



**HAL**  
open science

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

Jean-Francois Rontani, Lukas Smik, Simon Belt

► **To cite this version:**

Jean-Francois Rontani, Lukas Smik, Simon Belt. Autoxidation of the sea ice biomarker proxy IPSO25 in the near-surface oxic layers of Arctic and Antarctic sediments. *Organic Geochemistry*, 2019, 129, pp.63-76. 10.1016/j.orggeochem.2019.02.002 . hal-02325900

**HAL Id: hal-02325900**

**<https://hal.science/hal-02325900>**

Submitted on 22 Oct 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

1

2

3 Autoxidation of the sea ice biomarker proxy IPSO<sub>25</sub> in the near-surface oxic layers of Arctic

4 and Antarctic sediments

5

6 Jean-François Rontani<sup>a\*</sup>, Lukas Smik<sup>b</sup>, Simon T. Belt<sup>b</sup>

7

8 <sup>a</sup> *Aix Marseille Univ, Université de Toulon, CNRS/INSU/IRD, Mediterranean Institute of*  
9 *Oceanography (MIO) UM 110, 13288 Marseille, France*

10 <sup>b</sup> *Biogeochemistry Research Centre, School of Geography, Earth and Environmental*  
11 *Sciences, University of Plymouth, Drake Circus, Plymouth, Devon PL4 8AA, UK*

12

13

14

15

16

17

18

19 \* Corresponding author. Tel.: +33-4-86-09-06-02; fax: +33-4-91-82-96-41. *E-mail address:*  
20 *jean-francois.rontani@mio.osupytheas.fr (J.-F. Rontani)*

21

22 **ABSTRACT**

23

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

44

45 *Keywords:* IPSO<sub>25</sub>; Degradation; Autoxidation; Arctic and Antarctic sediments; Biotic and  
46 abiotic interactions; IP<sub>25</sub>; DIP<sub>25</sub>.

## 47 1. Introduction

48

49 C<sub>25</sub> and C<sub>30</sub> highly branched isoprenoid (HBI) alkenes (commonly exhibiting 1–6  
50 double bonds) are ubiquitous biomarkers found in a wide range of marine and lacustrine  
51 sediments (Rowland et al., 1990; Belt et al., 2000; Sinninghe Damsté et al., 2004). Despite  
52 this, HBIs appear to be biosynthesized by a relatively small number of diatom taxa belonging  
53 to the *Haslea*, *Navicula*, *Pleurosigma*, *Berkeleya*, *Rhizosolenia* and *Pseudosolenia* genera  
54 (Volkman et al., 1994; Sinninghe-Damsté et al., 1999; Belt et al., 2001a, 2001b, 2016; Grossi  
55 et al., 2004; Brown et al., 2014; Kaiser et al., 2016). Amongst the more recent investigations,  
56 a mono-unsaturated C<sub>25</sub> HBI alkene (3,9,13-trimethyl-6-(1,5-dimethylhexyl)-tetradec-1-ene)  
57 was identified in Arctic sea ice and in underlying sediments (Belt et al, 2007; Vare et al,  
58 2009). Since this HBI is believed to only be made by certain Arctic sea ice diatoms (Belt et  
59 al., 2007; Brown et al., 2014) and appears relatively stable in the geological record, its  
60 analysis in marine sedimentary archives provides a proxy measure of seasonal Arctic sea ice  
61 in the past. More commonly referred to as IP<sub>25</sub> (Ice Proxy with 25 carbon atoms), this HBI has  
62 been used as the basis for sea ice reconstructions spanning different Arctic regions and over a  
63 range of timescales (see Belt, 2018 for a recent compilation of sea ice reconstructions).

64 A related di-unsaturated HBI (2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-  
65 pentadec-6(17)-ene), sometimes referred to as diene II, is co-produced with IP<sub>25</sub> in the Arctic,  
66 and is also biosynthesized by some Antarctic sea ice diatoms (Nichols et al., 1993; Johns et  
67 al., 1999; Belt et al., 2016). Interestingly, however, IP<sub>25</sub> has not been reported in sea ice,  
68 sediments or the water column from around the Antarctic. As such, diene II has been  
69 proposed as a proxy measure for sea ice in the Southern Ocean, and the term IPSO<sub>25</sub> (Ice  
70 Proxy for the Southern Ocean with 25 carbon atoms) has been recently proposed (Belt et al.,  
71 2016). Although IPSO<sub>25</sub> appears to be a common constituent of Antarctic surface sediments

72 (for near-coastal regions, at least; Nichols et al., 1993; Johns et al., 1999; Belt et al., 2016;  
73 Belt, 2018, 2019), analysis of IPSO<sub>25</sub> in downcore Antarctic archives has so far resulted in  
74 only a relatively small number of palaeo sea ice reconstructions, at least in comparison with  
75 IP<sub>25</sub> for the Arctic (e.g., Collins et al., 2013; Etourneau et al., 2013; Barbara et al., 2016;  
76 Campagne et al., 2016; see also Belt, 2018, 2019 for a recent review and summary). Finally,  
77 in the Arctic, the ratio IPSO<sub>25</sub>/IP<sub>25</sub> (sometimes referred to as DIP<sub>25</sub>) has previously been  
78 proposed as a possible indicator of variability in sea ice conditions or even of sea surface  
79 temperatures (SST) (e.g., Fahl and Stein, 2012; Stein et al., 2012; Cabedo-Sanz et al., 2013).

80 As with all proxies, including those based on individual or combinations of  
81 biomarkers, their application requires careful consideration of alteration and preservation  
82 between their source and sedimentary environments. It is necessary, therefore, to determine  
83 the magnitude and relative importance of various biotic and/or abiotic processes that can  
84 influence the preservation of the original source signature. In the case of HBIs, bacterial  
85 degradation of some HBIs was studied several decades ago (Robson and Rowland, 1988), yet  
86 the effects of photo- and autoxidation on these compounds have been examined only  
87 relatively recently.

88 Motivation for the more recent studies stems partly from the proxy signatures of  
89 certain HBIs such as IP<sub>25</sub> and IPSO<sub>25</sub>, as described above, together with the now well-known  
90 high reactivity of terrestrial and marine organic matter, more generally, in the Arctic (Rontani  
91 et al., 2012, 2016, 2017). By studying the reactivity of a range of HBI alkenes towards  
92 different abiotic processes in solvents and in senescent diatoms (Rontani et al., 2011, 2014),  
93 extremely low reactivities of mono- and di-unsaturated HBIs were observed and attributed to  
94 the presence of relatively unreactive terminal double bonds. Such lack of reactivity is  
95 consistent with the general lack of degradation of IP<sub>25</sub> in the water column following sea ice  
96 melt (Brown et al., 2016; Rontani et al., 2018a). However, lipid autoxidation is not limited to

97 the water column, and can potentially be an important process in the oxic layers of sediments,  
98 especially for regions of low accumulation rates, where near-surface sediments may represent  
99 relatively long time intervals (decades to centuries). Indeed, as part of a recent laboratory-  
100 based investigation into the autoxidation of IP<sub>25</sub>, a series of oxidation products were  
101 characterized that could also be identified in sediment material from the Canadian Arctic  
102 (Rontani et al., 2018a). This study demonstrated the susceptibility of IP<sub>25</sub> towards  
103 autoxidation in Arctic sediments, a process that was more prevalent in cases where  
104 sequestered ice algal material experienced relatively long residence times in the oxic layer.  
105 On the other hand, the near-ubiquity of IP<sub>25</sub> in surface sediments from across the Arctic  
106 suggests that such oxidation reactions likely perturb its sedimentary content, rather than  
107 remove it.

108 In the present work, we aimed to determine whether IPSO<sub>25</sub> also undergoes  
109 autoxidation in near-surface Arctic and Antarctic sediments and, therefore, whether palaeo sea  
110 ice reconstructions using this proxy should consider the possible impact of this type of  
111 degradation. To achieve this, oxidation of purified IPSO<sub>25</sub> was carried out under more  
112 powerful oxidative conditions than previously employed (Rontani et al., 2014) and the main  
113 products were identified by high resolution mass spectral analysis. The same oxidation  
114 products were then analysed for, and quantified, in sediment samples from the Canadian  
115 Arctic and the West Antarctic Peninsula (WAP).

116

## 117 **2. Experimental**

118

### 119 *2.1. Sediment sampling*

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

122 2013). The box core was sectioned on board, with sub-samples (1 cm resolution) then frozen  
123 (−20 °C) prior to being freeze-dried and stored (−20 °C to +4 °C) prior to analysis (Rontani et  
124 al., 2018a). The redox boundary layer was identified using the change (reduction) in Mn  
125 content as described previously (Vare et al., 2009; Brown, 2011 and References cited therein).  
126 Sediment material from the WAP (see Belt et al., 2016 for details of locations) was obtained  
127 from the upper 0–1 cm of box cores collected between 2002 and 2011 and then held at the  
128 British Antarctic Survey (UK) or the British Ocean Sediment Core Research Facility  
129 (BOSCORF, UK) at +4 °C. Suspended particulate matter (SPM) were obtained off the coast  
130 of East Antarctica as described previously (Rontani et al., 2018b) (Supplementary Fig. S1).

131

## 132 2.2. Chemicals

133 A sample of purified IPSO<sub>25</sub> was obtained from a culture of the marine diatom *Haslea*  
134 *ostrearia* as described previously (Johns et al., 1999).

135 Treatment of IPSO<sub>25</sub> with a stoichiometric amount of perchloroperbenzoic acid in dry  
136 dichloromethane (4 h at 50 °C) mainly afforded 1,2-epoxy-2-(4-methylpentyl)-3-(3-  
137 methylpent-4-enyl)-6,10-dimethylundecane (**1**) (93%) (Belt et al., 2007) and to a lower extent  
138 1,2-epoxy-3,9,13-trimethyl-6-(1-methylidene-5-methylhexyl)-tetradecane (**2**) (7%) (total yield  
139 85%). Differentiation between these two isomers was difficult due to their very similar mass  
140 spectra and so required LiAlH<sub>4</sub>-reduction to the corresponding alcohols (see below).

141 Oxidation of IPSO<sub>25</sub> using RuCl<sub>3</sub> and *tert*-butyl hydroperoxide in cyclohexane at room  
142 temperature for 16 h (Seki et al., 2008) and subsequent NaBH<sub>4</sub>-reduction in ether-methanol  
143 (4:1, v/v) produced 6-methylidene-2,10,14-trimethyl-7-(3-methylpent-4-enyl)-pentadecan-5-  
144 ol (**3**) and 3,9,13-trimethyl-6-(1-methylidene-5-methylhexyl)-tetradec-1-en-3-ol (**4**) in low  
145 yield. It is interesting to note that using a mixture of RuCl<sub>3</sub> and *tert*-butyl hydroperoxide  
146 failed to attack the tertiary allylic position at C-7, likely due to steric hindrance.

147 LiAlH<sub>4</sub>-reduction of the mixture of epoxides **1** and **2** in dry diethyl ether (1 h at room  
148 temperature) afforded 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-pentadecan-6-ol (**5**) and  
149 3,9,13-trimethyl-6-(1-methylidene-5-methylhexyl)-tetradecan-2-ol (**6**), respectively (total  
150 yield 95%).

151 Treatment of IPSO<sub>25</sub> with a stoichiometric amount of OsO<sub>4</sub> in dioxane-pyridine (8:1,  
152 v/v) at room temperature for 1 h (McCloskey and McClelland, 1965) afforded 2-(4-  
153 methylpentyl)-3-(3-methylpent-4-enyl)-6,10-dimethylundecane-1,2-diol (**7**) (yield 60%).

154 3,9,13-Trimethyl-6-(1-methylene-5-methylhexyl)-tetradecane-1,2-diol (**8**) was  
155 obtained in small amounts after hydrolysis of the epoxide **2** in a mixture of MeOH and HCl  
156 2N (5:1, v/v) at 50 °C for 2 h. Under these conditions epoxide **1** mainly isomerized to allylic  
157 alcohols.

158 3,7,11,15-Tetramethylhexadecan-1,2-diol (**9**) was produced by Pd/CaCO<sub>3</sub>-catalysed  
159 hydrogenation of 3-methylidene-7,11,15-trimethylhexadecan-1,2-diol (**10**) (Rontani et al.,  
160 2018), whose synthesis from phytol was described previously (Rontani and Aubert, 2005).

161 2,6,10,14-Tetramethylpentadecan-2-ol (**11**) was produced by condensation of 6,10,14-  
162 trimethylpentadecan-2-one (**12**) with methyl lithium in anhydrous diethyl ether as previously  
163 described (Rontani et al., 2013a).

164

### 165 2.3. Induction of autoxidation in solvent

166 Autoxidation experiments were performed under an atmosphere of air in 15 ml screw-  
167 cap flasks containing IPSO<sub>25</sub> (10 µg), *tert*-butyl hydroperoxide (300 µl of a 6.0 M solution in  
168 decane), di-*tert*-butyl nitroxide (1.2 mg) and hexane (2 ml). After stirring, the flask was  
169 incubated in the dark at 65 °C. A relatively high temperature was selected in order to  
170 accelerate the autoxidation reactions. Aliquots (200 µl) were withdrawn from the reaction  
171 mixture after incubation for different times. Each sub-sample was evaporated to dryness under



172 a stream of nitrogen and analyzed by gas chromatography–electron ionization quadrupole  
173 time of flight mass spectrometry (GC–QTOF) after NaBH<sub>4</sub> reduction (Section 2.5) and  
174 derivatization (Section 2.7) for identification of hydroxylated oxidation products.

175

#### 176 *2.4. Reduction of oxidation products*

177 Hydroperoxides resulting from IPSO<sub>25</sub> oxidation were reduced to the corresponding  
178 alcohols by reaction with excess NaBH<sub>4</sub> in diethyl ether:methanol (4:1, v/v) at room  
179 temperature (1 h). After reduction, a saturated solution of NH<sub>4</sub>Cl (10 ml) was added  
180 cautiously to remove any unreacted reducing agent; the pH was adjusted to 1 with dilute HCl  
181 (2 N) and the mixture shaken and extracted with hexane:chloroform (5 ml, 4:1, v/v; ×3). The  
182 combined extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to dryness  
183 under a stream of nitrogen.

184

#### 185 *2.5. Sediment and SPM treatment*

186 Sediments or SPM material (collected on GF/F filters, porosity 0.8 μm) were placed in  
187 MeOH (15 ml) and hydroperoxides were reduced to the corresponding alcohols with excess  
188 NaBH<sub>4</sub> (70 mg, 30 min at 20 °C). Following the reduction step, water (15 ml) and KOH (1.7  
189 g) were added and the mixture saponified by refluxing (2 h). After cooling, the contents of the  
190 flask were acidified (HCl, to pH 1) and extracted three times with dichloromethane (DCM)  
191 (30 ml). The combined DCM extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and  
192 concentrated to give the total lipid extract (TLE). Since IPSO<sub>25</sub> oxidation product content was  
193 quite low relative to other lipids, accurate quantification required further separation of the  
194 TLE using column chromatography (silica; Kieselgel 60, 8 × 0.5 cm). IPSO<sub>25</sub> was recovered  
195 in the hexane eluate and its oxidation products in the dichloromethane eluate.

196

197 2.6. *Derivatization*

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

205

206 2.7. *GC-QTOF analyses*

207 Accurate mass spectra were obtained with an Agilent 7890B/7200 GC-QTOF System  
208 (Agilent Technologies, Parc Technopolis - ZA Courtaboeuf, Les Ulis, France). A cross-linked  
209 5% phenyl-methylpolysiloxane (Macherey Nagel; Optima 5-MS Accent) column (30 m ×  
210 0.25 mm, 0.25 µm film thickness) was employed. Analysis was performed with an injector  
211 operating in pulsed splitless at 280 °C and the oven temperature programmed from 70 °C to  
212 130 °C at 20 °C/min, then to 250 °C at 5 °C/min and then to 300 °C at 3 °C/min. The carrier  
213 gas (He) was maintained at  $0.69 \times 10^5$  Pa until the end of the temperature program.

214 Instrument temperatures were 300 °C for the transfer line and 230 °C for the ion source.

215 Accurate mass spectra were recorded across the range  $m/z$  50–700 at 4 GHz with nitrogen as  
216 collision gas (1.5 ml/min). The QTOF-MS instrument provided a typical resolution ranging  
217 from 8009 to 12252 from  $m/z$  68.9955 to 501.9706. Perfluorotributylamine (PFTBA) was  
218 utilized for daily MS calibration. Structural assignments were based on interpretation of  
219 accurate mass spectral fragmentations and confirmed by comparison of retention times and  
220 mass spectra of oxidation products with those of authentic synthesized compounds.

221

222 2.8. GC–MS/MS analyses

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

237 Quantification of oxidation products **3**, **5** and **7** was carried out with external standards  
238 in multiple reaction monitoring (MRM) mode. Precursor ions were selected from the more  
239 intense and specific ions observed in EI mass spectra. Due to the very low amounts of IPSO<sub>25</sub>  
240 available, these compounds could not be produced in sufficient amounts to be used as external  
241 standard during their quantification in sediment samples. TMS derivative of structurally  
242 similar isoprenoid compounds (3-methylidene-7,11,15-trimethylhexadecan-1,2-diol (**10**) for  
243 compound **3**, 2,6,10,14-tetramethylpentadecan-2-ol (**11**) for compound **5** and 3,7,11,15-  
244 tetramethylhexadecan-1,2-diol (**9**) for compound **7**) (see Appendix) were thus used as external  
245 standards. Correction factors that took into account the proportion of the selected precursor

246 ion in the EIMS of each compound and that of the selected MRM transition in each CID-MS  
247 were employed.

248

### 249 **3. Results**

250

#### 251 *3.1. Autoxidation of IPSO<sub>25</sub> in solvent*

252 A number of different oxidation products could be detected after incubation of IPSO<sub>25</sub>  
253 in hexane in the presence of *tert*-butyl hydroperoxide (radical enhancer) and di-*tert*-butyl  
254 nitroxide (radical initiator) (Porter et al., 1995) at 65 °C and subsequent NaBH<sub>4</sub>-reduction and  
255 silylation. Comparison of retention times and accurate mass spectra of these compounds  
256 (Figs. 1 and 2) with qualitative standards prepared by oxidation of purified IPSO<sub>25</sub> (Section  
257 2.2) allowed formal identification of compounds **1** (59.2%), **2** (5.9%), **3** (9.3%), **4** (10.2%)  
258 and **7** (traces). A compound derived from the attack of the terminal tertiary carbon atoms was  
259 also detected and tentatively attributed to 10-methylidene-2,6,14-trimethyl-9-(3-methylpent-  
260 4-enyl)-pentadecan-2-ol (**13**) or 6-methylidene-2,10,14-trimethyl-7-(3-methylpent-4-enyl)-  
261 pentadecan-2-ol (**14**) (7.6%) on the basis of the accurate mass fragmentations observed (Fig.  
262 1D).

263

#### 264 *3.2. Autoxidation of IPSO<sub>25</sub> in Arctic and Antarctic sediments*

265 The DCM eluates obtained after chromatographic fractionation of the total lipid  
266 extracts from the sediments investigated were analysed in MRM mode. The use of the  
267 transitions  $m/z$  365  $\rightarrow$  275,  $m/z$  365  $\rightarrow$  135 and  $m/z$  365  $\rightarrow$  149 and the comparison of  
268 retention time with the oxidation products characterized during the thermal incubation  
269 reactions allowed the unambiguous detection of the alcohol **3** (Fig. 3). In contrast, we failed to  
270 detect the oxidation products **1**, **2** and **4**. Taking into account: (i) the presence of the IPSO<sub>25</sub>

271 oxidation product **3** in the sediments and (ii) the well-known lability of epoxides, we searched  
272 for the presence of the reduction and hydrolysis products of the main oxidation product **1** (i.e.  
273 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-pentadecan-6-ol (**5**) (Fig. 2A) and 2-(4-  
274 methylpentyl)-3-(3-methylpent-4-enyl)-6,10-dimethylundecane-1,2-diol (**7**) (Fig. 2C)). By  
275 using appropriate MRM transitions, we were able to detect the tertiary alcohol **5** in DCM  
276 eluates of both Arctic and Antarctic sediments (Fig. 4). In contrast, diol **7** could only be  
277 identified in the Arctic sediment extracts (Fig. 5).

278 As described in Section 2.8, quantification of compounds **3**, **5** and **7** involved the use  
279 of TMS derivatives of structurally similar isoprenoid compounds as external standards. The  
280 transitions employed for quantification were (i)  $m/z$  365  $\rightarrow$  275 and  $m/z$  353  $\rightarrow$  263 (loss of  
281 trimethylsilanol by the precursor ion) for the alcohol **3** and the standard **10**, respectively; (ii)  
282  $m/z$  353  $\rightarrow$  117 and  $m/z$  341  $\rightarrow$  117 (formation of the product ion TMS-O<sup>+</sup>=CH-CH<sub>3</sub>) for the  
283 tertiary alcohol **5** and the standard **11**, respectively; (iii)  $m/z$  423  $\rightarrow$  333 and  $m/z$  355  $\rightarrow$  265  
284 (loss of trimethylsilanol by the precursor ion) for the diol **7** and the standard **9**, respectively.  
285 As indicated in Section 2.8, corrective factors were applied to accommodate structural  
286 differences between the oxidation product and the corresponding standard. The resulting  
287 concentrations of compounds **3**, **5** and **7** are given in Tables 1 and 2.

288

### 289 3.3. *Autoxidation of IPSO<sub>25</sub> in Antarctic SPM*

290 We also analysed for IPSO<sub>25</sub> oxidation products in lipid extracts of suspended particles  
291 collected at different water depths in the polynya region west of the Dalton Iceberg Tongue  
292 (East Antarctica) and where an intense autoxidation of some other lipids was previously  
293 observed (Rontani et al., 2018b). However, compounds **3**, **5** and **7** could not be identified in  
294 any of the samples analysed.

295

## 296 4. Discussion

297

### 298 4.1. Autoxidation of IPSO<sub>25</sub> in solvent

299 It is well-known that addition of ROO• radicals to a C=C bond competes with allylic  
300 hydrogen abstraction when there is a double bond that is either conjugated or 1,1-disubstituted  
301 (Schaich, 2005). Consistent with this, we observed efficient addition of peroxy radicals to the  
302 1,1-disubstituted 6-17 double bond of IPSO<sub>25</sub> affording epoxide **1** as the major product  
303 (59.2% of total oxidation products) after fast intramolecular homolytic substitution (Fossey et  
304 al., 1995) (Fig. 6). In contrast, addition to the terminal 23-24 double bond was relatively  
305 minor (5.9% of total oxidation products). Addition of peroxy radicals to the 6-17 double  
306 bond also resulted in the formation of trace amounts of the diol **7** after subsequent oxygen  
307 addition and hydrogen abstraction (Fig. 6).

308 Parallel to these peroxy radical addition reactions was a series of competitive  
309 hydrogen abstraction reactions leading to the formation of hydroperoxides **15-18** (see  
310 Appendix), which manifest as alcohols **3, 4, 13** and **14** following NaBH<sub>4</sub>-reduction during  
311 treatment. Hydrogen atom abstraction from the allylic carbon atoms 5 and 22 of IPSO<sub>25</sub> and  
312 subsequent oxidation of the resulting radicals to yield hydroperoxides **15** and **16**, respectively  
313 (Fig. 6), is as expected given the relatively stable allylic radicals formed (Fig. 6), with the  
314 additional formation of hydroperoxides **17** and **18** presumably attributable to the stability of  
315 their respective tertiary radical precursors. Surprisingly, we failed to detect oxidation products  
316 resulting from hydrogen atom abstraction at carbon 7, despite the stability of the tertiary  
317 allylic radical formed. These results are consistent with the very low efficiency of  
318 autoxidative processes at the allylic C-7 previously observed in the case of (6-17, 9-10, 23-24)  
319 HBI triene (Rontani et al., 2014). We suggest that the lack of reaction at C-7 results from  
320 steric hindrance during hydrogen abstraction by the bulky *tert*-butylperoxy radicals employed

321 during the incubation and is supported by the lack of oxidation of the allylic carbon 7  
322 observed during treatment of IPSO<sub>25</sub> with RuCl<sub>3</sub>- *tert*-butyl hydroperoxide (see Section 2.2).  
323 Hydrogen atom abstraction from non-allylic tertiary carbon atoms appeared to be limited to  
324 the external tertiary carbon atoms 2 and 14 of the molecule (and not to carbon 10), also likely  
325 due to steric hindrance.

326

#### 327 *4.2. Degradation of IPSO<sub>25</sub> in Arctic and Antarctic sediments*

328 Despite the relative recalcitrance of mono- and di-unsaturated HBIs towards free  
329 radical oxidation, reported previously (Rontani et al., 2011, 2014), oxidation product **3** could  
330 be detected in most of the Arctic and Antarctic sediments (Tables 1 and 2), confirming the  
331 partial autoxidation of IPSO<sub>25</sub> in both regions. On the other hand, the failure to detect the  
332 major oxidation product of this diene in the incubation experiments (i.e. compound **1**) likely  
333 results from: (i) the lack of specificity of its main MRM transitions, thus making it difficult to  
334 identify, (ii) an intense degradation during the treatment (NaBH<sub>4</sub>-reduction, alkaline  
335 hydrolysis and acidification) or (iii) the well-known biotic and abiotic lability of epoxides in  
336 sediments, more generally. Indeed, epoxides may undergo alcoholysis and hydrolysis during  
337 alkaline hydrolysis and are converted to chlorohydrins during acidification with HCl  
338 (Marchand and Rontani, 2001).

339 Some epoxides are also slowly reduced to alcohols during NaBH<sub>4</sub>-reduction (Zabeti et  
340 al., 2010), but this is not the case for epoxide **1**. From a biological perspective, these epoxides  
341 react readily with a large number of cell components such as DNA or proteins (Swaving and  
342 de Bont, 1998) so their removal is essential for bacteria to survive. This involves two main  
343 types of enzymes: glutathione transferases (GSTs) (which catalyse the reduction of the  
344 epoxide ring to an alcohol, Kieslich et al., 1986) and epoxide hydrolases (which catalyse the  
345 hydrolysis of the epoxide ring to a diol, Michaels et al., 1980; Rustemov et al., 1991).

346 Moreover, epoxides may also be hydrolysed abiotically (Minerath et al., 2009) and rearranged  
347 to carbonyl compounds in sediments with high clay content (Ruiz-Hitzky and Casal, 1985).

348 The presence of the tertiary alcohol **5** in the sediments investigated (Tables 1 and 2),  
349 may therefore potentially be attributed to the reduction of the epoxide ring of the IPSO<sub>25</sub>  
350 oxidation product **1** by sedimentary bacteria (Fig. 7). However, alcohol **5** might also be  
351 produced directly from IPSO<sub>25</sub> by bacteria after hydration (pathway II in Fig. 7) or  
352 epoxidation (pathway III in Fig. 7) and subsequent reduction (pathway IV in Fig. 7). Indeed,  
353 the involvement of hydration during anaerobic bacterial degradation of isoprenoid alkenes  
354 (squalene, pristenes and phytene, Rontani et al., 2002, 2013a) and *n*-alk-1-enes (Grossi et al.,  
355 2011) was demonstrated previously. On the other hand, bacterial epoxidation (mediated by  
356 cytochrome P-450-dependent monooxygenases) can produce epoxides from a broad range of  
357 lipophilic substrates such as *n*-alkenes (Soltani et al., 2004), terpenes (Duetz et al., 2003),  
358 unsaturated fatty acids (for a review see Ratledge, 1994) and alkenones (Zabeti et al., 2010).  
359 Since bacterial epoxidation should act more intensively on the terminal 23-24 double bond  
360 due to the better proximity of the terminal double bond to the heme iron of cytochrome P-450  
361 (Andersen et al., 1997), the formation of epoxide **2** (Fig. 7) and its degradation products  
362 would thus be expected. However, the absence of alcohol **6** (resulting from the reduction of  
363 epoxide **2** or hydration of the 23-24 double bond of IPSO<sub>25</sub> (Fig. 7)) in the sediments analyzed  
364 points to the lack of such bacterial processes, so the formation of alcohol **5** seems thus to  
365 mainly result from bacterial reduction of the epoxide ring of autoxidation product **1**.

366 Further, due to the probable low reactivity of monooxygenases towards the 6-17  
367 double bond of IPSO<sub>25</sub>, the formation of diol **7** may be attributed to the biotic (induced by  
368 epoxide hydrolases) or abiotic (clay-catalyzed) hydrolysis of epoxide **1** (pathways V and VI in  
369 Fig. 7). The lack of methoxyhydrins and chlorohydrins derived from the degradation of the  
370 epoxide **1** in the presence of methanol and hydrochloric acid, respectively, also allow us to



371 exclude the possible production of diol **7** during sample treatment (alkaline hydrolysis and  
372 acidification).

373 Surprisingly, diol **8** could not be detected during MRM analyses of the sediment  
374 extracts, despite the previous detection of its close structural analog (i.e. diol **19**) as an  
375 oxidation product of IP<sub>25</sub> in the same (STN 4) sediments (Rontani et al., 2018a). We attribute  
376 this to (i) the possible coelution of diols **7** and **8** and (ii) the very weak abundance of the  
377 precursor ion at *m/z* 423 in the mass spectrum of its TMS derivative (Fig. 2D), rather than  
378 from a lack of microbial degradation of IP<sub>SO</sub><sub>25</sub>.

379 In the sediments from the Arctic (STN 4), we also note the generally increasing  
380 proportion of IP<sub>SO</sub><sub>25</sub> oxidation products with depth below the redox boundary (Fig. 8),  
381 indicative of a progressive reduction of hydroperoxide **15** (produced in the oxic layer) to the  
382 corresponding alcohol **3**, together with reduction and hydrolysis of the epoxide **1** to yield  
383 alcohol **5** and diol **7**. However, due to the proposed action of sedimentary bacteria on the  
384 autoxidation products of IP<sub>SO</sub><sub>25</sub> (see earlier), the very low amounts of compounds **3**, **5** and **7**  
385 relative to their parent compound (< 1%; Fig. 8) likely underestimate the extent of abiotic  
386 degradation of IP<sub>SO</sub><sub>25</sub>, more generally.

387 In the Antarctic surface sediments, the proportion of oxidation products was always  
388 low, ranging from 0.02 to 1.1% of the residual IP<sub>SO</sub><sub>25</sub> (Table 1). These differences may  
389 potentially be attributed to: (i) the ability for sedimentary bacterial communities to degrade  
390 the primary IP<sub>SO</sub><sub>25</sub> autoxidation products, as described above, or (ii) the different residence  
391 times of algal material within the oxic layer of sediments, which may vary considerably  
392 according to location. On the other hand, the variable degradation extent may reflect the  
393 different times that the sediments have been kept in storage following collection; however, for  
394 the samples analyzed, the lowest percentages of degradation products were observed in the  
395 oldest samples (i.e. in BC 313/316 collected in 2002 compared to the other box cores

396 collected in 2008 and 2011; Table 1). These results, and those obtained previously for IP<sub>25</sub>  
397 (Rontani et al., 2018a), highlight the importance of the measurement of redox boundary layers  
398 in upper sections of sediment cores and sedimentation rates to estimate the residence time of  
399 algal material in the oxic environment and thus the extent of autoxidative degradation and its  
400 impact on paleo sea ice reconstruction based on the use of HBI tracers.

401

#### 402 *4.3. Degradation of IPSO<sub>25</sub> in Antarctic SPM*

403 The failure to detect compounds **3**, **5** and **7** in lipid extracts of strongly autoxidized  
404 suspended particles (Rontani et al., 2018b) collected at different water depths in the polynya  
405 region west of the Dalton Iceberg Tongue (East Antarctica) is in good agreement with: (i) the  
406 relative recalcitrance of di-unsaturated HBIs towards free radical oxidation processes  
407 (Rontani et al., 2011, 2014), and (ii) the expected short residence time of highly aggregated  
408 ice algae (i.e. the source of IPSO<sub>25</sub>) (Riebesell, 1991; Alldredge et al., 1993; Passow, 2002)  
409 within the water column. It also enables us to exclude the possible biological formation of  
410 these compounds in ice algae.

411

#### 412 *4.4. Potential effects of degradation processes on the DIP<sub>25</sub> index*

413 Due to the co-occurrence of IPSO<sub>25</sub> (generally reported as diene II in the Arctic) and  
414 IP<sub>25</sub> in Arctic sea ice, particles and sediments under sea ice (Belt et al., 2007; Vare et al.,  
415 2009), it has been suggested that the ratio between these two biomarkers (viz IPSO<sub>25</sub>/IP<sub>25</sub> or  
416 DIP<sub>25</sub> (Cabedo-Sanz et al., 2013)) may potentially provide further insights into Arctic sea ice  
417 conditions (e.g., Fahl and Stein, 2012; Stein et al., 2012; Cabedo-Sanz et al., 2013). It has also  
418 been suggested that variable DIP<sub>25</sub> might be indicative of changes to SST based on some  
419 empirical observations and alignment with other SST proxies (Vare et al., 2009; Cabedo-Sanz  
420 et al., 2013; Xiao et al., 2013; Müller and Stein, 2014; Ruan et al., 2017); however, there are

421 as yet no in situ data to support these interpretations (Belt, 2018). In general, proxies based on  
422 ratios of biomarkers are better at accommodating the effects of degradative processes, even if  
423 such effects cannot be totally eliminated. Indeed, it was previously demonstrated that, under  
424 some conditions, autoxidative and biodegradation processes may act selectively on C<sub>37:2</sub> and  
425 C<sub>37:3</sub> alkenones, thus negatively impacting on the  $U_{37}^{K'}$  index (for a review, see Rontani et al.,  
426 2013b). It is feasible, therefore, that differential degradation of IP<sub>25</sub> and IPSO<sub>25</sub> may also  
427 influence the DIP<sub>25</sub> ratio, with substantially increased values, as seen in some sedimentary  
428 records (Fahl and Stein, 2012; Müller and Stein, 2014) resulting from a preferential  
429 degradation of IP<sub>25</sub>. Previously, however, autoxidative degradation of these two HBIs  
430 measured in solvents (Rontani et al., 2014), showed a higher degradation rate for IPSO<sub>25</sub> ( $k =$   
431  $0.004 \text{ h}^{-1}$ ) compared to IP<sub>25</sub> ( $k = 0.001 \text{ h}^{-1}$ ). Unfortunately, due to the mineralisation of the  
432 major part of substrates by bacteria, comparison of the efficiency of bacterial degradation  
433 processes on IP<sub>25</sub> and IPSO<sub>25</sub> on the basis of the quantities of metabolites detected is difficult.  
434 However, we note that significant proportions (up to 35% of the residual substrate) of 2,8,12-  
435 trimethyl-5-(1,5-dimethylhexyl)-tridecanoic acid (**20**), resulting from bacterial cleavage of the  
436 23-24 double bond of IP<sub>25</sub>, were detected in sediments from Barrow Strait (i.e. STN 4)  
437 (Rontani et al., 2018c), while we failed to detect the corresponding metabolite of IPSO<sub>25</sub> (i.e.  
438 2,8,12-trimethyl-5-(1-methylidene-5-methylhexyl)-tridecanoic acid (**21**)) in the same  
439 sediments. This suggests a preferential bacterial degradation of IP<sub>25</sub>, which could potentially  
440 be attributed to the presence of toxic autoxidative epoxides in algal material containing  
441 IPSO<sub>25</sub>, which are in lower abundance (or absent) in the case of IP<sub>25</sub>. More detailed analyses  
442 of factors that control the DIP<sub>25</sub> ratio, however, will be required in the future.

443

444 *4.5. Consequences for IP<sub>25</sub>, IPSO<sub>25</sub> and DIP<sub>25</sub>-based sea ice reconstructions*

445 As with all lipid-based proxies, those involving HBIs such as IP<sub>25</sub> and IPSO<sub>25</sub> require  
446 careful consideration of their alteration and preservation during transport through the water  
447 column and deposition in sediments, including determining the magnitude and relative  
448 importance of biotic and/or abiotic processes. While both autoxidative and bacterial  
449 degradation products of IP<sub>25</sub> were identified and quantified previously in Arctic surficial  
450 sediments (Rontani et al., 2018c), here we demonstrated that IPSO<sub>25</sub> may also be affected by  
451 such processes in Arctic and Antarctic sediments. At this stage, the characterisation of  
452 signature degradation products from these biotic and abiotic processes mainly provides useful  
453 ‘qualitative’ indicators of diagenetic alteration of these two paleo sea ice tracers.  
454 Unfortunately, subsequent reaction of most of the primary oxidation products by sedimentary  
455 bacteria limits their accumulation in sediments, thereby preventing any accurate quantitative  
456 estimates of the extent of degradation of IP<sub>25</sub> and IPSO<sub>25</sub>, and thus of the ratio between them  
457 (i.e. DIP<sub>25</sub>). The impacts of sedimentary degradation of IP<sub>25</sub> and IPSO<sub>25</sub> on their use as paleo  
458 sea ice proxies therefore remains difficult to assess at this stage. On the other hand, the  
459 somewhat higher accumulation of 2,8,12-trimethyl-5-(1,5-dimethylhexyl)-tridecanoic acid  
460 (**20**) in some oxic sediments could potentially provide semi-quantitative estimates of the role  
461 of bacterial degradation of IP<sub>25</sub> (Rontani et al., 2018c).

462

## 463 **5. Conclusions**

464

465 The detection of reduced or hydrolyzed autoxidation products of IPSO<sub>25</sub> in Arctic and  
466 Antarctic sediments demonstrated that this proxy may be partially degraded abiotically in  
467 near-surface oxic sediments, especially in the case of sediment cores containing relatively  
468 thick oxic layers representing long times of deposition. Unfortunately, due to its high biotic  
469 and abiotic lability, the major autoxidation product formed (epoxide **1**) does not accumulate in

470 sediments. In contrast, IPSO<sub>25</sub> appeared to be essentially unaffected by autoxidation processes  
471 in the water column.

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

475 Autoxidation reactions of HBIs appear to occur primarily at the unsaturated or allylic  
476 carbon atoms within the lipid framework. However, the production of compounds such as **13**  
477 or **14** observed during IPSO<sub>25</sub> autoxidation, and the previous detection of degradation  
478 products of IP<sub>25</sub> in Arctic sediments resulting from the free radical oxidation of its saturated  
479 tertiary carbon atoms (Rontani et al., 2018a), clearly show that autoxidation processes can  
480 also affect saturated compounds when algal or bacterial material experiences long residence  
481 times in the oxic layer of sediments.

482

### 483 **Acknowledgements**

484

485 Financial support from the Centre National de la Recherche Scientifique (CNRS) and  
486 the Aix-Marseille University is gratefully acknowledged. Thanks are due to the FEDER  
487 OCEANOMED (N° 1166-39417) for the funding of the apparatus employed. LS and STB are  
488 grateful to the University of Plymouth for financial support. We thank Leanne Armand and  
489 Amy Leventer for providing the SPM samples. Thanks are due to two anonymous reviewers  
490 and to the Associate Editor for their useful and constructive comments.

491

492 *Associate Editor*–**Stuart Wakeham**

493

### 494 **References**

495 Alldredge, A.L., Passow, U., Logan, B.E., 1993. The abundance and significance of a class of  
496 large, transparent organic particles in the ocean. *Deep-Sea Research Part I*–  
497 *Oceanographic Research Papers* 40, 1131–1140.

498 Andersen, J.F., Walding, J.K., Evans, P.H., Bowers, W.S., Feyereisen, R., 1997. Substrate  
499 specificity for the epoxidation of terpenoids and active site topology of house fly  
500 cytochrome P450 6A1. *Chemical Research in Toxicology* 10, 156–164.

501 Barbara, L., Crosta, X., Leventer, A., Schmidt, S., Etourneau, J., Domack, E., Massé, G.,  
502 2016. Environmental responses of the Northeast Antarctic Peninsula to the Holocene  
503 climate variability. *Paleoceanography*, 31, 131–147.

504 Belt, S.T., Allard, W.G., Massé, G., Robert, J.-M., Rowland, S.J., 2000. Highly branched  
505 isoprenoids (HBIs): identification of the most common and abundant sedimentary  
506 isomers. *Geochimica et Cosmochimica Acta* 64, 3839–3851.

507 Belt, S.T., Massé, G., Allard, W.G., Robert, J.-M., Rowland, S.J., 2001a. Identification of a  
508 C<sub>25</sub> highly branched isoprenoid triene in the freshwater diatom *Navicula sclesvicensis*.  
509 *Organic Geochemistry* 32, 1169–1172.

510 Belt, S.T., Massé, G., Allard, W.G., Robert, J.-M., Rowland, S.J., 2001b. C<sub>25</sub> highly branched  
511 isoprenoid alkenes in planktonic diatoms of the *Pleurosigma* genus. *Organic*  
512 *Geochemistry* 32, 1271–1275.

513 Belt, S.T., Massé, G., Rowland, S.J., Poulin, M., Michel, C., LeBlanc, B., 2007. A novel  
514 chemical fossil of palaeo sea ice: IP<sub>25</sub>. *Organic Geochemistry* 38, 16–27.

515 Belt, S.T., Smik, L., Brown, T.A., Kim, J.H., Rowland, S.J., Allen, C.S., Gal, J.K., Shin,  
516 K.H., Lee, J.I., Taylor, K.W.R., 2016. Source identification and distribution reveals  
517 the potential of the geochemical Antarctic sea ice proxy IPSO<sub>25</sub>. *Nature*  
518 *Communications* 7, 12655.

519 Belt, S.T., 2018. Source-specific biomarkers as proxies for Arctic and Antarctic sea ice.  
520        Organic Geochemistry 125, 277–298.

521 Belt, S.T., 2019. What do IP<sub>25</sub> and related biomarkers really reveal about sea ice change?  
522        Quaternary Science Reviews 204, 216–219.

523 Brown, T.A., 2011. Production and preservation of the Arctic sea ice diatom biomarker IP<sub>25</sub>.  
524        PhD thesis, University of Plymouth, UK.

525 Brown, T.A., Belt, S.T., Cabedo-Sanz, P., 2014. Identification of a novel diunsaturated C<sub>25</sub>  
526        highly branched isoprenoid in the marine tube-dwelling diatom *Berkeleya rutilans*.  
527        Environmental Chemistry Letters 12, 455–460.

528 Cabedo-Sanz, P., Belt, S.T., Knies, J., Husum, K., 2013. Identification of contrasting seasonal  
529        sea ice conditions during the Younger Dryas. Quaternary Science Reviews 79, 74–86.

530 Campagne, P., Crosta, X., Schmidt, S., Houssais, M.N., Ther, O., Massé, G., 2016.  
531        Sedimentary response to sea ice and atmospheric variability over the instrumental  
532        period off Adélie Land, East Antarctica. Biogeosciences 13, 4205–4218.

533 Collins, L.G., Allen, C.S., Pike, J., Hodgson, D.A., Weckström, K., Massé, G., 2013.  
534        Evaluating highly branched isoprenoids (HBIs) as an Antarctic sea-ice proxy in deep-  
535        water glacial sediments. Quaternary Science Reviews 79, 87–98.

536 Duez, W.A., Bouwmeester, H., Beilen, J.B., Witholt, B., 2003. Biotransformation of limonene  
537        by bacteria, fungi, yeasts and plants. Applied Microbiology and Biotechnology 61,  
538        299–301.

539 Etourneau, J., Collins, L.G., Willmott, V., Kim, J.H., Barbara, L., Leventer, A., Schouten, S.,  
540        Sinninghe Damsté, J.S., Bianchini, A., Klein, V., Crosta, X., Massé, G., 2013.  
541        Holocene climate variations in the western Antarctic Peninsula: evidence for sea ice  
542        extent predominantly controlled by changes in insolation and ENSO variability.  
543        Climate of the Past 9, 1431–1446.

544 Fahl, K., Stein, R., 2012. Modern seasonal variability and deglacial/Holocene change of  
545 central Arctic Ocean sea-ice cover: New insights from biomarker proxy records. *Earth  
546 and Planetary Science Letters* 351–352, 123–133.

547 Fossey, J., Lefort, D., Sorba, J., 1995. *Free Radicals in Organic Chemistry*. Masson, Paris.

548 Grossi, V., Beker, B., Geenevasen, J.A.J., Schouten, S., Raphel, D., Fontaine, M.-F.,  
549 Sinninghe Damsté, J.S., 2004. C<sub>25</sub> highly branched isoprenoid alkenes from the marine  
550 benthic diatom *Pleurosigma strigosum*. *Phytochemistry* 65, 3049–3055.

551 Grossi, V., Cravo-Lauro, C., Rontani, J.-F., Cros, M., Hirschler-Réa, A., 2011. Anaerobic  
552 oxidation of *n*-alkenes by sulphate-reducing bacteria from the genus *Desulfatiferula*:  
553 *n*-ketones as potential metabolites. *Research in Microbiology* 162, 915–922.

554 Johns, L., Wraige, E.J., Belt, S.T., Lewis, C.A., Massé, G., Robert, J.M., Rowland, S.J., 1999.  
555 Identification of a C<sub>25</sub> highly branched isoprenoid (HBI) diene in Antarctic sediments,  
556 Antarctic sea-ice diatoms and cultured diatoms. *Organic Geochemistry* 30, 1471–  
557 1475.

558 Kaiser, J., Belt, S.T., Tomczak, T., Brown, T.A., Wasmund, N., Arz, H.W., 2016. C<sub>25</sub> highly  
559 branched isoprenoid alkenes in the Baltic Sea produced by the marine planktonic  
560 diatom *Pseudosolenia calcar-avis*. *Organic Geochemistry* 93, 51–58.

561 Kieslich, K. Abraham, W.R., Stumpf, B., Thede, B., Washausen, P., 1986. Transformation of  
562 terpenoids. In: Brunke, E.J. (Ed.), *Progress in Essential Oil Research*. Walter de  
563 Gruyter & Co., Berlin, pp. 368–394.

564 McCloskey, J.A., McClelland, M.J., 1965. Mass spectra of O-isopropylidene derivatives of  
565 unsaturated fatty esters, *Journal of the American Chemical Society* 87, 5090–5093.

566 Marchand, D., Rontani, J.-F., 2001. Characterisation of photooxidation and autoxidation  
567 products of phytoplanktonic monounsaturated fatty acids in marine particulate matter  
568 and recent sediments. *Organic Geochemistry* 32, 287–304.



569 Michaels, B.C., Ruettinger, R.T., Fulco, A.J., 1980. Hydration of 9,10-epoxypalmitic acid by  
570 a soluble enzyme from *Bacillus megaterium*. Biochemical and Biophysical Research  
571 Communications 92, 1189–1195.

572 Minerath, E.C., Schultz, M.P., Elrod, M.J., 2009. Kinetics of the reactions of isoprene-derived  
573 epoxides in model tropospheric aerosol solutions. Environmental Science Technology  
574 43, 8133–8139.

575 Müller, J., Stein, R., 2014. High-resolution record of late glacial sea ice changes in Fram  
576 Strait corroborates ice-ocean interactions during abrupt climate shifts. Earth and  
577 Planetary Science Letters 403, 446–455.

578 Nichols, D.S., Nichols, P.D., Sullivan, C.W., 1993. Fatty acid, sterol and hydrocarbon  
579 composition of Antarctic sea ice diatom communities during the spring bloom in  
580 McMurdo Sound. Antarctic Science 5, 271–278.

581 Passow, U., 2002. Transparent exopolymer particles (TEP) in aquatic environments. Progress  
582 in Oceanography 55, 287–333.

583 Porter, N.A., Caldwell, S.E., Mills, K.A., 1995. Mechanisms of free radical oxidation of  
584 unsaturated lipids. Lipids 30, 277–290.

585 Ratledge, C., 1994. Biodegradation of oils, fats and fatty acids. In: Ratledge, C. (Ed.),  
586 Biochemistry of Microbial Degradation. Kluwer Academic Publishers, Dordrecht, pp.  
587 89–142.

588 Riebesell U., Schloss I., Smetacek V., 1991. Aggregation of algae released from melting sea  
589 ice-implications for seeding and sedimentation. Polar Biology 11, 239–248.

590 Robson, J.N., Rowland, S.J., 1988. Biodegradation of highly branched isoprenoid  
591 hydrocarbons: a possible explanation of sedimentary abundance. Organic  
592 Geochemistry 13, 691–695.

593 Rontani, J.-F., Mouzdahir, A., Michotey, V., Bonin P., 2002. Aerobic and anaerobic  
594 metabolism of squalene by a new denitrifying *Marinobacter* sp. isolated from marine  
595 sediment. *Archives of Microbiology* 178, 279–287.

596 Rontani, J.-F., Aubert, C., 2005. Characterization of isomeric allylic diols resulting from  
597 chlorophyll phytyl side chain photo- and autoxidation by electron ionization gas  
598 chromatography/mass spectrometry. *Rapid Communications in Mass Spectrometry* 19,  
599 637–646.

600 Rontani, J.-F., Belt, S.T., Vaultier, F., Brown, T.A., 2011. Visible light-induced photo-  
601 oxidation of highly branched isoprenoid (HBI) alkenes: a significant dependence on  
602 the number and nature of the double bonds. *Organic Geochemistry* 42, 812–822.

603 Rontani, J.-F., Charriere, B., Forest, A., Heussner, S., Vaultier, F., Petit, M., Delsaut, N.,  
604 Fortier, L., Sempéré, R., 2012. Intense photooxidative degradation of planktonic and  
605 bacterial lipids in sinking particles collected with sediment traps across the Canadian  
606 Beaufort Shelf (Arctic Ocean). *Biogeosciences* 9, 4787–4802.

607 Rontani, J.-F., Bonin, P., Vaultier, F., Guasco, S., Volkman, J.K., 2013a. Anaerobic bacterial  
608 degradation of pristenes and phytanes in marine sediments does not lead to pristane  
609 and phytane. *Organic Geochemistry* 58, 43–55.

610 Rontani, J.-F., Volkman, J.K., Prahl, F.G., Wakeham, S.G., 2013b. Biotic and abiotic  
611 degradation of alkenones and implications for  $U_{37}^{K'}$  paleoproxy applications: A review.  
612 *Organic Geochemistry* 59, 93–113.

613 Rontani, J.-F., Belt, S., Vaultier, F., Brown, T., Massé, G., 2014. Autoxidative and  
614 photooxidative reactivity of highly branched isoprenoid (HBI) alkenes. *Lipids* 49,  
615 481–494.

616 Rontani, J.-F., Belt, S.T., Brown, T.A., Amiraux, R., Gosselin, M., Vaultier, F., Mundy, C.J.,  
617 2016. Monitoring abiotic degradation in sinking versus suspended Arctic sea ice algae

618 during a spring ice melt using specific lipid oxidation tracers. *Organic Geochemistry*  
619 98, 82–97.

620 Rontani, J.-F., Galeron, M.-A., Amiraux, R., Artigue, L., Belt, S.T., 2017. Identification of di-  
621 and triterpenoid lipid tracers confirms the significant role of autoxidation in the  
622 degradation of terrestrial vascular plant material in the Canadian Arctic. *Organic*  
623 *Geochemistry* 108, 43–50.

624 Rontani, J.-F., Belt, S.T., Amiraux R., 2018a. Biotic and abiotic degradation of the sea ice  
625 diatom biomarker IP<sub>25</sub> and selected algal sterols in near-surface Arctic sediments.  
626 *Organic Geochemistry* 118, 73–88.

627 Rontani, J.-F., Smik, L., Belt, S.T., Vaultier, F., Armbrecht, L., Leventer, A., Armand, L.K.,  
628 2018b. Abiotic degradation of highly branched isoprenoid alkenes and other lipids in  
629 the water column off East Antarctica. *Marine Chemistry* (Submitted).

630 Rontani, J.-F., Aubert, C., Belt S.T., 2018c. EIMS Fragmentation and MRM quantification of  
631 bacterial metabolites of the sea ice biomarker proxy IP<sub>25</sub> in Arctic sediments. *Rapid*  
632 *Communications in Mass Spectrometry* 32, 775–783.

633 Rowland, S.J., Hird, S.J., Robson, J.N., Venkatesan, M.I., 1990. Hydrogenation behaviour of  
634 two highly branched C<sub>25</sub> dienes from Antarctic marine sediments. *Organic*  
635 *Geochemistry* 15, 215–218.

636 Ruan, J., Huang, Y., Shi, X., Liu, Y., Xiao, W., Xu, Y., 2017. Holocene variability in sea  
637 surface temperature and sea ice extent in the northern Bering Sea: A multiple  
638 biomarker study. *Organic Geochemistry* 113, 1–9.

639 Ruiz-Hitzky, E., Casal, B., 1985. Epoxide rearrangements on mineral and silica-alumina  
640 surfaces. *Journal of Catalysis* 92, 291–295.

641 Rustemov, S.A., Golovieva, L.A., Alieva, R.M., Baskunov, B.P., 1991. New pathway of  
642 styrene oxidation by a *Pseudomonas putida* culture. *Mikrobiologiya* 61, 5–10.

643 Schaich, K.M., 2005. Lipid oxidation: Theoretical aspects. In: Shahidi, F. (Ed.), Bailey's  
644 Industrial Oil and Fat Products. John Wiley & Sons, Chichester, pp. 269–355.

645 Seki, H., Ohyama, K., Sawai, S., Mizutani, M., Ohnishi, T., Sudo, H., Akashi, T., Aoki, T.,  
646 Saito, K., Muranaka, T., 2008. Licorice  $\beta$ -amyirin 11-oxidase, a cytochrome P450 with  
647 a key role in the biosynthesis of the triterpene sweetener glycyrrhizin. Proceedings of  
648 the National Academy of Sciences 105, 14204–14209.

649 Sinninghe Damsté, J.S., Schouten, S., Rijpstra, W.I.C., Hopmans, E.C., Peletier, H., Gieskes,  
650 W.W.C., Geenevasen, J.A.J., 1999. Structural identification of the C<sub>25</sub> highly branched  
651 isoprenoid pentaene in the marine diatom *Rhizosolenia setigera*. Organic  
652 Geochemistry 30, 1581–1583.

653 Sinninghe Damsté, J.S., Muyzer, G., Abbas, B., Rampen, S.W., Massé, G., Allard, W.G.,  
654 Belt, S.T., Robert, J.-M., Rowland, S.J., Moldowan, J.M., Barbanti, S.M., Fago, F.J.,  
655 Denisevich, P., Dahl, J., Trinidade, L.A.F., Schouten, S., 2004. The rise of the  
656 rhizosolenid diatoms. Science 304, 584–587.

657 Soltani, M., Metzger, P., Largeau, C., 2004. Effects of hydrocarbon structure on fatty acid,  
658 fatty alcohols and  $\beta$ -hydroxy acid composition in the hydrocarbon-degrading  
659 bacterium *Marinobacter hydrocarbonoclasticus*. Lipids 39, 491–505.

660 Stein, R., Fahl, K., Müller, J., 2012. Proxy reconstruction of Arctic Ocean sea ice history:  
661 from IRD to IP<sub>25</sub>. Polarforschung 82, 37–71.

662 Swaving, J., de Bont, A.M., 1998. Microbial transformation of epoxides. Enzyme and  
663 Microbial Technology 22, 19–26.

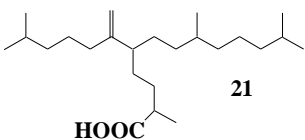
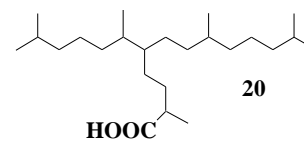
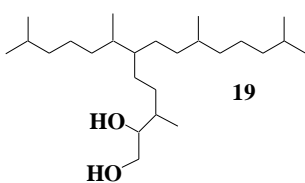
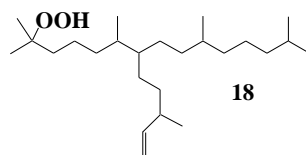
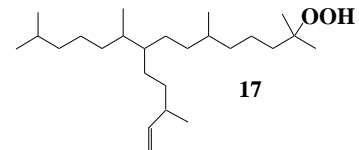
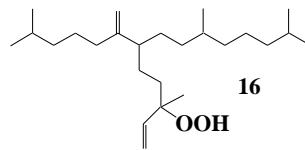
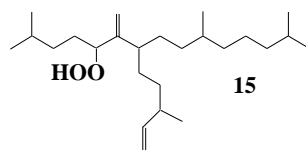
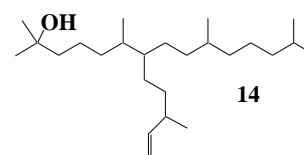
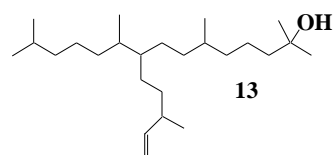
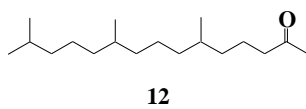
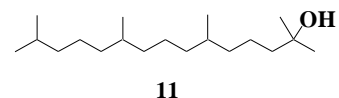
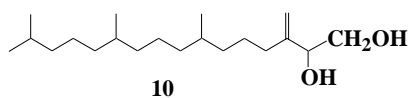
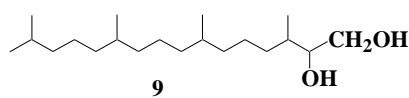
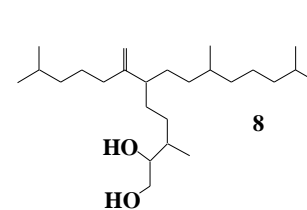
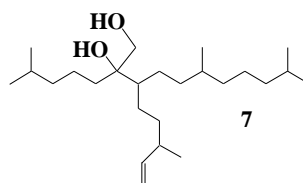
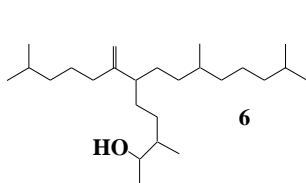
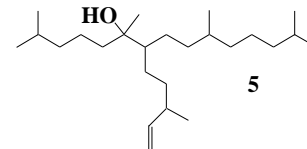
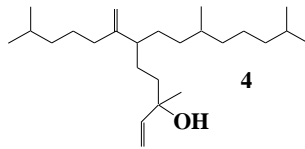
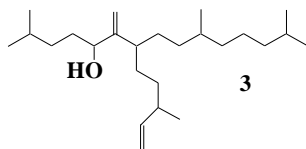
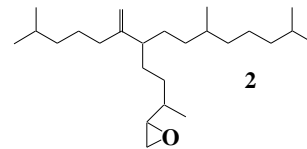
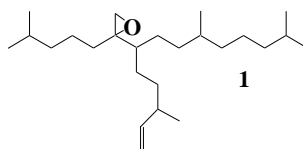
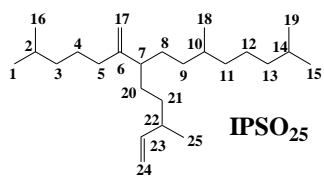
664 Vare, L.L., Massé, G., Gregory, T.R., Smart, C.W., Belt, S.T., 2009. Sea ice variations in the  
665 central Canadian Arctic Archipelago during the Holocene. Quaternary Science  
666 Reviews 28, 1354–1366.

667 Volkman, J.K., Barrett, S.M., Dunstan, G.A., 1994. C<sub>25</sub> and C<sub>30</sub> highly branched isoprenoid  
668 alkenes in laboratory cultures of two marine diatoms. *Organic Geochemistry* 21, 407–  
669 414.

670 Xiao, X., Stein, R., Fahl, K., 2013. Biomarker distributions in surface sediments from the  
671 Kara and Laptev Seas (Arctic Ocean): Indicators for organic-carbon sources and sea  
672 ice coverage. *Quaternary Science Reviews* 79, 40–52.

673 Zabeti, N., Bonin, P., Volkman, J.K., Jameson, I., Guasco, S., Rontani, J.-F., 2010. Potential  
674 alteration of  $U_{37}^{K'}$  paleothermometer due to selective degradation of alkenones by  
675 marine bacteria isolated from the haptophyte *Emiliana huxleyi*. *FEMS Microbiology*  
676 *and Ecology* 73, 83–94.

## APPENDIX



678 **Figure captions**

679

680 **Fig. 1.** TOFMS mass spectra of 1,2-epoxy-2-(4-methylpentyl)-3-(3-methylpent-4-enyl)-6,10-  
681 dimethylundecane (**1**) (A) and trimethylsilyl derivatives of: 6-methylidene-2,10,14-trimethyl-  
682 7-(3-methylpent-4-enyl)-pentadecan-5-ol (**3**) (B), 3,9,13-trimethyl-6-(1-methylidene-5-  
683 methylhexyl)-tetradec-1-en-3-ol (**4**) (C) and 10-methylidene-2,6,14-trimethyl-9-(3-  
684 methylpent-4-enyl)-pentadecan-2-ol (**13**) or 6-methylidene-2,10,14-trimethyl-7-(3-  
685 methylpent-4-enyl)-pentadecan-2-ol (**14**) (D).

686

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

692

693 **Fig. 3.** MRM chromatograms ( $m/z$  365  $\rightarrow$  275,  $m/z$  365  $\rightarrow$  149 and  $m/z$  425  $\rightarrow$  135) of  
694 silylated standard alcohol **3** (A) and DCM fractions obtained from the Antarctic station BC  
695 313 (B) and the 10–11 cm sediment layer of the box core from Barrow Strait (Canadian  
696 Arctic) (C).

697

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

701

702 **Fig. 5.** MRM chromatograms ( $m/z$  526  $\rightarrow$  231 and  $m/z$  526  $\rightarrow$  142) of silylated standard diol  
703 **7** (A) and DCM fractions obtained from the 2–3 cm (B) and the 10–11 cm (C) sediment layers  
704 of the box core from Barrow Strait (Canadian Arctic).

705

706 **Fig. 6.** Proposed mechanisms for the autoxidation of IPSO<sub>25</sub> in sediments and subsequent  
707 NaBH<sub>4</sub>-reduction of the resulting hydroperoxides during the treatment.

708

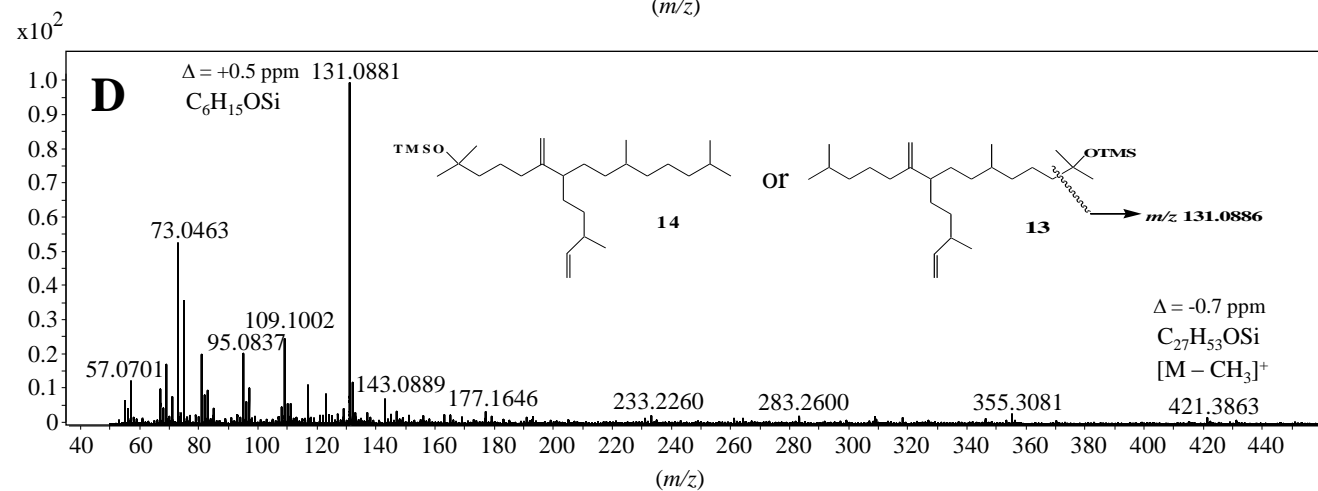
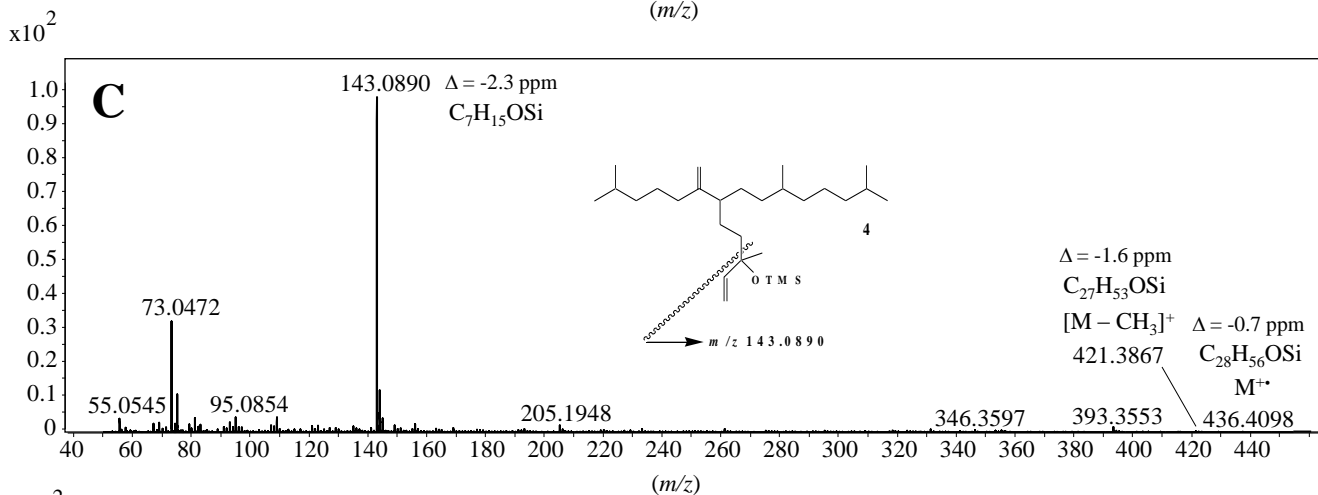
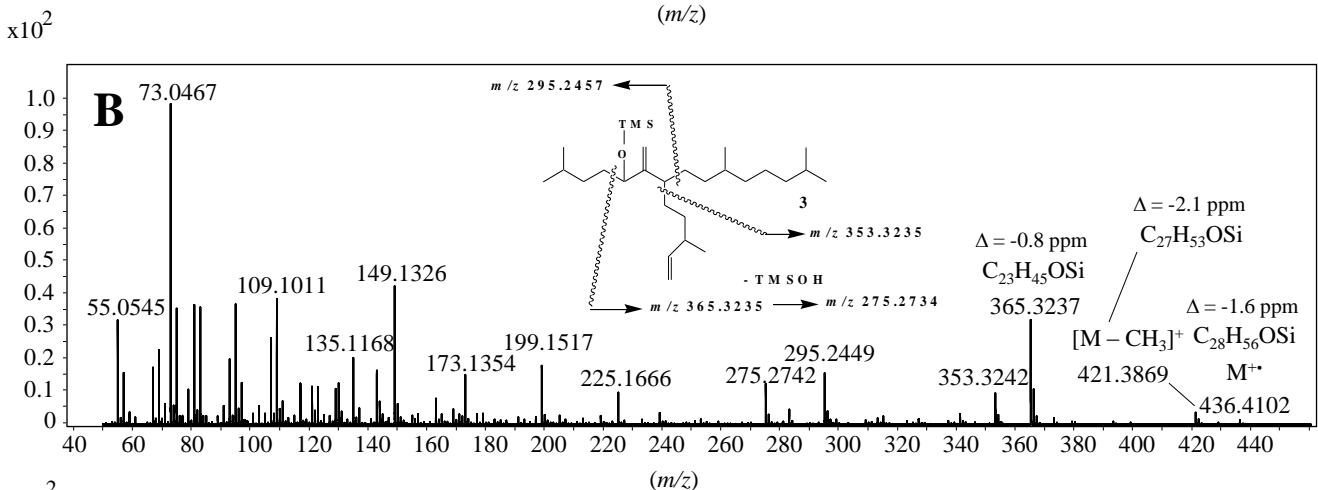
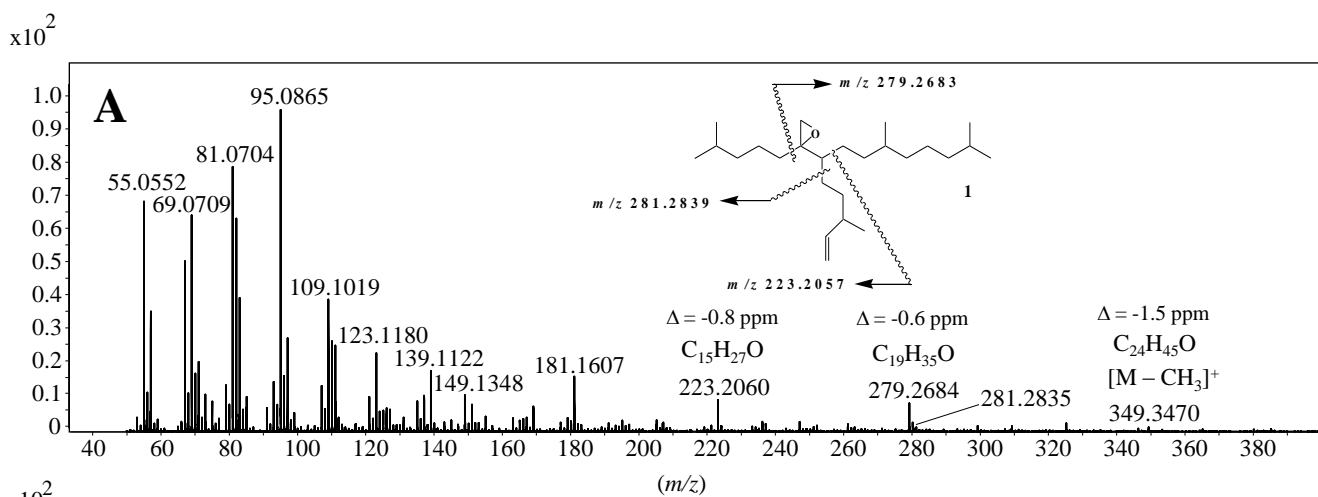
709 **Fig. 7.** Proposed mechanisms for the formation and degradation of epoxides **1** and **2** in  
710 sediments.

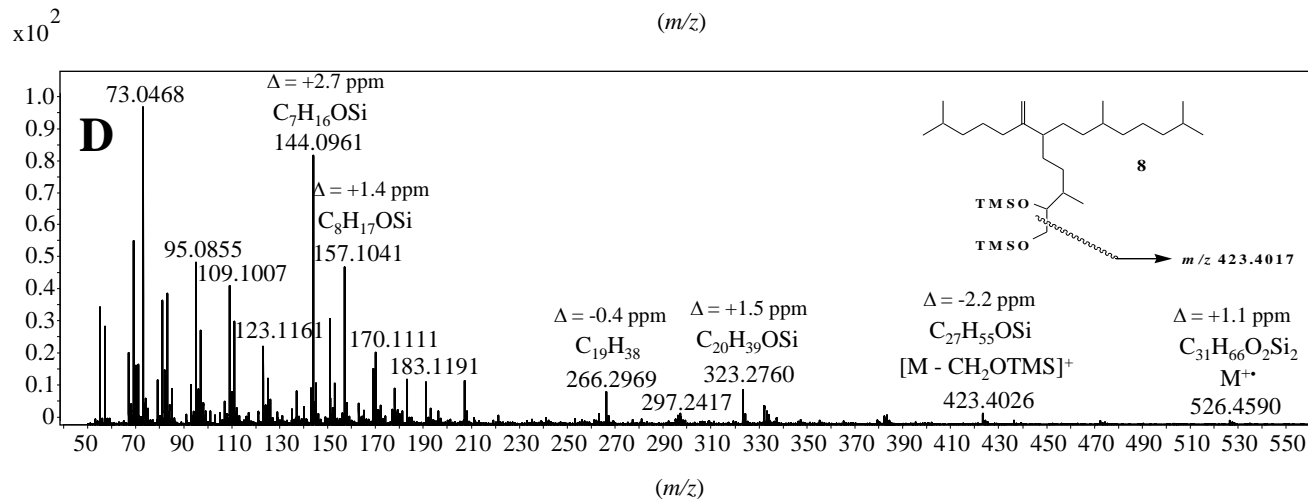
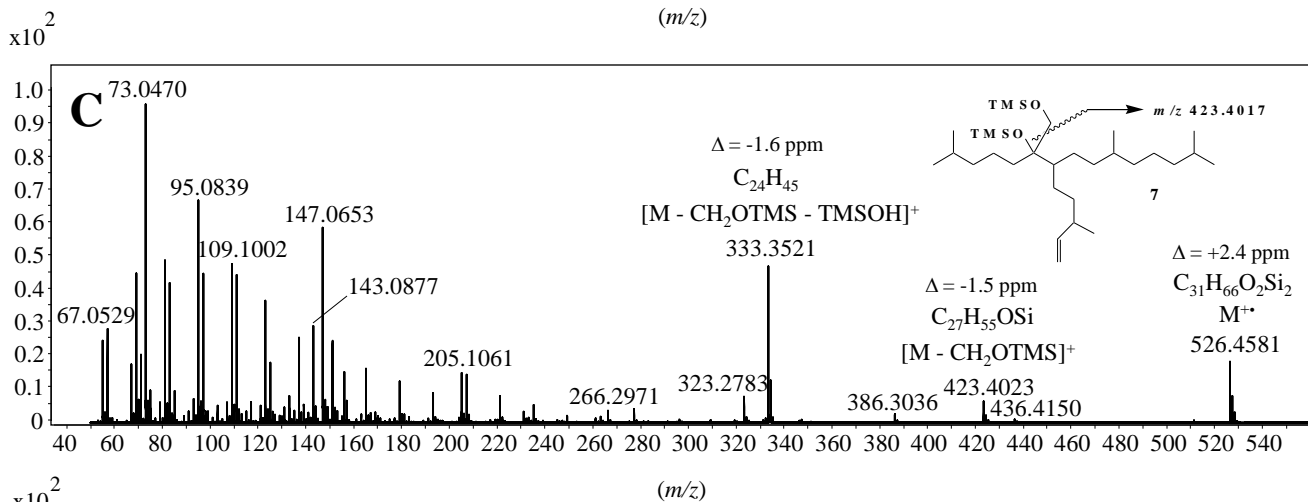
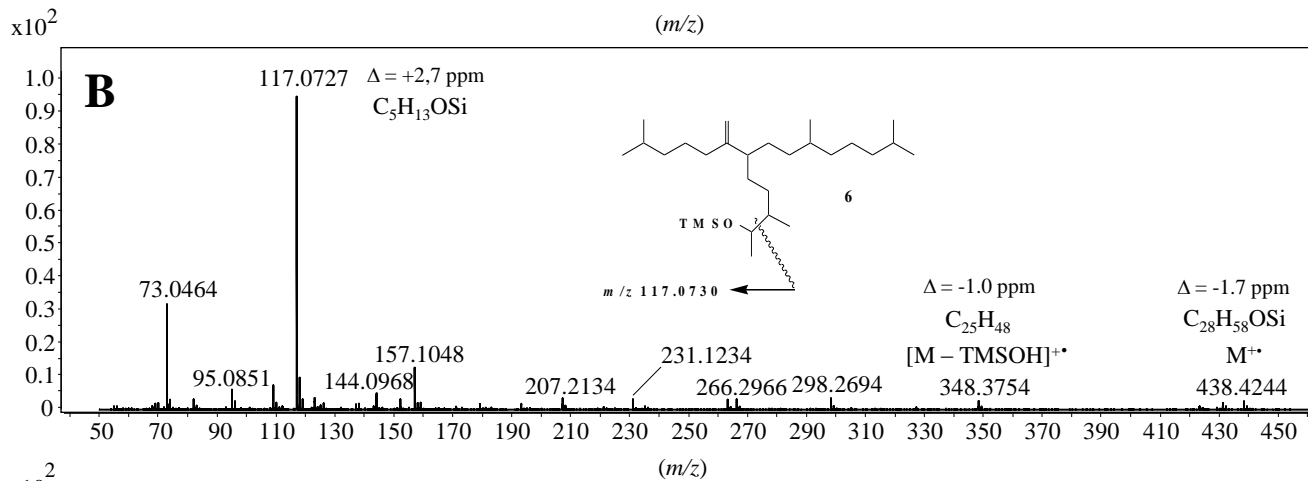
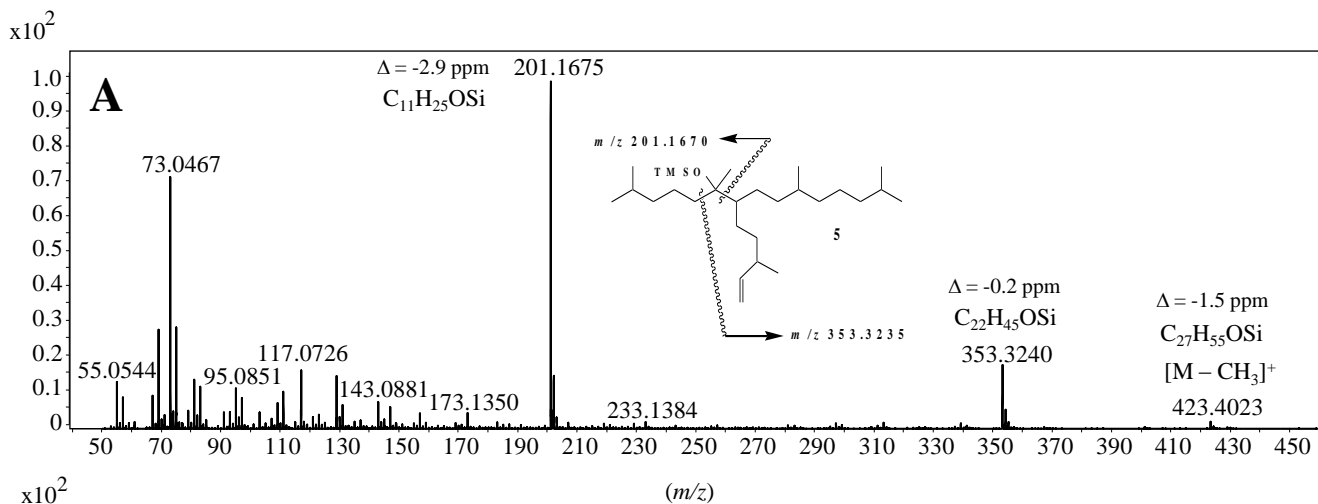
711

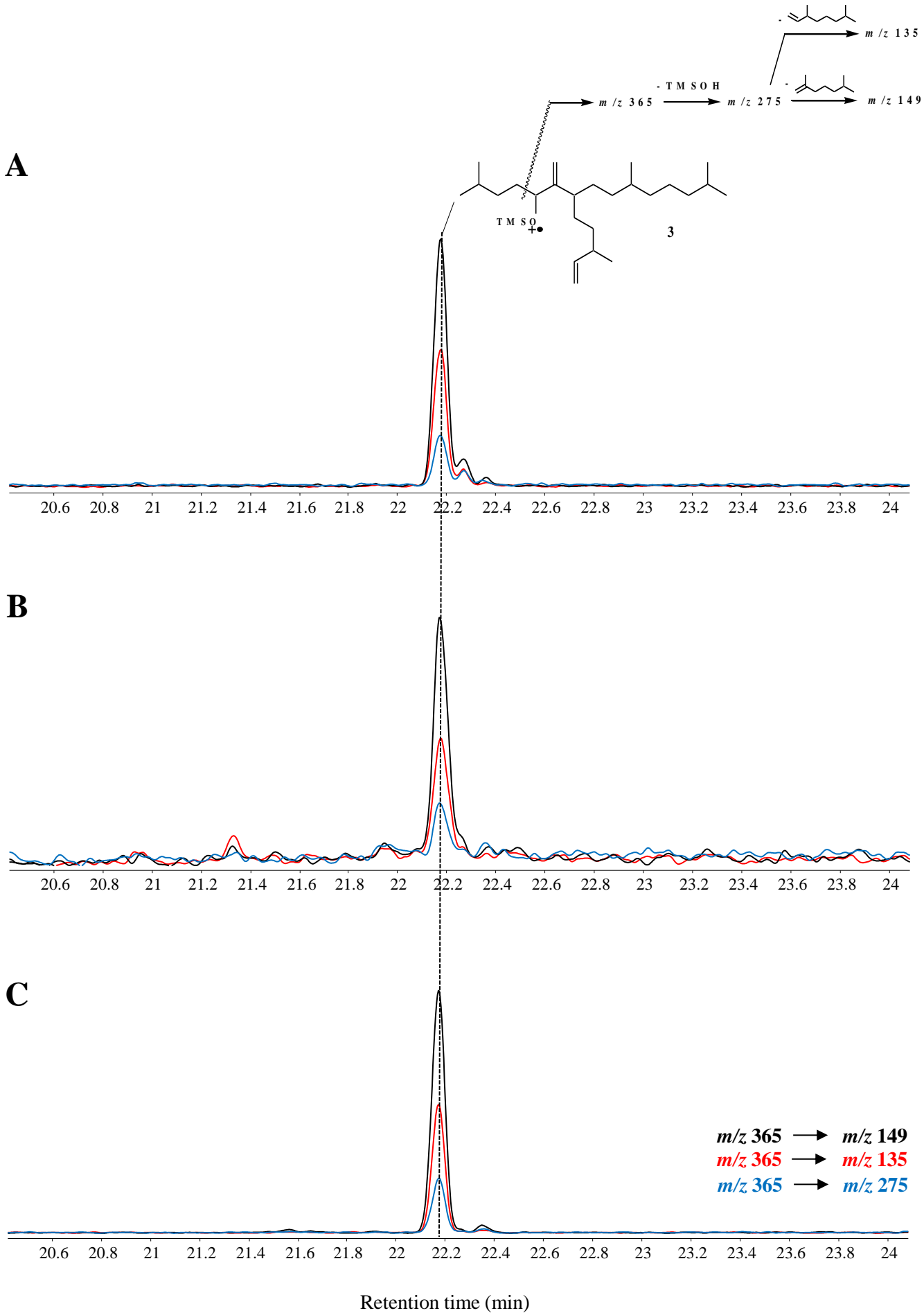
712 **Fig. 8.** Relative percentages of IPSO<sub>25</sub> and its degradation products in various sediment  
713 sections of the box core from Barrow Strait (Canadian Arctic).

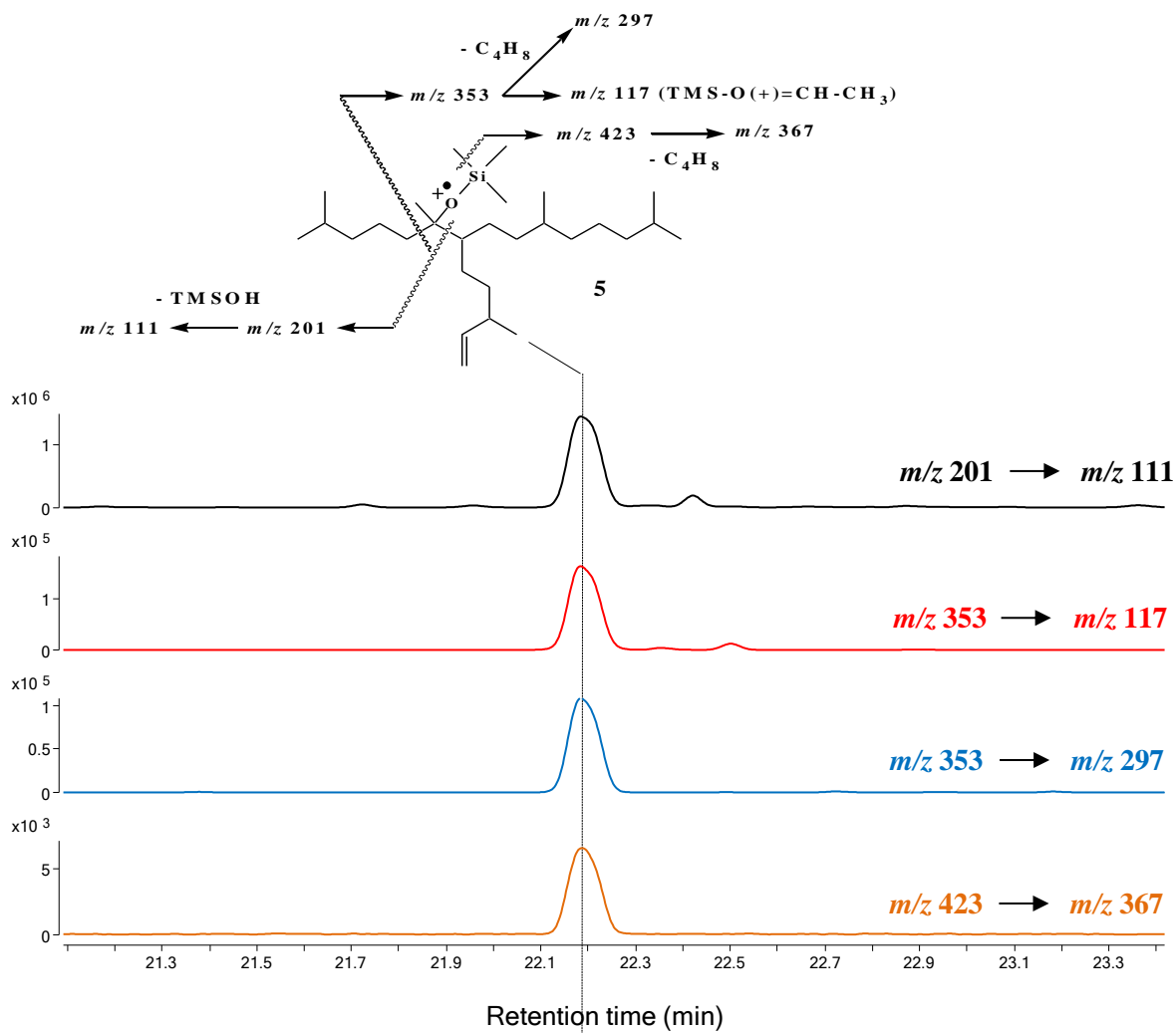
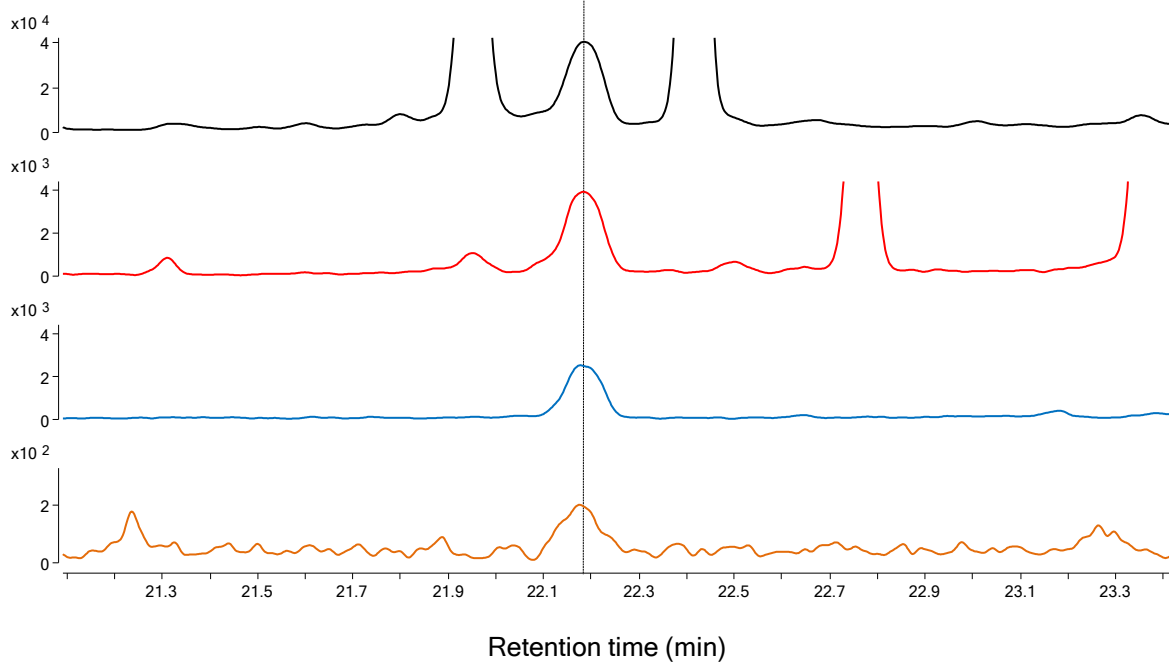
714

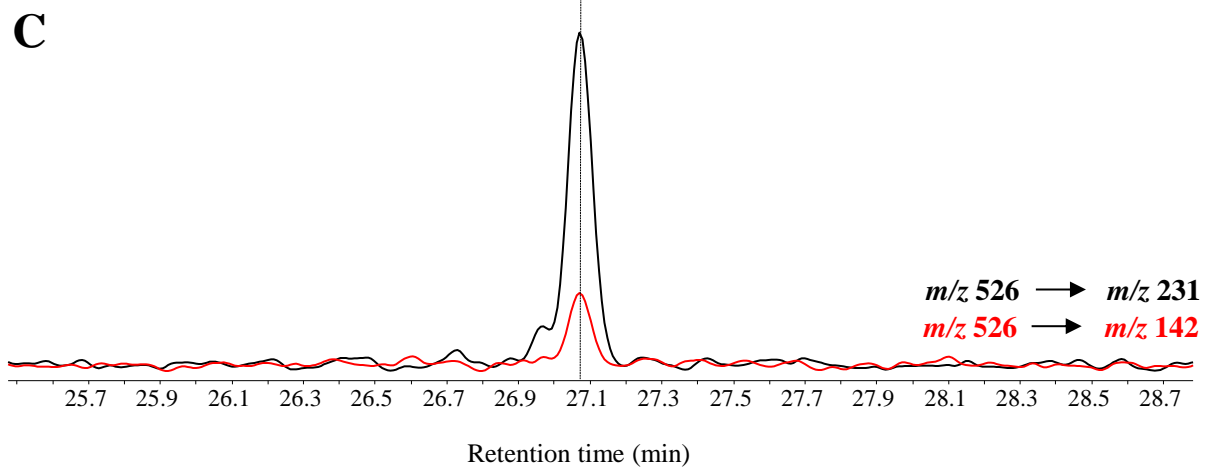
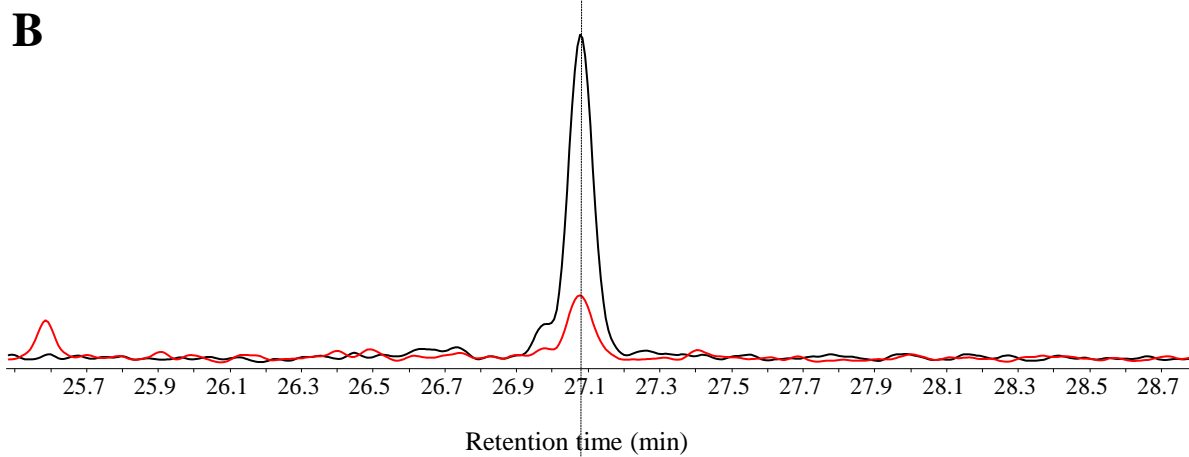
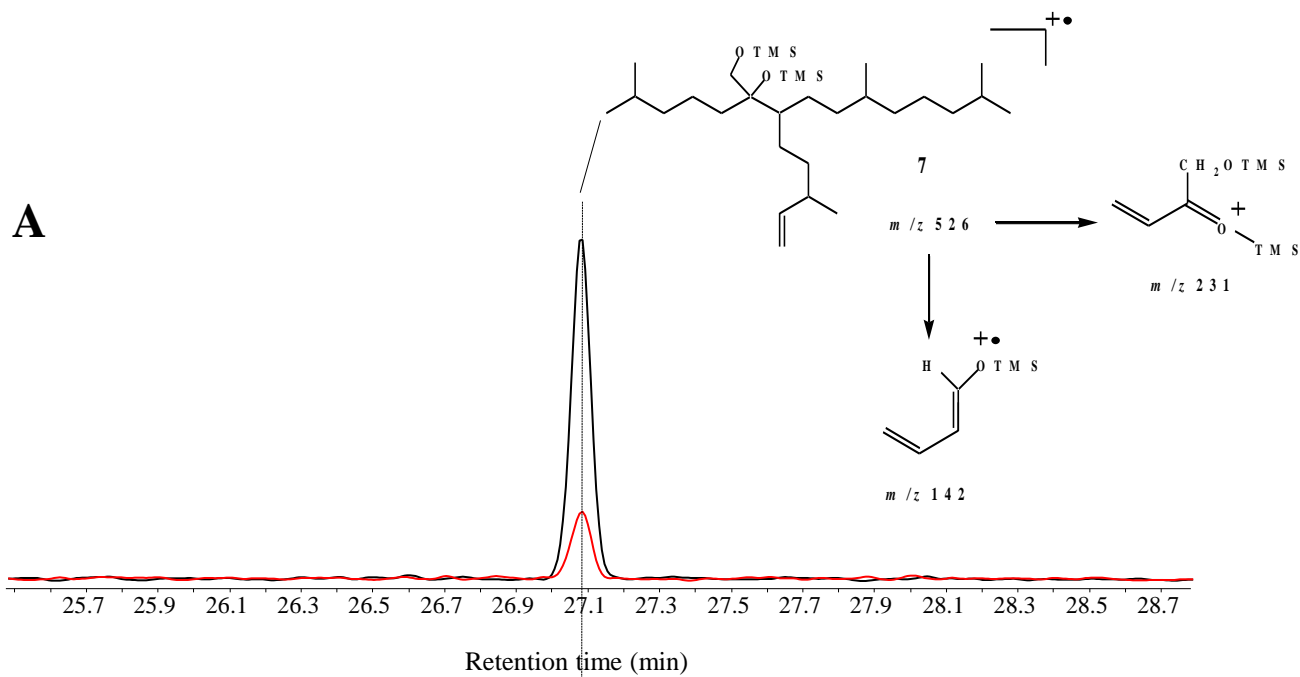




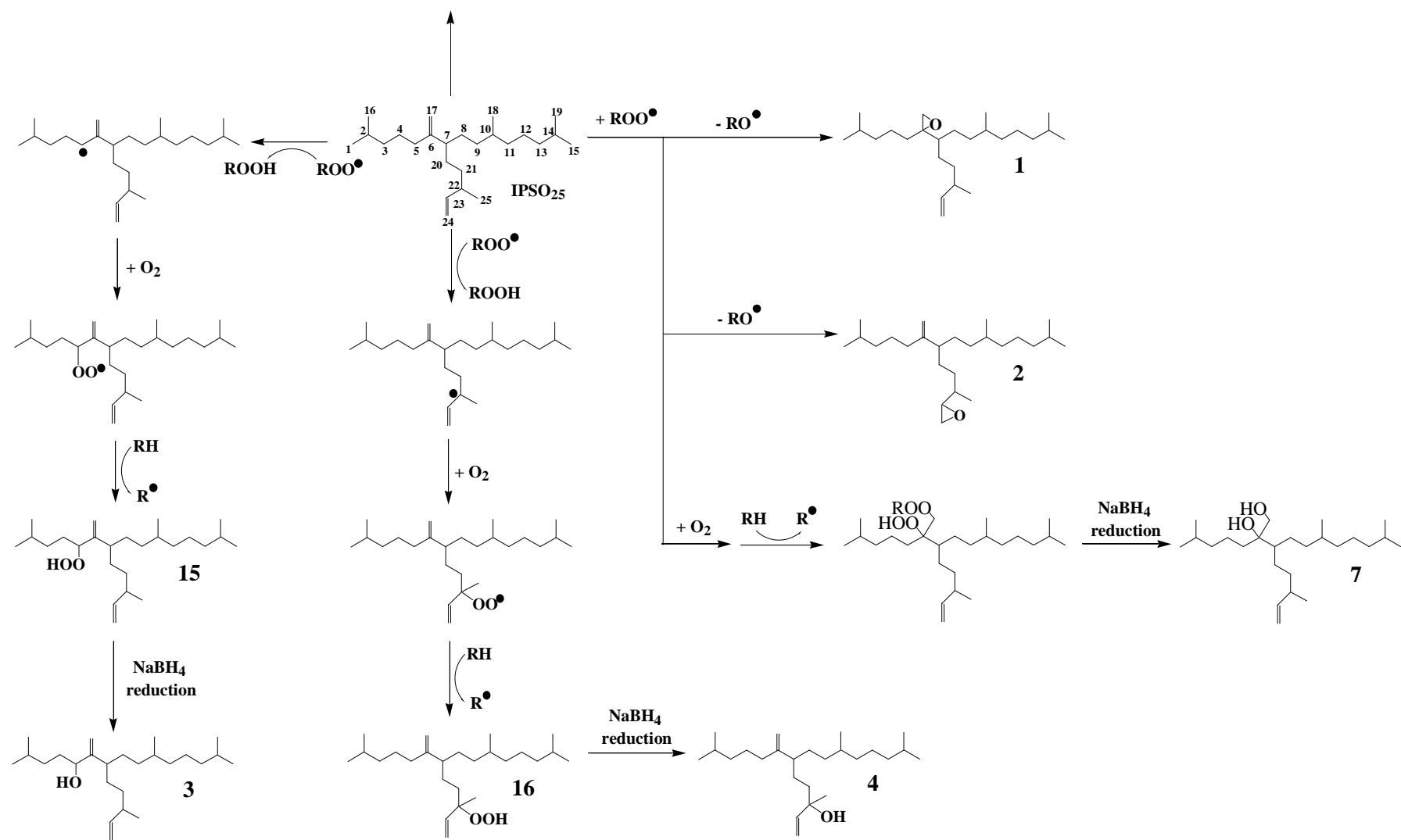


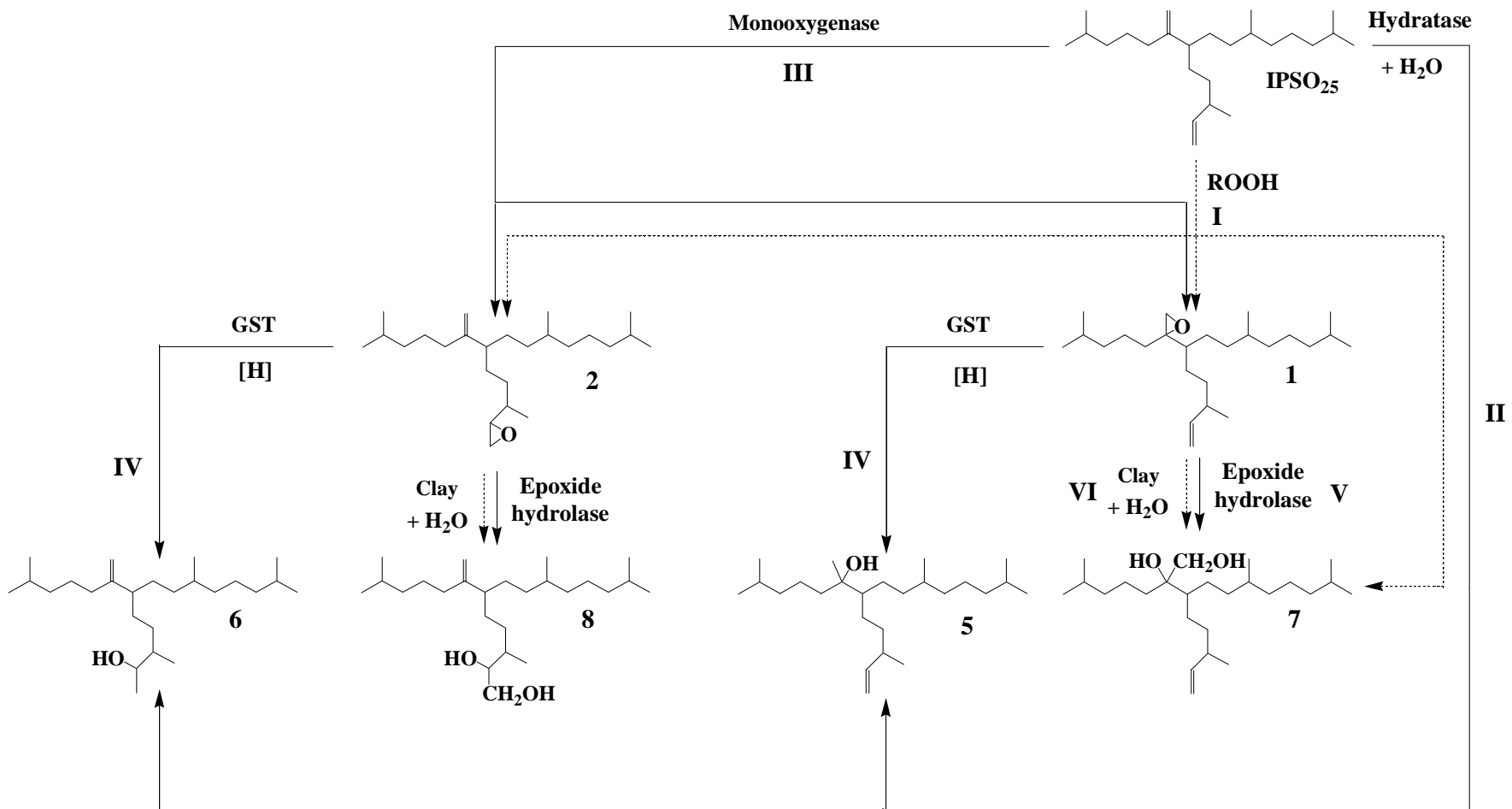


**A****B**



Oxidation of the terminal tertiary carbon atoms





..... Abiotic processes  
 — Biotic processes

Relative percentage of  $\text{IPSO}_{25}$  and its degradation products

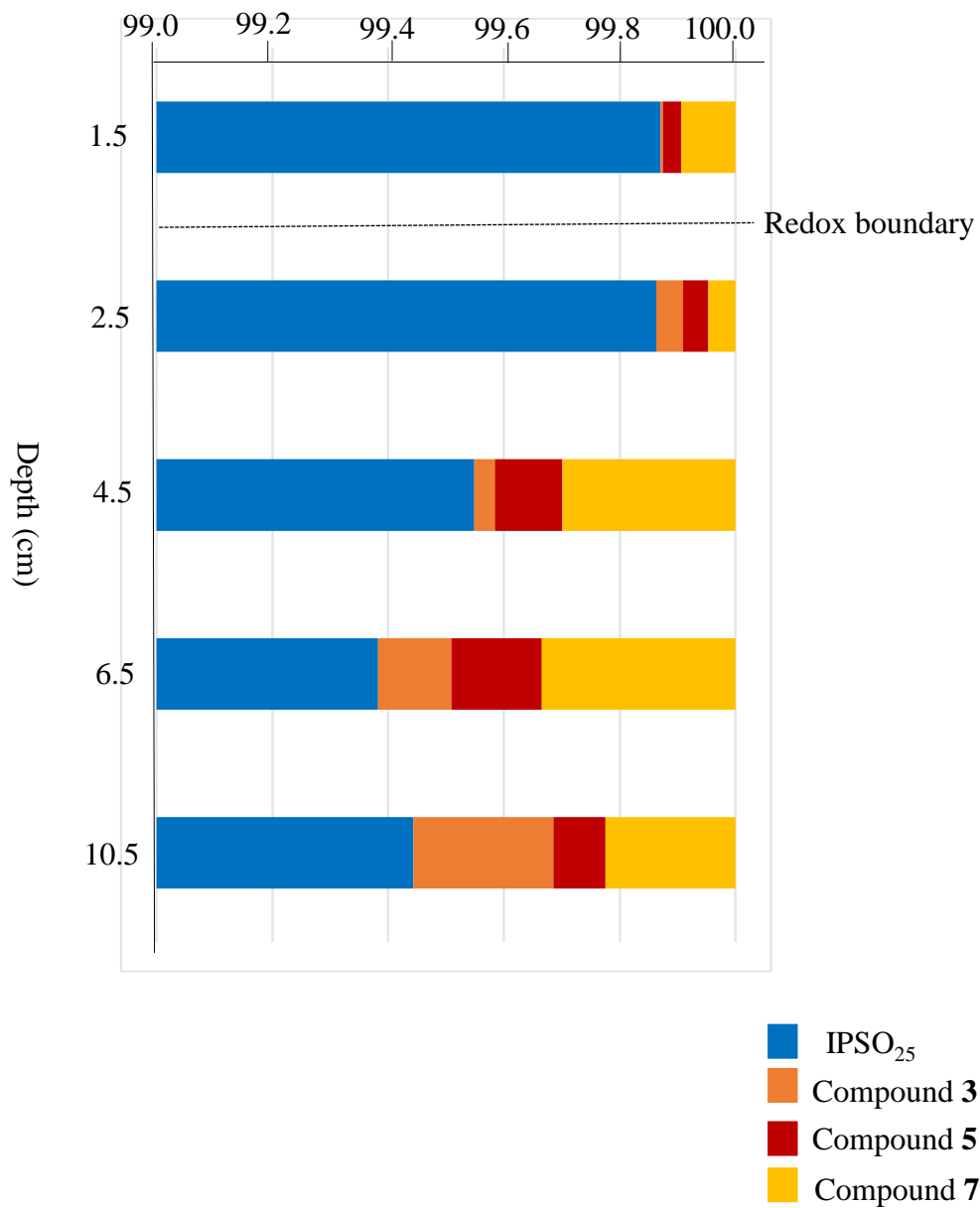




Table 1

Concentrations of IPSO<sub>25</sub> and its degradation products in Antarctic surface sediments (note the difference in units between IPSO<sub>25</sub> and its oxidation products).

Station	IPSO <sub>25</sub> (ng g <sup>-1</sup> )	Compound <b>3</b> (pg g <sup>-1</sup> )	Compound <b>5</b> (pg g <sup>-1</sup> )
BC 313	1201.0	101.3 (0.01) <sup>b</sup>	77.8 (0.01) <sup>b</sup>
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	- <sup>a</sup>	33.4 (0.04)
BC 628	29.0	54.5 (0.19)	25.4 (0.01)

<sup>a</sup> Not detected

<sup>b</sup> Percentage relative to the residual parent compound.

Table 2

Concentrations of IPSO<sub>25</sub> and its degradation products in sediments from the Arctic station 4 (Barrow Strait) (note the difference in units between IPSO<sub>25</sub> and its oxidation products).

Depth (cm)	IPSO <sub>25</sub> (μg g <sup>-1</sup> )	Compound 3 (ng g <sup>-1</sup> )	Compound 5 (ng g <sup>-1</sup> )	Compound 7 (ng g <sup>-1</sup> )
1–2	2.5	0.1	0.8	2.4
2–3	3.2	1.5	1.4	1.5
4–5	2.0	0.7	2.3	5.9
6–7	1.7	2.2	2.7	5.8
8–9	1.6	0.2	0.1	0.6
10–11	1.8	4.3	1.6	4.0