Faculty of Science and Engineering

School of Geography, Earth and Environmental Sciences

2019-03-20

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http://hdl.handle.net/10026.1/13533

10.1016/j.marchem.2019.02.004 Marine Chemistry Elsevier

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1	Abiotic degradation of highly branched isoprenoid alkenes
2	and other lipids in the water column off East Antarctica
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Abstract. In some previous studies, the ratio between a di-unsaturated highly branched 26 27 isoprenoid (HBI) lipid termed IPSO₂₅ and a structurally related tri-unsaturated counterpart (HBI III) (viz. IPSO₂₅/HBI III) has been used as a proxy measure of variable sea ice cover in 28 29 the Antarctic owing to their production by certain sea ice algae and open water diatoms, respectively. To investigate this further, we quantified selected lipids and their photo- and 30 autoxidation products in samples of suspended particulate matter (SPM) collected at different 31 water depths in the polynya region west of the Dalton Iceberg Tongue (East Antarctica). The 32 results obtained confirm the high efficiency of photo- and autoxidation processes in diatoms 33 from the region. The systematic increase of the ratio IPSO₂₅/HBI III with water depth in the 34 35 current samples appeared to be dependent on the sampling site and was due to both (i) a relatively higher contribution of ice algae to the deeper samples resulting from their increased 36 aggregation and therefore higher sinking rate, or (ii) a stronger abiotic degradation of HBI III 37 38 during settling through the water column. Analyses of samples taken from the water-sediment interface and some underlying near-surface sediments revealed a further increase of the ratio 39 IPSO₂₅/HBI III, indicative of further differential oxidation of the more unsaturated HBI. 40 Unfortunately, specific oxidation products of HBI III could not be detected in the strongly 41 oxidized SPM and sediment samples, likely due to their lability towards further oxidation. In 42 43 contrast, oxidation products of HBI III were detected in weakly oxidized samples of phytoplanktonic cells collected from Commonwealth Bay (also East Antarctica), thus 44 providing more direct evidence for the involvement of photo- and/or autoxidation of HBI III 45 in the region. This oxidative alteration of the ratio IPSO25/HBI III between their source and 46 sedimentary environments should be taken into account when using this parameter for palaeo 47 sea ice reconstruction purposes in the Antarctic. 48

49

- 51 Key words: East Antarctica; Suspended particulate matter; Near-surface sediments; Lipids;
- 52 Photo- and autoxidation; Alteration of IPSO₂₅/HBI III ratio; Paleoceanographic implications.

53 **1. Introduction**

54	Sea ice plays a central role in the overall climate structure of the Polar Regions
55	(Thomas, 2017). Amongst its various well known attributes, its high albedo (reflectivity)
56	means that sea ice serves as an efficient regulator of incoming solar radiation to the surface
57	oceans. Further, the physical structure of sea ice provides a physical barrier to the
58	exchange of gas, heat and moisture between the polar oceans and the atmosphere. It is also
59	an important contributor to near-surface stratification, bottom-water formation and
60	ventilation, in particular (e.g. Dickson et al., 2007 and references therein). From a
61	biogeochemical perspective, nutrient release during ice melt in spring, coupled with
62	surface layer stratification and increasing light and temperature, often leads to intense open
63	water phytoplankton production, especially along the retreating ice edge or the so-called
64	marginal ice zone (MIZ) (Smith and Nelson 1986; Smith, 1987; Sakshaug et al., 2009;
65	Perette et al., 2011).

Understanding the well documented abrupt changes in sea ice in the polar regions 66 (Stroeve et al., 2012; Fetterer et al., 2016, Serreze et al., 2016; Walsh et al., 2017) requires 67 more detailed knowledge of how it has changed in the past in response to other climatic 68 drivers. A common approach to achieve this is through the analysis of so-called sea ice 69 proxies present in marine sediment archives. The majority of these proxies possess some 70 kind of biological origin, although there are others (e.g. de Vernal et al., 2013 and 71 references therein). In the Antarctic, the identification of certain ice-associated diatoms in 72 polar marine sediments has a long history of use for palaeo sea ice determinations (Armand 73 et al., 2017). However, the growth habitat of the target species are normally more closely 74 75 associated with the open waters of the MIZ rather than that of sea ice itself (Leventer, 1998; Leventer et al., 2008). On the other hand, those diatoms that bloom within the sea ice 76

host (i.e. the strictly sympagic community), are often under-represented in sedimentary
records (Leventer, 2013).

Over the last decade or so, a number of diatom-derived lipid biomarkers have 79 emerged as useful complementary sea ice proxies to the more traditional 80 micropaleontological-based approaches. Thus a mono-unsaturated highly branched 81 isoprenoid (HBI) termed IP₂₅ (Ice Proxy with 25 carbon atoms; Belt et al., 2007) has 82 emerged as a useful proxy for seasonal Arctic sea ice (for reviews, see Belt and Muller, 83 2013; Belt, 2018), while a di-unsaturated structural homolog of IP₂₅ – sometimes referred 84 to as HBI II (1; see appendix) – appears to be a suitable counterpart for the Antarctic. A 85 86 recent source identification and the near ubiquity of the diene 1 in near-coastal sediments from around the Antarctic continent has led to its recent designation as IPSO₂₅ (Ice Proxy 87 for the Southern Ocean with 25 carbon atoms; Belt et al., 2016) by analogy with IP₂₅. A 88 89 further, tri-unsaturated HBI, often termed HBI III (2), is also showing potentially as a biomarker proxy indicator of the MIZ in both Polar Regions. Thus, enhanced 90 91 concentrations of the triene 2 have been observed in surface sediments from the MIZ of the Barents Sea in the Arctic (Belt et al., 2015) and in surface waters of the MIZ in East 92 Antarctica (Smik et al., 2016) and the Scotia Sea (Schmidt et al., 2018) shortly following 93 94 sea ice melt. As a result, some palaeo sea records based on HBI II (hereafter referred to as IPSO₂₅) (1) and HBI III (2) for the Antarctic have appeared in recent years (Barbara et al., 95 96 2010,2013,2016; Denis et al., 2010; Collins et al., 2013; Etourneau et al., 2013; Campagne et al., 2015,2016). A general interpretation of greater sea ice extent for relatively high 97 IPSO₂₅ (1) compared to HBI III (2), and more open water conditions for increased triene 2 98 concentrations has been applied. In some of these studies, variability in the ratio 1/2 has 99 been used as a qualitative measure of changes to sea ice cover; however, this assumption 100 has, as yet, not been validated through comparison of surface sediment biomarker data 101

102	with known overlying sea ice conditions in the same way as for IP_{25} (and HBI III (2) in
103	some cases) in the Arctic (see Belt, 2018 for a recent review). Nonetheless, such
104	interpretations are consistent with the data reported by Smik et al. (2016) following
105	analysis of IPSO ₂₅ (1) and HBI III (2) in surface waters from regions of variable sea ice
106	cover from East Antarctica, with highest concentrations found in the summer sea ice zone
107	and MIZ, respectively. Similar findings have also been reported for surface water samples
108	from the Scotia Sea (Schmidt et al., 2018). However, the extent to which the surface water
109	distributions of IPSO ₂₅ (1) and HBI III (2) are replicated in the underlying sediments for
110	palaeo sea ice reconstruction purposes was not investigated in the initial study by Smik et
111	al. (2016).
112	To provide further insight to this, here we carried out analysis of further water
113	samples from the polynya region proximal to the Dalton Ice Tongue in East Antarctica
114	with the primary aim of determining any variability of the ratio $1/2$ with water depth, and
115	to reconcile outcomes through the identification of pathway-specific oxidation products of
116	common phytoplankton lipids as indicators of well-known degradation processes (i.e.
117	bacterial degradation, photooxidation and autoxidation). Further evidence for the oxidation
118	of such lipids was obtained through the analysis of near-surface sediment material
119	collected from the main study region and from filtered phytoplankton samples collected
120	from Commonwealth Bay (also East Antarctica).
121	
122	2. Materials and methods
123	

124 *2.1. Sampling*

Water samples were obtained as part of the NBP1402 cruise aboard the RVIB *Nathaniel B Palmer* in February–March 2014 as described previously (Smik et al., 2016;

127	see also NBP1402 Scientific Cruise Report, 2014, Sabrina Coast: Marine record of
128	cryosphere-ocean dynamics (467 pages) for further details)
129	(http://www.marinegeo.org/tools/search/data/field/NBPalmer/NBP1402/docs/NBP1402Cru
130	iseReport_Final.pdf). For the current study, we focused on those locations that had
131	experienced seasonal sea ice cover within the polynya region west of the Dalton Iceberg
132	Tongue (East Antarctica). At each of the 12 sampling sites (Fig. 1), surface (0-10 m), sub-
133	surface (chlorophyll <i>a</i> maximum; ca. 25–60 m) and deep (ca. 500–1100 m) water samples
134	were obtained from CTD rosettes. At the five stations where we carried out lipid
135	degradation studies, the surface CTD samples had already been used for native lipid
136	analyses so we used water obtained from the ship's intake line (ca. <10 m); near-surface
137	and deep water samples were obtained from the CTD rosettes as per the other stations. In
138	each case, 1.5–3.0 l of sampled water was filtered onto 25 mm Whatman GF/F filters (as
139	supplied), wrapped in aluminium foil and stored frozen (-80°C). Sample data are detailed
140	in Supplementary Table 1. Megacoring was conducted using a Bowers and Connelly
141	MegaCorer, with 12 10-cm diameter core tubes, for sampling an undisturbed sediment
142	water interface. Surface water above the core tops and a layer of diatomaceous 'fluff' were
143	pipetted off the top of the core tubes and stored frozen (-80°C). Sediment material from the
144	cores was extruded at 0.5 to 2 cm intervals, depending on the core depth.
145	Three samples of phytoplankton cells (CB, AS607 and AS608) were collected in
146	Commonwealth Bay (East Antarctica, 66°56S; 142°27E) during the IPEV-COCA2012
147	cruise in January 2012. Surface waters were sampled using a 25-µm ring net deployed
148	from the R/V Astrolabe. Concentrated phytoplankton cell suspensions (ranging from 2.6 to
149	1.1 mg d.w. ml ⁻¹) were stored frozen (-20 °C) prior to freeze drying and analysis.
150	

2.2. Sample treatment

152	Lipids from all of the CTD samples, the waters above the sediment cores and the
153	diatomaceous 'fluff' were extracted and analyzed as described previously by Smik et al.
154	(2016). This treatment involved addition of internal standards (9-octyl-8-heptadecene for
155	HBI quantification, 5α -androstan- 3β -ol for Δ^5 -sterol quantification and nonadecanoic acid
156	for fatty acid quantification), saponification (5% KOH (9:1 v/v MeOH/H2O); 70 °C; 60
157	min) and separation of non-saponifiable (hexane 3x2 ml) and saponifiable fractions (+1 ml
158	HCl; hexane (3x2 ml)). For sediments, ca. 1 g of freeze-dried material was extracted by
159	sonication (dichloromethane/methanol; 2:1 v/v, 3x2 ml) to obtain a total organic extract
160	(TOE). Subsequent purification of the unsaponifiable fraction/TOE by open column
161	chromatography (SiO ₂) afforded HBIs (elution with hexane; 5 column volumes) and
162	sterols (elution with hexane-methyl acetate (4:1, v/v; 5 column volumes). In addition,
163	saturated non-polar components of TOEs were removed using silver-ion chromatography
164	(Belt et al., 2015).
165	Treatment of the filtered water samples from the five stations selected for lipid
166	oxidation product analyses and phytoplankton material collected from Commonwealth Bay
167	involved a different treatment. Following addition of MeOH (25 ml) and reduction with
168	excess NaBH4 (70 mg, 30 min) of labile hydroperoxides to alcohols, which are more
169	amenable to analysis using gas chromatography-mass spectrometry (GC-MS), water (25
170	ml) and KOH (2.8 g) were added and the resulting mixture saponified by refluxing (2 h).
171	After cooling, the mixture was acidified (HCl, 2 N) to pH 1 and extracted with
172	dichloromethane (DCM; 3 x 20 ml). The combined DCM extracts were dried over
470	

anhydrous sodium sulfate, filtered and concentrated via rotary evaporation at 40°C to give
total lipid extracts (TLEs).

A different treatment (Rontani et al., 2018) was employed to estimate the relative
proportions of hydroperoxides and their ketonic and alcoholic degradation products in

177	phytoplankton samples from Commonwealth Bay. This involved ultrasonic extraction of
178	lipids with chloroform-MeOH-water (1:2:0.8, $v/v/v$), separation of the supernatant by
179	centrifugation at 3500G, evaporation to dryness, and division of the residue into two equal
180	parts. The first sub-sample was acetylated in acetic anhydride-pyridine (1:2, v/v) overnight,
181	which converted hydroperoxides to the corresponding ketones (Mihara and Tateba, 1986),
182	and then saponified. The second sub-sample was reduced with NaBD4 and saponified.
183	Comparison of the amounts of alcohols present after acetylation and NaBD4 reduction
184	made it possible to estimate the amount of hydroperoxides and alcohols present in the
185	samples, while deuterium labeling (via NaBD4 reduction) allowed us to estimate the
186	proportion of ketones in the samples.
187	
188	2.3. Derivatization
189	For all samples containing hydroxylic components, an aliquot was dissolved in 300
190	µl pyridine/bis(trimethylsilyl)trifluoroacetamide (BSTFA, Supelco; 2:1, v:v) and silylated
191	(1 h) at 50 °C. After evaporation to dryness under a stream of N_2 , the derivatized residue
192	was dissolved in a mixture of ethyl acetate and BSTFA (to avoid desilylation) and
193	analyzed by GC-MS, GC-QTOF or GC-MS/MS.
194	
195	2.4. Assignment and quantification of lipids
196	Native lipids were identified and quantified using GC-MS in total ion current (TIC)
197	or selected ion monitoring (SIM) mode using a Hewlett-Packard 5890 Series II gas
198	chromatograph, fitted with a 30 m fused silica HP _{5ms} column (0.25 mm i.d., 0.25 μ m film)
199	coupled to a 5970 Series Mass Selective Detector (MSD) (Belt et al., 2012). Individual
200	lipids (and their derivatised products) were identified on the basis of their characteristic
201	GC retention indices (e.g. RI _{HP5ms} 2082 and 2044 for IPSO ₂₅ and HBI III, respectively) and

202	mass spectra (Belt, 2018), together with comparison of both parameters with those
203	obtained from purified standards (Smik et al., 2016). Quantification of individual lipids
204	was achieved first by manual integration of GC-MS peak areas, division of these by those
205	of the respective internal standards, and normalization of the resulting ratios using
206	instrumental response factors obtained for each lipid (Belt et al., 2014; Smik et al., 2016).
207	These normalised ratios were then multiplied by the mass of the internal standard and
208	finally converted to their corresponding seawater concentrations using the volume of water
209	filtered or mass of sediment extracted. All analytical data can be found in Supplementary
210	Table 1.
211	
212	2.5. Assignment and quantification of lipid oxidation products
213	Lipid oxidation products were identified by comparison of retention times, accurate
214	masses and mass spectra with those of standards and quantified (calibration with external
215	standards) using gas chromatography-electron ionization quadrupole time of flight mass
216	spectrometry (GC-QTOF). GC-QTOF analyses were carried out with an Agilent
217	7890B/7200A GC-QTOF System (Agilent Technologies, Parc Technopolis - ZA
218	Courtaboeuf, Les Ulis, France). A cross-linked 5% phenyl-methylpolysiloxane (Macherey
219	Nagel; Optima 5-MS Accent) column (30 m \times 0.25 mm, 0.25 μ m film thickness) was
220	employed. Analyses were performed with an injector operating in pulsed splitless mode at
221	280 °C and the oven temperature programmed from 70 °C to 130 °C at 20 °C min ⁻¹ , then to
222	250 °C at 5 °C min ⁻¹ , and then to 300 °C at 3 °C min ⁻¹ . The carrier gas (He) was
223	maintained at 0.69×10^5 Pa until the end of the temperature program. Instrument
224	temperatures were 300 °C for the transfer line and 230 °C for the ion source. Accurate
225	mass spectra were obtained across the range m/z 50-700 at 4 GHz. The QTOF-MS

- instrument provided a typical resolution ranging from 8009 to 12252 from m/z 68.9955 to 501.9706. Perfluorotributylamine (PFTBA) was utilized for daily MS calibration.
- 228

229 2.6. Assignment and quantification of HBI oxidation products

Quantification of HBI oxidation products was carried out using an Agilent 7850-A 230 gas chromatograph connected to an Agilent 7010-OOO mass spectrometer working in 231 multiple reaction monitoring (MRM) mode. The following conditions were employed: 30 232 m x 0.25 mm (i.d.) fused silica column coated with HP-5MS (Agilent; film thickness: 0.25 233 μm); oven programmed from 70 to 130 °C at 20 °C min⁻¹, then to 250 °C at 5 °C min⁻¹ and 234 then to 300 °C at 3 °C min⁻¹; carrier gas (He), 1.0 bar; injector (splitless), 250 °C; electron 235 energy, 70 eV; source temperature, 230 °C; quadrupole temperature, 150 °C; scan range 236 m/z 40-700; collision energy, ranging from 5 to 15 eV; collision flow, 1.5 ml min⁻¹ (N₂); 237 quench flow, 2.25 ml min⁻¹ (He); cycle time, 0.2 s. Oxidation products were assigned by 238 comparison of retention times and mass spectra with those of standards. Due to the 239 240 presence of two highly photo-reactive tri-substituted double bonds (C-7/20 and C-9/10) in HBI III (2), it was not possible to quantify its primary oxidation products directly using 241 standards, since they are not accumulated due to rapid further oxidation (Rontani et al., 242 2014a). We therefore quantified photoproducts of a related HBI triene **3** (possessing only 243 one reactive tri-substituted double bond (C-9/10); see appendix) as an external standard 244 and estimated the quantities of oxidation products from the triene 2 by applying a 245 correction factor (Rontani et al., 2014b). 246

247

248 2.7. Standard compounds

The synthesis of 3-methylidene-7,11,15-trimethylhexadecan-1,2-diol (phytyldiol) (7)
was described previously by Rontani and Aubert (2005). (8-11)-Hydroperoxyhexadec-(8-

251	10)-enoic acids (Z and E) (36-41) and (8-11)-Hydroperoxyoctadec-(8-10)-enoic (Z and E)
252	(30-35) acids were produced by Fe ²⁺ /ascorbate-induced autoxidation (Loidl-Stahlhofen and
253	Spiteller, 1994) of palmitoleic and oleic acids, respectively. Subsequent reduction of these
254	different hydroperoxides in methanol with excess NaBH4 afforded the corresponding
255	hydroxyacids. 3,6-Dihydroxy-cholest-4-ene (18) (employed for sterol photooxidation
256	estimates) was obtained from Maybridge Ltd. Treatment of sitosterol (42) with meta-
257	chloroperoxy-benzoic acid in dry DCM yielded a mixture of 5α , 6α -and 5β , 6β -epoxides.
258	Heating of these epoxides in the presence of water afforded the corresponding 24-
259	ethylcholesta- 3β , 5α , 6β -triol (43) (Holland and Diakow, 1979). IPSO ₂₅ (1) and HBI triene
260	3 were purified from cultures of <i>Haslea ostrearia</i> (Belt et al., 1996; Johns et al., 1999),
261	while HBI triene 2 was obtained from a culture of <i>Pleurosigma intermedium</i> (Belt et al.,
262	2000). Photosensitized oxidation products (hydroperoxides) of these HBI alkenes were
263	produced in pyridine in the presence of haematoporphyrin as photosensitizer and then
264	reduced with NaBH4 to the corresponding alcohols (Rontani et al., 2014a).
265	
266	2.8 Diatom taxonomy
267	Diatom identification and enumeration were carried out for selected water and
268	sediment samples. Specifically, three water samples of 200 ml each were collected at

269 CTD015 (5, 40, 563 m). Overlying bottom water (100 μ l), diatomaceous fluff (50 μ l) and

sediment samples were collected from MC061. Sediment was also collected from MC045.

271 The water samples were immediately fixed with Lugol's solution (~0.5 ml). Back at the

laboratory, the preserved water samples were concentrated (CTD015) or diluted (MC061)

into Utermöhl chambers to a final volume of 3 ml. After sedimentation of 48 hrs, a

274 minimum total of 400 cells (including microphyto- and microzooplankton live at the time

of preservation), were identified and counted following the Utermöhl method (Utermöhl,

276	1958) at a magnification of 400x under an inverted microscope (Olympus IMT-2, Japan).
277	Microplankton were identified to species level where possible using appropriate taxonomic
278	literature (Hasle, 1965; Tomas, 1997; Scott and Marchant, 2005, Kim et al. 2013). Final
279	counts were converted to cells 1 ⁻¹ . Sediment samples were dried at 50 °C. Quantitative
280	slides were made using a settling method (Scherer, 1994). Approximately 5 ml of water
281	and hydrogen peroxide was added to several mg of each sample, and the samples were
282	placed on a warming tray at 50 °C for 2–3 days. After complete reaction and removal of
283	organic material, the samples were poured into water-filled 1 l beakers and allowed to
284	settle onto coverslips. The coverslips were mounted on glass slides using Norland Optical
285	Adhesive #61 cured under UV light. These quantitative slides were used for assessment of
286	the diatom assemblage, by identification and counting of a minimum of 400 diatom valves
287	along cross-slide transects, at a magnification of 1000x. Counting followed the method
288	described by Schrader and Gersonde (1978) and Crosta and Koc (2007). Diatom
289	concentration (diatom valves per gram) and relative abundance (percentage) of diatom
290	species were calculated.
291	For the purposes of the current investigation, we determined the distribution of three
292	common Fragilariopsis spp. to provide a semi-quantitative assessment of the relative
293	contribution from sea ice-associated (F. curta and F. cylindrus) and open water (F.
294	kerguelensis) diatoms. (Armand et al., 2005; Crosta et al., 2005; Crosta et al., 2008). Thus,

- 295
- 296
- 297 **3. Results and discussion**

The identification and quantification of the various lipids and their degradation
products are described here according to the individual lipid classes at each sampling
location. The sequence of presentation is arranged so as to first provide sufficient evidence

the ratio (F. curta + F. cylindrus)/F. kerguelensis was determined (Table 2).

301	for the oxidation state of the lipids, in order that the variability in the ratio of IPSO ₂₅
302	(1)/HBI III (2) can then be put into context.

303

304 3.1. Lipids and their degradation products in water samples from west of the Dalton
305 Iceberg Tongue

306

307 3.1.1. Chlorophyll phytyl side-chain

308 In addition to phytol (4), which mainly arises from the hydrolysis of the chlorophyll phytyl side-chain during alkaline hydrolysis, significant amounts of 3,7,11,15-309 tetramethylhexadecanoic acid (phytanic acid) (5), 3,7,11,15-tetramethylhexadec-1-en-ol-3 310 311 (isophytol) (6) and 3-methylidene-7,11,15-trimethylhexadecan-1,2-diol (phytyldiol) (7) could also be detected in the different samples. However, phytanic acid (5) was not 312 quantified in the present work due to its lack of specificity. Indeed, this isoprenoid acid is 313 also formed during the aerobic and anaerobic bacterial degradation of phytol (Rontani and 314 Volkman, 2003) and the grazing of phytoplankton (Prahl et al., 1984). 315 In contrast, there have been very few reports of the presence of isophytol (6) in the 316 marine environment (Fang et al., 2006), so its relatively high proportion compared to 317

phytol (1) in some samples (Table 1) is potentially surprising. Isophytol (6) may be formed in sediments either by enzyme-catalyzed allylic rearrangement during bacterial degradation of phytol under denitrifying conditions (Rontani et al., 1999), or by clay-catalyzed dehydration of phytol (de Leeuw et al., 1974). It is interesting to note that relatively high proportions of isophytol were also recently observed after NaBH₄-reduction and alkaline hydrolysis of phytoplanktonic cells collected from Commonwealth Bay, Antarctica (Rontani and Galeron, 2016). In order to explain this observation, it was proposed that

325	allylation (Berkessel, 2009) of the chlorophyll phytyl side-chain by peroxyl radicals could
326	result in the formation of the precursor 3-peroxy-3,7,11,15-tetramethylhexadec-1-ene (8),
327	with subsequent reduction to isophytol (6) (Fig. 2) (Rontani and Galeron, 2016). The
328	absence of the initial reduction step employed here (i.e. using NaBH4) during conventional
329	treatment of environmental samples is likely at the origin of the very few reports of
330	isophytol (6) in previous studies. In any case, the high values of the ratio isophytol/phytol
331	observed at station 25, and to a lesser extent at station 28B (Table 1), attest to the presence
332	of high concentrations of peroxides, and thus of a strong photo- or autoxidation state of
333	POM.
334	The formation of phytyldiol (7) results from initial Type II photosensitized oxidation
335	(i.e. involving singlet oxygen $({}^{1}O_{2})$) of the chlorophyll phytyl side-chain and subsequent
336	hydrolysis of the photoproducts thus formed (Rontani et al., 1994). On the basis of its high
337	specificity and widespread occurrence in the environment (Cuny and Rontani, 1999), this
338	diol can be used as a specific tracer of chlorophyll photodegradation. Further, Cuny et al.
339	(2002) proposed that the amount of chlorophyll photodegradation in the marine
340	environment could be estimated from the so-called Chlorophyll Phytyl side-chain
341	Photodegradation Index (CPPI) derived from the molar ratio phytyldiol/phytol. Using this
342	approach, the highest photooxidation state of POM was confirmed as being at station 25
343	and the lowest at station 32 (<1%, not included in the figure) (Fig. 3).
344	
345	3.1.2. Sterols
346	The major sterols in the filtered water sample were 24-norcholest-5,22 <i>E</i> -dien-3 β -ol
347	(22-dehydrocholesterol) (10), cholest-5-en-3 β -ol (cholesterol) (11), 24-methylcholesta-

348 5,22*E*-dien-3β-ol (*epi*-brassicasterol) (**12**), 24-methylcholesta-5,24(28)-dien-3β-ol (24-

methylenecholesterol) (13) and 24-ethylcholest-7-en- 3β -ol (22-dihydrocondrillasterol) (14)

350	(Supplementary Table 1). 22-Dehydrocholesterol (10) has been found in diatoms and
351	notably in <i>Thalassiosira aff. antarctica</i> (Rampen et al., 2007). Although cholesterol (11)
352	may be derived from diatoms or Prymnesiophycean algae (Volkman, 1986), its dominance
353	generally suggests an important contribution of zooplanktonic faecal material to the
354	samples. Indeed, it is well known that zooplankton convert much of the sterols produced
355	by algae into cholesterol (11) (Volkman et al., 1980; Prahl et al., 1984). Epi-brassicasterol
356	(12) and 24-methylenecholesterol (13) are major constituents of several diatom species
357	(Lee et al., 1980) including sea ice diatoms (Belt et al., 2018). However, it may be noted
358	that <i>epi</i> -brassicasterol (12) is also present in some dinoflagellates and in many haptophytes
359	(Volkman, 1986, 2003). The unusual sterol 22-dihydrochondrillasterol (14) was detected
360	previously in some Chlorophyceae (Martin-Creuzburg et al., 2011; Martin-Creuzburg and
361	Merkel, 2016). The sterol profiles observed in these samples (Supplementary Table 1) are
362	thus typical of mixed assemblages of diatoms, Prymnesiophytes and Chlorophytes.
363	Type II photosensitized oxidation of Δ^5 -sterols produces mainly unstable Δ^6 -5 α -
364	hydroperoxides with low amounts of Δ^4 -6 α/β -hydroperoxides (Smith, 1981). Here, we
365	selected Δ^4 -6 α/β -hydroperoxides as tracers of photooxidation of Δ^5 -sterols due to their
366	high specificity and relative stability (Rontani et al., 2009; Christodoulou et al., 2009).
367	These compounds were quantified after NaBH4 reduction to the corresponding diols and
368	photooxidation percentage was obtained from the equation: photooxidation $\% = (\Delta^4$ -stera-
369	$6\alpha/\beta$ -diols % × (1+0.3)/0.3) (Christodoulou et al., 2009). The values obtained for <i>epi</i> -
370	brassicasterol (12) and 24-methylenecholesterol (13) (the two main algal sterols present in
371	the samples analyzed) are shown in Fig. 3. Photooxidation of these two sterols exhibits the
372	same general trend as that seen for chlorophyll, with the highest photooxidation state
373	observed at station 25 (Fig. 3). Interestingly, as observed previously in the Arctic (Rontani
374	et al., 2012; 2014a), photodegradation processes appeared to have acted more intensively

375	on 24-methylenecholesterol (13) (mainly arising from diatoms) than on epi-brassicasterol
376	(12) (arising from diatoms and/or Prymnesiophytes). These differences confirm the higher
377	efficiency of Type II photosensitized oxidation processes in diatoms compared to
378	Prymnesiophytes.
379	Stanols constitute useful indicators of bacterial degradation of Δ^5 -sterols (Gagosian
380	et al., 1982; de Leeuw and Baas, 1986; Wakeham, 1989). We thus quantified the ratio 24-
381	methyl-5 α -cholest-22 <i>E</i> -en-3 β -ol (<i>epi</i> -brassicastanol) (15)/ <i>epi</i> -brassicasterol (12) to
382	indicate the extent of bacterial degradation of algal material. (Note: the ratio 24-methyl-
383	5α -cholest-24(28)-en-3 β -ol (16)/24-methylenecholesterol (13) could not be quantified due
384	to co-elution of the stanol 16 with the isobaric campesterol (17)). The values of the ratio
385	epi-brassicastanol (15)/epi-brassicasterol (12) (Table 1) show only a weak increase with
386	depth suggesting that bacterial degradation processes acted only weakly on algal material.
387	
388	3.1.3. Fatty acids
389	The fatty acid content of the SPM samples is characterized by a very low content of
390	polyunsaturated fatty acids (PUFAs) and notably of $C_{18:4}$ (19), $C_{20:5}$ (20) and $C_{22:6}$ (21)
391	acids, which are typical for marine plankton (Kattner et al., 1983). Instead, the dominant
392	fatty acids are the saturated and monounsaturated fatty acids (MUFAs) (i.e. C14:0 (22),
393	C16:1 ₀₇ (palmitoleic acid) (23), C16:0 (palmitic acid) (24), C18:1 ₀₉ (oleic acid) (25), C18:1 ₀₇
394	(vaccenic acid) (26) and C _{18:0} (27)) (Supplementary Table 1). The reactivity of unsaturated
395	fatty acids with respect to auto- and photooxidative processes increases, logically, with the
396	number of double bonds (Frankel, 1998; Rontani et al., 1998). The very low amounts of
397	PUFAs is therefore suggestive of intense photo- or autoxidation of the samples. In order to
208	
330	confirm this, the oxidation products of MUFAs (oleic and palmitoleic acids) (25 and 23)

markers of these abiotic degradative processes (Marchand and Rontani, 2001, 2003). 400 401 Photo- and autoxidation of monounsaturated fatty acids affords mixtures of isomeric allylic hydroperoxyacids (Frankel, 1998). Based on the specific formation of cis isomers by 402 403 autoxidation (Porter et al., 1995), the relative importance of photooxidation and autoxidation can easily be distinguished by quantifying the respective hydroxyacids that 404 result from NaBH₄-reduction of these compounds (Marchand and Rontani, 2001). The 405 406 results obtained (Fig. 4) show a clear difference in reactivity between palmitoleic (23) and oleic (25) acids. Indeed, photo- and autoxidation states appeared to be considerably higher 407 in the case of palmitoleic acid (23) (the main MUFA of diatoms, Fahl and Kattner, 1993; 408 409 Leu et al., 2010) compared to oleic acid (25) (dominant in Prymnesiophytes, Rossi et al., 2006). These outcomes are consistent with previous observations of more efficient photo-410 and autoxidation processes in diatoms than in Prymnesiophytes (Rontani et al., 2012; 411 412 2014b). Such differences in reactivity were attributed previously to the involvement of intra-cellular compartmentalization effects, which may significantly modify the reactivity 413 414 of lipids towards autoxidative and photooxidative processes according to their location in phytoplanktonic cells (Rontani, 2012). 415 The palmitoleic (23)/palmitic acid (24) ratio is often employed to follow diatom 416 blooms (Pedersen et al., 1999; Reuss and Poulsen, 2002). Due to the strong oxidation of 417

418 palmitoleic acid (23) observed in some of our samples (Fig. 4), we employed the ratio (Σ

419 palmitoleic acid (23) and its oxidation products)/palmitic acid (24) to estimate the relative

proportion of diatom in the mixed phytoplankton assemblages. Using this approach, we

421 observed a relatively high proportion of (strongly oxidized) diatoms in the surface water

sample of station 25 and an increase in their proportion with water depth at station 28B

423 (Table 1).

424

420

425 3.1.4. Cutin components

426	Relatively high amounts of 9,16-dihydroxyhexadecanoic (29) and 10,16-
427	dihydroxyhexadecanoic (28) acids were observed in some samples (Table 1). These
428	compounds are well-known depolymerisation products of cutins (insoluble polyester
429	polymers) present in the outer layer of the epidermal cells of primary plant tissues, such as
430	leaves) (Deas and Holloway, 1977; Kolattukudy, 1977, 1980). The presence of such
431	compounds is very surprising since the Antarctic biome is an unfavorable environment for
432	higher plant growth. Only two native phanerogams, Deschampsia antarctica Desv. and
433	Colobanthus quitensis (Kunth) Bartl., occur in Antarctica to almost 69°S (Smith 1994).
434	The high concentrations of dihydroxyacids 28 and 29 detected in some sub-surface water
435	samples (Table 1) is therefore attributed to the accumulation of low density debris of such
436	plants.

437

438 3.1.5. HBI alkenes

The two HBI lipids, IPSO₂₅ (1) and HBI III (2), reported previously by Smik et al. 439 (2016) in the surface water samples described here, were also present in each of the sub-440 surface and deep water samples investigated for the first time within the current study. 441 Although there was some variability in the absolute and relative concentrations of these 442 HBIs between the surface and sub-surface samples, The IPSO₂₅(1)/HBI III (2) ratio was 443 444 mainly slightly higher in the majority of the sub-surface samples compared to the surface water counterparts, with CTD-004 and -014 the only exceptions. More striking changes to 445 this ratio were observed with the corresponding deep water samples, however, with mean 446 (i.e. across all samples) relative enhancements in IPSO₂₅(1)/HBI III (2) of ca. 8 and 6 447 when compared with the surface and sub-surface samples, respectively (Table 1). 448

449	The systematic increase of the ratio $1/2$ with depth (Table 1) may potentially be
450	attributed to: (i) a relatively higher contribution of ice algae (and thus $IPSO_{25}(1)$) to the
451	deeper samples resulting from their stronger aggregation and therefore higher sinking rate,
452	or (ii) a stronger abiotic degradation of HBI III (2) during settling through the water
453	column. One characteristic of sea ice algae is their ability to produce high amounts of
454	extracellular polymeric substances (EPS); the production of which facilitates the
455	attachment of algae to their substrate (sea ice) but also allows the formation of aggregates
456	of algal cells (Riebesell, 1991; Alldredge et al., 1993; Passow, 2002), thus shortening their
457	residence time within the euphotic zone. In the case of station 28B, the simultaneous
458	increase of the ratios $1/2$ and (Σ palmitoleic acid (23) and its oxidation products)/palmitic
459	acid (24) with depth (Table 2) suggests a dominance of aggregated ice diatom material in
460	the deepest SPM sample.
461	Photo- and autoxidation of IPSO ₂₅ (1) were previously studied in vitro (Rontani et
462	al., 2011; 2014a). Based on its very low degradation rates (resulting from the poor
463	reactivity of its two terminal double bonds (i.e. at C6-17 and C23-24) towards ${}^{1}O_{2}$ and free
464	radicals), it is feasible that this diene (1) could be largely unaffected by abiotic oxidation
465	within the water column of the oceans, at least in comparison with some more unsaturated
466	lipids, or those containing more reactive double bonds. Indeed, HBI triene 2 possesses two
467	tri-substituted double bonds (i.e. at C7–20 and C9–10), both of which are more reactive
468	towards ${}^{1}O_{2}$ (Frimer, 1983) than the two double bonds in IPSO ₂₅ . In addition, the relative
469	positions of these two double bonds in HBI III (2) creates a bis-allylic methylene group (at
470	C-8) that can lose a hydrogen atom even more readily (Yin et al., 2011). HBI triene 2 is
471	thus very sensitive towards photo- and autoxidation processes and exhibits degradation
472	rates close to those of PUFAs (Rontani et al., 2014a). On the basis of the very intense
473	abiotic alteration of these fatty acids in the samples investigated here (see section 3.1.3), a

474	similar oxidation of HBI triene (2) was thus expected. However, we were not able to detect
475	the previously identified primary oxidation products of 2 (Rontani et al., 2014a), probably
476	due to their further oxidation to polar and oligomeric compounds, which are not generally
477	detectable using the GC-MS methods employed here. This conclusion is consistent with
478	the strong photo- and autoxidation states of palmitoleic acid (23) observed in these samples
479	(Fig. 4) and the differences of reactivity observed previously between HBI III (2) and this
480	acid in diatom cells (kphoto HBI III /kphoto palmitoleic acid ≈ 4 and kauto HBI III/kauto palmitoleic acid > 10)
481	(Rontani et al., 2011; 2014a).
482	In order to provide further evidence for the influence of autoxidative processes upon
483	the ratio $1/2$, we measured it, together with the autoxidation state of sitosterol (42)
484	(estimated on the basis of 3β , 5α , 6β -trihydroxysitosterol (43) as previously proposed by
485	Christodoulou et al. (2009)) and palmitoleic acid (23) in the water column samples from
486	station 32 (T32/CTD015) and in two near-surface sediment samples from nearby locations
487	(MC45 and MC61; Fig. 1), with one of these (MC61) located directly at the station where
488	the CTD015 samples were taken. The ratio $1/2$ was also measured in the surface waters
489	recovered from the top of the MC61 sediment core and in the suspension of diatomaceous
490	'fluff' taken at the water-sediment interface, thereby providing a near-continuous depth
491	sequence from surface waters to underlying sediments. Although sitosterol (42) is
492	commonly associated with higher plants ((Lütjohann, 2004), it is also present in
493	phytoplankton, and notably in diatoms (Volkman, 1986; 2003). Due to the absence of lipid
494	signatures of terrestrial material in the water samples collected at station 32 and in the
495	sediments from nearby locations, the presence of sitosterol (42) in these samples was thus
496	attributed to an algal origin. The results obtained (Table 2) show a clear increase in both
497	the ratio $1/2$ and the autoxidation state of algal material with water depth and then into the
498	surface sediments (Table 2). The failure to detect oxidation products of sitosterol in the

water column samples is attributed to the relatively poor chromatographic properties of the
only partially silylated (at positions 3 and 6) triol 43, which hinders its detection at low
concentrations.

502 Although we do not currently have detailed taxonomic data from all sampling stations/types, we do have data from the station for which we have lipid profiles from both 503 the water column and underlying Megacore (viz. CTD015 & MC61). The most striking 504 feature is the consistent decrease in the ratio (F. curta + F. cylindrus)/F. kerguelensis505 through the water column, the water-sediment interface and then into the sub-surface 506 sediment (Table 2), suggesting a progressive decrease in the relative contribution of sea 507 508 ice-associated and open-water diatoms. However, this conclusion is contrary to what might be inferred from the (increasing) IPSO₂₅ (1) /HBI III (2) ratio, suggesting that changes in 509 the latter, at some locations, are determined more by the enhanced degradation of HBI III 510 (relative to IPSO₂₅) as shown from the lipid data described above; the caveat being that the 511 aforementioned *Fragilariopsis* spp. are not known HBI-producers. We also assume that the 512 513 water column data derived from samples taken in a single sampling season are also representative of multi-annual accumulation that the sediment samples likely reflect. 514 Unfortunately, the known sources of IPSO₂₅ and HBI III were of too low abundance for 515 516 more direct comparisons between lipid and taxonomic distributions to be made for these samples. Interestingly, a positive relationship between IPSO₂₅ (1)/HBI triene (2) and the 517 ratio F. curta/F. kerguelensis (i.e., a slight modification to our diatom ratio) was reported 518 in a previous downcore sediment study from the region (Massé et al., 2011), suggesting 519 that the modifications to the former described herein for the water column and water-520 521 sediment interface may not necessarily have an adverse impact on its use as a proxy measure of sea ice change in palaeo records, especially for qualitative purposes. Further 522 studies comparing these two approaches will, however, be required, before the generality 523

- of this observation can be confirmed, and the most reliable use of IPSO₂₅/HBI III as a
 proxy measure of sea ice change can be deciphered.
- 526

527 *3.2. Phytoplanktonic material from Commonwealth Bay (East Antarctica)*

To demonstrate the efficiency of photo- and autoxidation processes on HBI III (2) in 528 529 this region, more generally, we also analysed phytoplanktonic cells collected from surface 530 waters of Commonwealth Bay (also East Antarctica; see Fig. 1). In this weakly oxidized material (oxidation percentage of palmitoleic acid (23) < 5%), MRM analyses allowed us 531 532 to detect the HBI alcohols 44–48 (Figs. 5B and 6B, Table 3). The assignment of these compounds was confirmed by comparison with the MRM chromatograms of standards 533 obtained by photo- and autoxidation of HBI III (2) (Figs. 5A and 6A) (Rontani et al., 534 2014b). Alcohol 48 is produced specifically by photooxidation of HBI III (2), while 535 alcohols 44–47 result from both its photo- and autoxidation (Rontani et al., 2014a). On the 536 basis of the detection of these oxidation products in a weakly oxidized phytoplanktonic 537 sample from Commonwealth Bay, the strong increase of the ratio IPSO₂₅ (1)/HBI III (2) 538 observed in the deeper SPM samples from stations 25, 27, 32 and 34 and in near-surface 539 sediments from the polynya region west of the Dalton Iceberg Tongue (Tables 1 and 2) 540 may be thus attributed to an intense photo- and/or autoxidation of HBI III (2) within the 541 water column, with further autoxidation of (2), relative to (1), at the water-sediment 542 interface and in the oxic layer of the underlying sediment. 543 During the NaBH₄-reduction step employed to avoid thermal degradation of 544 hydroperoxides during the subsequent saponification reaction, the sum of hydroperoxides 545

and their degradation products (alcohols and ketones) was obtained via quantification of

- 547 their respective alcohols. Two different treatments were employed (acetylation and
- 548 saponification vs NaBD4-reduction and saponification) (see Section 2.2) in order to

549	specifically quantify hydroperoxides and their main degradation products (i.e. alcohols and
550	ketones). The results obtained (summarized in Table 4) show that a substantial proportion
551	(ca. 55–81%) of HBI III (2) oxidation products were still present as hydroperoxides.
552	Interestingly, the decrease in unlabeled phytol (4) concentration (5–20%) observed
553	when the treatment of phytoplanktonic cells involved acetylation and saponification
554	instead of NaBD4-reduction and saponification, provides further evidence for the formation
555	pathway of isophytol (6) proposed previously (Rontani and Galeron, 2016) (Fig. 2).
556	Indeed, this decrease likely results from the presence of 1-peroxy-3,7,11,15-
557	tetramethylhexadec-3-ene (9) , which is formed by allylic rearrangement of its isomer 8
558	(Fig. 2).
559	
560	4. Conclusions
561	Selected lipids and their oxidation products were quantified in SPM samples
562	collected at different water depths in the polynya region west of the Dalton Iceberg Tongue
563	(East Antarctica). The sterol profiles were typical of mixed assemblages of diatoms,
564	prymnesiophytes and chlorophytes. Surprisingly, some samples contained
565	depolymerisation products of cutins, the presence of which was attributed to the
566	accumulation of low-density debris of the two phanerogams present in Antarctica.
567	We identified an intense photo- and autoxidation of unsaturated diatom components
568	(e.g. palmitoleic acid (23), 24-methylenecholesterol (13), chlorophyll phytyl side-chain
569	(4)), but not of the HBI triene 2, despite its known reactivity towards such processes, likely
570	due to its susceptibility towards further oxidation. However, oxidation products of HBI
571	triene (2) could be detected in weakly oxidized SPM samples collected from
572	Commonwealth Bay (East Antarctica), clearly demonstrating the oxidation of this lipid in
573	this region.

574	The systematic increase of the ratio $IPSO_{25}$ (1)/HBI triene (2) observed with depth in
575	the water column and in some underlying sediments thus appears to result, in part, from an
576	intense and preferential abiotic degradation of the HBI triene (2) due to a combination of
577	photo- and autoxidation processes. At one sampling site, the increase in the IPSO ₂₅
578	(1)/HBI triene (2) ratio with depth was opposite to that of the ratio of selected sea ice-
579	associated versus open-water diatoms, suggesting that the differential biomarker
580	degradation was a dominant factor. However, for another sampling site, the increase in the
581	IPSO ₂₅ (1)/HBI triene (2) ratio appeared to be more influenced by the accumulation of ice
582	algal material, although we do not yet have the complementary taxonomic data to confirm
583	this.
584	Distinguishing between these two factors will require more detailed and combined
585	lipid and taxonomic analysis in the future. In the meantime, it is evident from the results
586	presented here, that the differential degradation of IPSO ₂₅ (2) and HBI triene (3) in the
587	water column and in near-surface sediments (at least) can impact on the ratio between
588	these two HBIs between their source and sedimentary environments. The latter should be
589	taken into account when using this parameter for palaeo sea ice reconstruction purposes in
590	the Antarctic. The extent to which the IPSO ₂₅ (1) /HBI triene (2) ratio reflects established
591	proxy measures of past sea ice change (e.g., the ratio of certain Fragilariopsis spp. as
592	described herein) will require more studies of both parameters in further downcore records
593	from the Antarctic.
594	
595	Acknowledgements
596	
597	The FEDER OCEANOMED (N° 1166-39417) is acknowledged for the funding of the

apparatus employed. Thanks are due to the scientific party and crew of cruise NBP1402;

599	the project (P.I. A. Leventer) was funded by NSF ANT-1143836. We also thank G. Massé
600	for the donation of the phytoplankton samples collected in the Commonwealth Bay during
601	the IPEV-COCA2012 cruise funded by IPEV (1010-ICELIPIDS program) and ANR
602	(CLIMICE program).
603	
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APPENDIX







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895 FIGURE CAPTIONS

896	
897	Figure 1. Summary map showing sampling locations (CB = Commonwealth Bay).
898	
899	Figure 2. Proposed pathways for autoxidation of chlorophyll phytyl side chain.
900	
901	Figure 3. Photooxidation percentages of <i>epi</i> -brassicasterol (12), 24-methylenecholesterol
902	(13) and chlorophyll in the CTD samples collected at the stations selected for lipid
903	oxidation product analyses. The very low photooxidation percentages of sterols in the
904	samples collected at the station 32 were not included in this figure.
905	
906	Figure 4. Photo- and autoxidation percentages of palmitoleic (23) and oleic (25) acids in
907	the CTD samples collected at the stations selected for lipid oxidation product analyses. The
908	weak oxidation percentages of palmitoleic acid in the samples collected at the station 32
909	are given in Table 3.
910	
911	Figure 5. MRM chromatograms (m/z 213 \rightarrow 117, m/z 213 \rightarrow 123 and m/z 213 \rightarrow 157) for
912	standard oxidation products of the HBI triene 2 (A) and CB phytoplanktonic sample
913	collected in Commonwealth Bay (B).
914	

915	Figure 6. MRM chromatograms (m/z 295 \rightarrow 93, m/z 295 \rightarrow 107 and m/z 295 \rightarrow 183) for
916	standard oxidation products of the HBI triene 2 (A) and CB phytoplanktonic sample
917	collected from Commonwealth Bay (B).

- Figure 7. Conceptual scheme summarizing sedimentation and degradation of ice algae and
- 920 open water phytoplankton in east Antarctica. Note that in some cases the increase of the
- ratio IPSO₂₅(1)/HBI III (2) with depth may be due to the faster sedimentation rate of
- aggregated sympagic algae relative to open water phytoplankton and in other cases to an
- 923 intense photooxidation (in the euphotic layer) or autoxidation (in the entire water column
- and in the oxic layer of sediments) of the HBI triene **2**.



- Detailed lipid analysis (oxidation products)
- Other CTD stations (native lipids only)
- Sediments (Megacores)



 $\mathbf{R}_2 = \begin{cases} ---(\mathbf{CH}_2)_2 - \mathbf{Pyr} \end{cases}$

Pyr = More or less oxidized tetrapyrrolic structure











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Retention time (min)



Retention time (min)



Table 1

Different indicators measured at the five stations selected for lipid degradation analyses.

Station	Depth (m)	IPSO ₂₅ (1)/ HBI triene (2)	Cuticular waxes ^a / palmitic acid (24)	<i>Epi</i> -brassicastanol (12)/ <i>epi</i> -brassicasterol (16)	(Palmitoleic acid (23)+ ox ^b)/ palmitic acid (24)	Isophytol (6)/ phytol (4)
25	10<	0 21	0	0.24	30.91	0.45
25	49	0.26	ů 0	0.20	3 42	1 64
25	1083	2.57	0	0.32	1.65	0.60
27	10<	0.26	0.07	0.17	1.82	0
27	50	0.14	2.15	0.21	0.42	0.01
27	654	1.74	0	0.29	0.25	0.08
28B	10<	0.51	0.02	0.14	1.01	0.30
28B	50	0.44	0.03	0.24	3.11	0.06
28B	596	1.61	0	0.16	4.02	0.20
32	10<	0.21	0	0.10	0.05	0.13
32	40	0.37	0	0.09	0.08	0.08
32	563	0.88	0	0.17	0.02	0.07
34	10<	0.25	0.04	0.14	1 11	0.04
34	25	0.23	1 23	0.17	1.11	0.04
34	487	1.54	0	0.28	1.36	0.03

^a Mixtures of 9,16-dihydroxyhexadecanoic (29) and 10,16-dihydroxyhexadecanoic (28) acids

^b Photo- and autoxidation products

Table 2

Comparison of the ratio 1/2 and the autoxidation state of some other algal lipids in SPM and underlying sediments. See Fig. 1 for sample locations.

Station – sample type	Depth (m)	IPSO ₂₅ (1)/ HBI triene (2)	Sitosterol (42) autoxidation %	Palmitoleic acid (23) autoxidation %	(F. curta + F. cylindrus) /F. kerguelensis
T32 - SPM	10<	0.2	0	1.3	20.6
CTD015 – SPM	40	0.4	0	9.3	18.8
CTD015 – SPM	563	0.9	0	21.8	8.0
MC61 – overlying water	579	1.6	*	*	0.5
MC61 – diatomaceous 'fluff'	579	2.6	*	*	N/A
MC61 – sediment (1–2 cm)	579	7.5	28.4	53.4	0.7
MC45 – sediment (1–2 cm)	538	11.3	46.3	51.6	0.8

* - not measured

N/A - abundances too low

Table 3

Percentage^a of oxidation products of HBI triene (2) detected after NaBH₄-reduction of filtered phytoplankton from Commonwealth Bay (East Antarctica)



^a Relative to the residual parent HBI

^b Coelution problem

Table 4

Relative percentages of intact hydroperoxides and their ketonic and alcoholic degradation products measured in the case of the main HBI oxidation products present in phytoplankton from Commonwealth Bay (East Antarctica) (CB sample).

X-				↓ ↓ ↓ × ↓ ↓ ↓
HO-	18	22	21	45
O=	1	3	-	-
HOO-	81	75	79	55

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Supplementary Table 1

Sample ID	Latitude	Longitude	Collection Date (2014)	Water depth (m)	IPSO ₂₅ (pg mL ⁻¹)	HBI III (pg mL ⁻¹)	IPSO25/ HBI III	Epi-brassicasterol (pg ml ⁻¹)	24-Methylenecholesterol (pg ml ⁻¹)	22-Dehydrocholesterol (pg mL ⁻¹)	Cholesterol (pg mL ⁻¹)	22-dihydrocondrillasterol (pg mL ⁻¹)
surface												
T-25	-66.883	119.437	20/02	<10	0.215	1.039	0.21	690	112	1033	319	241
T-27	-66.406	119.694	25/02	<10	0.180	0.698	0.26	236	47	352	190	82
T-28B	-66.488	120.340	25/02	<10	0.371	0.724	0.51	275	52	246	171	97
T-32	-66.184	120.503	05/03	<10	0.246	1.160	0.25	249	49	264	155	115
T-34	-66.501	120.457	06/03	<10	0.347	1.414	0.21	220	42	196	166	120
CTD-002	-66.086	120.037	10/02	1	0.317	0.600	0.53	248	59	325	192	49
CTD-004	-66.367	120.006	12/02	0	0.105	0.395	0.27	525	80	983	370	227
CTD-005	-66.364	119.331	17/02	10	0.099	0.288	0.35	277	45	326	204	55
CTD-006	-66.389	119.231	17/02	10	0.302	1.669	0.18	437	72	542	270	205
CTD-007	-66.386	118.960	17/02	10	0.188	0.415	0.45	279	55	456	125	31
CTD-008	-66.567	119.217	18/02	9	0.112	0.441	0.25	467	66	509	280	125
CTD-009	-66.893	119.418	20/02	7	0.151	0.705	0.21	664	94	1135	397	224
CTD-010	-66.185	120.504	21/02	5	0.195	1.056	0.18	270	56	375	191	779
CTD-012	-66.388	119.749	25/02	5	0.351	1.143	0.31	336	62	527	207	134
CTD-013	-66.485	120.333	25/02	5	0.147	0.690	0.21	265	46	340	225	134
CTD-014	-66.506	120.487	06/03	5	0.156	0.523	0.30	221	33	212	183	107
CTD-015	-66.129	120.464	06/03	5	0.141	0.965	0.15	266	57	270	194	200
Mean							0.28					

Sample ID	Latitude	Longitude	Collection Date (2014)	Water depth (m)	C ₁₄ FA (pg mL ⁻¹)	C ₁₆ FA (pg mL ⁻¹)	C _{16:1ω7} FA (pg mL ⁻¹)	C ₁₈ FA (pg mL ⁻¹)
surface								
T-25	-66.883	119.437	20/02	<10	2432	2624	1622	277
T-27	-66.406	119.694	25/02	<10	852	1258	637	244
T-28B	-66.488	120.340	25/02	<10	923	1287	720	218
T-32	-66.184	120.503	05/03	<10	697	971	502	169
T-34	-66.501	120.457	06/03	<10	884	1216	688	214
CTD-002	-66.086	120.037	10/02	1	1071	1624	661	357
CTD-004	-66.367	120.006	12/02	0	520	1510	797	381
CTD-005	-66.364	119.331	17/02	10	549	1610	259	596
CTD-006	-66.389	119.231	17/02	10	2394	2853	1452	296
CTD-007	-66.386	118.960	17/02	10	279	674	312	154
CTD-008	-66.567	119.217	18/02	9	1968	2474	1279	157
CTD-009	-66.893	119.418	20/02	7	2509	3367	1412	541
CTD-010	-66.185	120.504	21/02	5	786	1331	539	339
CTD-012	-66.388	119.749	25/02	5	1647	1904	882	207
CTD-013	-66.485	120.333	25/02	5	1021	1588	650	349
CTD-014	-66.506	120.487	06/03	5	1117	1594	649	327
CTD-015	-66.129	120.464	06/03	5	850	1357	521	284

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Supplementary Table 1

Sample ID	Latitude	Longitude	Collection Date (2014)	Water depth (m)	IPSO ₂₅ (pg mL ⁻¹)	HBI III (pg mL ⁻¹)	IPSO25/ HBI III	Epi-brassicasterol (pg ml ⁻¹)	24-Methylenecholesterol (pg ml ⁻¹)	22-Dehydrocholesterol (pg mL ⁻¹)	Cholesterol (pg mL ⁻¹)	22-dihydrocondrillasterol (pg mL ⁻¹)
sub-surface												
CTD-002	-66.086	120.037	10/02	20	0.187	0.245	0.77	82	9	97	63	12
CTD-004	-66.367	120.006	12/02	60	0.279	1.103	0.25	326	62	624	156	117
CTD-005	-66.364	119.331	17/02	60	0.296	0.671	0.44	119	20	157	94	33
CTD-006	-66.389	119.231	17/02	40	0.321	1.564	0.21	289	66	336	228	88
CTD-007	-66.386	118.960	17/02	25	0.346	0.757	0.46	506	76	801	259	35
CTD-008	-66.567	119.217	18/02	50	0.126	0.268	0.47	140	18	221	67	10
CTD-009	-66.893	119.418	20/02	60	0.194	0.750	0.26	233	30	307	102	95
CTD-010	-66.185	120.504	21/02	35	0.311	1.297	0.24	111	18	137	87	36
CTD-012	-66.388	119.749	25/02	50	0.288	2.021	0.14	203	37	331	136	80
CTD-013	-66.485	120.333	25/02	50	0.588	1.348	0.44	137	30	165	120	65
CTD-014	-66.506	120.487	06/03	25	0.257	1.250	0.21	145	26	125	98	88
CTD-015	-66.129	120.464	06/03	40	0.440	1.181	0.37	125	24	102	82	87
Mean							0.36					

Sample ID	Latitude	Longitude	Collection Date (2014)	Water depth (m)	C ₁₄ FA (pg mL ⁻¹)	C ₁₆ FA (pg mL ⁻¹)	C _{16:1ω7} FA (pg mL ⁻¹)	C ₁₈ FA (pg mL ⁻¹)
sub-surface								
CTD-002	-66.086	120.037	10/02	20	394	899	205	366
CTD-004	-66.367	120.006	12/02	60	658	1599	592	415
CTD-005	-66.364	119.331	17/02	60	841	1384	462	329
CTD-006	-66.389	119.231	17/02	40	1542	2463	908	501
CTD-007	-66.386	118.960	17/02	25	512	1399	593	369
CTD-008	-66.567	119.217	18/02	50	522	1089	255	242
CTD-009	-66.893	119.418	20/02	60	1379	2060	704	507
CTD-010	-66.185	120.504	21/02	35	700	1329	384	267
CTD-012	-66.388	119.749	25/02	50	1188	1756	667	280
CTD-013	-66.485	120.333	25/02	50	1067	1754	656	442
CTD-014	-66.506	120.487	06/03	25	956	1411	596	334
CTD-015	-66.129	120.464	06/03	40	981	1366	601	195

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Supplementary Table 1

Sample ID	Latitude	Longitude	Collection Date (2014)	Water depth (m)	IPSO ₂₅ (pg mL ⁻¹)	HBI III (pg mL ⁻¹)	IPSO ₂₅ / HBI III	Epi-brassicasterol (pg ml ⁻¹)	24-Methylenecholesterol (pg ml ⁻¹)	22-Dehydrocholesterol (pg mL ⁻¹)	Cholesterol (pg mL ⁻¹)	22-dihydrocondrillasterol (pg mL ⁻¹)
deep												
CTD-002	-66.086	120.037	10/02	480	0.086	0.042	2.02	24	2	18	30	8
CTD-004	-66.367	120.006	12/02	610	0.157	0.067	2.36	52	10	61	50	6
CTD-005	-66.364	119.331	17/02	830	0.061	0.017	3.49	22	5	24	56	LOD
CTD-006	-66.389	119.231	17/02	860	0.080	0.028	2.87	28	5	26	34	LOD
CTD-007	-66.386	118.960	17/02	890	0.121	0.028	4.31	30	4	20	26	LOD
CTD-008	-66.567	119.217	18/02	670	0.092	0.043	2.13	36	6	42	47	LOD
CTD-009	-66.893	119.418	20/02	1080	0.128	0.050	2.57	104	20	110	73	LOD
CTD-010	-66.185	120.504	21/02	530	0.169	0.146	1.16	44	5	42	37	2
CTD-012	-66.388	119.749	25/02	650	0.105	0.060	1.74	62	11	81	83	LOQ
CTD-013	-66.485	120.333	25/02	600	0.126	0.078	1.61	66	8	94	319	7
CTD-014	-66.506	120.487	06/03	490	0.086	0.056	1.54	25	8	42	43	LOQ
CTD-015	-66.129	120.464	06/03	560	0.127	0.144	0.88	39	6	34	112	15
Mean							2.22					

Sample ID	Latitude	Longitude	Collection Date (2014)	Water depth (m)	C ₁₄ FA (pg mL ⁻¹)	C ₁₆ FA (pg mL ⁻¹)	C _{16:1ω7} FA (pg mL ⁻¹)	C ₁₈ FA (pg mL ⁻¹)
deep								
CTD-002	-66.086	120.037	10/02	480	104	373	55	226
CTD-004	-66.367	120.006	12/02	610	100	694	98	566
CTD-005	-66.364	119.331	17/02	830	121	678	111	432
CTD-006	-66.389	119.231	17/02	860	154	503	102	231
CTD-007	-66.386	118.960	17/02	890	117	357	85	140
CTD-008	-66.567	119.217	18/02	670	164	537	103	181
CTD-009	-66.893	119.418	20/02	1080	1162	1952	613	534
CTD-010	-66.185	120.504	21/02	530	254	592	117	142
CTD-012	-66.388	119.749	25/02	650	433	1433	234	510
CTD-013	-66.485	120.333	25/02	600	592	2937	2230	1202
CTD-014	-66.506	120.487	06/03	490	166	455	194	155
CTD-015	-66.129	120.464	06/03	560	187	905	158	846

Sample ID	Latitude	Longitude	Collection Date (2014)	Water depth (m)	IPSO ₂₅ (ng g ⁻¹)	HBI III (ng g ⁻¹)	IPSO25/ HBI III	Epi-brassicasterol (ng g ⁻¹)	24-Methylenecholesterol (ng g ⁻¹)	22-Dehydrocholesterol (ng g ⁻¹)	Cholesterol (ng g ⁻¹)	22-dihydrocondrillasterol (ng g ⁻¹)
sediments *												
(1-2 cm)												
MC-45	-66.398	120.589	26/02	538	34.5	3.1	11.3	1272	LOD	981	1881	LOQ
MC-61	-66.128	120.464	05/03	579	45.1	6.0	7.5	957	LOD	458	688	LOQ

LOD-below detection limit

LOQ-present, at the level of quantification

*No fatty acids measured for sediment samples