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Autoxidation of the sea ice biomarker proxy IPSO ²⁵ in the near-surface oxic layers of Arctic and Antarctic sediments

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3 Autoxidation of the sea ice biomarker proxy IPSO₂₅ in
4 the near-surface oxic layers of Arctic and Antarctic
5 sediments

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23 **Abstract**

24

25 Over the last decade or so, the mono- and di-unsaturated highly branched isoprenoid (HBI)
26 lipids IP₂₅ (Ice Proxy with 25 carbon atoms) and IPSO₂₅ (Ice Proxy for the Southern Ocean
27 with 25 carbon atoms) have emerged as useful proxies for sea ice in the Arctic and Antarctic,
28 respectively. A more complete understanding of their respective proxy signatures, however,
29 requires more detailed knowledge of their stability in the water column and in sediments. In
30 the current study, we focused on the autoxidation of IPSO₂₅, first by performing laboratory-
31 based oxidation reactions on a purified sample and characterizing products based on detailed
32 mass spectral analysis. We then analysed for the same oxidation products in near-surface
33 sediments retrieved from the Arctic and the Antarctic, and some suspended organic matter
34 from the Antarctic. Our data show that IPSO₂₅ is susceptible to partial autoxidation within
35 the oxic layers of Arctic and Antarctic sediments, while the same processes appear not to be
36 so important in the water column. Although the number of primary autoxidation reactions
37 identified in sediments was not as large as in laboratory experiments, there was evidence for
38 their subsequent modification by biotic degradation. Quantifying the extent of degradation
39 of IPSO₂₅ and IP₂₅ in sediments, and thus the impact of such process on the use of these
40 biomarkers as paleo sea ice proxies, remains challenging at this stage, since most of the
41 primary oxidation products do not accumulate, likely due to secondary biodegradation
42 reactions. Some interesting differences in reactivity were also observed between IPSO₂₅ and
43 IP₂₅ present in the same Arctic sediments. This suggests that factors other than
44 environmental control may influence the IPSO₂₅/IP₂₅ ratio (i.e. DIP₂₅) in Arctic sediments.

45

46 **Key words:** IPSO₂₅; Degradation; Autoxidation; Arctic and Antarctic sediments; Biotic and
47 abiotic interactions; IP₂₅; DIP₂₅.

48 1. Introduction

49

50 C₂₅ and C₃₀ highly branched isoprenoid (HBI) alkenes (commonly exhibiting
51 between one and six double bonds) are ubiquitous biomarkers found in a wide range of
52 marine and lacustrine sediments (Rowland et al., 1990; Belt et al., 2000; Sinninghe Damsté
53 et al., 2004). Despite this, HBIs appear to be biosynthesized by a relatively small number of
54 diatom taxa belonging to the *Haslea*, *Navicula*, *Pleurosigma*, *Berkeleya*, *Rhizosolenia* and
55 *Pseudosolenia* genera (Volkman et al., 1994; Sinninghe-Damsté et al., 1999; Belt et al.,
56 2001a, 2001b, 2016; Grossi et al., 2004; Brown et al., 2014; Kaiser et al., 2016). Amongst
57 the more recent investigations, a mono-unsaturated C₂₅ HBI alkene (3,9,13-trimethyl-6-(1,5-
58 dimethylhexyl)-tetradec-1-ene) was identified in Arctic sea ice and in underlying sediments
59 (Belt et al, 2007; Vare et al, 2009). Since this HBI is believed to only be made by certain
60 Arctic sea ice diatoms (Belt et al., 2007; Brown et al., 2014) and appears relatively stable in
61 the geological record, its analysis in marine sedimentary archives provides a proxy measure
62 of seasonal Arctic sea ice in the past. More commonly referred to as IP₂₅ (Ice Proxy with 25
63 carbon atoms), this HBI has been used as the basis for sea ice reconstructions spanning
64 different Arctic regions and over a range of timescales (see Belt, 2018 for a recent
65 compilation of sea ice reconstructions). A related di-unsaturated HBI (2,6,10,14-
66 tetramethyl-7-(3-methylpent-4-enyl)-pentadec-6(17)-ene), sometimes referred to as diene II,
67 is co-produced with IP₂₅ in the Arctic, and is also biosynthesized by some Antarctic sea ice
68 diatoms (Nichols et al., 1993; Johns et al., 1999; Belt et al., 2016). Interestingly, however,
69 IP₂₅ has not been reported in sea ice, sediments or the water column from around the
70 Antarctic. As such, diene II has been proposed as a proxy measure for sea ice in the Southern
71 Ocean, and the term IPSO₂₅ (Ice Proxy for the Southern Ocean with 25 carbon atoms) has
72 been recently proposed (Belt et al., 2016). Although IPSO₂₅ appears to be a common

73 constituent of Antarctic surface sediments (for near-coastal regions, at least; Nichols et al.,
74 1993; Johns et al., 1999; Belt et al., 2016; Belt, 2018,2019), analysis of IPSO₂₅ in downcore
75 Antarctic archives has so far resulted in only a relatively small number of palaeo sea ice
76 reconstructions, at least in comparison with IP₂₅ for the Arctic (e.g., Collins et al., 2013;
77 Etourneau et al., 2013; Barbara et al., 2016; Campagne et al., 2016; see also Belt, 2018,2019
78 for a recent review and summary). Finally, in the Arctic, the ratio IPSO₂₅/IP₂₅ (sometimes
79 referred to as DIP₂₅) has previously been proposed as a possible indicator of variability in
80 sea ice conditions or even of sea surface temperatures (SST) (e.g. Fahl and Stein, 2012; Stein
81 et al., 2012; Cabedo-Sanz et al., 2013).

82 As with all proxies, including those based on individual or combinations of
83 biomarkers, their application requires careful consideration of alteration and preservation
84 between their source and sedimentary environments. It is necessary, therefore, to determine
85 the magnitude and relative importance of various biotic and/or abiotic processes that can
86 influence the preservation of the original source signature. In the case of HBIs, bacterial
87 degradation of some HBIs was studied several decades ago (Robson and Rowland, 1988),
88 yet the effects of photo- and autoxidation on these compounds have been examined only
89 relatively recently. Motivation for the more recent studies stems partly from the proxy
90 signatures of certain HBIs such as IP₂₅ and IPSO₂₅, as described above, together with the
91 now well-known high reactivity of terrestrial and marine organic matter, more generally, in
92 the Arctic (Rontani et al., 2012,2016,2017). By studying the reactivity of a range of HBI
93 alkenes towards different abiotic processes in solvents and in senescent diatoms (Rontani et
94 al., 2011,2014), extremely low reactivities of mono- and di-unsaturated HBIs were observed,
95 and attributed to the presence of relatively unreactive terminal double bonds. Such lack of
96 reactivity is consistent with the general lack of degradation of IP₂₅ in the water column
97 following sea ice melt (Brown et al., 2016; Rontani et al., 2018a). However, lipid

98 autoxidation is not limited to the water column, and can potentially be an important process
99 in the oxic layers of sediments, especially for regions of low accumulation rates, where near-
100 surface sediments may represent relatively long time intervals (decades to centuries). Indeed,
101 as part of a recent laboratory-based investigation into the autoxidation of IP₂₅, a series of
102 oxidation products were characterized that could also be identified in sediment material from
103 the Canadian Arctic (Rontani et al., 2018a). This study demonstrated the susceptibility of
104 IP₂₅ towards autoxidation in Arctic sediments, a process that was more prevalent in cases
105 where sequestered ice algal material experienced relatively long residence times in the oxic
106 layer. On the other hand, the near-ubiquity of IP₂₅ in surface sediments from across the Arctic
107 suggests that such oxidation reactions likely perturb its sedimentary content, rather than
108 remove it.

109 In the present work, we aimed to determine whether IPSO₂₅ also undergoes
110 autoxidation in near-surface Arctic and Antarctic sediments and, therefore, whether palaeo
111 sea ice reconstructions using this proxy should consider the possible impact of this type of
112 degradation. To achieve this, oxidation of purified IPSO₂₅ was carried out under more
113 powerful oxidative conditions than previously employed (Rontani et al., 2014) and the main
114 products were identified by high resolution mass spectral analysis. The same oxidation
115 products were then analysed for, and quantified, in sediment samples from the Canadian
116 Arctic and the West Antarctic Peninsula (WAP).

117

118 **2. Experimental**

119

120 *2.1. Sediment sampling*

121 Sediment material from the Arctic was taken from a box core obtained from Barrow
122 Strait (STN 4) in the Canadian Arctic on board the CCGS Amundsen in 2005 (Belt et al.,

123 2013). The box core was sectioned on board, with sub-samples (1 cm resolution) then frozen
124 (-20° C) prior to being freeze-dried and stored (-20° C to +4° C) prior to analysis (Rontani
125 et al., 2018a). The redox boundary layer was identified using the change (reduction) in Mn
126 content as described previously (Vare et al., 2009; Brown, 2011 and references cited therein).
127 Sediment material from the WAP (see Belt et al., 2016 for details of locations) was obtained
128 from the upper 0–1 cm of box cores collected between 2002 and 2011 and then held at the
129 British Antarctic Survey (UK) or the British Ocean Sediment Core Research Facility
130 (BOSCORF, UK) at +4° C. suspended particulate matter (SPM) were obtained off the coast
131 of East Antarctica as described previously (Rontani et al., 2018b) (Supplementary Figure 1).

132

133 2.2. Chemicals

134 A sample of purified IPSO₂₅ was obtained from a culture of the marine diatom *Haslea*
135 *ostrearia* as described previously (Johns et al., 1999).

136 Treatment of IPSO₂₅ with a stoichiometric amount of perchloroperbenzoic acid in
137 dry dichloromethane (4h at 50 °C) mainly afforded 1,2-epoxy-2-(4-methylpentyl)-3-(3-
138 methylpent-4-enyl)-6,10-dimethylundecane (**1**) (93%) (Belt et al., 2007) and to a lower
139 extent 1,2-epoxy-3,9,13-trimethyl-6-(1-methylidene-5-methylhexyl)-tetradecane (**2**) (7%)
140 (total yield 85%). Differentiation between these two isomers was difficult due to their very
141 similar mass spectra and needed LiAlH₄-reduction to the corresponding alcohols (see
142 below).

143 Oxidation of IPSO₂₅ using RuCl₃ and *tert*-butyl hydroperoxide in cyclohexane at
144 room temperature for 16 h (Seki et al., 2008) and subsequent NaBH₄-reduction in ether-
145 methanol (4:1, v/v) produced 6-methylidene-2,10,14-trimethyl-7-(3-methylpent-4-enyl)-
146 pentadecan-5-ol (**3**) and 3,9,13-trimethyl-6-(1-methylidene-5-methylhexyl)-tetradec-1-en-

147 3-ol (**4**) in low yield. It is interesting to note that using a mixture of RuCl₃ and *tert*-butyl
148 hydroperoxide failed to attack the tertiary allylic position at C-7, likely due to steric
149 hindrance.

150 LiAlH₄-reduction of the mixture of epoxides **1** and **2** in dry diethyl ether (1 h at room
151 temperature) afforded 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-pentadecan-6-ol (**5**)
152 and 3,9,13-trimethyl-6-(1-methylidene-5-methylhexyl)-tetradecan-2-ol (**6**), respectively
153 (total yield 95%).

154 Treatment of IPSO₂₅ with a stoichiometric amount of OsO₄ in dioxane-pyridine (8:1,
155 v/v) at room temperature for 1h (MacCloskey and MacClelland, 1965) afforded 2-(4-
156 methylpentyl)-3-(3-methylpent-4-enyl)-6,10-dimethylundecane-1,2-diol (**7**) (yield 60%).

157 3,9,13-trimethyl-6-(1-methylene-5-methylhexyl)-tetradecane-1,2-diol (**8**) was
158 obtained in small amounts after hydrolysis of the epoxide **2** in a mixture of MeOH and HCl
159 2N (5:1, v/v) at 50 °C for 2 h. Under these conditions epoxide **1** mainly isomerized to allylic
160 alcohols.

161 3,7,11,15-Tetramethylhexadecan-1,2-diol (**9**) was produced by Pd/CaCO₃-catalysed
162 hydrogenation of 3-methylidene-7,11,15-trimethylhexadecan-1,2-diol (**10**) (Rontani et al.,
163 2018), whose synthesis from phytol was described previously (Rontani and Aubert, 2005).

164 2,6,10,14-Tetramethylpentadecan-2-ol (**11**) was produced by condensation of
165 6,10,14-trimethylpentadecan-2-one (**12**) with methylolithium in anhydrous diethyl ether as
166 previously described (Rontani et al., 2013a).

167

168 *2.3. Induction of autoxidation in solvent*

169 Autoxidation experiments were performed under an atmosphere of air in 15 ml
170 screw-cap flasks containing IPSO₂₅ (10 µg), *tert*-butyl hydroperoxide (300 µl of a 6.0 M
171 solution in decane), di-*tert*-butyl nitroxide (1.2 mg) and hexane (2 ml). After stirring, the
172 flask was incubated in the dark at 65 °C. A relatively high temperature was selected in order
173 to accelerate the autoxidation reactions. Aliquots (200 µl) were withdrawn from the reaction
174 mixture after incubation for different times. Each sub-sample was evaporated to dryness
175 under a stream of nitrogen and analyzed by gas chromatography–electron ionization
176 quadrupole time of flight mass spectrometry (GC-QTOF) after NaBH₄ reduction (Section
177 2.5) and derivatization (Section 2.7) for identification of hydroxylated oxidation products.

178

179 *2.4. Reduction of oxidation products*

180 Hydroperoxides resulting from IPSO₂₅ oxidation were reduced to the corresponding
181 alcohols by reaction with excess NaBH₄ in diethyl ether:methanol (4:1, v/v) at room
182 temperature (1 h). After reduction, a saturated solution of NH₄Cl (10 ml) was added
183 cautiously to remove any unreacted reducer; the pH was adjusted to 1 with dilute HCl (2 N)
184 and the mixture shaken and extracted with hexane:chloroform (5 ml, 4:1, v/v; x3). The
185 combined extracts were dried over anhydrous Na₂SO₄, filtered and evaporated to dryness
186 under a stream of nitrogen.

187

188 *2.5. Sediment and SPM treatment*

189 Sediments or SPM material (collected on GF/F filters, porosity 0.8 µm) were placed
190 in MeOH (15 ml) and hydroperoxides were reduced to the corresponding alcohols with
191 excess NaBH₄ (70 mg, 30 min at 20 °C). Following the reduction step, water (15 ml) and
192 KOH (1.7 g) were added and the mixture saponified by refluxing (2 h). After cooling, the
193 contents of the flask were acidified (HCl, to pH 1) and extracted three times with

194 dichloromethane (DCM) (30 ml). The combined DCM extracts were dried over anhydrous
195 Na₂SO₄, filtered and concentrated to give the total lipid extract (TLE). Since IPSO₂₅
196 oxidation product content was quite low relative to other lipids, accurate quantification
197 required further separation of the TLE using column chromatography (silica; Kieselgel 60,
198 8 x 0.5 cm). IPSO₂₅ was recovered in the hexane eluate and its oxidation products in the
199 dichloromethane eluate.

200

201 *2.6. Derivatization*

202 In order to analyse for hydroxylated products (i.e. alcohols and carboxylic acids),
203 lipid extracts were derivatized by dissolving them in 300 µl pyridine/bis-
204 (trimethylsilyl)trifluoroacetamide (BSTFA; Supelco; 2:1, v/v) and silylated (50 °C, 1 h).
205 After evaporation to dryness under a stream of N₂, the derivatized residue was re-dissolved
206 in 100 µl BSTFA (to avoid desilylation of fatty acids), together with an amount of solvent
207 (ethyl acetate) dependent on the mass of the extract, and then analyzed using GC-QTOF and
208 GC-MS/MS.

209

210 *2.7. GC-QTOF analyses*

211 Accurate mass spectra were obtained with an Agilent 7890B/7200 GC-QTOF System
212 (Agilent Technologies, Parc Technopolis - ZA Courtaboeuf, Les Ulis, France). A cross-
213 linked 5% phenyl-methylpolysiloxane (Macherey Nagel; Optima 5-MS Accent) column (30
214 m × 0.25 mm, 0.25 µm film thickness) was employed. Analysis was performed with an
215 injector operating in pulsed splitless at 280 °C and the oven temperature programmed from
216 70 °C to 130 °C at 20 °C/min, then to 250 °C at 5 °C/min and then to 300 °C at 3 °C/min.
217 The carrier gas (He) was maintained at 0.69 × 10⁵ Pa until the end of the temperature

218 program. Instrument temperatures were 300 °C for transfer line and 230 °C for the ion
219 source. Accurate mass spectra were recorded across the range m/z 50-700 at 4 GHz with
220 nitrogen as collision gas (1.5 ml/min). The QTOF-MS instrument provided a typical
221 resolution ranging from 8009 to 12252 from m/z 68.9955 to 501.9706.
222 Perfluorotributylamine (PFTBA) was utilized for daily MS calibration. Structural
223 assignments were based on interpretation of accurate mass spectral fragmentations and
224 confirmed by comparison of retention times and mass spectra of oxidation products with
225 those of authentic synthesized compounds.

226

227 2.8. GC-MS/MS analyses

228 GC/EIMS/MS experiments were performed using an Agilent 7890A/7010 tandem
229 quadrupole gas chromatograph system equipped with a HES source (Agilent Technologies,
230 Parc Technopolis - ZA Courtaboeuf, Les Ulis, France). A cross-linked 5% phenyl-
231 methylpolysiloxane (Agilent; HP-5MS) (30 m × 0.25 mm, 0.25 μm film thickness) capillary
232 column was employed. Analyses were performed with an injector operating in pulsed
233 splitless mode set at 270 °C and the oven temperature programmed from 70 °C to 130 °C at
234 20 °C/min, then to 250 °C at 5 °C/min and then to 300 °C at 3 °C/min. The pressure of the
235 carrier gas (He) was maintained at 0.69×10^5 Pa until the end of the temperature program
236 and then programmed from 0.69×10^5 Pa to 1.49×10^5 Pa at 0.04×10^5 Pa/min. The
237 following mass spectrometric conditions were employed: electron energy, 70 eV; transfer
238 line, 300 °C; source temperature, 230 °C; quadrupole 1 temperature, 150 °C; quadrupole 2
239 temperature, 150 °C; collision gas (N₂) flow, 1.5 ml/min; quench gas (He) flow, 2.25 ml
240 /min; mass range, 50-700 Dalton; cycle time, 313 ms. Collision induced dissociation (CID)
241 was optimized by using collision energies at 5, 10, 15 and 20 eV. Quantification of oxidation

242 products **3**, **5** and **7** was carried out with external standards in multiple reaction monitoring
243 (MRM) mode. Precursor ions were selected from the more intense and specific ions observed
244 in EI mass spectra. Due to the very low amounts of IPSO₂₅ available, these compounds could
245 not be produced in sufficient amounts to be used as external standard during their
246 quantification in sediment samples. TMS derivative of structurally similar isoprenoid
247 compounds (3-methylidene-7,11,15-trimethylhexadecan-1,2-diol (**10**) for compound **3**,
248 2,6,10,14-tetramethylpentadecan-2-ol (**11**) for compound **5** and 3,7,11,15-
249 tetramethylhexadecan-1,2-diol (**9**) for compound **7**) (see appendix) were thus used as
250 external standards. Correction factors that took into account the proportion of the selected
251 precursor ion in the EIMS of each compound and that of the selected MRM transition in
252 each CID-MS were employed.

253

254 **3. Results**

255

256 *3.1. Autoxidation of IPSO₂₅ in solvent*

257 A number of different oxidation products could be detected after incubation of
258 IPSO₂₅ in hexane in the presence of *tert*-butyl hydroperoxide (radical enhancer) and di-*tert*-
259 butyl nitroxide (radical initiator) (Porter et al., 1995) at 65 °C and subsequent NaBH₄-
260 reduction and silylation. Comparison of retention times and accurate mass spectra of these
261 compounds (Figs. 1 and 2) with qualitative standards prepared by oxidation of purified
262 IPSO₂₅ (Section 2.2) allowed formal identification of compounds **1** (59.2%), **2** (5.9%), **3**
263 (9.3%), **4** (10.2%) and **7** (traces). A compound derived from the attack of the terminal tertiary
264 carbon atoms was also detected, and tentatively attributed to 10-methylidene-2,6,14-
265 trimethyl-9-(3-methylpent-4-enyl)-pentadecan-2-ol (**13**) or 6-methylidene-2,10,14-

266 trimethyl-7-(3-methylpent-4-enyl)-pentadecan-2-ol (**14**) (7.6%) on the basis of the accurate
267 mass fragmentations observed (Fig. 1D).

268

269 *3.2. Autoxidation of IPSO₂₅ in Arctic and Antarctic sediments*

270 The DCM eluates obtained after chromatographic fractionation of the total lipid
271 extracts from the sediments investigated were analysed in MRM mode. The use of the
272 transitions m/z 365 \rightarrow 275, m/z 365 \rightarrow 135 and m/z 365 \rightarrow 149 and the comparison of
273 retention time with the oxidation products characterized during the thermal incubation
274 reactions allowed the unambiguous detection of the alcohol **3** (Fig. 3). In contrast, we failed
275 to detect the oxidation products **1**, **2** and **4**. Taking into account: (i) the presence of the IPSO₂₅
276 oxidation product **3** in the sediments and (ii) the well-known lability of epoxides, we
277 searched for the presence of the reduction and hydrolysis products of the main oxidation
278 product **1** (i.e. 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-pentadecan-6-ol (**5**) (Fig. 2A)
279 and 2-(4-methylpentyl)-3-(3-methylpent-4-enyl)-6,10-dimethylundecane-1,2-diol (**7**) (Fig.
280 2C)). By using appropriate MRM transitions, we were able to detect the tertiary alcohol **5** in
281 DCM eluates of both Arctic and Antarctic sediments (Fig. 4). In contrast, diol **7** could only
282 be identified in the Arctic sediment extracts (Fig. 5).

283 As described in Section 2.8, quantification of compounds **3**, **5** and **7** involved the use
284 of TMS derivatives of structurally similar isoprenoid compounds as external standards. The
285 transitions employed for quantification were (i) m/z 365 \rightarrow 275 and m/z 353 \rightarrow 263 (loss of
286 trimethylsilanol by the precursor ion) for the alcohol **3** and the standard **10**, respectively; (ii)
287 m/z 353 \rightarrow 117 and m/z 341 \rightarrow 117 (formation of the product ion TMS-O⁺=CH-CH₃) for the
288 tertiary alcohol **5** and the standard **11**, respectively; (iii) m/z 423 \rightarrow 333 and m/z 355 \rightarrow 265
289 (loss of trimethylsilanol by the precursor ion) for the diol **7** and the standard **9**, respectively.

290 As indicated in Section 2.8, corrective factors were applied to accommodate for structural
291 differences between the oxidation product and the corresponding standard. The resulting
292 concentrations of compounds **3**, **5** and **7** are given in Tables 1 and 2.

293

294 *3.3. Autoxidation of IPSO₂₅ in Antarctic SPM*

295 We also analysed for IPSO₂₅ oxidation products in lipid extracts of suspended
296 particles collected at different water depths in the polynya region west of the Dalton Iceberg
297 Tongue (East Antarctica) and where an intense autoxidation of some other lipids was
298 previously observed (Rontani et al., 2018b). However, compounds **3**, **5** and **7** could not be
299 identified in any of the samples analysed.

300

301 **4. Discussion**

302

303 *4.1. Autoxidation of IPSO₂₅ in solvent*

304 It is well-known that addition of ROO• radicals to a C=C bond competes with allylic
305 hydrogen abstraction when there is a double bond that is either conjugated or 1,1-
306 disubstituted (Schaich, 2005). Consistent with this, we observed efficient addition of peroxy
307 radicals to the 1,1-disubstituted 6-17 double bond of IPSO₂₅ affording epoxide **1** as the major
308 product (59.2% of total oxidation products) after fast intramolecular homolytic substitution
309 (Fossey et al., 1995) (Fig. 6). In contrast, addition to the terminal 23-24 double bond was
310 relatively minor (5.9% of total oxidation products). Addition of peroxy radicals to the 6-17
311 double bond also resulted in the formation of trace amounts of the diol **7** after subsequent
312 oxygen addition and hydrogen abstraction (Fig. 6). Parallel to these peroxy radical addition

313 reactions was a series of competitive hydrogen abstraction reactions leading to the formation
314 of hydroperoxides **15-18** (see appendix), which manifest as alcohols **3, 4, 13** and **14**
315 following NaBH₄-reduction during treatment. Hydrogen atom abstraction from the allylic
316 carbon atoms 5 and 22 of IPSO₂₅ and subsequent oxidation of the resulting radicals to yield
317 hydroperoxides **15** and **16**, respectively (Fig. 6), is as expected given the relatively stable
318 allylic radicals formed (Fig. 6), with the additional formation of hydroperoxides **17** and **18**
319 presumably attributable to the stability of their respective tertiary radical precursors.
320 Surprisingly, we failed to detect oxidation products resulting from hydrogen atom
321 abstraction at carbon 7, despite the stability of the tertiary allylic radical formed. These
322 results are consistent with the very low efficiency of autoxidative processes at the allylic C-
323 7 previously observed in the case of (6-17, 9-10, 23-24) HBI triene (Rontani et al., 2014).
324 We suggest that the lack of reaction at C-7 results from steric hindrance during hydrogen
325 abstraction by the bulky *tert*-butylperoxyl radicals employed during the incubation, and is
326 supported by the lack of oxidation of the allylic carbon 7 observed during treatment of
327 IPSO₂₅ with RuCl₃- *tert*-butyl hydroperoxide (see Section 2.2). Hydrogen atom abstraction
328 from non-allylic tertiary carbon atoms appeared to be limited to the external tertiary carbon
329 atoms 2 and 14 of the molecule (and not to carbon 10), also likely due to steric hindrance.

330

331 *4.2. Degradation of IPSO₂₅ in Arctic and Antarctic sediments*

332 Despite the relative recalcitrance of mono- and di-unsaturated HBIs towards free
333 radical oxidation, reported previously (Rontani et al., 2011, 2014), oxidation product **3** could
334 be detected in most of the Arctic and Antarctic sediments (Tables 1 and 2), confirming the
335 partial autoxidation of IPSO₂₅ in both regions. On the other hand, the failure to detect the
336 major oxidation product of this diene in the incubation experiments (i.e. compound **1**) likely
337 results from: (i) the lack of specificity of its main MRM transitions, thus making it difficult

338 to identify, (ii) an intense degradation during the treatment (NaBH₄-reduction, alkaline
339 hydrolysis and acidification) or (iii) the well-known biotic and abiotic lability of epoxides in
340 sediments, more generally. Indeed, epoxides may undergo alcoholysis and hydrolysis during
341 alkaline hydrolysis and are converted to chlorohydrins during acidification with HCl
342 (Marchand and Rontani, 2001). Some epoxides are also slowly reduced to alcohols during
343 NaBH₄-reduction (Zabeti et al., 2010), but this is not the case for epoxide **1**. From a
344 biological perspective, these epoxides react readily with a large number of cell components
345 such as DNA or proteins (Swaving and de Bont, 1998) so their removal is essential for
346 bacteria to survive. This involves two main types of enzymes: glutathione transferases
347 (GSTs) (which catalyse the reduction of the epoxide ring to an alcohol, Kieslich et al., 1986)
348 and epoxide hydrolases (which catalyse the hydrolysis of the epoxide ring to a diol, Michaels
349 et al., 1980; Rustemov et al., 1991). Moreover, epoxides may also be hydrolysed abiotically
350 (Minerath et al., 2009) and rearranged to carbonyl compounds in sediments with high clay
351 content (Ruiz-Hitzky and Casal, 1985).

352 The presence of the tertiary alcohol **5** in the sediments investigated (Tables 1 and 2),
353 may therefore potentially be attributed to the reduction of the epoxide ring of the IPSO₂₅
354 oxidation product **1** by sedimentary bacteria (Fig. 7). However, alcohol **5** might also be
355 produced directly from IPSO₂₅ by bacteria after hydration (pathway II in Fig. 7) or
356 epoxidation (pathway III in Fig. 7) and subsequent reduction (pathway IV in Fig. 7). Indeed,
357 the involvement of hydration during anaerobic bacterial degradation of isoprenoid alkenes
358 (squalene, pristenes and phytene, Rontani et al., 2002, 2013a) and *n*-alk-1-enes (Grossi et
359 al., 2011) was demonstrated previously. On the other hand, bacterial epoxidation (mediated
360 by cytochrome P-450-dependent monooxygenases) can produce epoxides from a broad
361 range of lipophilic substrates such as *n*-alkenes (Soltani et al., 2004), terpenes (Duetz et al.,
362 2003), unsaturated fatty acids (for a review see Ratledge, 1994) and alkenones (Zabeti et al.,

2010). Since bacterial epoxidation should act more intensively on the terminal 23-24 double bond due to the better proximity of the terminal double bond to the heme iron of cytochrome P-450 (Andersen et al., 1997), the formation of epoxide **2** (Fig. 7) and its degradation products would thus be expected. However, the absence of alcohol **6** (resulting from the reduction of epoxide **2** or hydration of the 23-24 double bond of IPSO₂₅ (Fig. 7)) in the sediments analyzed points to the lack of such bacterial processes, so the formation of alcohol **5** seems thus to mainly result from bacterial reduction of the epoxide ring of autoxidation product **1**.

Further, due to the probable low reactivity of monooxygenases towards the 6-17 double bond of IPSO₂₅, the formation of diol **7** may be attributed to the biotic (induced by epoxide hydrolases) or abiotic (clay-catalyzed) hydrolysis of epoxide **1** (pathways V and VI in Fig. 7). The lack of methoxyhydrins and chlorohydrins derived from the degradation of the epoxide **1** in the presence of methanol and hydrochloric acid, respectively, also allow us to exclude the possible production of diol **7** during sample treatment (alkaline hydrolysis and acidification).

Surprisingly, diol **8** could not be detected during MRM analyses of the sediment extracts, despite the previous detection of its close structural analog (i.e. diol **19**) as an oxidation product of IP₂₅ in the same (STN 4) sediments (Rontani et al., 2018a). We attribute this to (i) the possible coelution of diols **7** and **8** and (ii) the very weak abundance of the precursor ion at *m/z* 423 in the mass spectrum of its TMS derivative (Fig. 2D), rather than from a lack of microbial degradation of IPSO₂₅.

In the sediments from the Arctic (STN 4), we also note the generally increasing proportion of IPSO₂₅ oxidation products with depth below the redox boundary (Fig. 8), indicative of a progressive reduction of hydroperoxide **15** (produced in the oxic layer) to the corresponding alcohol **3**, together with reduction and hydrolysis of the epoxide **1** to yield

388 alcohol **5** and diol **7**. However, due to the proposed action of sedimentary bacteria on the
389 autoxidation products of IPSO₂₅ (see earlier), the very low amounts of compounds **3**, **5** and
390 **7** relative to their parent compound (< 1%; Fig. 8) likely underestimates the extent of abiotic
391 degradation of IPSO₂₅, more generally.

392 In the Antarctic surface sediments, the proportion of oxidation products was always
393 low, ranging from 0.02 to 1.1% of the residual IPSO₂₅ (Table 1). These differences may
394 potentially be attributed to: (i) the ability for sedimentary bacterial communities to degrade
395 the primary IPSO₂₅ autoxidation products, as described above, or (ii) the different residence
396 times of algal material within the oxic layer of sediments, which may vary considerably
397 according to location. On the other hand, the variable degradation extent may reflect the
398 different times that the sediments have been kept in storage following collection; however,
399 for the samples analyzed, the lowest percentages of degradation products were observed in
400 the oldest samples (i.e. in BC 313/316 collected in 2002 compared to the other box cores
401 collected in 2008 and 2011; Table 1). These results, and those obtained previously for IP₂₅
402 (Rontani et al., 2018a), highlight the importance of the measurement of redox boundary
403 layers in upper sections of sediment cores and sedimentation rates to estimate the residence
404 time of algal material in the oxic environment and thus the extent of autoxidative degradation
405 and its impact on paleo sea ice reconstruction based on the use of HBI tracers.

406

407 *4.3. Degradation of IPSO₂₅ in Antarctic SPM*

408 The failure to detect compounds **3**, **5** and **7** in lipid extracts of strongly autoxidized
409 suspended particles (Rontani et al., 2018b) collected at different water depths in the polynya
410 region west of the Dalton Iceberg Tongue (East Antarctica) is in good agreement with: (i)
411 the relative recalcitrance of di-unsaturated HBIs towards free radical oxidation processes

412 (Rontani et al., 2011, 2014), and (ii) the expected short residence time of highly aggregated
413 ice algae (i.e. the source of IPSO₂₅) (Riebesell, 1991; Alldredge et al., 1993; Passow, 2002)
414 within the water column. It also enables us to exclude the possible biological formation of
415 these compounds in ice algae.

416

417 *4.4. Potential effects of degradation processes on the DIP₂₅ index*

418 Due to the co-occurrence of IPSO₂₅ (generally reported as diene II in the Arctic) and
419 IP₂₅ in Arctic sea ice, particles and sediments under sea ice (Belt et al., 2007; Vare et al.,
420 2009), it has been suggested that the ratio between these two biomarkers (viz. IPSO₂₅/IP₂₅
421 or DIP₂₅ (Cabedo-Sanz et al., 2013)) may potentially provide further insights into Arctic sea
422 ice conditions (e.g. Fahl and Stein, 2012; Stein et al., 2012; Cabedo-Sanz et al., 2013). It has
423 also been suggested that variable DIP₂₅ might be indicative of changes to SST based on some
424 empirical observations and alignment with other SST proxies (Vare et al., 2009; Cabedo-
425 Sanz et al., 2013; Xiao et al., 2013; Müller and Stein, 2014; Ruan et al., 2017); however,
426 there are as yet no in situ data to support these interpretations (Belt, 2018). In general, proxies
427 based on ratios of biomarkers are better at accommodating the effects of degradative
428 processes, even if such effects cannot be totally eliminated. Indeed, it was previously
429 demonstrated that, under some conditions, autoxidative and biodegradation processes may
430 act selectively on C_{37:2} and C_{37:3} alkenones, thus negatively impacting on the $U_{37}^{K'}$ index (for
431 a review, see Rontani et al., 2013b). It is feasible, therefore, that differential degradation of
432 IP₂₅ and IPSO₂₅ may also influence the DIP₂₅ ratio, with substantially increased values, as
433 seen in some sedimentary records (Fahl and Stein, 2012; Müller and Stein, 2014) resulting
434 from a preferential degradation of IP₂₅. Previously, however, autoxidative degradation of
435 these two HBIs measured in solvents (Rontani et al., 2014), showed a higher degradation

436 rate for IPSO₂₅ ($k = 0.004 \text{ h}^{-1}$) compared to IP₂₅ ($k = 0.001 \text{ h}^{-1}$). Unfortunately, due to the
437 mineralisation of the major part of substrates by bacteria, comparison of the efficiency of
438 bacterial degradation processes on IP₂₅ and IPSO₂₅ on the basis of the quantities of
439 metabolites detected is difficult. However, we note that significant proportions (up to 35%
440 of the residual substrate) of 2,8,12-trimethyl-5-(1,5-dimethylhexyl)-tridecanoic acid (**20**),
441 resulting from bacterial cleavage of the 23-24 double bond of IP₂₅, were detected in
442 sediments from Barrow Strait (i.e. STN 4) (Rontani et al., 2018c), while we failed to detect
443 the corresponding metabolite of IPSO₂₅ (i.e. 2,8,12-trimethyl-5-(1-methylidene-5-
444 methylhexyl)-tridecanoic acid (**21**)) in the same sediments. This suggests a preferential
445 bacterial degradation of IP₂₅, which could potentially be attributed to the presence of toxic
446 autoxidative epoxides in algal material containing IPSO₂₅, which are in lower abundance (or
447 absent) in the case of IP₂₅. More detailed analyses of factors that control the DIP₂₅ ratio,
448 however, will be required in the future.

449

450 *4.5. Consequences for IP₂₅, IPSO₂₅ and DIP₂₅-based sea ice reconstructions*

451 As with all lipid-based proxies, those involving HBIs such as IP₂₅ and IPSO₂₅ require
452 careful consideration of their alteration and preservation during transport through the water
453 column and deposition in sediments, including determining the magnitude and relative
454 importance of biotic and/or abiotic processes. While both autoxidative and bacterial
455 degradation products of IP₂₅ were identified and quantified previously in Arctic surficial
456 sediments (Rontani et al., 2018c), here we demonstrated that IPSO₂₅ may also be affected
457 by such processes in Arctic and Antarctic sediments. At this stage, the characterisation of
458 signature degradation products from these biotic and abiotic processes mainly provides
459 useful ‘qualitative’ indicators of diagenetic alteration of these two paleo sea ice tracers.
460 Unfortunately, subsequent reaction of most of the primary oxidation products by

461 sedimentary bacteria limits their accumulation in sediments, thereby preventing any accurate
462 quantitative estimates of the extent of degradation of IP₂₅ and IPSO₂₅, and thus of the ratio
463 between them (i.e. DIP₂₅). The impacts of sedimentary degradation of IP₂₅ and IPSO₂₅ on
464 their use as paleo sea ice proxies therefore remains difficult to assess at this stage. On the
465 other hand, the somewhat higher accumulation of 2,8,12-trimethyl-5-(1,5-dimethylhexyl)-
466 tridecanoic acid (**20**) in some oxic sediments could potentially provide semi-quantitative
467 estimates of the role of bacterial degradation of IP₂₅ (Rontani et al., 2018c).

468

469 **5. Conclusions**

470

471 The detection of reduced or hydrolyzed autoxidation products of IPSO₂₅ in Arctic
472 and Antarctic sediments demonstrated that this proxy may be partially degraded abiotically
473 in near-surface oxic sediments, especially in the case of sediment cores containing relatively
474 thick oxic layers representing long times of deposition. Unfortunately, due to its high biotic
475 and abiotic lability, the major autoxidation product formed (epoxide **1**) does not accumulate
476 in sediments. In contrast, IPSO₂₅ appeared to be essentially unaffected by autoxidation
477 processes in the water column.

478 The results obtained during this work also confirmed that, in the environment, biotic
479 and abiotic degradation processes cannot be considered separately. Indeed, their interactions,
480 although complex, need to be taken into account in any organic geochemical assessment.

481 Autoxidation reactions of HBIs appear to occur primarily at the unsaturated or allylic
482 carbon atoms within the lipid framework. However, the production of compounds such as
483 **13** or **14** observed during IPSO₂₅ autoxidation, and the previous detection of degradation
484 products of IP₂₅ in Arctic sediments resulting from the free radical oxidation of its saturated

485 tertiary carbon atoms (Rontani et al., 2018a), clearly show that autoxidation processes can
486 also affect saturated compounds when algal or bacterial material experiences long residence
487 times in the oxic layer of sediments.

488

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490

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497

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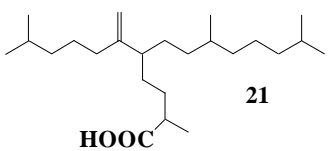
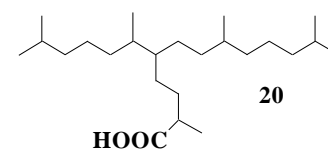
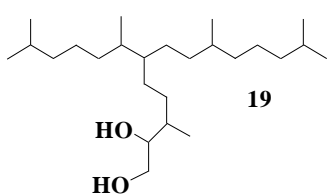
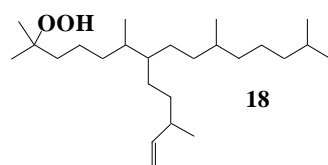
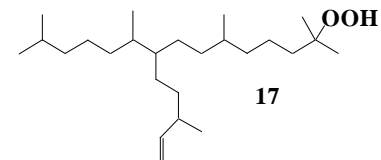
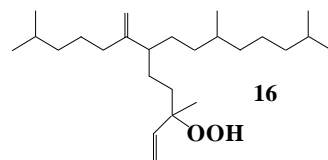
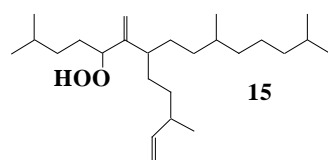
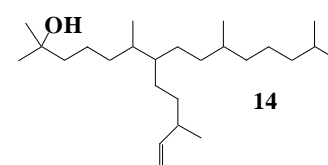
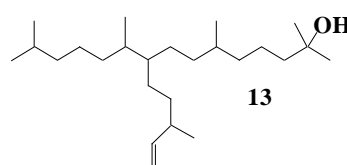
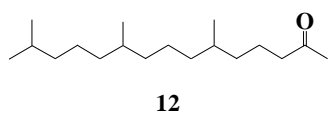
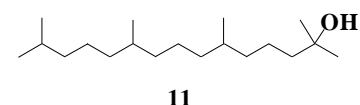
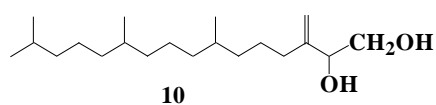
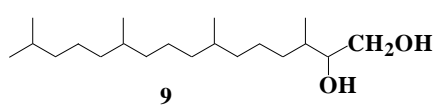
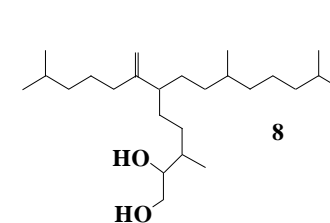
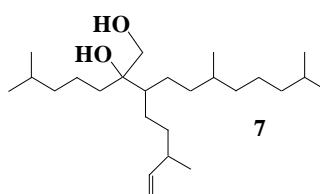
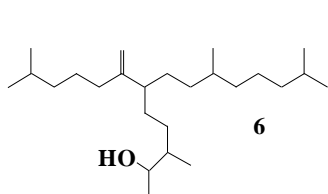
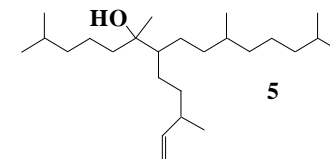
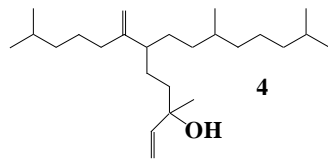
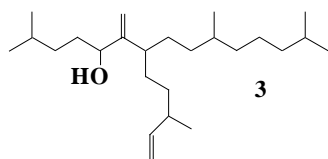
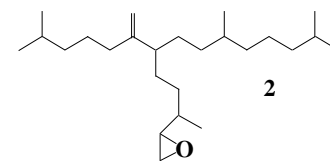
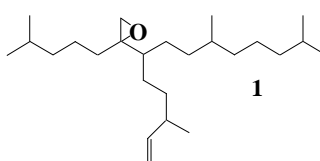
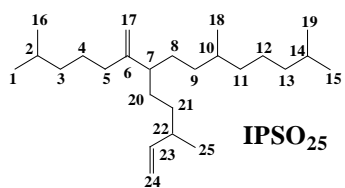
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APPENDIX



681 FIGURE CAPTIONS

682

683 **Figure 1.** TOFMS mass spectra of 1,2-epoxy-2-(4-methylpentyl)-3-(3-methylpent-4-enyl)-
684 6,10-dimethylundecane (**1**) (A) and trimethylsilyl derivatives of: 6-methylidene-2,10,14-
685 trimethyl-7-(3-methylpent-4-enyl)-pentadecan-5-ol (**3**) (B), 3,9,13-trimethyl-6-(1-
686 methylidene-5-methylhexyl)-tetradec-1-en-3-ol (**4**) (C) and 10-methylidene-2,6,14-
687 trimethyl-9-(3-methylpent-4-enyl)-pentadecan-2-ol (**13**) or 6-methylidene-2,10,14-
688 trimethyl-7-(3-methylpent-4-enyl)-pentadecan-2-ol (**14**) (D).

689

690 **Figure 2.** TOFMS mass spectra of trimethylsilyl derivatives of: 2,6,10,14-tetramethyl-7-(3-
691 methylpent-4-enyl)-pentadecan-6-ol (**5**) (A), 3,9,13-trimethyl-6-(1-methylidene-5-
692 methylhexyl)-tetradecan-2-ol (**6**) (B), 2-(4-methylpentyl)-3-(3-methylpent-4-enyl)-6,10-
693 dimethylundecane-1,2-diol (**7**) (C) and 3,9,13-trimethyl-6-(1-methylene-5-methylhexyl)-
694 tetradecane-1,2-diol (**8**) (D) .

695

696 **Figure 3.** MRM chromatograms (m/z 365 \rightarrow 275, m/z 365 \rightarrow 149 and m/z 425 \rightarrow 135) of
697 silylated standard alcohol **3** (A) and DCM fractions obtained from the Antarctic station BC
698 313 (B) and the 10-11 cm sediment layer of the box core from Barrow Strait (Canadian
699 Arctic) (C).

700

701 **Figure 4.** MRM chromatograms (m/z 201 \rightarrow 111, m/z 353 \rightarrow 117, m/z 353 \rightarrow 297 and m/z
702 423 \rightarrow 367) of silylated standard alcohol **5** (A) and DCM fraction obtained from the 2-3 cm
703 sediment layer of the box core from Barrow Strait (Canadian Arctic) (B).

704

705 **Figure 5.** MRM chromatograms (m/z 526 \rightarrow 231 and m/z 526 \rightarrow 142) of silylated standard
706 diol **7** (A) and DCM fractions obtained from the 2-3 cm (B) and the 10-11 cm (C) sediment
707 layers of the box core from Barrow Strait (Canadian Arctic).

708

709 **Figure 6.** Proposed mechanisms for the autoxidation of IPSO₂₅ in sediments and subsequent
710 NaBH₄-reduction of the resulting hydroperoxides during the treatment.

711

712 **Figure 7.** Proposed mechanisms for the formation and degradation of epoxides **1** and **2** in
713 sediments.

714

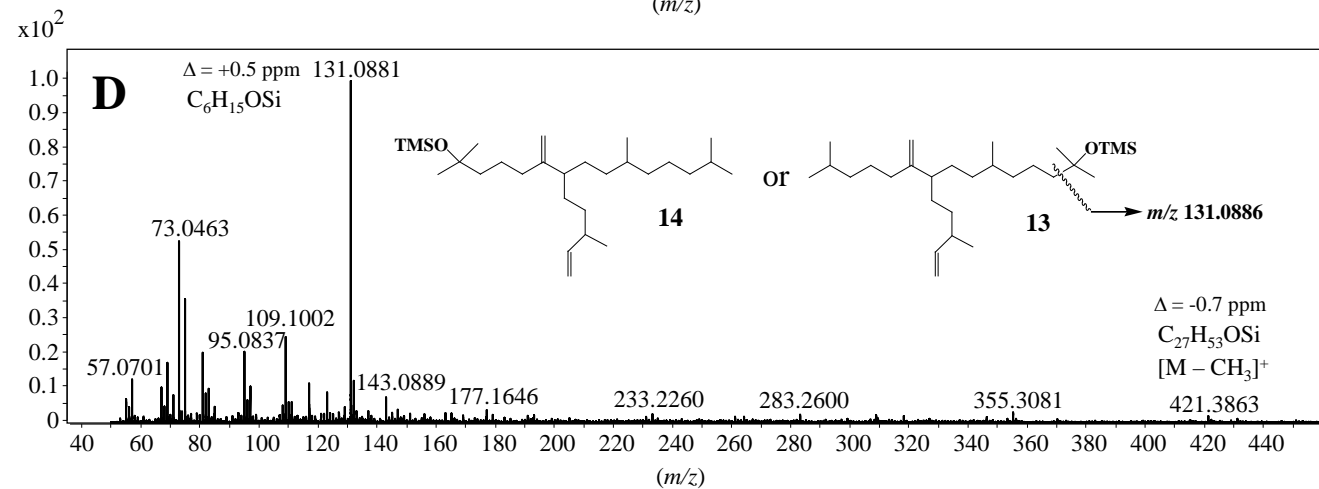
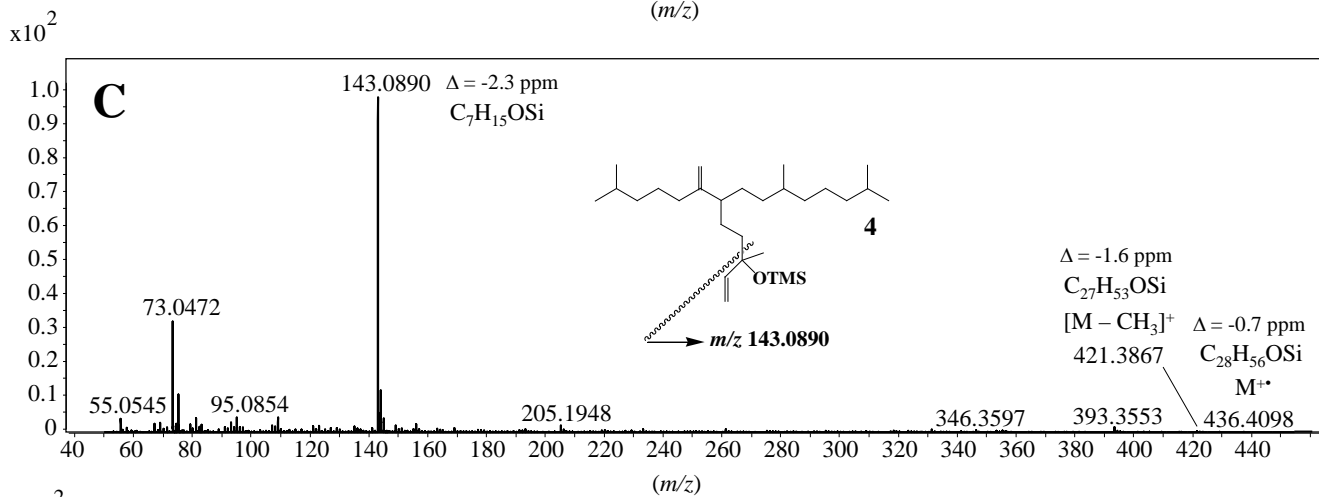
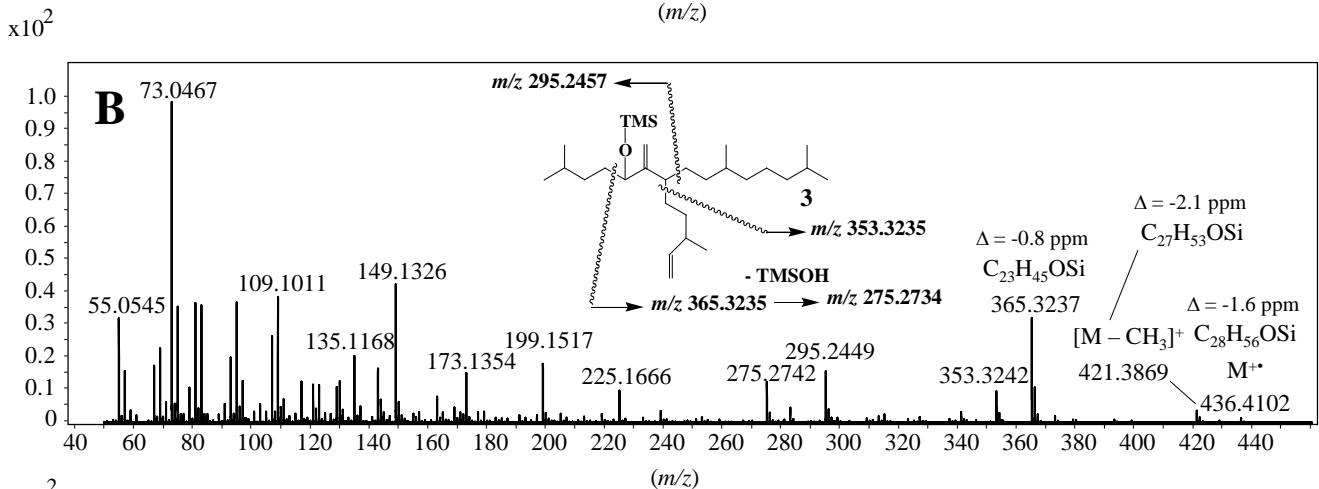
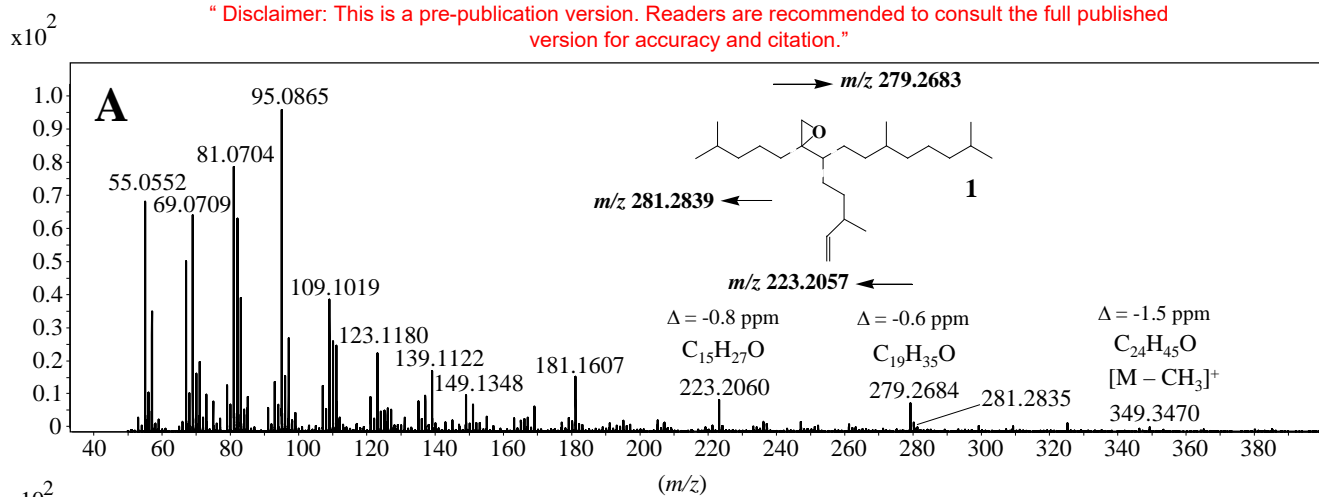
715 **Figure 8.** Relative percentages of IPSO₂₅ and its degradation products in various sediment
716 sections of the box core from Barrow Strait (Canadian Arctic).

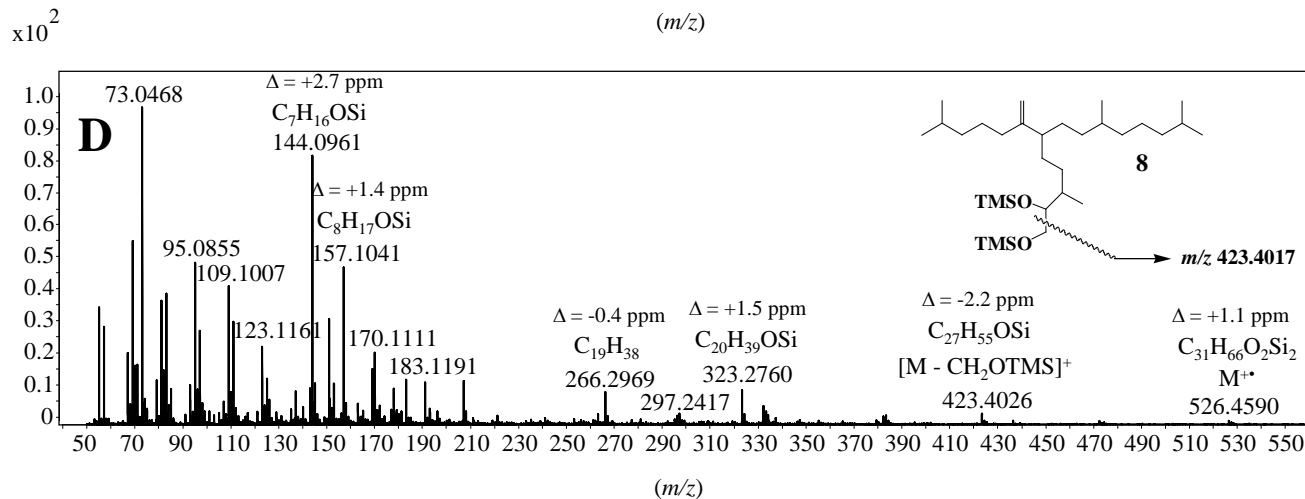
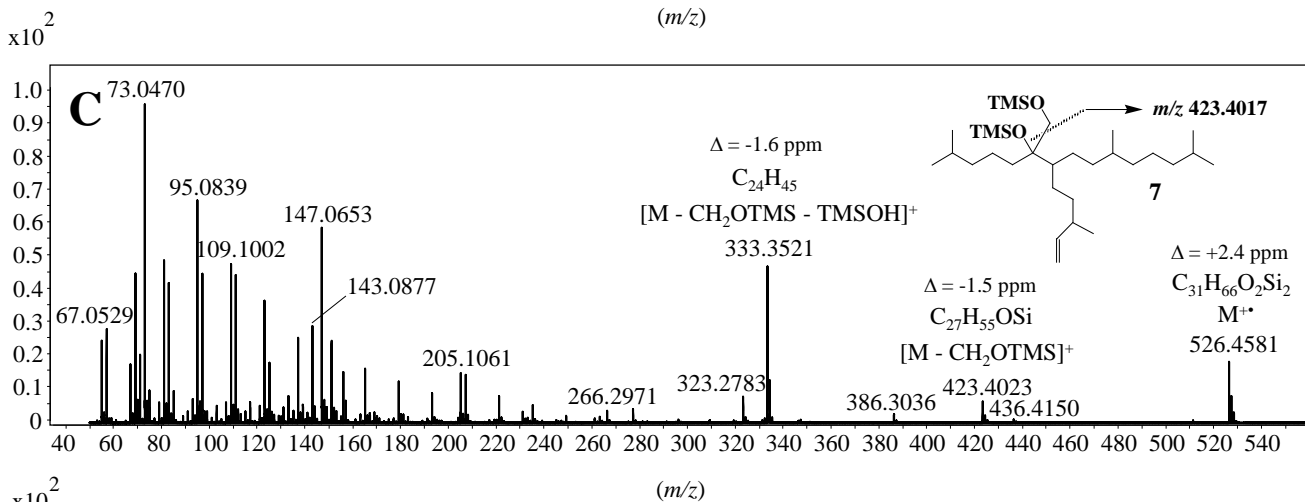
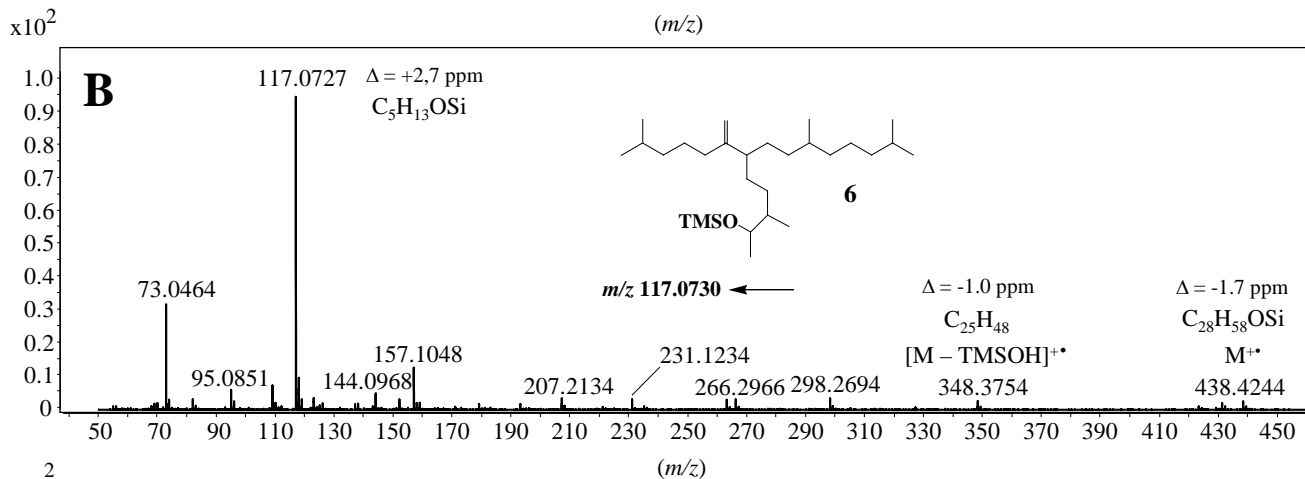
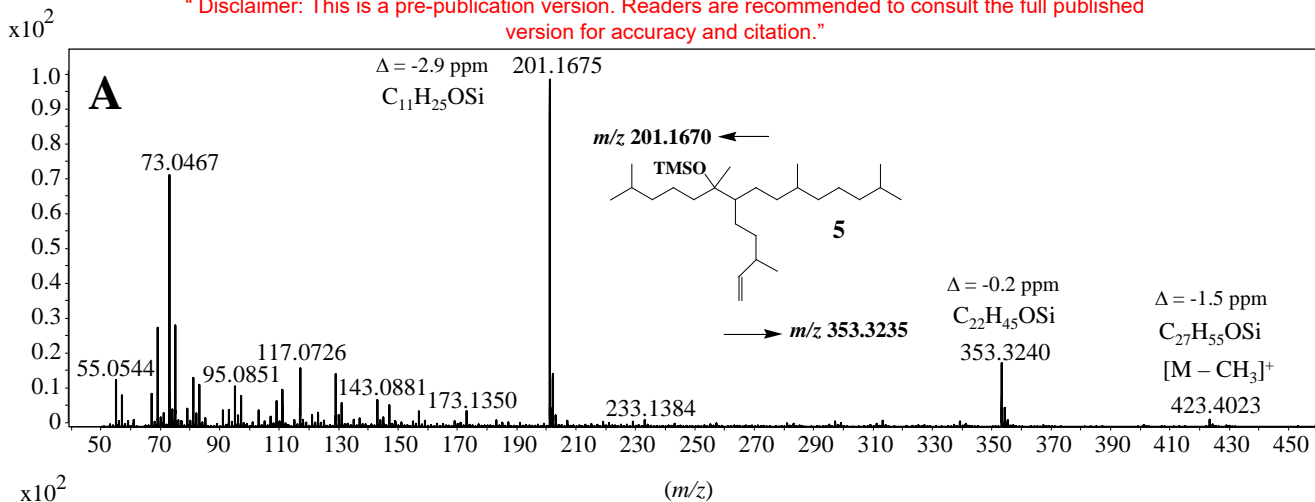
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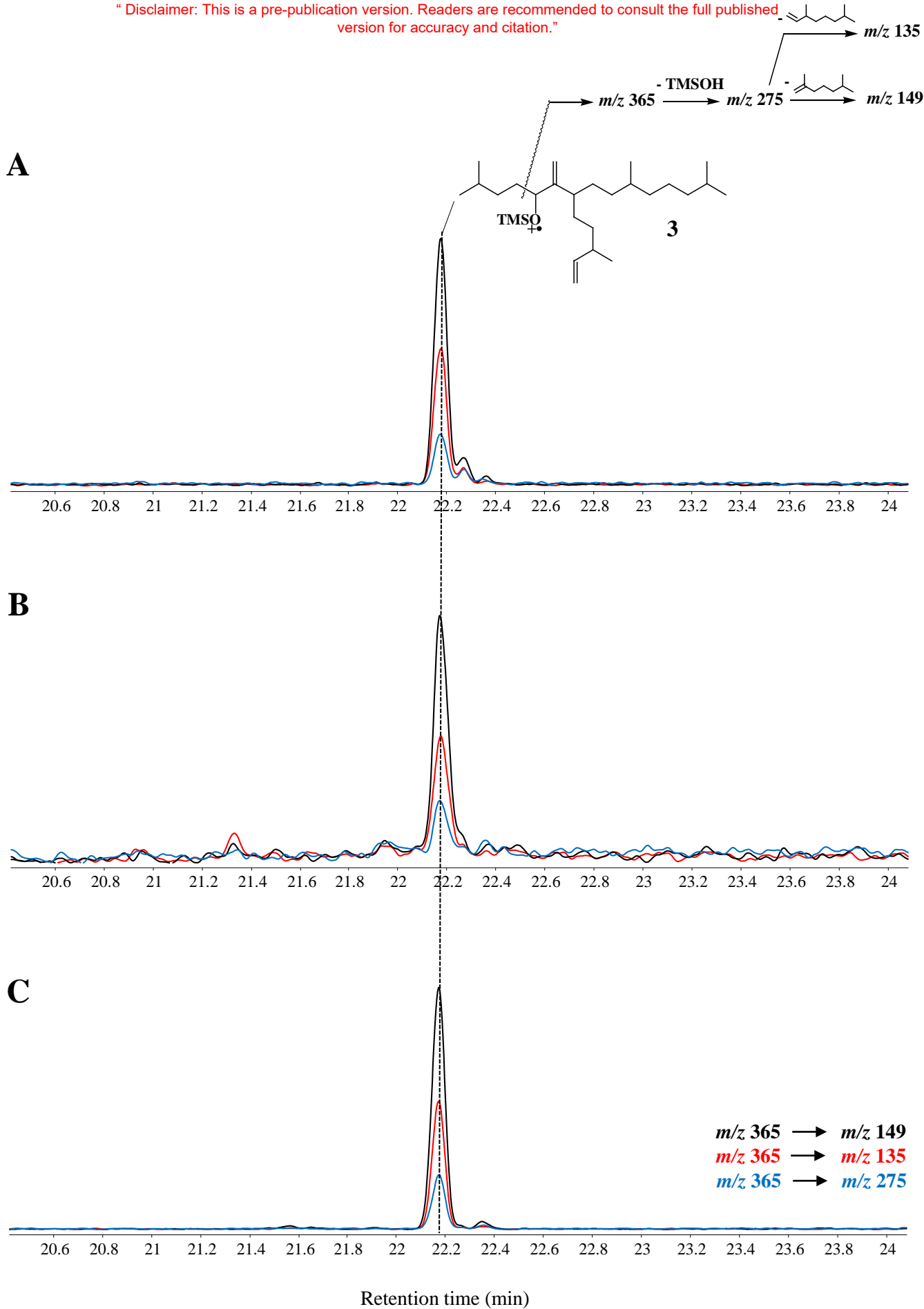
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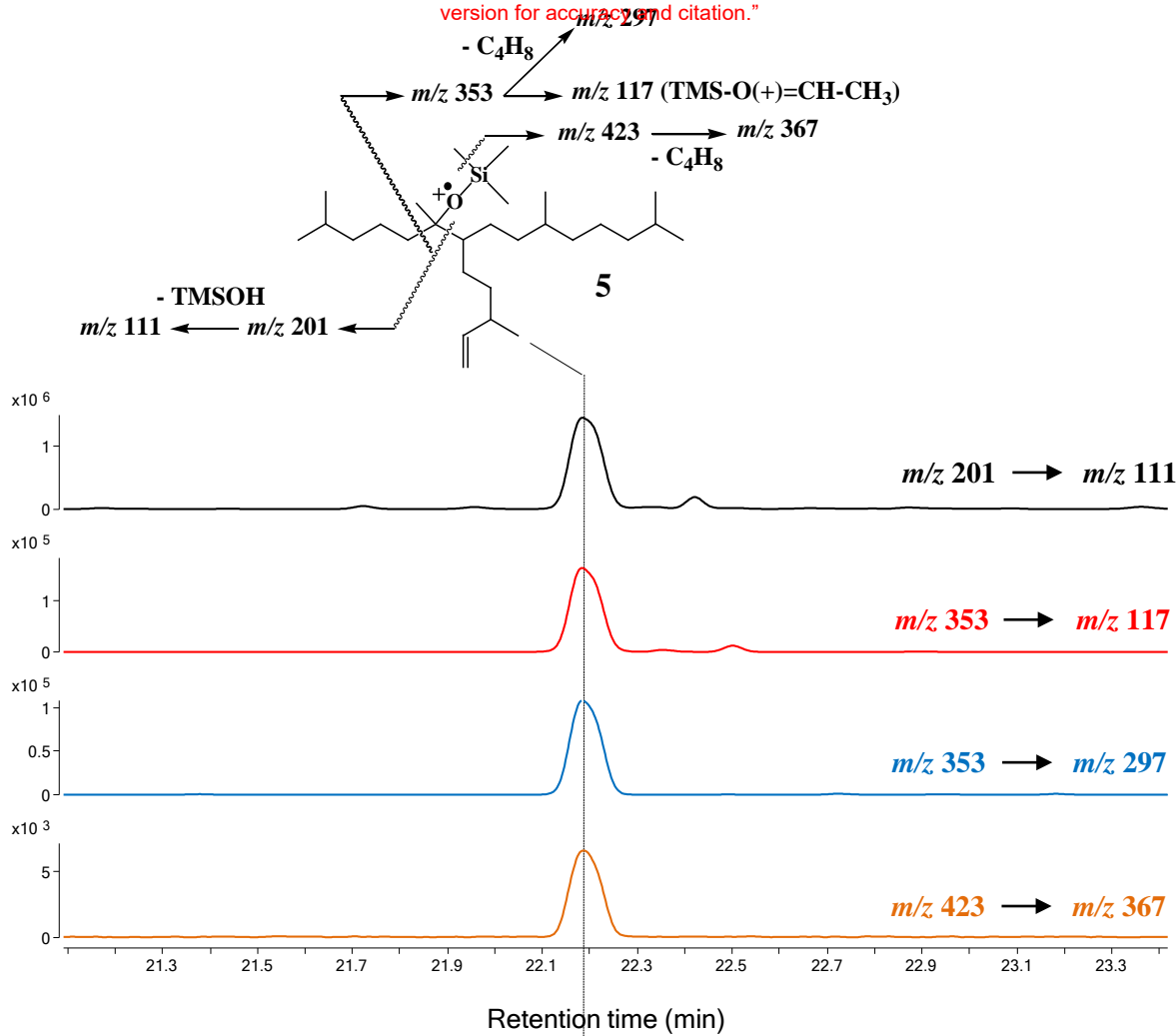
720 **Supplementary Figure 1.** Antarctic (a) and Arctic (b) sampling locations. (The rectangle
721 corresponds to the sampling zone of SPM, see Rontani et al., 2018b for more precise
722 locations).



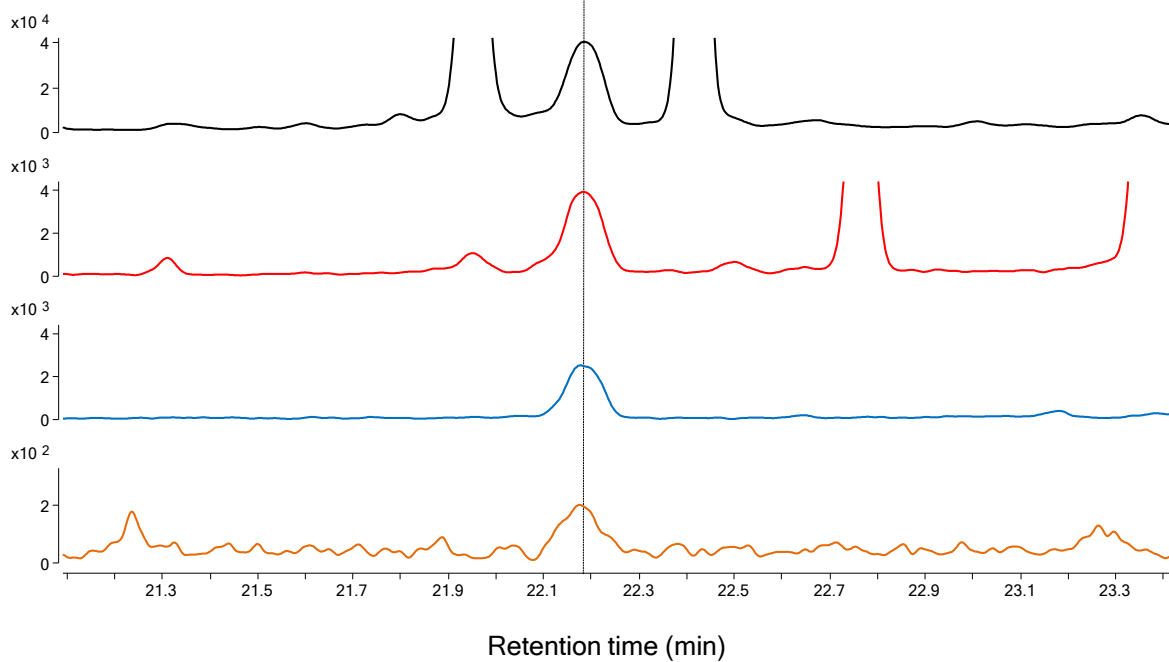


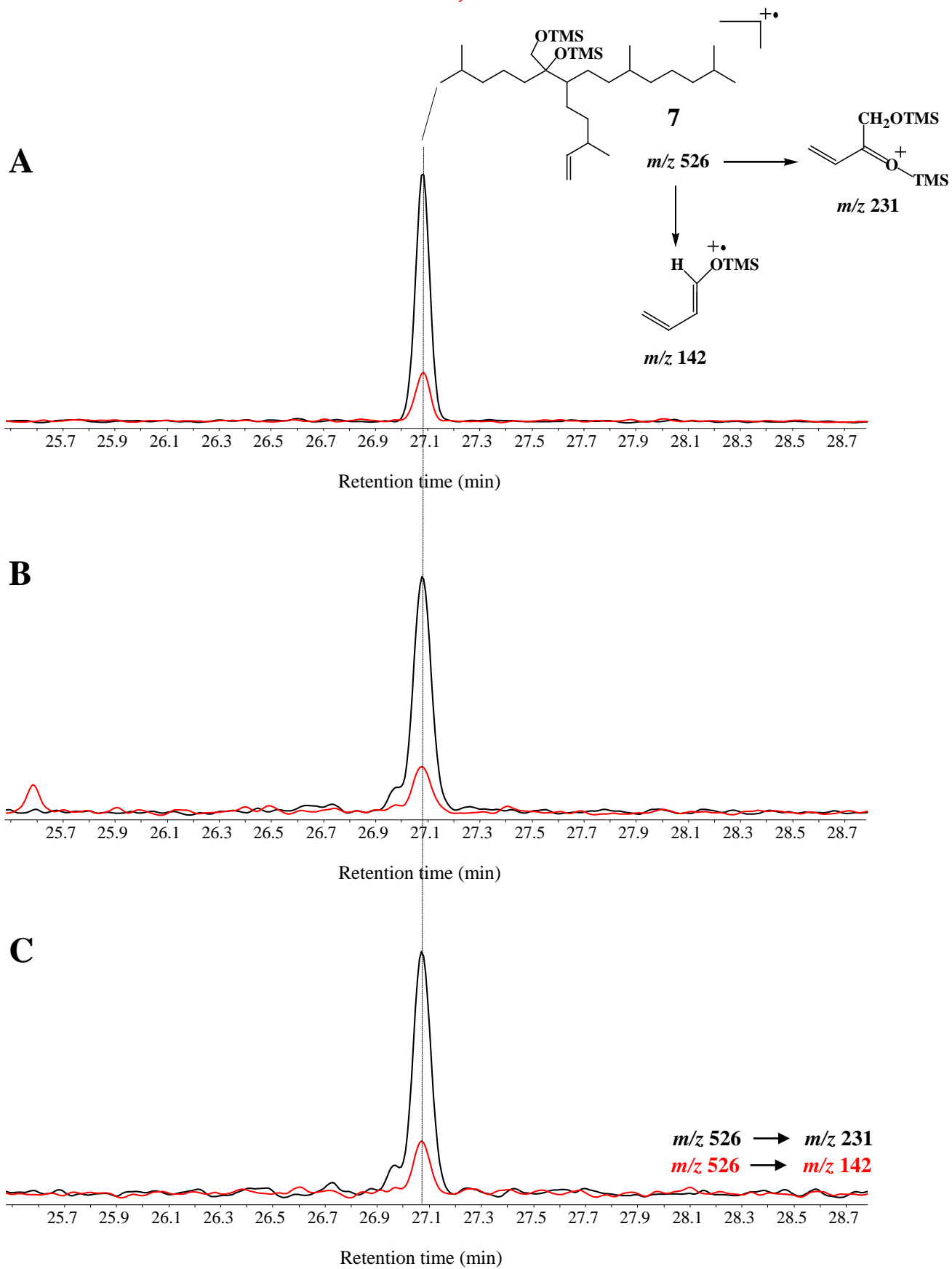


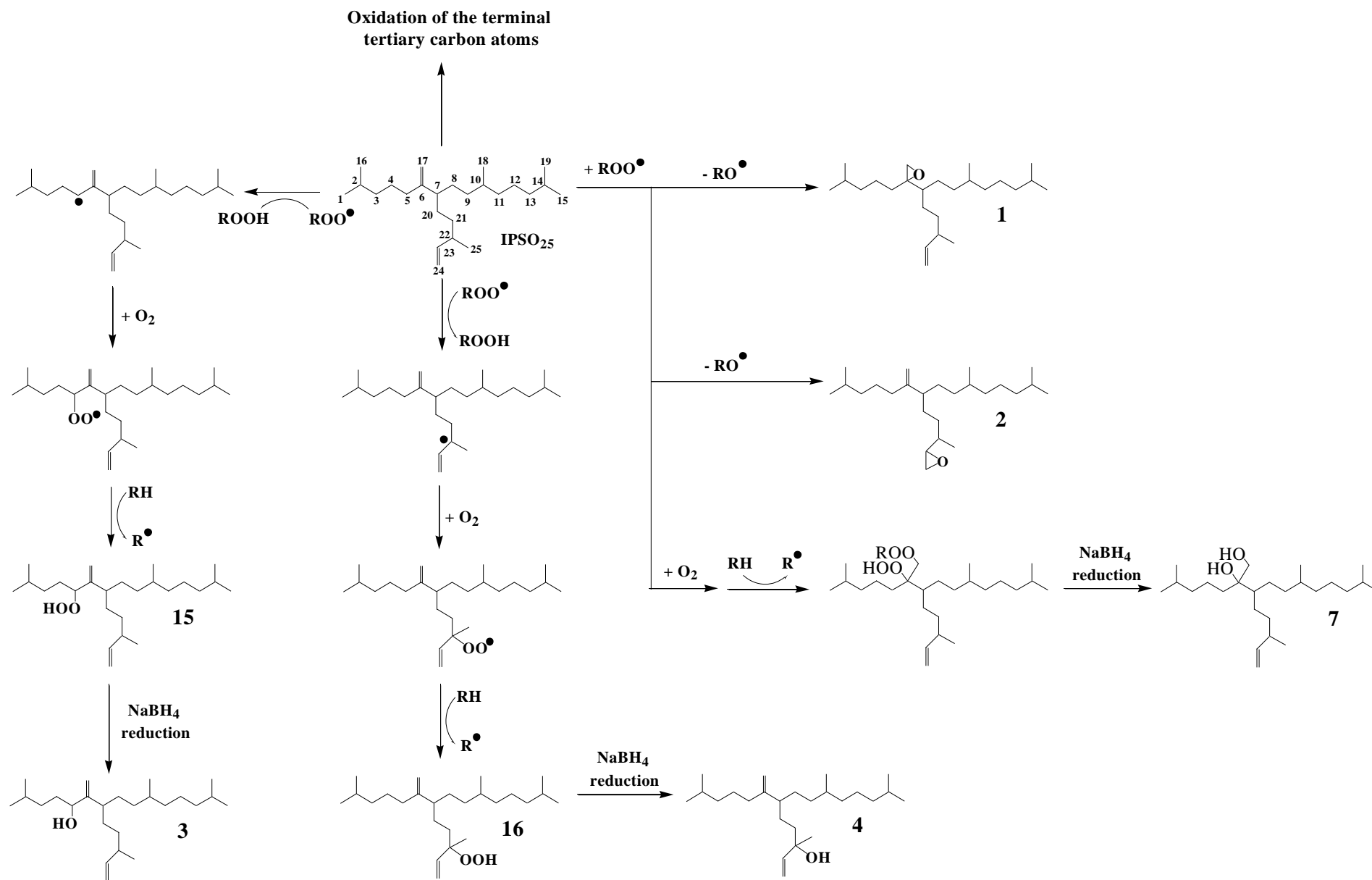
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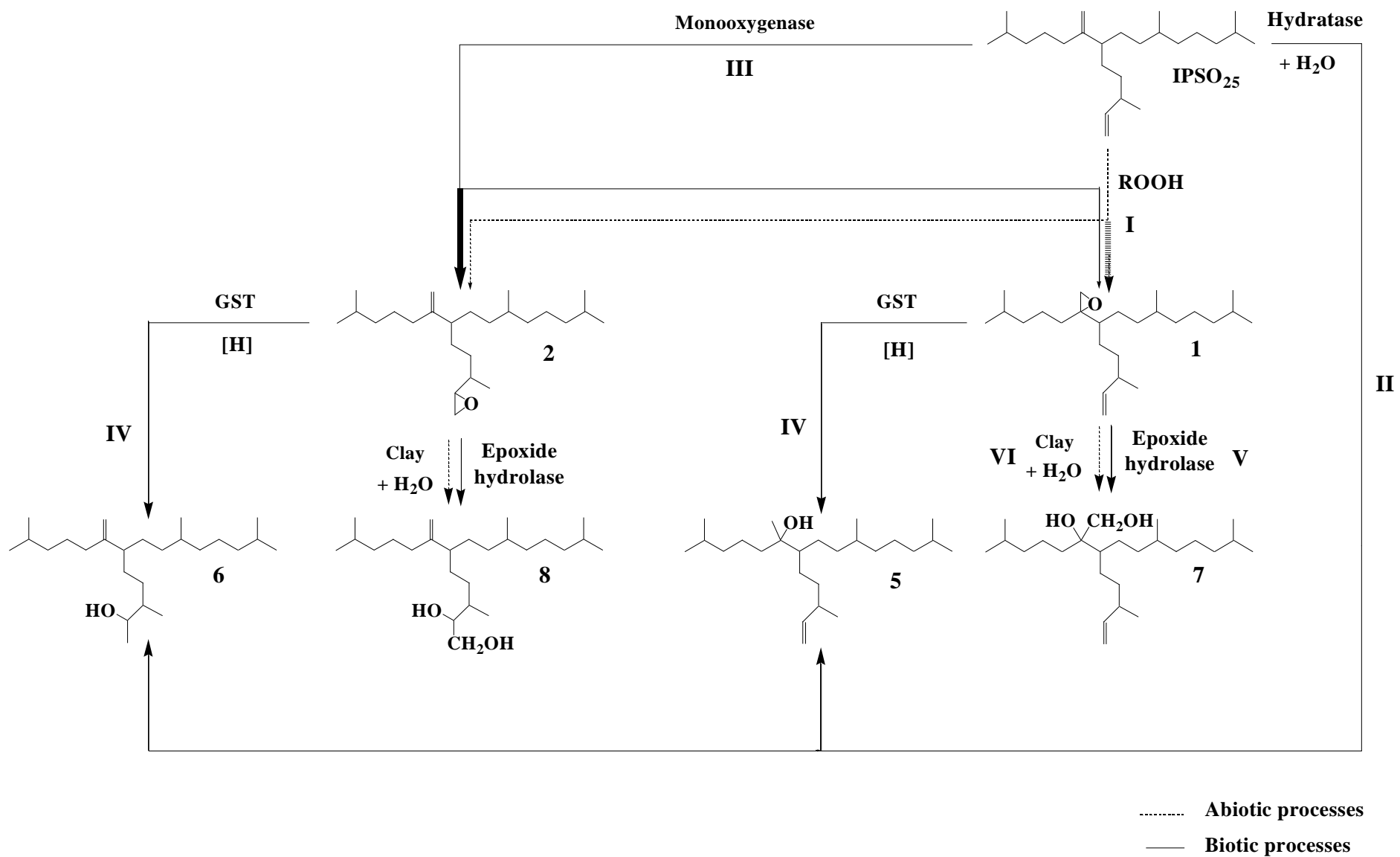


B









Relative percentage of IPSO_{25} and its degradation products

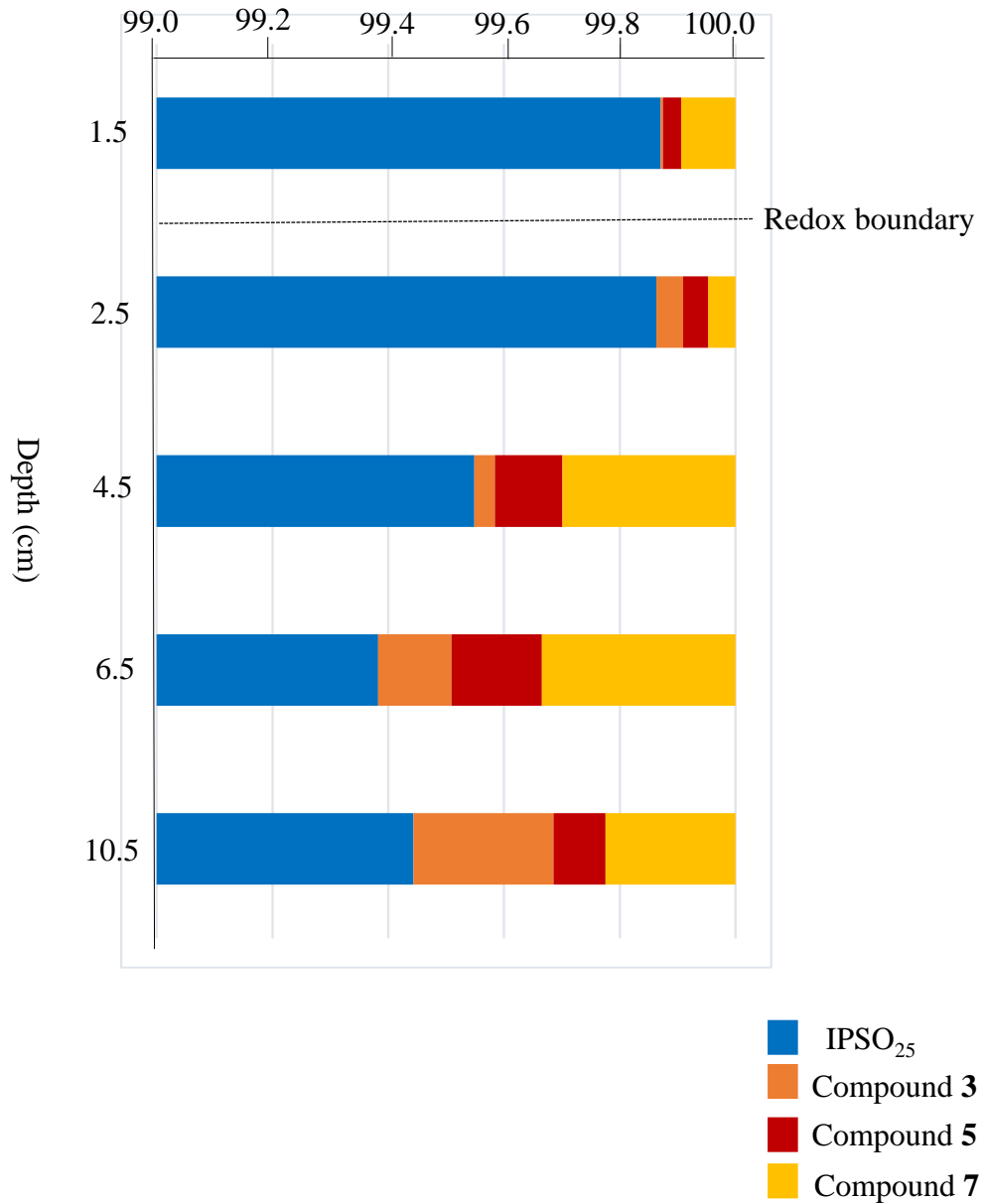


Table 1

Concentrations of IPSO₂₅ and its degradation products in Antarctic surface sediments

Station	IPSO ₂₅ (ng g ⁻¹)	Compound 3 (pg g ⁻¹)	Compound 5 (pg g ⁻¹)
BC 313	1201.0	101.3 (0.01) ^b	77.8 (0.01) ^b
BC 316	396.0	569.2 (0.14)	38.1 (0.01)
BC 516	49.0	50.0 (0.10)	-
BC 566	42.0	230.3 (0.55)	231.7 (0.55)
BC 571	14.0	44.4 (0.32)	37.0 (0.26)
BC 615	93.0	- ^a	33.4 (0.04)
BC 628	29.0	54.5 (0.19)	25.4 (0.01)

^a Not detected

^b Percentage relative to the residual parent compound.

Table 2

Concentrations of IPSO₂₅ and its degradation products in sediments from the Arctic station 4 (Barrow Strait)

Depth (cm)	IPSO ₂₅ (μg g ⁻¹)	Compound 3 (ng g ⁻¹)	Compound 5 (ng g ⁻¹)	Compound 7 (ng g ⁻¹)
1.5	2.5	0.1	0.8	2.4
2.5	3.2	1.5	1.4	1.5
4.5	2.0	0.7	2.3	5.9
6.5	1.7	2.2	2.7	5.8
8.5	1.6	0.2	0.1	0.6
10.5	1.8	4.3	1.6	4.0