciences, UiT The Arctic University of Norway, 9037 Tromsø, Norway.

11 <sup>d</sup> Geological Survey of Norway, N-7491 Trondheim, Norway.

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15 \*Author for correspondence

16 E-mail: sbelt@plymouth.ac.uk

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19 Keywords: Arctic; Sea ice; HBI; Biomarker; Classification Tree; IP<sub>25</sub>; PIP<sub>25</sub>; Barents Sea

## 20 **Abstract**

21 The development of various combinative methods for Arctic sea ice reconstruction using the  
22 sympagic highly-branched isoprenoid (HBI) IP<sub>25</sub> in conjunction with pelagic biomarkers has  
23 often facilitated more detailed descriptions of sea ice conditions than using IP<sub>25</sub> alone. Here,  
24 we investigated the application of the Phytoplankton-IP<sub>25</sub> index (PIP<sub>25</sub>) and a recently  
25 proposed Classification Tree (CT) model for describing temporal shifts in sea ice conditions  
26 to assess the consistency of both methods. Based on biomarker data from three downcore  
27 records from the Barents Sea spanning millennial timescales, we showcase apparent and  
28 potential limitations of both approaches, and provide recommendations for their identification  
29 or prevention. Both methods provided generally consistent outcomes and, within the studied  
30 cores, captured abrupt shifts in sea ice regimes, such as those evident during the Younger  
31 Dryas, as well as more gradual trends in sea ice conditions during the Holocene. The most  
32 significant discrepancies occurred during periods of highly unstable climate change, such as  
33 those characteristic of the Younger Dryas–Holocene transition. Such intervals of increased  
34 discrepancy were identifiable by significant changes of HBI distributions and correlations to  
35 values not observed in proximal surface sediments. We suggest that periods of highly-  
36 fluctuating climate that are not represented in modern settings may hinder the performance  
37 and complementary application of PIP<sub>25</sub> and CT-based methods, and that data visualisation  
38 techniques should be employed to identify such occurrences in downcore records.  
39 Additionally, due to the reliance of both methods on biomarker distributions, we emphasise  
40 the importance of accurate and consistent biomarker quantification.

## 41 **1. Introduction**

42 Arctic sea ice is a pivotal component of the global ecosystem. The receding sea ice edge  
43 is a site of primary productivity during the spring-summer melt season (e.g., Wassmann et al.,  
44 2006; Vancoppenolle et al., 2013, and references therein), while ice formation facilitates deep  
45 water formation and helps to maintain the global thermohaline circulation (e.g., Bitz et al.,  
46 2006). Additionally, sea ice is an effective reflector of incoming shortwave solar radiation,  
47 thus regulating the oceanic heat budget (e.g., Meier et al., 2014, and references therein) and  
48 the ocean-atmosphere heat exchange (Maykut, 1978). The sensitivity of the melting-freezing  
49 cycle and physical properties of sea ice to the global atmospheric and oceanic circulation of  
50 moisture and heat (e.g., Smedsrud et al., 2013) makes seasonal and interannual variability of  
51 sea ice cover a prime indicator of climate change (Vihma, 2014). The decline of Arctic sea  
52 ice extent and thickness observed via satellite passive microwave sensors since the 1970’s  
53 (Lindsay and Schweiger, 2015; Fetterer et al., 2017) is unprecedented within observational  
54 records covering recent centuries, at least (Divine and Dick, 2006; Walsh et al., 2017).

55 Cumulative thinning and retreat of Arctic sea ice leads to pre-disposition of the ice cover for  
56 accelerated melting via various positive feedback mechanisms (Perovich and Polashenski,  
57 2012), and augments the global temperature increase at high latitudes (Serreze and Barry,  
58 2011). Thus, the Arctic is projected to become ice-free at its September minimum within the  
59 next few decades (Overland and Wang, 2013) due to potentially irreversible loss of ice cover  
60 (e.g., Lindsay and Zhang, 2005; Eisenman and Wettlaufer, 2009), with important  
61 implications for global oceanographic regimes, atmospheric heat circulation (Smedsrud et al.,  
62 2013), mid-latitude weather (Mori et al., 2014), Arctic food webs (Harada, 2016), and human  
63 activities (Meier et al., 2014). The assessment of such implications and accurate prediction of  
64 future trends requires the reconstruction of sea ice cover over geologically significant  
65 timescales (Stroeve et al., 2015).

66 IP<sub>25</sub>, a source-specific highly-branched isoprenoid (HBI) biomarker synthesized by  
67 sympagic diatoms (Brown et al., 2014), has emerged as a relatively direct proxy of seasonal  
68 Arctic sea ice (Belt et al., 2007; Belt and Müller, 2013). Consistent with its source, IP<sub>25</sub> has  
69 been detected throughout the Arctic in surface sediments characterised by seasonal sea ice  
70 cover (Belt et al., 2007, 2015; Navarro-Rodriguez et al., 2013; Stoyanova et al., 2013;  
71 Weckström et al., 2013; Xiao et al., 2013, 2015a; Ribeiro et al., 2017), and is mostly absent  
72 in ice-free settings (Müller et al., 2012; Méheust et al., 2013). Additionally, IP<sub>25</sub> appears to be  
73 relatively stable within sedimentary records for millions of years (Stein and Fahl, 2013; Knies  
74 et al., 2014; Stein et al., 2016). Combined, the seasonal sea ice selectivity, source-specificity  
75 and stability have facilitated the use of IP<sub>25</sub> for palaeo-sea ice reconstructions throughout the  
76 Arctic spanning a range of timescales (e.g., Andrews et al., 2009; Müller et al., 2009, 2012;  
77 Vare et al., 2010; Stein and Fahl, 2012, 2013; Berben et al., 2014, 2017; Knies et al., 2014,  
78 2017; Müller and Stein, 2014; Belt et al., 2015; Xiao et al., 2015b; Cabedo-Sanz and Belt,  
79 2016; Cabedo-Sanz et al., 2016; Hoff et al., 2016; Stein et al., 2016; Bartels et al., 2017).  
80 However, while relative changes in IP<sub>25</sub> concentration are generally consistent with  
81 corresponding shifts in sea ice conditions (Massé et al., 2008; Andrews et al., 2009; Vare et  
82 al., 2010; Axford et al., 2011), the considerable differences between absolute sedimentary  
83 IP<sub>25</sub> concentration ranges for locations experiencing similar sea ice conditions (Stoyanova et  
84 al., 2013; Xiao et al., 2015b) limits comparison of sea ice variability for different Arctic  
85 regions.

86 To help provide more detailed and regionally comparable descriptions of sea ice  
87 conditions, Müller et al. (2011) first introduced the Phytoplankton-IP<sub>25</sub> index (PIP<sub>25</sub>; Eq. 1),  
88 based on IP<sub>25</sub> abundance relative to that of open-water biomarkers produced by marine  
89 phytoplankton, such as brassicasterol and dinosterol (Volkman, 1986, 2006). Thus, a  
90 normalised uniform scale (0–1) removed the influence of absolute concentrations, allowing

91 more consistent comparisons of sea ice conditions between Arctic regions, while a  
92 concentration balance factor (i.e.  $c$ -factor) compensated for different concentration ranges  
93 commonly observed for IP<sub>25</sub> and sterols (Müller et al., 2011; Cabedo-Sanz and Belt, 2016). In  
94 practice, correlation of sterol-based PIP<sub>25</sub> indices and overlying sea ice concentrations yielded  
95 variable results for different Arctic regions (Müller et al., 2011; Navarro-Rodriguez et al.,  
96 2013; Xiao et al., 2015b), partially attributed to the lower source specificity of sterols, which  
97 are produced ubiquitously by a variety of marine, terrigenous (Yunker et al., 2005; Rampen  
98 et al., 2010), and even ice-obligate sources (Belt et al., 2013, 2018). Moreover, the value of  
99 the  $c$ -factor greatly affected PIP<sub>25</sub> estimates in downcore records due to large and variable  
100 differences in IP<sub>25</sub> and sterol concentration ranges in different core sections representing  
101 periods of abrupt shifts between contrasting climate conditions (Belt and Müller, 2013;  
102 Berben et al., 2014; Cabedo-Sanz and Belt, 2016). More recently, substitution of sterols with  
103 a source-specific tri-unsaturated HBI biomarker (hereafter referred to as HBI III (Z); Fig. 1)  
104 derived from some pelagic *Pleurosigma* and *Rhizosolenia* spp. (Belt et al., 2000, 2017;  
105 Rowland et al., 2001) has significantly reduced the influence of the  $c$ -factor, in some cases  
106 (e.g., Belt et al., 2015; Cabedo-Sanz and Belt, 2016), as a result of comparable concentration  
107 ranges of IP<sub>25</sub> and HBI III (Z). A regional calibration of P<sub>III</sub>IP<sub>25</sub> (i.e. PIP<sub>25</sub> using HBI III (Z)  
108 as the pelagic biomarker) versus satellite-derived spring sea ice concentration (%SpSIC)  
109 allowed calculation of semi-quantitative SpSIC estimates in the Barents Sea and the western  
110 Svalbard margin (Eq. 2; Cabedo-Sanz and Belt, 2016; Smik et al., 2016; Berben et al., 2017).  
111 Nonetheless, the magnitude of the  $c$ -factor, which relies on average biomarker concentrations  
112 throughout a dataset when a regional P<sub>III</sub>IP<sub>25</sub>–SpSIC calibration is not available (Müller et al.,  
113 2011), could still potentially introduce bias to P<sub>III</sub>IP<sub>25</sub>-derived SpSIC estimates. Further, the  
114 objective choice of a suitable pelagic counterpart to the sympagic IP<sub>25</sub> remains a challenge,  
115 and is made more difficult by the inherent limitation of the PIP<sub>25</sub> index to one such

116 biomarker. To address these challenges, Köseoğlu et al. (2018) recently constructed a  
117 multivariate classification tree (CT) model (Breiman et al., 1984) using percentage  
118 abundances of a group of HBI biomarkers (Fig. 1) in surface sediments encompassing the full  
119 range of sea ice variability in the Barents Sea. Each surface sediment was classified into  
120 marginal (<10 % satellite SpSIC), intermediate (10–50 % SpSIC) or extensive (>50 %  
121 SpSIC) class of sea ice conditions (Fig. 2). The CT model was subsequently used to  
122 reconstruct classes of sea ice conditions throughout recent centuries in four short sediment  
123 cores collected from Barents Sea sites experiencing variable modern sea ice cover (Vare et  
124 al., 2010). For these cores, the CT class predictions were consistent with P<sub>III</sub>IP<sub>25</sub>-derived  
125 semi-quantitative SpSIC estimates and, perhaps more importantly, the observational record of  
126 sea ice cover (Divine and Dick, 2006; Walsh et al., 2017). The CT method offered automatic  
127 selection of HBI biomarkers that achieved the highest classification rate, quantitative model  
128 evaluation via performance metrics, and independence from the *c*-factor. Thus, the CT model  
129 was ca.  $92 \pm 6$  % accurate using IP<sub>25</sub> and a further tri-unsaturated HBI (hereafter HBI III (E);  
130 Fig. 1) as primary descriptive variables representing ice algal and pelagic productivity,  
131 respectively. HBIs II and III (Z) were utilised as surrogate variables, probably due to their  
132 high correlation to IP<sub>25</sub> and HBI III (E), respectively.

133 Despite this development, CT models require further evaluation before their wider  
134 applicability as a statistical tool for classification of sea ice conditions can be established.  
135 Specifically, the agreement of model-derived categorical assessment of sea ice conditions and  
136 PIP<sub>25</sub>-derived semi-quantitative SpSIC estimates in sediment cores needs to be determined  
137 across longer timescales encompassing major changes in sea ice dynamics, such as those  
138 occurring during the Younger Dryas–Holocene transition (e.g., Ślubowska et al., 2005;  
139 Rasmussen et al., 2007; Cabedo-Sanz et al., 2013; Kristensen et al., 2013) and the Holocene  
140 cooling (e.g., Duplessy et al., 2001, 2005; Risebrobakken et al., 2010, 2011). Potential error

141 sources that could impact the accuracy and applicability of both methods also require  
142 discussion, such as the possibility of differential degradation of HBIs based on their variable  
143 degree of unsaturation (Rontani et al., 2014a, 2018a). To achieve this, in the current study we  
144 assessed the agreement of P<sub>III</sub>IP<sub>25</sub>-based SpSIC estimates (Smik et al., 2016) and CT model  
145 predictions (Köseoğlu et al., 2018) in three marine sediment cores located at sites of  
146 contrasting contemporary sea ice conditions in the Barents Sea (Fig. 2) and spanning periods  
147 of both abrupt and gradual climate shifts throughout the last ca. 16 cal kyr BP. The core sites  
148 were chosen based on the availability of previous climatological reconstructions (Cabedo-  
149 Sanz et al., 2013; Berben et al., 2014, 2017), a comprehensive suite of HBI concentrations  
150 (Belt et al., 2015), and surface sediment-based regional calibrations for both P<sub>III</sub>IP<sub>25</sub> and CT  
151 approaches (Smik et al., 2016; Köseoğlu et al., 2018). This allowed us to readily identify the  
152 causes of discrepancies between the two methods and provide recommendations regarding  
153 their complementary application to downcore records.

154

## 155 **2. Regional setting**

156 The Barents Sea is a seasonally ice-covered shelf area of the Arctic Continental Shelf,  
157 which experiences extensive seasonal sea ice cover in winter (October–March) and remains  
158 almost entirely ice-free in September following the insolation-induced summer melt (May–  
159 August; Sakshaug et al., 2009). It is also characterised by phytoplankton blooms occurring in  
160 the highly-productive Marginal Ice Zone (MIZ) along the receding sea ice edge (e.g.,  
161 Wassmann et al., 1999). The steep salinity and temperature gradients created through mixing  
162 of Atlantic Water (AW) and Arctic Water (ArW) mark the position of the Polar Front (PF)  
163 and define the winter maximum sea ice extent. The PF position is relatively stable in the  
164 western and central Barents Sea (Loeng and Drinkwater, 2007), but becomes more variable to  
165 the east where it is characterised by separate temperature and salinity gradients (Oziel et al.,

166 2016). Most of the inter-annual sea ice variability occurs in winter and is largely dictated by  
167 the volume and temperature of inflowing AW (e.g., Loeng et al., 1997; Smedsrud et al.,  
168 2010). While most of the Atlantic-derived heat energy is lost to the atmosphere (Smedsrud et  
169 al., 2010, 2013), the volume and temperature of AW inflow have been increasing due to  
170 forcing from atmospheric circulation modes, such as the North Atlantic Oscillation (e.g.,  
171 Loeng et al., 1997; Vinje, 2001; Ingvaldsen et al., 2004; Sorteberg and Kvingedal, 2006), and  
172 further amplification via positive feedback mechanisms, including the ice-albedo feedback  
173 (Smedsrud et al., 2013). Strengthening of AW inflow has been linked to the diminishing sea  
174 ice extent and increasing temperature of the Barents Sea, and continued ‘Atlantification’ of  
175 the region could influence its capacity to limit heat flux to the central Arctic Ocean and  
176 hinder sequestration of atmospheric CO<sub>2</sub> by halting deep water formation (Screen and  
177 Simmonds, 2010; Årthun et al., 2012).

178

### 179 **3. Materials and methods**

#### 180 *3.1 Sediment material*

181 Three sediment cores from sites characterised by different modern sea ice conditions in  
182 the Barents Sea were selected for this study. Specific descriptions of all core locations and  
183 chronologies are available elsewhere (Ebbesen and Hald, 2004; R  ther et al., 2012; Berben et  
184 al., 2014, 2017; Belt et al., 2015). Core NP05-11-70GC (78.67°N, 32.70°E; 293 m water  
185 depth), hereafter referred to as core 70, was collected from the Olga Basin to the South of  
186 Kong Karls Land (East Svalbard) aboard the *RV Lance* in August of 2005. Core chronology  
187 is based on three calibrated <sup>14</sup>C Accelerated Mass Spectrometry (AMS) dates from mixed  
188 foraminifera (Berben et al., 2017). Concentrations of IP<sub>25</sub> and HBI III (Z) (Fig. 1), P<sub>III</sub>IP<sub>25</sub>  
189 indices, and associated semi-quantitative SpSIC estimates of core 70 for the last ca. 9.4 cal  
190 kyr BP were presented previously (Belt et al., 2015; Berben et al., 2017). Core JM09-KA11-

191 GC (74.87°N, 16.48°E; 345 m water depth), hereafter referred to as core 11, was obtained  
192 from the Kveithola Trough (South off Svalbard) aboard *RV Jan Mayen* in 2009. We use the  
193 age model spanning ca. 16 cal kyr BP presented in Belt et al. (2015) and based on merged <sup>14</sup>C  
194 AMS dates from previous studies (Rüther et al., 2012; Berben et al., 2014).  
195 Micropaleontological distributions, stable isotope analyses (Dylmer et al., 2013; Groot et al.,  
196 2014), IP<sub>25</sub> and HBI III (Z) concentrations (and P<sub>III</sub>IP<sub>25</sub> values) were presented previously for  
197 core 11 (Belt et al., 2015), but not SpSIC estimates. Piston core JM99-1200 (69.27°N,  
198 16.42°E; 475 m water depth), hereafter referred to as core 1200, was retrieved from  
199 Andfjorden (northern Norway) aboard the *RV Jan Mayen* in November 1999. Herein, we  
200 used the age model of Cabedo-Sanz et al. (2013) corresponding to ca. 14.0–7.0 cal kyr BP  
201 (Bølling-Allerød to middle Holocene). Concentrations of IP<sub>25</sub> and HBI III (Z) and P<sub>III</sub>IP<sub>25</sub>  
202 values (but not P<sub>III</sub>IP<sub>25</sub>-derived SpSICs) of core 1200 were reported previously (Cabedo-Sanz  
203 et al., 2013; Belt et al., 2015), in addition to sedimentological, isotopic and  
204 micropaleontological analyses (Knies et al., 2003; Ebbesen and Hald, 2004). The CT model  
205 outputs for cores 70, 11 and 1200 are presented here for the first time.

206

### 207 *3.2 Proxy and statistical methods*

208 Modern SpSIC (April-June average for the 1988–2007 period) for each core site was  
209 inferred from the Nimbus-7 SMMR and DMSP SSM/I-SSMIS satellite dataset (Cavalieri et  
210 al., 1996) used for PIP<sub>25</sub> and CT model calibrations (Xiao et al., 2015a; Smik et al., 2016;  
211 Köseoğlu et al., 2018). Previously published concentrations of IP<sub>25</sub> and HBI III (Z) for cores  
212 1200 (Cabedo-Sanz et al., 2013) and 11 (Belt et al., 2015) were re-examined to calculate  
213 P<sub>III</sub>IP<sub>25</sub> indices (Eq. 1; Müller et al., 2011) and derive SpSIC estimates (Eq. 2) using the  
214 regional *c*-factor (*c* = 0.63) and P<sub>III</sub>IP<sub>25</sub>–SpSIC calibration of Smik et al. (2016), respectively.  
215 Additionally, a threshold P<sub>III</sub>IP<sub>25</sub> value of 0.8, corresponding to a SpSIC of 68% (Eq. 2), was

216 used to indicate the occurrence of at least some (>5%) sea ice cover during the summer  
217 months (July–September; Smik et al., 2016). Absolute concentrations (ng/g dry sed.) are  
218 denoted by square brackets in all equations.

$$P_{III}IP_{25} = \frac{[IP_{25}]}{([IP_{25}] + [HBI III (Z)] \times 0.63)} \#(\text{Eqn. 1})$$

$$SpSIC (\%) = \frac{(P_{III}IP_{25} - 0.0692)}{0.0107} \#(\text{Eqn. 2})$$

219 Previously obtained chromatographic and mass spectrometric (MS) data were re-  
220 examined to quantify additional HBI lipids (viz. HBIs II and III (E)) required to obtain CT  
221 model predictions of sea ice conditions following the method of Köseoğlu et al. (2018).  
222 Briefly, percentage abundances of IP<sub>25</sub> and HBIs II, III (Z) and III (E) (Fig. 1) to their totals  
223 were calculated for each core horizon from absolute concentrations (ng/g dry sed.) using Eq.  
224 3.

$$HBI (\%) = \frac{[HBI]}{\sum([IP_{25}], [HBI II], [HBI III (Z)], [HBI III (E)])} \times 100 \#(\text{Eqn. 3})$$

225 Subsequently, the CT model constructed from a Barents Sea surface sediment dataset via  
226 the R Statistical Package (R Core Team, 2017) was used to classify each core horizon into  
227 one of three classes representing marginal (<10% satellite SpSIC), intermediate (10–50%  
228 SpSIC), and extensive (>50% SpSIC) spring sea ice conditions. The performance metrics of  
229 the CT model used for classification of core horizons are shown in Supplementary Table S1  
230 (Köseoğlu et al., 2018). Biomarker concentrations, P<sub>III</sub>IP<sub>25</sub>-derived SpSIC and CT model  
231 outcomes for all cores are available at <https://doi.pangaea.de/10.1594/PANGAEA.891102>.

232 Additional statistical analyses were carried out to supplement the comparison of CT and  
233 P<sub>III</sub>IP<sub>25</sub>-based sea ice assessments. Thus, Pearson’s correlations for IP<sub>25</sub> versus HBI II and  
234 HBI III (Z) versus HBI III (E) were calculated from surface sediment data (Fig. 2; Köseoğlu  
235 et al., 2018). The biomarker pairings for correlation were chosen due to previous evidence of  
236 co-production of sympagic IP<sub>25</sub> and HBI II (Navarro-Rodriguez et al., 2013; Brown et al.,

237 2014, Belt et al., 2016), pelagic HBIs III (Z) and III (E) (Belt et al., 2000; Rowland et al.,  
238 2001), as well as significant correlation of these biomarker pairs in the Barents Sea and other  
239 Arctic regions (Navarro-Rodriguez et al., 2013; Navarro-Rodriguez, 2014). Thus, the  
240 product-moment correlation coefficient was used as a measure of correlation to distinguish  
241 between negative and positive linear relationships and identify periods of anomalously  
242 deteriorated correlations in downcore records compared to those characteristic of relatively  
243 modern settings represented by surface sediments. Further, rolling Pearson’s correlations  
244 were calculated for all downcore records using a sampling window of nine, corresponding to  
245 a time window of between ca. 0.5–2.0 cal kyr BP. All correlation and CT model analyses  
246 were incorporated into functions within the R statistical package (R Core Team, 2017). The  
247 source code and supporting materials are available at  
248 <https://doi.org/10.5281/zenodo.1346305>.

249

#### 250 **4. Results and Discussion**

251 The applicability of multivariate CT models and  $P_{III}IP_{25}$ -based semi-quantitative SpSIC  
252 estimates (Eq. 1 and 2) as complementary methods for sea ice reconstruction spanning both  
253 abrupt and gradual climate shifts of the Younger Dryas and Holocene (ca. last 13.0 cal kyr  
254 BP) was assessed by comparing the results of both approaches in cores 11, 70 and 1200 (Figs.  
255 3–6). The assessment of consistency between the two methods was contextualised further by  
256 considering findings of previous studies (e.g., Belt et al., 2015).

257

##### 258 *4.1 Core 70 (northern Barents Sea)*

259 The core 70 site is characterised by extensive modern sea ice conditions ( $\approx 80\%$   
260 SpSIC) and the downcore record represents a gradual evolution of sea ice cover in the

261 northern Barents Sea from ice-free conditions during the early Holocene to prolonged  
262 seasonal sea ice presence prevalent in the region today. The primarily insolation-controlled  
263 southward expansion of sea ice cover previously inferred for the core site throughout the  
264 Holocene (Belt et al., 2015; Berben et al., 2017) is reflected in the CT model assessment (Fig.  
265 3). Consistent with the onset of the Holocene Thermal Maximum and the resulting proximity  
266 of the annual maximum sea ice edge to the core site between ca. 9.5–8.5 cal kyr BP evident  
267 from low  $P_{III}IP_{25}$ -derived SpSIC (ca. 5–15%), the CT model predicts mostly marginal sea ice  
268 conditions during this interval. Similarly, the southward migration of sea ice beginning ca.  
269 8.5 cal kyr BP as a response to decreasing summer insolation (Berben et al., 2017) is also  
270 reflected by a switch of CT model assessment from marginal to intermediate sea ice  
271 conditions. Finally, following a period of consistent intermediate ice conditions (ca.  $30 \pm 4 \%$   
272 SpSIC), a further southward migration of the ice edge between ca. 6.5–5.9 cal kyr BP,  
273 previously attributed to further decreasing solar insolation and reduced AW influence  
274 (Berben et al., 2017), is reflected by an associated shift of CT model predictions from  
275 intermediate to extensive sea ice conditions at ca. 6.0 cal kyr BP. This trend agrees with  
276 previous reports of Neoglaciation in the Barents Sea, a period characterised by glacier  
277 advances and increased sea ice export via the Fram Strait when modern-type oceanic  
278 circulation was re-established (Werner et al., 2013, 2016; Rasmussen and Thomsen, 2015).

279 Overall, the timing of CT prediction shifts was consistent with previously inferred  
280 climate evolution at the core 70 site (Berben et al., 2017), and no discrepancies from semi-  
281 quantitative SpSIC estimates were observed (Fig. 3), with all horizons consistently classified  
282 within the satellite SpSIC boundaries defined in the CT model training set (Fig. 2). Our data  
283 supports the complementary application of both approaches when describing gradual changes  
284 in sea ice conditions at millennial timescales, where CT predictions have the potential to  
285 identify the timing of switches between distinct sea ice conditions, as hypothesized

286 previously (Köseoğlu et al., 2018). However, we note that the CT model is limited by the  
287 class boundaries assigned to the training set (Fig. 2), which may result in insufficiently  
288 detailed assessment of changing sea ice conditions. In this case, a distinct ice expansion ca.  
289 2.7 cal kyr BP (SpSIC values of <80%; Fig. 3b) previously linked to insolation decreases  
290 (Berben et al., 2017) was not identified by the CT model since the 50–100% SpSIC range is  
291 only represented by a single class within the training set (Fig. 2). Such limitations of the  
292 training set, in this case driven by reduced sample density around Svalbard, should be  
293 considered when interpreting model output. The otherwise high agreement with the  $P_{III}IP_{25}$   
294 approach is potentially attributable, at least in part, to significantly similar HBI distributions  
295 and data structure between the surface sediment training set and core 70. Like most  
296 supervised classification methods, CTs rely on distributional similarity of predictive variables  
297 (e.g., HBI percentages) between the training set and new samples to be classified. Thus, in  
298 our study, the model is only likely to function correctly when the overall relative abundance  
299 ranges and relationships between HBIs observed in the surface sediment training set (Fig. 2)  
300 are reproduced in downcore records. This is the case for core 70, where consistently  
301 significant positive correlations are observed for  $IP_{25}$  versus HBI II and HBI III (Z) versus  
302 HBI III (E) biomarker pairs (Fig. 3c), also evident in surface sediments with different  
303 overlying SpSIC (Fig. 7) used to build the CT model. Relative HBI abundances (Eq. 3) are  
304 also comparable and generally dominated by sympagic biomarkers in both datasets (Fig. 8);  
305 although we stress that inherent HBI variability in surface sediments and core 70 prevent any  
306 detailed interpretation of spatially and temporally averaged values. Nonetheless, such  
307 visualisations of data ranges and structure help inform the expected CT performance for a  
308 given dataset and suggest that the model is likely to perform well for core 70.

309

310 *4.2 Core 1200 (southwestern Barents Sea)*

311 In contrast to contemporary ice-free conditions that characterise the core 1200 site, harsh  
312 glacial conditions with short ice-free summers during the majority of the Younger Dryas cold  
313 stadial spanning ca.13.0–11.9 cal kyr BP were previously inferred (Cabedo-Sanz et al., 2013;  
314 Belt et al., 2015). Accordingly, our records show elevated  $P_{III}IP_{25}$ -derived SpSIC values  
315 (>75%) accompanied by CT model predictions of extensive sea ice conditions during this  
316 period (Fig. 4b–c). Subsequently, ameliorated conditions are evident during the Younger  
317 Dryas–Holocene transition, with precipitous decrease of SpSIC estimates (to ca. 10–40%)  
318 and a switch of CT model assessment from extensive to marginal (<10% SpSIC) sea ice  
319 conditions. In core 1200, the ice retreat is characterised by rapid fluctuations of SpSIC  
320 estimates, consistent with switching of CT model assessment between intermediate and  
321 marginal classification of sea ice cover during the 11.9–11.5 cal kyr BP period, which is  
322 followed by ice-free conditions for the remainder of the record (Fig. 4b). Similar unstable  
323 conditions, likely attributable to the return of thermohaline circulation during this period  
324 (e.g., Bakke et al., 2009), were previously inferred for core 1200 from  $PIP_{25}$  records (Cabedo-  
325 Sanz et al., 2013; Belt et al., 2015), as well as sea surface temperature (SST) and sea surface  
326 salinity (SSS) reconstructions based on stable isotope measurements of planktic foraminifera  
327 (Ebbesen and Hald, 2004).

328 The apparent consistency of CT predictions and  $P_{III}IP_{25}$ -derived SpSIC in core 1200  
329 suggests that both methods respond similarly to extremes of sea ice conditions observed both  
330 during (ca. 13.0–12.0 cal kyr BP) and after (11.5 cal kyr BP onwards) the Younger Dryas  
331 stadial. However, while the CT model also detected rapid fluctuations of sea ice cover during  
332 the climatically unstable YD–Holocene transition (11.9–11.5 cal kyr BP), several horizons (n  
333 = 7) were classified outside of the categorical sea ice boundaries based on satellite SpSIC  
334 thresholds (Fig. 2 and 3b). Nonetheless, such discrepancies with the  $P_{III}IP_{25}$ -based SpSIC  
335 record were always within the RMSE of the regional  $P_{III}IP_{25}$ –SpSIC calibration (ca.  $\pm 11\%$

336 SpSIC; Smik et al., 2016), and are potentially attributable to various error sources associated  
337 with  $P_{III}IP_{25}$ -based SpSIC estimates and CT models. For example, the dependence of  $P_{III}IP_{25}$   
338 values on the  $c$ -factor may significantly influence the regional comparability of the resulting  
339 SpSIC estimates. While the general trends of  $P_{III}IP_{25}$ -derived SpSIC were previously shown  
340 to be unaffected by the magnitude of the  $c$ -factor (Belt et al., 2015; Smik et al., 2016),  $P_{III}IP_{25}$   
341 values (and associated SpSIC estimates; Eq. 1 and 2) may vary by ca. 10% when omitting the  
342  $c$ -factor ( $c = 1$ ; Smik et al., 2016). Further, the  $c$ -factor used in the current study ( $c = 0.63$ ;  
343 Eq. 1) was calculated based on average  $IP_{25}$  and HBI III (Z) concentrations from a wide range  
344 of Barents Sea locations characterised by different sea ice conditions (Smik et al., 2016).  
345 Thus, the regional applicability of a spatially averaged  $c$ -factor remains a challenge, and the  
346 same value may not provide fully comparable SpSIC estimates for all downcore locations in  
347 our study. In contrast, the CT approach is based on a multivariate set of HBI biomarkers, is  
348 therefore independent of the  $c$ -factor, and probably provides results that are more comparable  
349 between locations within the geographical coverage of the surface sediment dataset used for  
350 model training (Köseoğlu et al., 2018). Together, these caveats imply that the interpretation  
351 of  $P_{III}IP_{25}$ -derived SpSIC variability and any discrepancies with CT model predictions within  
352 the associated RMSE ( $\pm 11\%$  SpSIC) should be avoided, and broader changes beyond this  
353 error range should instead be considered. Additionally, unlike core 70, the data structure in  
354 core 1200 is significantly unstable during rapid climate fluctuations, with correlations  
355 degrading to near-zero values (Fig. 4c). This potentially hinders CT performance due to  
356 unpredictable data structure differences with the surface sediment training set. The CT model  
357 was previously shown to lose performance (with a ca. 20% misclassification error;  
358 Supplementary Table S1) in areas characterised by highly variable sea ice and primary  
359 productivity regimes, such as the MIZ of western Svalbard and the central Barents Sea. The  
360 period of high misclassification spanning 11.9–11.5 cal kyr BP in core 1200 was

361 characterised by the return of enhanced biogenic production (Knies, 2005), fluctuating AW  
362 inflow, and similarly variable sea ice conditions resulting from meltwater and nutrient input  
363 from waning ice sheets (Cabedo-Sanz et al., 2013). It is possible that CT performance  
364 suffered during this interval of significantly unstable sea ice cover and primary productivity  
365 regimes, of which the latter could potentially have contributed to degraded correlations  
366 observed in our record (Fig. 4c) due to inconsistent, variable HBI production. Overall, our  
367 results suggest that CT predictions potentially become more prone to misclassification, and  
368 therefore less consistent with semi-quantitative SpSIC estimates, in rapidly shifting climate  
369 conditions observed during stadial-interstadial transitions. Finally, misclassification errors  
370 may also be associated with information loss due to insufficient representation of the SpSIC  
371 range (0–100%) in the CT model. Specifically, the surface sediment dataset used for model  
372 construction contains no samples with modern overlying SpSIC of 16–22% and 56–67%  
373 (Köseoğlu et al., 2018), potentially resulting in an incomplete model definition near the  
374 marginal-intermediate (10% satellite SpSIC) and intermediate-extensive (50% satellite  
375 SpSIC) sea ice class boundaries, respectively. Such potential error sources may be mitigated  
376 by expansion of the model training set to increase sample density and include such under-  
377 represented SpSIC ranges. In the meantime, we suggest that shifts in CT model class  
378 predictions should be interpreted as broader changes between sea ice regimes, rather than  
379 between definitive SpSIC threshold values. Thus, the marginal, intermediate, and extensive  
380 sea ice classes included in the model (Fig. 2) likely represent ice-free or proximal maximum  
381 ice edge conditions, the highly-productive MIZ during the spring melt season, and more  
382 northern regions where ice cover persists until ca. August–September (e.g., North-East of  
383 Svalbard), respectively.

384

385 *4.3 Core 11 (western Barents Sea)*

386 The core 11 site in our dataset is presently characterised by marginal SpSIC (<5%)  
387 with a proximal spring sea ice edge (Fig. 2). As seen for core 1200, the site experienced  
388 SpSIC values of ca. 80% during the Younger Dryas (ca. 13.0–12.0 cal kyr BP), but exhibited  
389 a more gradual ice retreat and a step-wise switch of CT model predictions from extensive  
390 towards marginal sea ice conditions during the 12.0–11.5 cal kyr BP period (Fig. 5b). A  
391 period of highly unstable sea ice cover is instead observed between ca. 11.0–10.0 cal kyr BP,  
392 with fluctuating SpSIC estimates (ca. 0–65%) and CT model predictions. This is consistent  
393 with the return of enhanced sub-surface AW inflow to the core site after ca. 11.5 cal kyr BP  
394 inferred from benthic foraminiferal census data (Groot et al., 2014), with a contrastingly  
395 colder surface water layer dominated by ArW inferred from reduced SSTs (Berben et al.,  
396 2014). From ca. 10.0–1.5 cal kyr BP, ice-free conditions characterised the core 11 site, as  
397 evidenced by consistently low SpSIC (ca. <10%) and marginal sea ice conditions predicted  
398 by the CT model, and further supported by an enhancement of AW inflow to the core site  
399 from ca. 9.8 cal kyr BP (Groot et al., 2014). Finally, re-emergence of highly fluctuating sea  
400 ice cover during the last ca. 0.9–0.6 cal kyr BP (Berben et al., 2014; Belt et al., 2015), despite  
401 increasing AW inflow (Dylmer et al., 2013), was also captured by the CT model, which  
402 switches from marginal to intermediate sea ice conditions at this time (Fig. 5b).

403 Consistent with outcomes from core 1200, several horizons ( $n = 20$ ) from core 11  
404 were classified outside of the sea ice class boundaries based on satellite SpSIC thresholds.  
405 Notably, these differences also exceeded the standard RMSE ( $\pm 11\%$  SpSIC) of the regional  
406  $P_{III}IP_{25}$ -SpSIC calibration (Eq. 2; Smik et al., 2016) for four horizons, where marginal sea ice  
407 cover (<10% satellite SpSIC) was inferred for  $P_{III}IP_{25}$ -derived SpSIC values in excess of ca.  
408 40% (Fig. 5b). Most significant misclassification was observed during periods of high  
409 climatic variability (11.5–10.0 and 0.9–0.6 cal kyr BP), consistent with the return of variable  
410 sub-surface AW inflow. As with core 1200, we suggest that this stems from considerably

411 different distributions and data structure of HBIs in the misclassified horizons compared to  
412 those of surface sediments used for model construction, potentially caused by climate  
413 fluctuations during intervals of rapid climate change. Indeed, running correlations between  
414 IP<sub>25</sub> and HBI II severely degrade towards negative  $r$  values during the 11.5–10.0 cal kyr BP  
415 interval and the last 0.7 cal kyr BP (Fig. 5c), thus deviating from the consistently high  
416 positive associations observed in the surface training set (Fig. 7). Indeed, these distributional  
417 changes coincide with CT misclassification beyond the P<sub>III</sub>IP<sub>25</sub>-based SpSIC error of 11% and  
418 are better illustrated when considering individual concentration profiles of IP<sub>25</sub> and HBI II, as  
419 well as rolling correlations of corresponding relative differences (Fig. 6). It is evident that  
420 disproportional increases of HBI II relative to IP<sub>25</sub> contribute to the correlation reduction.  
421 Similar increases in the HBI II/IP<sub>25</sub> ratio were previously observed across the Arctic during  
422 periods of increased warm water inflow from the North Atlantic and North Pacific (e.g., Fahl  
423 and Stein, 2012; Hörner et al., 2016; Ruan et al., 2017), conditions that also characterised the  
424 core 11 site during intervals of elevated HBI II concentration (Berben et al., 2014; Belt et al.,  
425 2015). Overall, our data support the results from core 1200 and suggest that CT performance  
426 and consistency with the P<sub>III</sub>IP<sub>25</sub> approach suffer when HBI distributions included in the  
427 model training set are not represented in downcore records characterised by different or  
428 unstable climate. Visualisation of the variables used in the CT assessment (Fig. 5 and 6) is  
429 essential when identifying such cases. It is important to acknowledge that this limitation is  
430 potentially amplified as variations in relative abundances of any biomarker included in the  
431 model inherently affect the overall HBI composition due to data normalisation used for the  
432 CT (Eq. 3). The dependence of CT performance and viability on the consistency of data  
433 distribution in the training set with that of new samples highlights the necessity of  
434 constructing separate training sets for different Arctic regions, which often exhibit  
435 significantly different HBI distributions despite similar seasonal ice conditions (Stoyanova et

436 al., 2013; Xiao et al., 2015a). Ideally, downcore records to be classified should be within the  
437 geographical coverage of the surface sediment training set, as is the case in our study.  
438 Further, the choice of an optimal time interval for the satellite SpSIC data is potentially  
439 problematic due to the often unavailability of accumulation rates for surface sediments. Thus,  
440 the integrated biomarker signal at each surface location potentially corresponds to a variable  
441 temporal window (Köseoğlu et al., 2018) and some surface sediments may not even represent  
442 recent accumulation. This is likely to influence the accuracy of both the CT model and  
443  $P_{III}IP_{25}$ -based SpSIC estimates.

444 Another important consideration is the consistent quantification of all biomarkers  
445 between the training set and new samples. Accurate quantification of HBIs via mass  
446 spectrometric techniques involves the use of an instrumental Response Factor (RF), usually  
447 obtained from calibration with authentic standards, to account for mass spectral  
448 fragmentation efficiency differences between individual biomarkers and the internal standard  
449 (Belt et al., 2012; Belt et al., 2014). Moreover, HBIs usually exhibit vastly different RF  
450 values (Belt et al., 2014), necessitating instrument calibration via separate standard series for  
451 each biomarker and subsequent quality monitoring using a reference sediment material of  
452 known HBI concentration. Any RF changes thus affect the HBI distribution and resulting CT  
453 model rules, such that the use of different quantification methods (RF values) for the model  
454 training set and new samples will cause the model to fail when classifying the latter. For our  
455 data, assigning the same value to all RFs shifts the HBI composition towards higher relative  
456 abundances of HBI III (Z) and HBI III (E) (Fig. 8a). When these modified downcore  
457 distributions are classified using the CT model trained with correctly quantified surface  
458 sediments (Köseoğlu et al., 2018), the model fails to identify the extensive sea ice class  
459 completely and exhibits a high discrepancy with  $P_{III}IP_{25}$ -based SpSIC. On the other hand,  
460 when consistent methods are used to obtain the RFs, model performance is largely unaffected

461 (Fig. 8b). Directly comparable quantification is therefore necessary for the training and new  
462 sample sets, and the CT must be re-built with a new training set should a change in  
463 quantification methods occur.

464 Finally, the relatively high susceptibility of more unsaturated HBIs, particularly those  
465 with trisubstituted double bonds (HBIs III (Z) and III (E) in this case), towards degradative  
466 processes could also alter biomarker distributions in downcore sedimentary sequences  
467 relative to those in surface sediments. The lower stability of HBI trienes towards  
468 photodegradation and autoxidation in sea ice and the water column (Rontani et al., 2014a,b)  
469 possibly implies their increased potential for aerobic degradation in upper oxic sediments,  
470 which was shown recently to affect even the more diagenetically stable IP<sub>25</sub> (Rontani et al.,  
471 2018a,b). Thus, selective removal of HBIs III (Z) and III (E) from the HBI distribution may  
472 adversely affect P<sub>III</sub>IP<sub>25</sub>-based SpSIC estimates and CT model performance, especially under  
473 conditions of high light penetration, long residence times of algal cells in the photic zone, and  
474 low sedimentation rates, where diagenetic processes are more likely to have an effect. While  
475 it is not feasible to analytically diagnose the relative impacts of climate change and selective  
476 HBI degradation due to the extremely high reactivity of associated photo- and oxidation  
477 products (Rontani et al., 2014a,b), examination of HBI triene concentration profiles suggests  
478 a prevailing influence of climate on our data. Specifically, the concentrations of pelagic HBI  
479 III (Z) reach and surpass those of IP<sub>25</sub> (Fig. 3a, 4a, and 5a) during periods of reduced sea ice  
480 cover and generally ameliorated climate conditions inferred in previous studies, while  
481 reduced concentrations only coincide with harsh glacial conditions of the Younger Dryas and  
482 the late Holocene ice expansion (Cabedo-Sanz et al., 2013; Berben et al., 2014, 2017).  
483 Moreover, downcore concentrations of HBIs III (Z) and III (E) are often higher than  
484 maximum values observed in surface sediments from the highly-productive MIZ, which are  
485 ca. 40 ng/g and 20 ng/g for HBIs III (Z) and III (E), respectively (Köseoğlu et al., 2018). This

486 suggests that, in this case, sedimentary aerobic degradation or other processes prior to  
487 deposition are unlikely to significantly alter downcore HBI content relative to that of  
488 proximal surface sediments. Finally, as noted previously, the alteration of HBI distributions  
489 and data structure due to disproportional and even opposing concentration increases of II  
490 relative to those of IP<sub>25</sub> is the likely cause of discrepancies between P<sub>III</sub>IP<sub>25</sub>- and CT-based  
491 methods for cores 1200 and 11, in particular (Fig. 4–6). Nonetheless, a diagenetic influence  
492 on downcore HBI concentrations cannot be discounted, particularly in older core sections or  
493 when overlying climate conditions are more likely to promote accelerated or prolonged  
494 oxidation and photodegradation. Thus, we suggest that HBI distributions should be combined  
495 with degradation proxies, such as the recently utilized ratio of brassicasterol to 24-  
496 methylenecholesterol (Rontani et al., 2018a), and that uncharacteristically low concentrations  
497 of HBIs III (Z) and III (E) relative to otherwise inferred climate conditions (e.g., using other  
498 proxies) should be interpreted with caution.

499

## 500 **5. Conclusions**

501 Downcore records encompassing different modern sea ice conditions in the Barents Sea  
502 were used to assess the spatio-temporal consistency between CT model predictions and  
503 P<sub>III</sub>IP<sub>25</sub>-based SpSIC estimates. A good overall agreement between both approaches was  
504 observed for all cores, and the CT model was able to capture both abrupt and fluctuating  
505 shifts in sea ice regimes, such as those evident during the Younger Dryas stadial, as well as  
506 more gradual trends in sea ice conditions during the Holocene. However, shifts of CT model  
507 predictions occurred at variable threshold values of P<sub>III</sub>IP<sub>25</sub>-based SpSIC estimates in  
508 different downcore records (ca. ±11% for 16 samples, >11% for 4 samples). This variability  
509 was attributed partially to the occurrence of downcore HBI distributions, which are not

510 represented in the model training dataset, most notably during intervals of unstable and rapid  
511 climate change characterising stadial-interstadial transitions. While it is not feasible to avoid  
512 this limitation, examination of data structure and distribution may pinpoint intervals where  
513 CT performance is likely to decrease. A consequence of CT dependency on HBI  
514 distributional changes is the necessity to use consistent quantification methods for model  
515 training and new (downcore) samples, and to use separate training sets for different Arctic  
516 regions. Selective removal of more unsaturated HBIs via degradation processes represents  
517 another potential error source, although this was likely not the case for our data. Further  
518 potential error sources of both methods were also identified, including the uncertain regional  
519 applicability of a uniform  $c$ -factor and insufficient sample density for representation of the  
520 entire SpSIC range (0–100%) within the CT model. We suggest, therefore, that only  
521 variations of  $P_{III}IP_{25}$ -based SpSIC exceeding the associated RMSE of 11% be considered  
522 significant, and that CT model predictions should be interpreted in terms of broader changes  
523 in sea ice regimes (i.e. open water or proximal ice edge, MIZ conditions, and stable sea ice  
524 cover) rather than inflexible satellite-based numeric SpSIC thresholds (i.e. 10% and 50%  
525 SpSIC).

526

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535 **6. References**

- 536 Andrews, J.T., Belt, S.T., Olafsdottir, S., Massé, G., Vare, L.L., 2009. Sea ice and marine  
537 climate variability for NW Iceland/Denmark Strait over the last 2000 cal. yr BP. *The*  
538 *Holocene* 19, 775-784.
- 539 Árrthun, M., Eldevik, T., Smedsrud, L.H., Skagseth, Ø., Ingvaldsen, R.B., 2012. Quantifying  
540 the influence of Atlantic heat on Barents Sea ice variability and retreat. *Journal of*  
541 *Climate* 25, 4736-4743.
- 542 Axford, Y., Andresen, C.S., Andrews, J.T., Belt, S.T., Geirsdóttir, Á., Massé, G., Miller,  
543 G.H., Ólafsdóttir, S., Vare, L.L., 2011. Do paleoclimate proxies agree? A test  
544 comparing 19 late Holocene climate and sea-ice reconstructions from Icelandic  
545 marine and lake sediments. *Journal of Quaternary Science* 26, 645-656.
- 546 Bakke, J., Lie, Ø., Heegaard, E., Dokken, T., Haug, G.H., Birks, H.H., Dulski, P., Nilsen, T.,  
547 2009. Rapid oceanic and atmospheric changes during the Younger Dryas cold period.  
548 *Nature Geoscience* 2, 202-205.
- 549 Bartels, M., Titschack, J., Fahl, K., Stein, R., Seidenkrantz, M.S., Hillaire-Marcel, C.,  
550 Hebbeln, D., 2017. Atlantic Water advection vs glacier dynamics in northern  
551 Spitsbergen since early deglaciation. *Climate of the Past Discussions* 2017, 1-53.
- 552 Belt, S.T., Müller, J., 2013. The Arctic sea ice biomarker IP<sub>25</sub>: a review of current  
553 understanding, recommendations for future research and applications in palaeo sea ice  
554 reconstructions. *Quaternary Science Reviews* 79, 9-25.
- 555 Belt, S.T., Allard, W.G., Massé, G., Robert, J.-M., Rowland, S.J., 2000. Highly branched  
556 isoprenoids (HBIs): identification of the most common and abundant sedimentary  
557 isomers. *Geochimica et Cosmochimica Acta* 64, 3839-3851.

- 558 Belt, S.T., Massé, G., Rowland, S.J., Poulin, M., Michel, C., LeBlanc, B., 2007. A novel  
559 chemical fossil of palaeo sea ice: IP<sub>25</sub>. *Organic Geochemistry* 38, 16-27.
- 560 Belt, S.T., Brown, T.A., Rodriguez, A.N., Sanz, P.C., Tonkin, A., Ingle, R., 2012. A  
561 reproducible method for the extraction, identification and quantification of the Arctic  
562 sea ice proxy IP<sub>25</sub> from marine sediments. *Analytical Methods* 4, 705-713.
- 563 Belt, S.T., Brown, T.A., Ringrose, A.E., Cabedo-Sanz, P., Mundy, C.J., Gosselin, M., Poulin,  
564 M., 2013. Quantitative measurement of the sea ice diatom biomarker IP<sub>25</sub> and sterols  
565 in Arctic sea ice and underlying sediments: Further considerations for palaeo sea ice  
566 reconstruction. *Organic Geochemistry* 62, 33-45.
- 567 Belt, S.T., Brown, T.A., Ampel, L., Cabedo-Sanz, P., Fahl, K., Kocis, J.J., Massé, G.,  
568 Navarro-Rodriguez, A., Ruan, J., Xu, Y., 2014. An inter-laboratory investigation of  
569 the Arctic sea ice biomarker proxy IP<sub>25</sub> in marine sediments: key outcomes and  
570 recommendations. *Climate of the Past* 10, 155-166.
- 571 Belt, S.T., Cabedo-Sanz, P., Smik, L., Navarro-Rodriguez, A., Berben, S.M.P., Knies, J.,  
572 Husum, K., 2015. Identification of paleo Arctic winter sea ice limits and the marginal  
573 ice zone: optimised biomarker-based reconstructions of late Quaternary Arctic sea ice.  
574 *Earth and Planetary Science Letters* 431, 127-139.
- 575 Belt, S.T., Smik, L., Brown, T.A., Kim, J.H., Rowland, S.J., Allen, C.S., Gal, J.K., Shin,  
576 K.H., Lee, J.I., Taylor, K.W.R., 2016. Source identification and distribution reveals  
577 the potential of the geochemical Antarctic sea ice proxy IPSO<sub>25</sub>. *Nature*  
578 *Communications* 7, 12655. DOI: <https://doi.org/10.1038/ncomms12655>.
- 579 Belt, S.T., Brown, T.A., Smik, L., Tatarek, A., Wiktor, J., Stowasser, G., Assmy, P., Allen,  
580 C.S., Husum, K., 2017. Identification of C<sub>25</sub> highly branched isoprenoid (HBI)  
581 alkenes in diatoms of the genus *Rhizosolenia* in polar and sub-polar marine  
582 phytoplankton. *Organic Geochemistry* 110, 65-72.

- 583 Belt, S.T., Brown, T.A., Smik, L., Assmy, P., Mundy, C.J., 2018. Sterol identification in  
584 floating Arctic sea ice algal aggregates and the Antarctic sea ice diatom *Berkeleya*  
585 *adeliensis*. *Organic Geochemistry* 118, 1-3.
- 586 Berben, S.M.P., Husum, K., Cabedo-Sanz, P., Belt, S.T., 2014. Holocene sub-centennial  
587 evolution of Atlantic water inflow and sea ice distribution in the western Barents Sea.  
588 *Climate of the Past* 10, 181-198.
- 589 Berben, S.M.P., Husum, K., Navarro-Rodriguez, A., Belt, S.T., Aagaard-Sørensen, S., 2017.  
590 Semi-quantitative reconstruction of early to late Holocene spring and summer sea ice  
591 conditions in the northern Barents Sea. *Journal of Quaternary Science* 32, 587-603.
- 592 Bitz, C.M., Gent, P.R., Woodgate, R.A., Holland, M.M., Lindsay, R., 2006. The influence of  
593 sea ice on ocean heat uptake in response to increasing CO<sub>2</sub>. *Journal of Climate* 19,  
594 2437-2450.
- 595 Breiman, L., Friedman, J., Stone, C.J., Olshen, R.A., 1984. Classification and regression  
596 trees. CRC press, New York, ISBN: 9780412048418.
- 597 Brown, T.A., Belt, S.T., Tatarek, A., Mundy, C.J., 2014. Source identification of the Arctic  
598 sea ice proxy IP<sub>25</sub>. *Nature Communications* 5, 4197. DOI:  
599 <https://doi.org/10.1038/ncomms5197>.
- 600 Cabedo-Sanz, P., Belt, S.T., 2016. Seasonal sea ice variability in eastern Fram Strait over the  
601 last 2000 years. *Arktos* 2, 22. DOI: <https://doi.org/10.1007/s41063-016-0023-2>.
- 602 Cabedo-Sanz, P., Belt, S.T., Jennings, A.E., Andrews, J.T., Geirsdóttir, Á., 2016. Variability  
603 in drift ice export from the Arctic Ocean to the North Icelandic Shelf over the last  
604 8000 years: a multi-proxy evaluation. *Quaternary Science Reviews* 146, 99-115.
- 605 Cabedo-Sanz, P., Belt, S.T., Knies, J., Husum, K., 2013. Identification of contrasting seasonal  
606 sea ice conditions during the Younger Dryas. *Quaternary Science Reviews* 79, 74-86.

- 607 Cavalieri, D.J., Parkinson, C.L., Gloersen, P., Zwally, H.J., 1996. Sea Ice Concentrations  
608 from Nimbus-7 SMMR and DMSP SSM/I-SSMIS Passive Microwave Data, ver 1.1.  
609 NASA DAAC at the National Snow and Ice Data Center, Boulder, Colorado. DOI:  
610 <https://doi.org/10.5067/8GQ8LZQVL0VL> [Accessed 08.06.2018]
- 611 Divine, D.V., Dick, C., 2006. Historical variability of sea ice edge position in the Nordic  
612 Seas. *Journal of Geophysical Research: Oceans* 111, C01001. DOI:  
613 <https://doi.org/10.1029/2004JC002851>.
- 614 Duplessy, J.-C., Ivanova, E., Murdmaa, I., Paterne, M., Labeyrie, L., 2001. Holocene  
615 paleoceanography of the northern Barents Sea and variations of the northward heat  
616 transport by the Atlantic Ocean. *Boreas* 30, 2-16.
- 617 Duplessy, J.C., Cortijo, E., Ivanova, E., Khusid, T., Labeyrie, L., Levitan, M., Murdmaa, I.,  
618 Paterne, M., 2005. Paleoceanography of the Barents Sea during the Holocene.  
619 *Paleoceanography* 20, PA4004. DOI: <https://doi.org/10.1029/2004PA001116>
- 620 Dylmer, C.V., Giraudeau, J., Eynaud, F., Husum, K., De Vernal, A., 2013. Northward  
621 advection of Atlantic water in the eastern Nordic Seas over the last 3000 yr. *Climate*  
622 *of the Past* 9, 1505-1518.
- 623 Ebbesen, H., Hald, M., 2004. Unstable Younger Dryas climate in the northeast North  
624 Atlantic. *Geology* 32, 673-676.
- 625 Eisenman, I., Wettlaufer, J.S., 2009. Nonlinear threshold behavior during the loss of Arctic  
626 sea ice. *Proceedings of the National Academy of Sciences* 106, 28-32.
- 627 Fahl, K., Stein, R., 2012. Modern seasonal variability and deglacial/Holocene change of  
628 central Arctic Ocean sea-ice cover: new insights from biomarker proxy records. *Earth*  
629 *and Planetary Science Letters* 351-352, 123-133.

- 630 Fetterer, F., Knowles, K., Meier, W.N., Savoie, M., 2017. Sea Ice Index, in: NSIDC: National  
631 Snow and Ice Data Center, ver. 3. NSIDC: National Snow and Ice Data Center,  
632 Boulder, Colorado. DOI: <https://doi.org/10.7265/N5736NV7> [Accessed 08.06.2018]
- 633 Groot, D.E., Aagaard-Sørensen, S., Husum, K., 2014. Reconstruction of Atlantic water  
634 variability during the Holocene in the western Barents Sea. *Climate of the Past* 10, 51-  
635 62.
- 636 Harada, N., 2016. Review: Potential catastrophic reduction of sea ice in the western Arctic  
637 Ocean: Its impact on biogeochemical cycles and marine ecosystems. *Global and  
638 Planetary Change* 136, 1-17.
- 639 Hoff, U., Rasmussen, T.L., Stein, R., Ezat, M.M., Fahl, K., 2016. Sea ice and millennial-scale  
640 climate variability in the Nordic seas 90 kyr ago to present. *Nature Communications*  
641 7, 12247. DOI: <https://doi.org/10.1038/ncomms12247>.
- 642 Hörner, T., Stein, R., Fahl, K., Birgel, D., 2016. Post-glacial variability of sea ice cover, river  
643 run-off and biological production in the western Laptev Sea (Arctic Ocean) – A high-  
644 resolution biomarker study. *Quaternary Science Reviews* 143, 133-149.
- 645 Ingvaldsen, R.B., Asplin, L., Loeng, H., 2004. Velocity field of the western entrance to the  
646 Barents Sea. *Journal of Geophysical Research: Oceans* 109, C03021. DOI:  
647 <https://doi.org/10.1029/2003JC001811>.
- 648 Knies, J., 2005. Climate-induced changes in sedimentary regimes for organic matter supply  
649 on the continental shelf off northern Norway. *Geochimica et Cosmochimica Acta* 69,  
650 4631-4647.
- 651 Knies, J., Cabedo-Sanz, P., Belt, S.T., Baranwal, S.F., Rosell-Melé, A., 2014. The emergence  
652 of modern sea ice cover in the Arctic Ocean. *Nature Communications* 5, 5608. DOI:  
653 <https://doi.org/10.1038/ncomms6608>.

- 654 Knies, J., Hald, M., Ebbesen, H., Mann, U., Vogt, C., 2003. A deglacial–middle Holocene  
655 record of biogenic sedimentation and paleoproductivity changes from the northern  
656 Norwegian continental shelf. *Paleoceanography* 18, 1096. DOI:  
657 <https://doi.org/10.1029/2002PA000872>.
- 658 Knies, J., Pathirana, I., Cabedo-Sanz, P., Banica, A., Fabian, K., Rasmussen, T.L., Forwick,  
659 M., Belt, S.T., 2017. Sea-ice dynamics in an Arctic coastal polynya during the past  
660 6500 years. *Arktos* 3, 1. DOI: <https://doi.org/10.1007/s41063-016-0027-y>.
- 661 Köseoğlu, D., Belt, S.T., Smik, L., Yao, H., Panieri, G., Knies, J., 2018. Complementary  
662 biomarker-based methods for characterising Arctic sea ice conditions: A case study  
663 comparison between multivariate analysis and the PIP<sub>25</sub> index. *Geochimica et*  
664 *Cosmochimica Acta* 222, 406-420.
- 665 Kristensen, D.K., Rasmussen, T.L., Koç, N., 2013. Palaeoceanographic changes in the  
666 northern Barents Sea during the last 16,000 years – new constraints on the last  
667 deglaciation of the Svalbard–Barents Sea Ice Sheet. *Boreas* 42, 798-813.
- 668 Lindsay, R., Schweiger, A., 2015. Arctic sea ice thickness loss determined using subsurface,  
669 aircraft, and satellite observations. *The Cryosphere* 9, 269-283.
- 670 Lindsay, R.W., Zhang, J., 2005. The Thinning of Arctic Sea Ice, 1988–2003: Have We  
671 Passed a Tipping Point? *Journal of Climate* 18, 4879-4894.
- 672 Loeng, H., Drinkwater, K., 2007. An overview of the ecosystems of the Barents and  
673 Norwegian Seas and their response to climate variability. *Deep Sea Research Part II:*  
674 *Topical Studies in Oceanography* 54, 2478-2500.
- 675 Loeng, H., Ozhigin, V., Ådlandsvik, B., 1997. Water fluxes through the Barents Sea. *ICES*  
676 *Journal of Marine Science* 54, 310-317.

- 677 Massé, G., Rowland, S.J., Sicre, M.-A., Jacob, J., Jansen, E., Belt, S.T., 2008. Abrupt climate  
678 changes for Iceland during the last millennium: evidence from high resolution sea ice  
679 reconstructions. *Earth and Planetary Science Letters* 269, 565-569.
- 680 Maykut, G.A., 1978. Energy exchange over young sea ice in the central Arctic. *Journal of*  
681 *Geophysical Research: Oceans* 83, 3646-3658.
- 682 Méheust, M., Fahl, K., Stein, R., 2013. Variability in modern sea surface temperature, sea ice  
683 and terrigenous input in the sub-polar North Pacific and Bering Sea: reconstruction  
684 from biomarker data. *Organic Geochemistry* 57, 54-64.
- 685 Meier, W.N., Hovelsrud, G.K., van Oort, B.E.H., Key, J.R., Kovacs, K.M., Michel, C., Haas,  
686 C., Granskog, M.A., Gerland, S., Perovich, D.K., Makshtas, A., Reist, J.D., 2014.  
687 Arctic sea ice in transformation: a review of recent observed changes and impacts on  
688 biology and human activity. *Reviews of Geophysics* 52, 185-217.
- 689 Mori, M., Watanabe, M., Shiogama, H., Inoue, J., Kimoto, M., 2014. Robust Arctic sea-ice  
690 influence on the frequent Eurasian cold winters in past decades. *Nature Geoscience* 7,  
691 869-873.
- 692 Müller, J., Massé, G., Stein, R., Belt, S.T., 2009. Variability of sea-ice conditions in the Fram  
693 Strait over the past 30,000 years. *Nature Geoscience* 2, 772-776.
- 694 Müller, J., Stein, R., 2014. High-resolution record of late glacial and deglacial sea ice  
695 changes in Fram Strait corroborates ice–ocean interactions during abrupt climate  
696 shifts. *Earth and Planetary Science Letters* 403, 446-455.
- 697 Müller, J., Wagner, A., Fahl, K., Stein, R., Prange, M., Lohmann, G., 2011. Towards  
698 quantitative sea ice reconstructions in the northern North Atlantic: a combined  
699 biomarker and numerical modelling approach. *Earth and Planetary Science Letters*  
700 306, 137-148.

- 701 Müller, J., Werner, K., Stein, R., Fahl, K., Moros, M., Jansen, E., 2012. Holocene cooling  
702 culminates in sea ice oscillations in Fram Strait. *Quaternary Science Reviews* 47, 1-  
703 14.
- 704 Navarro-Rodriguez, A. (2014) Reconstruction of Recent Palaeo Sea Ice Conditions in the  
705 Barents Sea. Ph.D. thesis, Plymouth University. URI:  
706 <http://hdl.handle.net/10026.1/3085>.
- 707 Navarro-Rodriguez, A., Belt, S.T., Knies, J., Brown, T.A., 2013. Mapping recent sea ice  
708 conditions in the Barents Sea using the proxy biomarker IP<sub>25</sub>: implications for palaeo  
709 sea ice reconstructions. *Quaternary Science Reviews* 79, 26-39.
- 710 Overland, J.E., Wang, M., 2013. When will the summer Arctic be nearly sea ice free?  
711 *Geophysical Research Letters* 40, 2097-2101.
- 712 Oziel, L., Sirven, J., Gascard, J.C., 2016. The Barents Sea frontal zones and water masses  
713 variability (1980–2011). *Ocean Science* 12, 169-184.
- 714 Perovich, D.K., Polashenski, C., 2012. Albedo evolution of seasonal Arctic sea ice.  
715 *Geophysical Research Letters* 39, L08501. DOI:  
716 <https://doi.org/10.1029/2012GL051432>.
- 717 R Core Team, 2017. R: A language and environment for statistical computing. R Foundation  
718 for Statistical Computing, Vienna. <<https://www.r-project.org>>
- 719 Rampen, S.W., Abbas, B.A., Schouten, S., Sinninghe Damste, J.S., 2010. A comprehensive  
720 study of sterols in marine diatoms (Bacillariophyta): implications for their use as  
721 tracers for diatom productivity. *Limnology and Oceanography* 55, 91-105.
- 722 Rasmussen, T.L., Thomsen, E., 2015. Palaeoceanographic development in Storfjorden,  
723 Svalbard, during the deglaciation and Holocene: evidence from benthic foraminiferal  
724 records. *Boreas* 44, 24-44.

- 725 Rasmussen, T.L., Thomsen, E., Ślubowska, M.A., Jessen, S., Solheim, A., Koç, N., 2007.  
726 Paleocceanographic evolution of the SW Svalbard margin (76°N) since 20,000 <sup>14</sup>C yr  
727 BP. *Quaternary Research* 67, 100-114.
- 728 Ribeiro, S., Sejr, M.K., Limoges, A., Heikkilä, M., Andersen, T.J., Tallberg, P., Weckström,  
729 K., Husum, K., Forwick, M., Dalsgaard, T., Massé, G., Seidenkrantz, M.-S.,  
730 Rysgaard, S., 2017. Sea ice and primary production proxies in surface sediments from  
731 a High Arctic Greenland fjord: Spatial distribution and implications for  
732 palaeoenvironmental studies. *Ambio* 46, 106-118.
- 733 Risebrobakken, B., Dokken, T., Smedsrud, L.H., Andersson, C., Jansen, E., Moros, M.,  
734 Ivanova, E.V., 2011. Early Holocene temperature variability in the Nordic Seas: The  
735 role of oceanic heat advection versus changes in orbital forcing. *Paleoceanography*  
736 26, PA4206. DOI: <https://doi.org/10.1029/2011PA002117>.
- 737 Risebrobakken, B., Moros, M., Ivanova, E.V., Chistyakova, N., Rosenberg, R., 2010. Climate  
738 and oceanographic variability in the SW Barents Sea during the Holocene. *The*  
739 *Holocene* 20, 609-621.
- 740 Rontani, J.-F., Belt, S.T., Amiraux, R., 2018a. Biotic and abiotic degradation of the sea ice  
741 diatom biomarker IP<sub>25</sub> and selected algal sterols in near-surface Arctic sediments.  
742 *Organic Geochemistry* 118, 73-88.
- 743 Rontani, J.-F., Belt, S.T., Brown, T.A., Vaultier, F., Mundy, C.J., 2014a. Sequential photo-  
744 and autoxidation of diatom lipids in Arctic sea ice. *Organic Geochemistry* 77, 59-71.
- 745 Rontani, J.F., Aubert, C., Belt, S.T., 2018b. Electron ionization mass spectrometry  
746 fragmentation and multiple reaction monitoring quantification of bacterial metabolites  
747 of the sea ice biomarker proxy IP<sub>25</sub> in Arctic sediments. *Rapid Communications in*  
748 *Mass Spectrometry* 32, 775-783.

- 749 Rontani, J.F., Belt, S.T., Vaultier, F., Brown, T.A., Massé, G., 2014b. Autoxidative and  
750 photooxidative reactivity of highly branched isoprenoid (HBI) alkenes. *Lipids* 49,  
751 481-494.
- 752 Rowland, S.J., Allard, W.G., Belt, S.T., Massé, G., Robert, J.M., Blackburn, S., Frampton,  
753 D., Revill, A.T., Volkman, J.K., 2001. Factors influencing the distributions of  
754 polyunsaturated terpenoids in the diatom, *Rhizosolenia setigera*. *Phytochemistry* 58,  
755 717-728.
- 756 Ruan, J., Huang, Y., Shi, X., Liu, Y., Xiao, W., Xu, Y., 2017. Holocene variability in sea  
757 surface temperature and sea ice extent in the northern Bering Sea: a multiple  
758 biomarker study. *Organic Geochemistry* 113, 1-9.
- 759 Rüter, D.C., Bjarnadóttir, L.R., Junntila, J., Husum, K., Rasmussen, T.L., Lucchi, R.G.,  
760 Andreassen, K., 2012. Pattern and timing of the northwestern Barents Sea Ice Sheet  
761 deglaciation and indications of episodic Holocene deposition. *Boreas* 41, 494-512.
- 762 Sakshaug, E., Johnsen, G.H., Kovacs, K.M., 2009. *Ecosystem Barents Sea*. Tapir Academic  
763 Press, Trondheim, Norway. ISBN: 9788251924610.
- 764 Screen, J.A., Simmonds, I., 2010. The central role of diminishing sea ice in recent Arctic  
765 temperature amplification. *Nature* 464, 1334-1337.
- 766 Serreze, M.C., Barry, R.G., 2011. Processes and impacts of Arctic amplification: a research  
767 synthesis. *Global and Planetary Change* 77, 85-96.
- 768 Ślubowska, M.A., Koç, N., Rasmussen, T.L., Klitgaard-Kristensen, D., 2005. Changes in the  
769 flow of Atlantic water into the Arctic Ocean since the last deglaciation: Evidence  
770 from the northern Svalbard continental margin, 80°N. *Paleoceanography* 20, PA4014.  
771 DOI: <https://doi.org/10.1029/2005PA001141>.
- 772 Smedsrud, L.H., Esau, I., Ingvaldsen, R.B., Eldevik, T., Haugan, P.M., Li, C., Lien, V.S.,  
773 Olsen, A., Omar, A.M., Otterå, O.H., Risebrobakken, B., Sandø, A.B., Semenov,

- 774 V.A., Sorokina, S.A., 2013. The role of the Barents Sea in the Arctic climate system.  
775 *Reviews of Geophysics* 51, 415-449.
- 776 Smedsrud, L.H., Ingvaldsen, R., Nilsen, J.E.Ø., Skagseth, Ø., 2010. Heat in the Barents Sea:  
777 transport, storage, and surface fluxes. *Ocean Science* 6, 219-234.
- 778 Smik, L., Cabedo-Sanz, P., Belt, S.T., 2016. Semi-quantitative estimates of paleo Arctic sea  
779 ice concentration based on source-specific highly branched isoprenoid alkenes: a  
780 further development of the PIP<sub>25</sub> index. *Organic Geochemistry* 92, 63-69.
- 781 Sorteberg, A., Kvingedal, B., 2006. Atmospheric forcing on the Barents Sea winter ice  
782 extent. *Journal of Climate* 19, 4772-4784.
- 783 Stein, R., Fahl, K., 2012. A first southern Lomonosov Ridge (Arctic Ocean) 60 ka IP<sub>25</sub> sea-  
784 ice record. *Polarforschung*, 83-86.
- 785 Stein, R., Fahl, K., 2013. Biomarker proxy shows potential for studying the entire Quaternary  
786 Arctic sea ice history. *Organic Geochemistry* 55, 98-102.
- 787 Stein, R., Fahl, K., Schreck, M., Knorr, G., Niessen, F., Forwick, M., Gebhardt, C., Jensen,  
788 L., Kaminski, M., Kopf, A., Matthiessen, J., Jokat, W., Lohmann, G., 2016. Evidence  
789 for ice-free summers in the late Miocene central Arctic Ocean. *Nature*  
790 *Communications* 7, 11148. DOI: <https://doi.org/10.1038/ncomms11148>.
- 791 Stoyanova, V., Shanahan, T.M., Hughen, K.A., de Vernal, A., 2013. Insights into Circum-  
792 Arctic sea ice variability from molecular geochemistry. *Quaternary Science Reviews*  
793 79, 63-73.
- 794 Stroeve, J.C., Blanchard-Wrigglesworth, E., Guemas, V., Howell, S., Massonnet, F.,  
795 Tietsche, S., 2015. Improving predictions of Arctic sea ice extent. *Eos* 96. DOI:  
796 <https://doi.org/10.1029/2015EO031431>.
- 797 Vancoppenolle, M., Meiners, K.M., Michel, C., Bopp, L., Brabant, F., Carnat, G., Delille, B.,  
798 Lannuzel, D., Madec, G., Moreau, S., Tison, J.-L., van der Merwe, P., 2013. Role of

- 799 sea ice in global biogeochemical cycles: emerging views and challenges. *Quaternary*  
800 *Science Reviews* 79, 207-230.
- 801 Vare, L.L., Massé, G., Belt, S.T., 2010. A biomarker-based reconstruction of sea ice  
802 conditions for the Barents Sea in recent centuries. *The Holocene* 20, 637-643.
- 803 Vihma, T., 2014. Effects of Arctic sea ice decline on weather and climate: a review. *Surveys*  
804 *in Geophysics* 35, 1175-1214.
- 805 Vinje, T., 2001. Anomalies and trends of sea-ice extent and atmospheric circulation in the  
806 Nordic Seas during the period 1864–1998. *Journal of Climate* 14, 255-267.
- 807 Volkman, J.K., 1986. A review of sterol markers for marine and terrigenous organic matter.  
808 *Organic Geochemistry* 9, 83-99.
- 809 Volkman, J.K., 2006. Lipid markers for marine organic matter, In: Volkman, J.K. (Ed.),  
810 *Marine organic matter: biomarkers, isotopes and DNA*. Springer Berlin Heidelberg,  
811 Berlin, Heidelberg, pp. 27-70.
- 812 Walsh, J.E., Fetterer, F., Scott Stewart, J., Chapman, W.L., 2017. A database for depicting  
813 Arctic sea ice variations back to 1850. *Geographical Review* 107, 89-107.
- 814 Wassmann, P., Ratkova, T., Andreassen, I., Vernet, M., Pedersen, G., Rey, F., 1999. Spring  
815 bloom development in the marginal ice zone and the central Barents Sea. *Marine*  
816 *Ecology* 20, 321-346.
- 817 Wassmann, P., Reigstad, M., Haug, T., Rudels, B., Carroll, M.L., Hop, H., Gabrielsen, G.W.,  
818 Falk-Petersen, S., Denisenko, S.G., Arashkevich, E., Slagstad, D., Pavlova, O., 2006.  
819 Food webs and carbon flux in the Barents Sea. *Progress in Oceanography* 71, 232-  
820 287.
- 821 Weckström, K., Massé, G., Collins, L.G., Hanhijärvi, S., Bouloubassi, I., Sicre, M.-A.,  
822 Seidenkrantz, M.-S., Schmidt, S., Andersen, T.J., Andersen, M.L., Hill, B., Kuijpers,

823 A., 2013. Evaluation of the sea ice proxy IP<sub>25</sub> against observational and diatom proxy  
824 data in the SW Labrador Sea. *Quaternary Science Reviews* 79, 53-62.

825 Werner, K., Müller, J., Husum, K., Spielhagen, R.F., Kandiano, E.S., Polyak, L., 2016.  
826 Holocene sea subsurface and surface water masses in the Fram Strait – Comparisons  
827 of temperature and sea-ice reconstructions. *Quaternary Science Reviews* 147, 194-  
828 209.

829 Werner, K., Spielhagen, R.F., Bauch, D., Hass, H.C., Kandiano, E., 2013. Atlantic Water  
830 advection versus sea-ice advances in the eastern Fram Strait during the last 9 ka:  
831 multiproxy evidence for a two-phase Holocene. *Paleoceanography* 28, 283-295.

832 Xiao, X., Fahl, K., Müller, J., Stein, R., 2015a. Sea-ice distribution in the modern Arctic  
833 Ocean: Biomarker records from trans-Arctic Ocean surface sediments. *Geochimica et*  
834 *Cosmochimica Acta* 155, 16-29.

835 Xiao, X., Fahl, K., Stein, R., 2013. Biomarker distributions in surface sediments from the  
836 Kara and Laptev seas (Arctic Ocean): indicators for organic-carbon sources and sea-  
837 ice coverage. *Quaternary Science Reviews* 79, 40-52.

838 Xiao, X., Stein, R., Fahl, K., 2015b. MIS 3 to MIS 1 temporal and LGM spatial variability in  
839 Arctic Ocean sea ice cover: reconstruction from biomarkers. *Paleoceanography* 30,  
840 969-983.

841 Yunker, M.B., Belicka, L.L., Harvey, H.R., Macdonald, R.W., 2005. Tracing the inputs and  
842 fate of marine and terrigenous organic matter in Arctic Ocean sediments: a  
843 multivariate analysis of lipid biomarkers. *Deep Sea Research Part II: Topical Studies*  
844 *in Oceanography* 52, 3478-3508.

845

846 **Figure Legends**

847 **Figure 1.** Structures of C<sub>25</sub> Highly-Branched Isoprenoid (HBI) biomarkers used for sea ice  
848 reconstruction in the current study.

849 **Figure 2.** Map of the Barents Sea showing locations of downcore records 1200, 11, and 70  
850 (labelled black squares). The maximum April–June sea ice edge for the 1988–2007 period  
851 corresponding to an SpSIC threshold of 0 % is shown by a solid black line. Circles  
852 correspond to surface sediments used for CT model training, with overlying marginal (<10%  
853 satellite SpSIC; red markers), intermediate (10–50% SpSIC; yellow markers), and extensive  
854 (>50% SpSIC; green markers) sea ice cover. A simplified representation of the major AW  
855 surface currents is illustrated by red arrows, with abbreviations for: WSC – West Spitsbergen  
856 Current; NCaC – North Cape Current.

857 **Figure 3.** Proxy data and correlations for core 70 (northern Barents Sea): (a) Absolute  
858 concentrations of IP<sub>25</sub> (black line with circle markers) and HBI III (Z; green line); (b) P<sub>III</sub>IP<sub>25</sub>-  
859 based % SpSIC profile (black line) with an RMSE error of ca. 11% (thin black lines; Smik et  
860 al., 2016; Köseoğlu et al., 2018) and superimposed CT predictions of marginal (red circles),  
861 intermediate (yellow squares), and extensive (green diamonds) sea ice cover. Dashed  
862 horizontal lines represent the satellite SpSIC boundaries used to separate the sea ice classes in  
863 the CT model (Köseoğlu et al., 2018), where 10% and 50% satellite SpSIC thresholds  
864 correspond to the marginal-intermediate and intermediate-extensive boundaries, respectively;  
865 (c) Running Pearson’s correlations for IP<sub>25</sub> versus HBI II (black line with circle markers) and  
866 HBI III (Z) versus HBI III (E; red line) with a sampling window of 9 core horizons. Grey  
867 diamonds represent correlations significant at  $p = 0.05$ , and the dashed line separates positive  
868 ( $r > 0$ ) and negative ( $r < 0$ ) correlations.

869 **Figure 4.** Proxy data and correlations for core 1200 (southwestern Barents Sea). The  
870 illustrated profiles are analogous to those shown in Fig. 3. The light blue vertical bar  
871 highlights the Younger Dryas stadial (12.95–11.70 cal kyr BP).

872 **Figure 5.** Proxy data and correlations for core 11 (western Barents Sea). The illustrated  
873 profiles are analogous to those shown in Figs. 3 and 4. In (b), crossed red squares represent  
874 horizons where the discrepancy between CT predictions and  $P_{III}IP_{25}$ -based SpSIC estimates  
875 exceeded the  $P_{III}IP_{25}$ -SpSIC calibration RMSE of ca. 11% (Smik et al., 2016). The light blue  
876 vertical bar highlights the Younger Dryas stadial (12.95–11.70 cal kyr BP).

877 **Figure 6.** Biomarker profiles and correlations for core 11: (a) Concentrations of  $IP_{25}$  and HBI  
878 II represented by black (with circle markers) and green lines, respectively; (b) Running  
879 correlation of first relative (%) differences, with a sampling window of 9 horizons. Positive  
880 and negative correlations are separated by a dashed horizontal line, while grey diamonds  
881 show correlations significant at a 95% confidence level. In both (a) and (b), crossed red  
882 squares represent samples for which CT model predictions significantly differed from  
883  $P_{III}IP_{25}$ -derived % SpSIC values, with a discrepancy exceeding the RMSE of the  $P_{III}IP_{25}$ -  
884 SpSIC calibration (ca.  $\pm 11\%$  SpSIC). The light blue vertical bar highlights the Younger  
885 Dryas stadial (12.95–11.70 cal kyr BP).

886 **Figure 7.** Pearson’s correlations of  $IP_{25}$  versus HBI II (upper panel series A) and HBI III (Z)  
887 versus HBI III (E) (lower panel series B) in Barents Sea surface sediments with marginal  
888 (<10% SpSIC; red circles), intermediate (10–50% SpSIC; yellow triangles), and extensive  
889 (>50% SpSIC; green squares) overlying sea ice conditions. Surface sediment biomarker data  
890 was taken from Köseoğlu et al. (2018).

891 **Figure 8.** Biomarker composition and CT model output for cores 70, 1200, and 11 using  
892 different RF combinations: (a) Averaged relative abundances of  $IP_{25}$  and HBIs II, III (Z) and

893 III (E) in surface sediments and cores using calibrated and arbitrarily equated (uncalibrated)  
894 RFs; (b) Percentage distribution of core horizons classified into three categories of sea ice  
895 conditions by the CT model. “Correct RFs” and “incorrect RFs” indicate the respective use of  
896 calibrated RFs and arbitrarily equated RFs for both the CT training set (surface sediments)  
897 and cores. “Mismatched RFs” represents the use of calibrated and uncalibrated RFs for the  
898 training set and downcore records, respectively. Values within white circles correspond to the  
899 number of horizons classified into a given category of sea ice conditions where a discrepancy  
900 with  $P_{III}IP_{25}$ -based SpSIC estimates of at least 1% was observed. No samples were  
901 misclassified into the extensive (>50% SpSIC) sea ice category.

Figure 1

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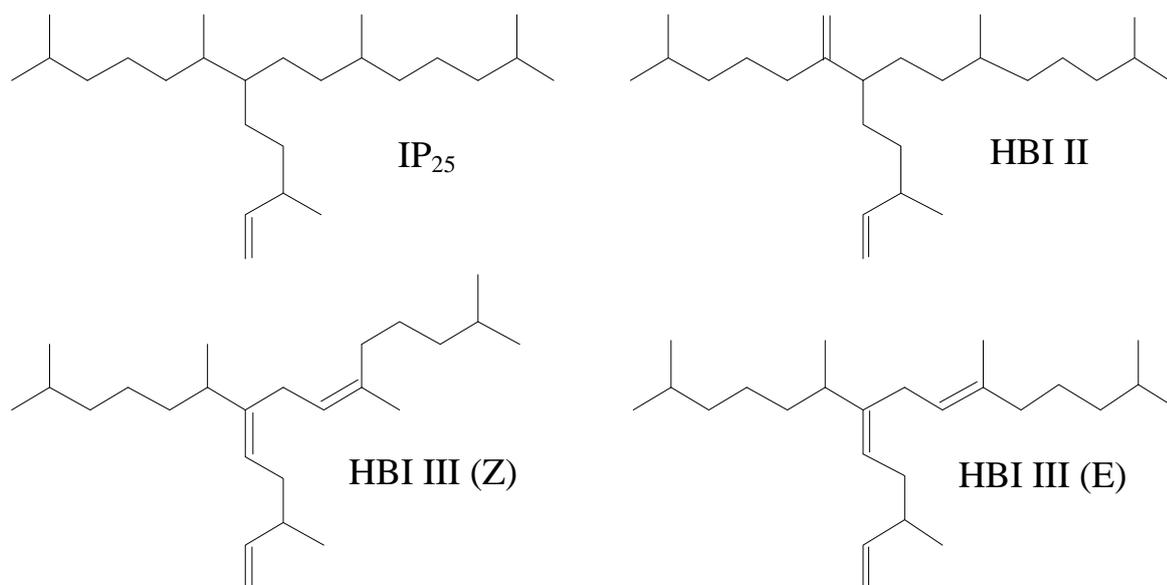


Figure 2

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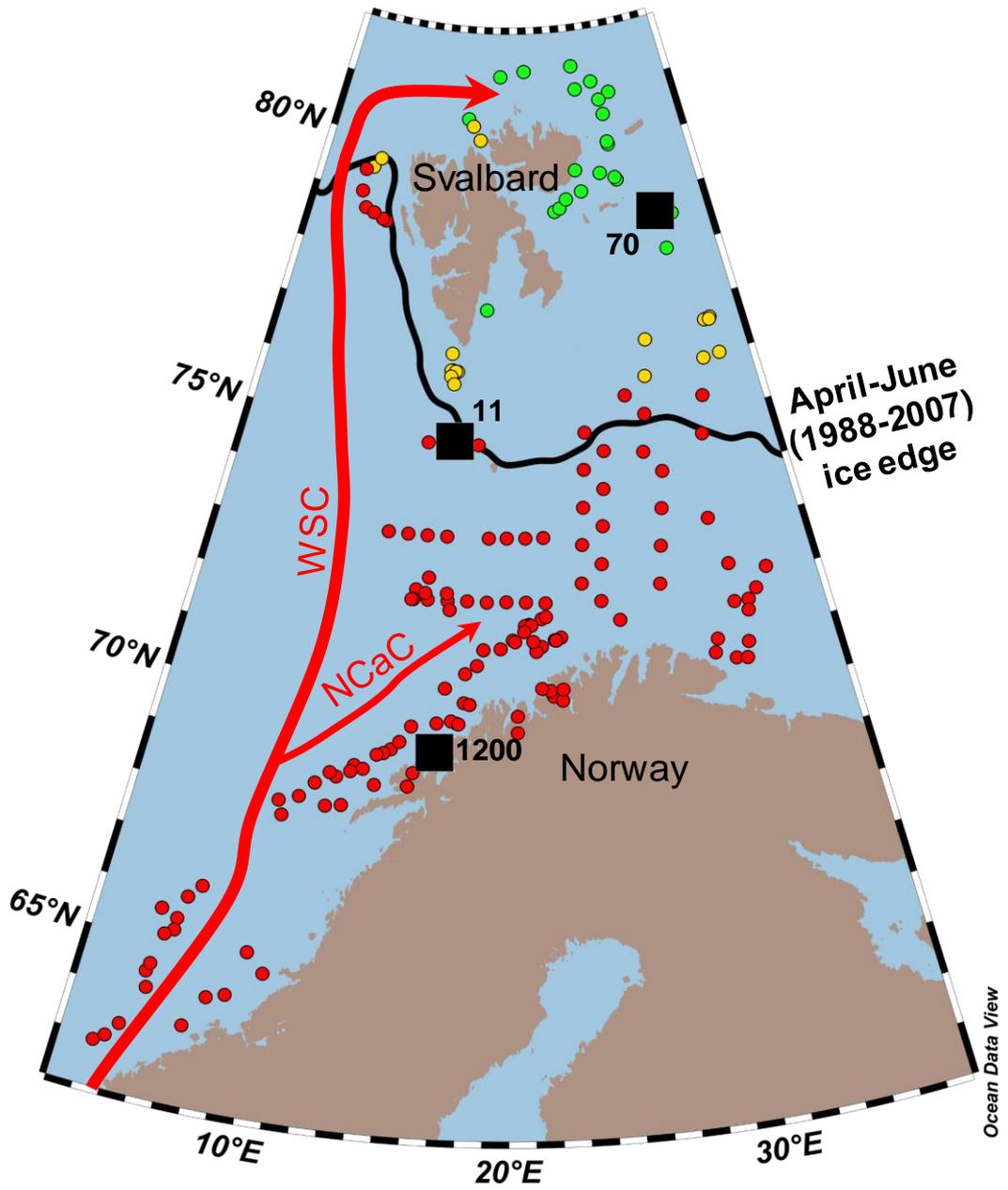


Figure 3

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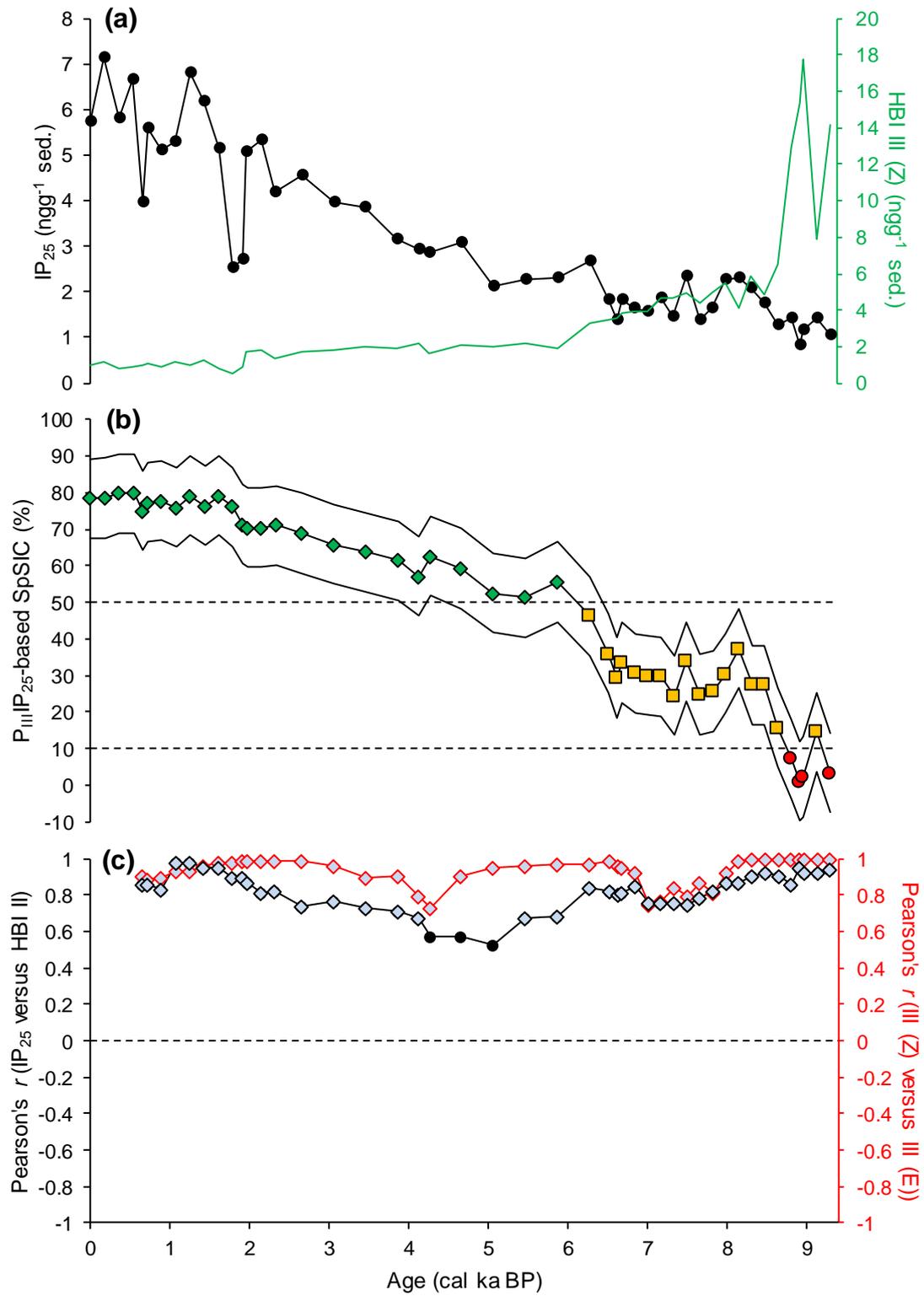


Figure 4

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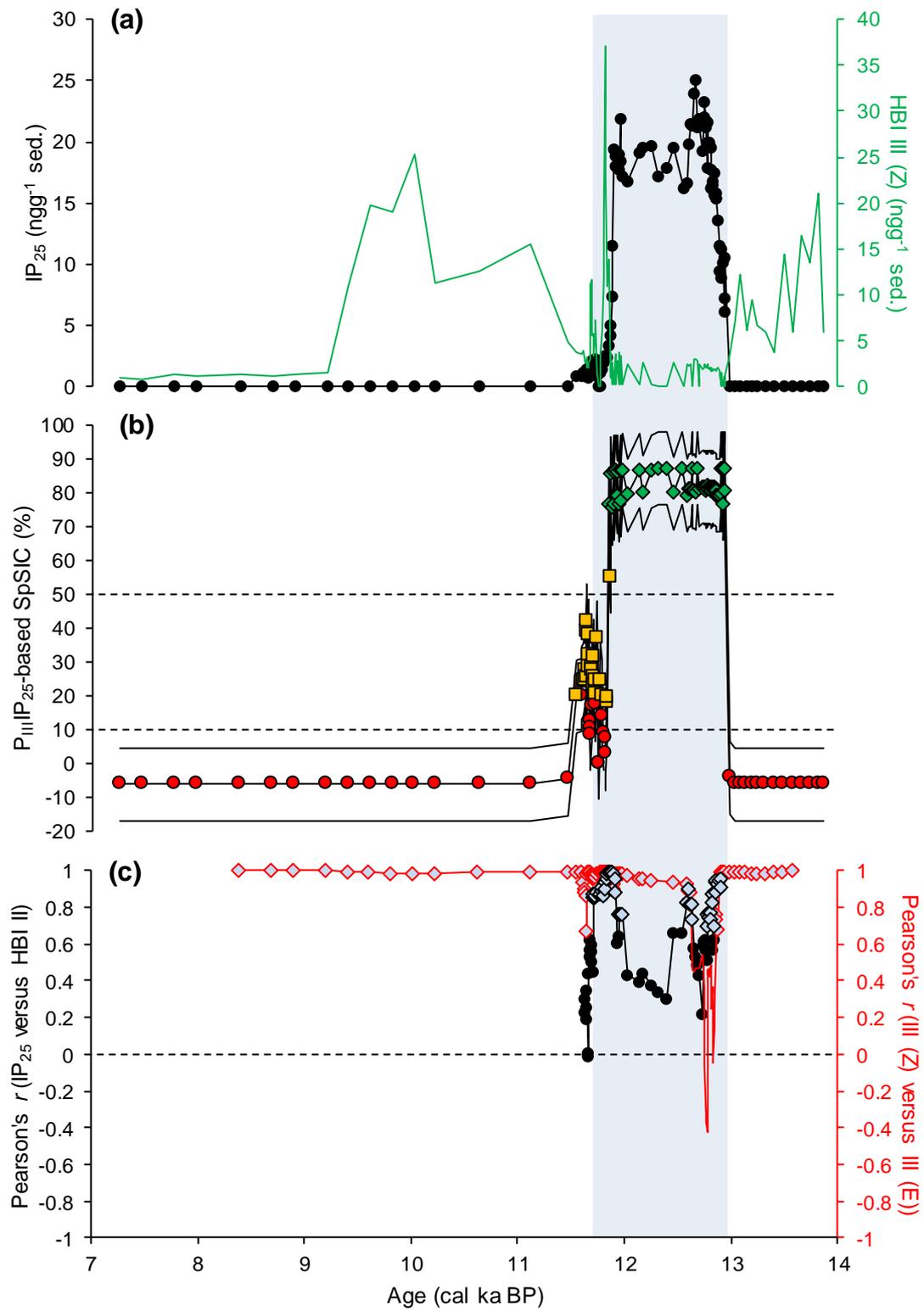


Figure 5

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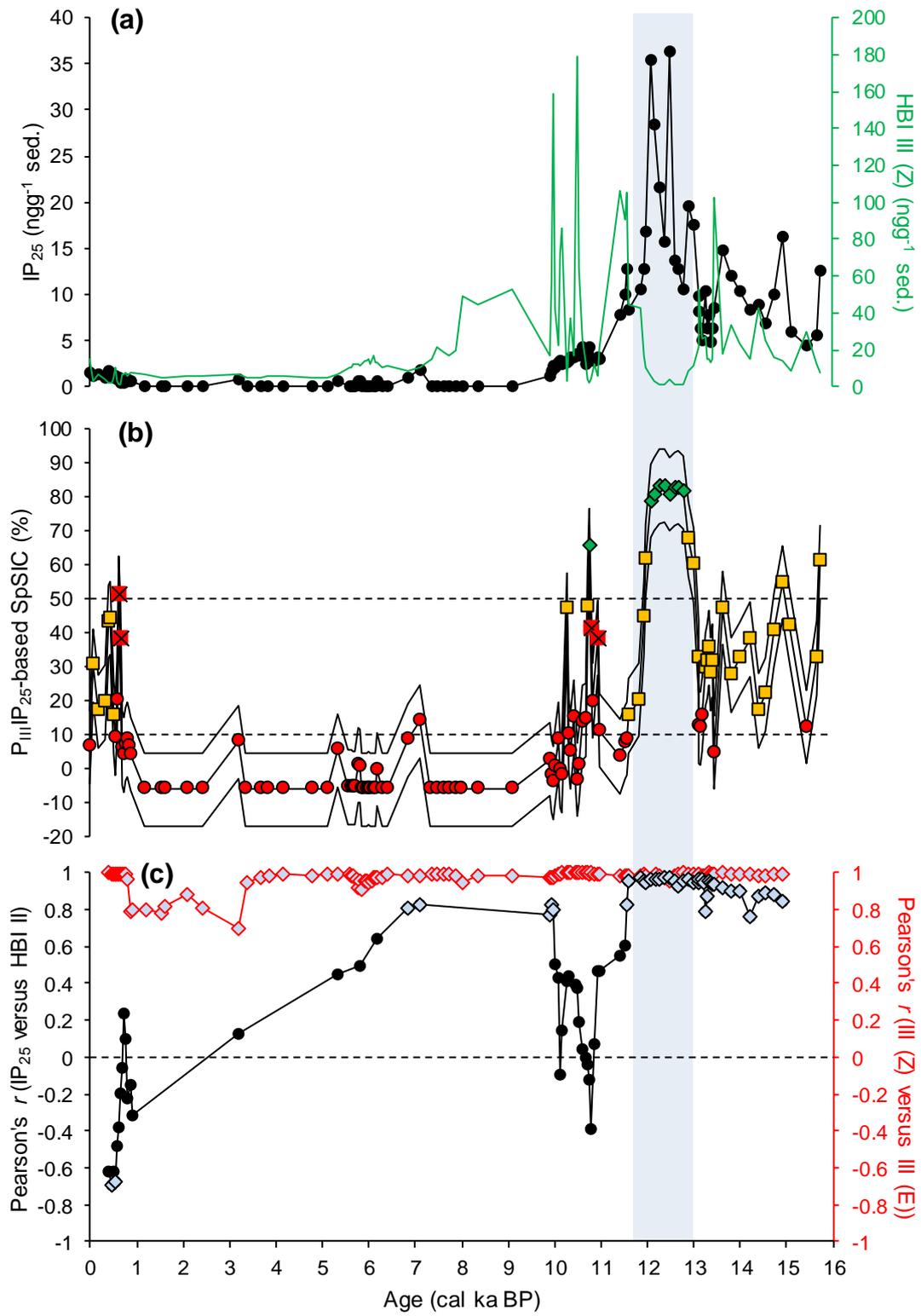
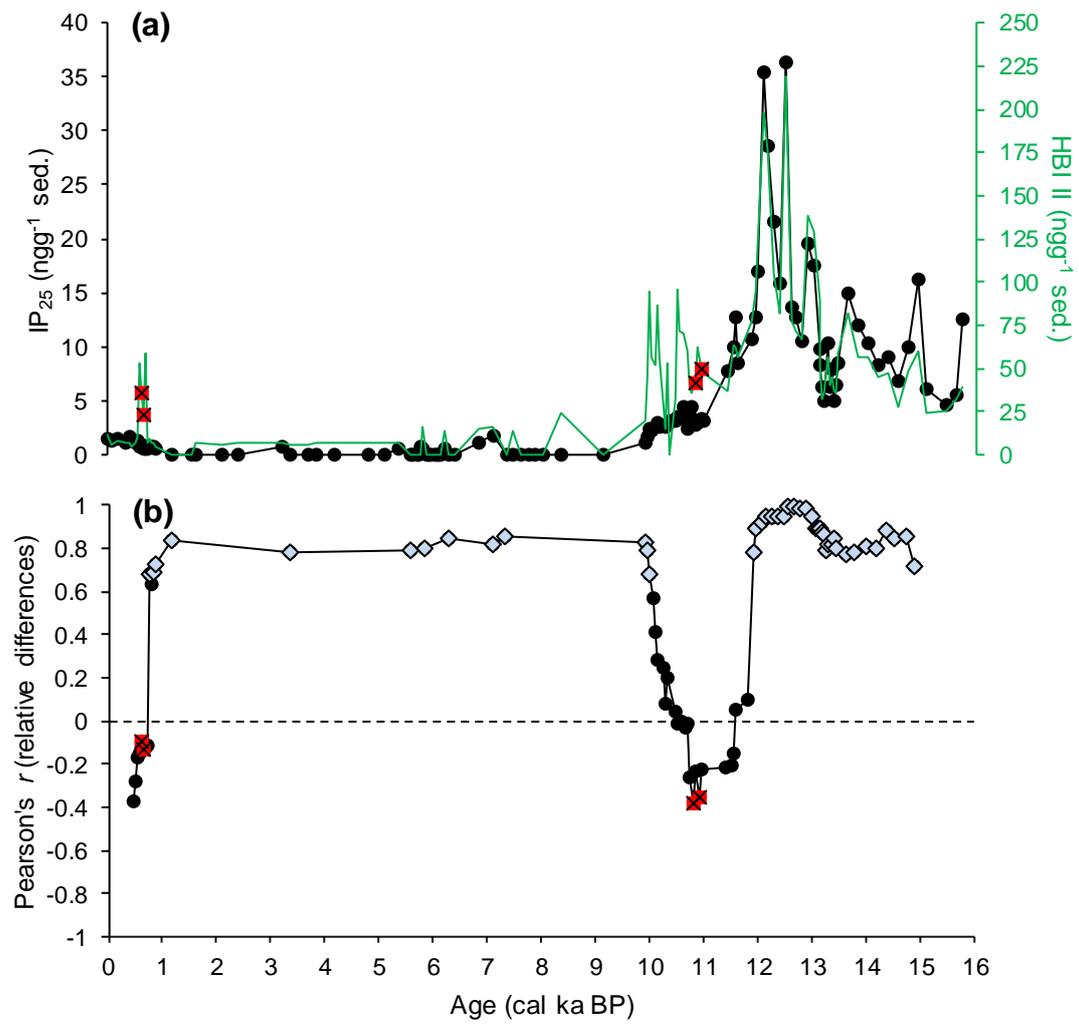


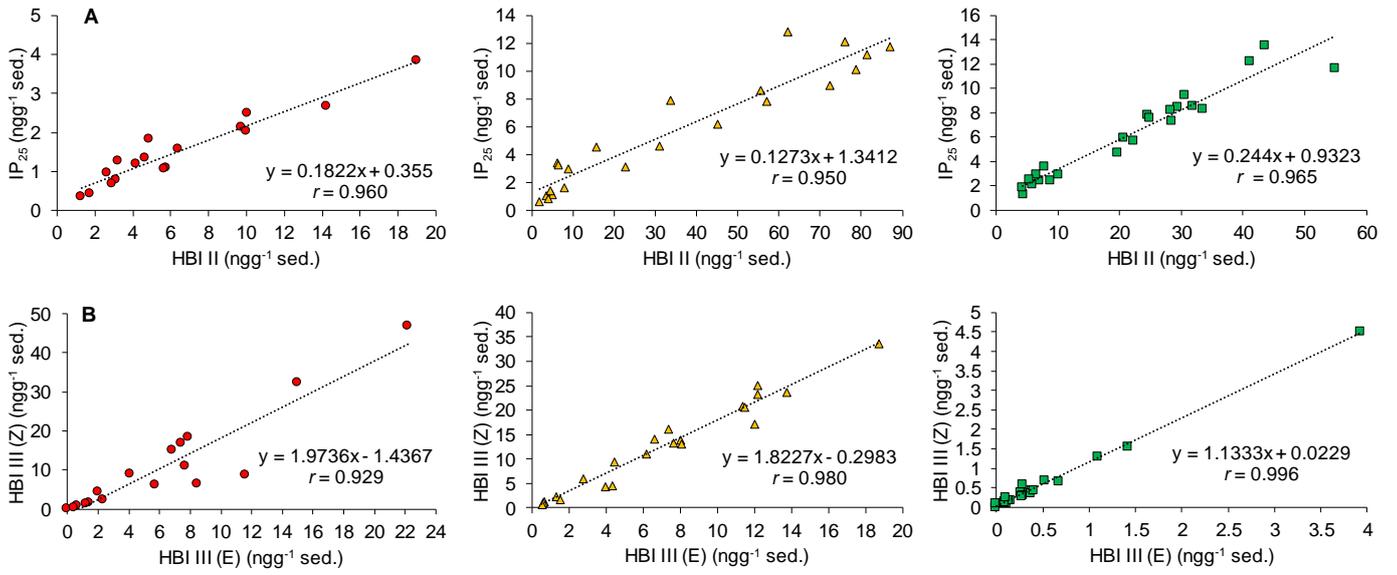
Figure 6

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Figure 7



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Figure 8

