

2018-04

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Belt, Simon

<http://hdl.handle.net/10026.1/11250>

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10.1016/j.orggeochem.2018.01.008

Organic Geochemistry

Elsevier BV

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1 Sterol identification in floating Arctic sea ice algal aggregates and the Antarctic  
2 sea ice diatom *Berkeleya adeliensis*.

3 Simon T. Belt<sup>a,\*</sup>, Thomas A. Brown<sup>a,b</sup>, Lukas Smik<sup>a</sup>, Philipp Assmy<sup>c</sup>, C. J.  
4 Mundy<sup>d</sup>

5 \* Author for correspondence. Tel.: +44 (0)1752 584959.

6 *E-mail address:* [sbelt@plymouth.ac.uk](mailto:sbelt@plymouth.ac.uk) (Simon Belt)

7 *a. Biogeochemistry Research Centre, School of Geography, Earth and*  
8 *Environmental Sciences, University of Plymouth, Drake Circus, Plymouth,*  
9 *Devon PL4 8AA, UK*

10 *b. Marine Ecology and Chemistry, Scottish Association for Marine Science,*  
11 *Oban, Argyll, UK, PA37 1QA.*

12 *c. Norwegian Polar Institute, Fram Centre, NO-9296 Tromsø, Norway*

13 *d. Centre for Earth Observation Science (CEOS), University of Manitoba,*  
14 *Winnipeg, Manitoba R3T 2N2, Canada.*

15

16 ABSTRACT

17 A number of common sterols were identified in sea ice diatoms from the  
18 Arctic and the Antarctic. The main sterols in floating sea ice algal aggregates  
19 collected from Resolute Passage (Canadian Arctic) and Nansen Basin (North  
20 Svalbard) in 2012 were 22E-dehydrocholesterol, cholesterol, epi-brassicasterol,  
21 24-methylenecholesterol and 24-ethylcholesterol, although the distribution  
22 varied between the two locations, likely reflecting compositional differences in

23 diatom taxa. The three major sterols in cells of *Berkeleya adeliensis* picked from  
24 a melted sea ice core collected from Ryder Bay in the Antarctic Peninsula in  
25 2014, were 24-ethylcholesterol, cholesterol and 22E-dehydrocholesterol. We  
26 suggest that certain sea ice diatoms may thus contribute to the sedimentary  
27 budget of common sterols in seasonally sea ice-covered locations following ice  
28 melt.

29

## 30 **1. Introduction**

31 Sterols are amongst the most common lipid constituents of diatoms (e.g.  
32 Volkman, 1986; Rampen et al., 2010). In recent years, the analysis of a number  
33 of sterols including 24-methylcholesta-5,22E-dien-3 $\beta$ -ol (brassicasterol or epi-  
34 brassicasterol) has been used to provide information regarding surface ocean  
35 settings in palaeo Arctic sea ice reconstructions based on the organic geochemical  
36 sea ice proxy IP<sub>25</sub> (Belt et al., 2007; Belt and Muller, 2013). In particular, the  
37 occurrence of, respectively, relatively high or low sedimentary concentrations of  
38 certain sterols has been employed as a means of distinguishing between  
39 permanently open-water versus perennially ice-covered regimes when IP<sub>25</sub> is  
40 typically absent (or very low in concentration), as first demonstrated by Müller et  
41 al. (2009). However, such interpretations are likely made more complicated by  
42 the fact that many sterols also have non-marine sources (Huang and Meinschein,  
43 1976; Volkman, 1986), such that the possibility of, for example, terrestrial input  
44 via fluvial discharge may complicate the marine sedimentary signal. Further, for  
45 regions of seasonal sea ice cover, there is the additional likely biosynthesis of  
46 sterols by common sympagic biota, especially as sterols appear to be common to

47 all diatoms, the most abundant phototrophs found in sea ice. Consistent with  
48 this, a number of sterols have previously been reported in both Arctic and  
49 Antarctic sea ice samples containing high diatom content (Nichols et al., 1989,  
50 1993; Brown et al., 2011; Belt et al., 2013). However, since some sea ice also  
51 contains material entrained from the water column during freeze-up (e.g.  
52 suspended sediment), a question remains as to the true origin of certain sterols  
53 in previously analysed sea ice samples. On the other hand, the magnitude of  
54 sterol concentrations in sea ice reported in previous studies (typically tens to  
55 hundreds of ng sterol per ml sea ice melt; Brown et al., 2011; Belt et al., 2013)  
56 likely precludes allochthonous sources as major contributors, albeit in the  
57 relatively few studies reported thus far. To help clarify matters, here we  
58 analysed the sterol content in (i) floating sea ice diatom aggregates from two  
59 different regions of the Arctic, including some from which the sources of the sea  
60 ice diatom biomarker IP<sub>25</sub> had previously been identified (Brown et al., 2014) and  
61 (ii) picked cells of *Berkeleya adeliensis*, a well-known constituent of Antarctic  
62 sympagic diatom communities, and a recently identified source of IPSO<sub>25</sub>, the  
63 proposed counterpart sea ice proxy to IP<sub>25</sub> in the Southern Ocean (Belt et al.,  
64 2016). Our data confirm the biosynthesis of certain sterols by sympagic diatoms,  
65 as proposed in previous studies (Nichols et al., 1989, 1993; Brown et al., 2011;  
66 Belt et al., 2013).

## 67 **2. Methods**

68 Floating sea ice algal aggregates (four samples from Resolute Passage,  
69 Arctic Canada and one from the Nansen Basin north of Nordaustlandet,

70 Svalbard (both 2012)) and sea ice cores (Ryder Bay, Antarctic Peninsula (2014))  
71 were obtained as described previously (Assmy et al., 2013; Brown et al., 2014;  
72 Belt et al., 2016). Floating algal aggregates were washed with de-ionised water  
73 to remove salts and then freeze-dried. Individual cells of *B. adeliensis* were  
74 picked from a partially thawed section of sea ice by hand using a modified  
75 pipette. In all cases, the resulting sympagic diatom samples were extracted with  
76 hexane (1 ml, ultrasonication; 5 min) and fractionated using column  
77 chromatography (0.5 g SiO<sub>2</sub>) to obtain apolar lipids (5 ml hexane) and sterols (5  
78 ml hexane/methyl acetate (4:1 v/v)). Sterol fractions were derivatised using N,O-  
79 Bis(trimethylsilyl)trifluoroacetamide (BSTFA; 50 µl; 70°C; 60 min) and analysed  
80 using gas chromatography–mass spectrometry (GC–MS) in total ion current  
81 (TIC) or selected ion monitoring (SIM) mode using an Agilent 7890a Series II gas  
82 chromatograph, fitted with a 30 m fused silica HP<sub>5</sub>ms column (0.25 mm i.d., 0.25  
83 µm film) coupled to a 5975c Series Mass Selective Detector (MSD). Individual  
84 sterols were identified by comparison of the mass spectra of their TMS ethers  
85 with published data (e.g. Volkman, 1986). 24-methylcholest-5,22E-dien-3β-ol was  
86 assumed to be epi-brassicasterol since this isomer is found in diatoms (e.g.  
87 Volkman, 1986; Volkman et al., 1998).

### 88 **3. Results and Discussion**

#### 89 *3.1 Sterols in Arctic sea ice diatoms*

90 The most abundant sterols in the four floating ice algal aggregate samples  
91 from Resolute Passage in the Canadian Arctic could be readily identified by  
92 comparison of their characteristic mass spectra with those reported previously.

93 Some other components were either too low in concentration to permit reliable  
94 identification or had mass spectra that did not match those of known sterol-TMS  
95 ethers. For each of the four samples, the principal identifiable sterols were  
96 cholesta-5,22E-dien-3 $\beta$ -ol (22E-dehydrocholesterol), cholest-5-en-3 $\beta$ -ol  
97 (cholesterol), 24-methylcholest-5,22E-dien-3 $\beta$ -ol (epi-brassicasterol), 24-  
98 methylcholest-5,24(28)-dien-3 $\beta$ -ol (24-methylenecholesterol), 24-methylcholest-5-  
99 en-3 $\beta$ -ol (methylcholesterol) and 24-ethylcholest-5-en-3 $\beta$ -ol (24-ethylcholesterol),  
100 with epi-brassicasterol, 24-methylenecholesterol and 24-ethylcholesterol as the  
101 major constituents (Fig. 1a; Table 1). These findings are consistent with those of  
102 Belt et al. (2013) who reported very similar sterol compositions in filtered sea ice  
103 samples collected from the same region and season in 2011 and 2012. A similar  
104 series of sterols was also present in the floating ice algal sample collected from  
105 Nansen Basin, northern Svalbard, although with a slightly different distribution  
106 compared to those found for the samples from Resolute Passage (Fig. 1b; Table  
107 1), probably due to changes in diatom taxa content. Indeed, the ice-associated  
108 pennate diatoms *Navicula pelagica*, *Nitzschia frigida* and *Pauliella taeniata*  
109 were the major taxa in the aggregates from Resolute Passage (Brown et al.,  
110 2014), while *N. pelagica*, *Hantzschia weyprechtii*, *Entomoneis paludosa* and  
111 *Cylindrotheca closterium* were the most abundant species in the sample from the  
112 Nansen Basin (Assmy et al., 2013).

### 113 3.2 Sterols in the Antarctic sympagic diatom *B. adeliensis*

114 The main sterols in the picked cells of *B. adeliensis* were 22-  
115 dehydrocholesterol, cholesterol and 24-ethylcholesterol (Fig. 1c; Table 1).  
116 Previously, Nichols et al. (1989, 1993) identified the same three sterols in filtered

117 sea ice samples from McMurdo Sound, Antarctica, containing mixed diatom  
118 communities, in which *Berkeleya spp.* were also identified. In our picked cells of  
119 *B. adeliensis*, trace amounts of epi-brassicasterol and 24-methylcholesterol could  
120 also be identified by GC–MS in SIM mode. These sterols were more prominent in  
121 some of the mixed assemblages of sea ice diatoms analysed by Nichols et al.  
122 (1989, 1993), presumably reflecting the changes in diatom composition in those  
123 samples.

124 Finally, since the deposition of Arctic and Antarctic sea ice diatoms in  
125 underlying sediments is well known from micropalaentological (Armand et al.,  
126 2017) and biomarker studies (e.g. via the detection of IP<sub>25</sub> and IPSO<sub>25</sub>; Belt et al.,  
127 2007, 2016; Belt and Müller, 2013), it follows that they likely also contribute to  
128 the sedimentary sterol budget in seasonally sea ice-covered locations.

#### 129 **4. Conclusions**

130 The results presented herein confirm the production of certain common  
131 sterols by sympagic algae in both the Arctic and Antarctic, as proposed in some  
132 previous studies. Of course, these findings do not preclude the possibility of some  
133 sterol entrainment (e.g. from sediments) in sea ice from other locations, which  
134 subsequently become deposited in underlying sediments following ice melt.  
135 Indeed, resolving the relative source contributions of various sterols in marine  
136 sediments will likely remain a challenge for such common lipid biomarkers.

#### 137 **5. Acknowledgments**

138 We thank the University of Plymouth for funding. Sample collection  
139 (Resolute Passage) was supported through a Natural Sciences and Engineering

140 Research Council of Canada grant to C.M. P.A. was supported by the Centre of  
141 Ice, Climate and Ecosystems at the Norwegian Polar Institute and the Research  
142 Council of Norway (project no. 244646). We thank Mairi Fenton for providing the  
143 sea ice sample from Ryder Bay. Finally, we acknowledge John Volkman and  
144 Andy Revill for providing constructive feedback on the original manuscript.

## 145 **6. References**

- 146 Armand, L.K., Ferry, A., Leventer, A., 2017. Advances in palaeo sea ice  
147 estimation. In: Thomas, D.N., (Ed.), *Sea Ice*. John Wiley & Sons, Ltd,  
148 Chichester, pp. 600–629.
- 149 Assmy, P., Ehn, J.K., Fernández-Méndez, M., Hop, H., Katlein, C., Sundfjord, A.,  
150 Bluhm, K., Daase, M., Engel, A., Fransson, A., Granskog, M.A., Hudson,  
151 S.R., Kristiansen, S., Nicolaus, M., Peeken, I., Renner, A.H.H., Spreen, G.,  
152 Tatarek, A., Wiktor, J., 2013. Floating ice-algal aggregates below melting  
153 Arctic sea ice. *PLoS ONE* 8, e76599.
- 154 Belt, S.T., Massé, G., Rowland, S.J., Poulin, M., Michel, C., LeBlanc, B., 2007. A  
155 novel chemical fossil of palaeo sea ice: IP<sub>25</sub>. *Organic Geochemistry* 38, 16–  
156 27.
- 157 Belt, S.T., Brown, T.A., Ringrose, A.E., Cabedo-Sanz, P., Mundy, C.J., Gosselin,  
158 M., Poulin, M., 2013. Quantitative measurements of the sea ice diatom  
159 biomarker IP<sub>25</sub> and sterols in Arctic sea ice and underlying sediments:  
160 Further considerations for palaeo sea ice reconstruction. *Organic*  
161 *Geochemistry* 62, 33–45.

- 162 Belt, S.T., Müller, J., 2013. The Arctic sea ice biomarker IP<sub>25</sub>: a review of current  
163 understanding, recommendations for future research and applications in  
164 palaeo sea ice reconstructions. *Quaternary Science Reviews* 79, 9–25.
- 165 Belt, S.T., Smik, L., Brown, T.A., Kim, J.-H., Rowland, S.J., Allen, C.S., Gal, J.-  
166 K., Shin, K.-H., Lee, J.I., Taylor, K.W.R., 2016. Source identification and  
167 distribution reveals the potential of the geochemical Antarctic sea ice  
168 proxy IPSO<sub>25</sub>. *Nature Communications* 7, 12655.
- 169 Brown, T.A., Belt, S.T., Mundy, C., Philippe, B., Massé, G., Poulin, M., Gosselin,  
170 M., 2011. Temporal and vertical variations of lipid biomarkers during a  
171 bottom ice diatom bloom in the Canadian Beaufort Sea: further evidence  
172 for the use of the IP<sub>25</sub> biomarker as a proxy for spring Arctic sea ice. *Polar*  
173 *Biology* 34, 1857–1868.
- 174 Brown, T.A., Belt, S.T., Tatarek, A., Mundy, C.J., 2014. Source identification of  
175 the Arctic sea ice proxy IP<sub>25</sub>. *Nature Communications* 5, 4197.
- 176 Huang, W.Y., Meinschein W.G., 1976. Sterols as source indicators of organic  
177 material in sediments. *Geochimica et Cosmochimica Acta* 40, 323–330.
- 178 Müller, J., Massé, G., Stein, R., Belt, S.T., 2009. Variability of sea-ice conditions  
179 in the Fram Strait over the past 30,000 years. *Nature Geoscience* 2, 772–  
180 776.
- 181 Nichols, P.D., Palmisano, A.C., Rayner, M.S., Smith, G.A., White, D.C., 1989.  
182 Changes in the lipid composition of Antarctic sea-ice diatom communities  
183 during a spring bloom: an indication of community physiological status.  
184 *Antarctic Science* 1, 133–140.

185 Nichols, D.S., Nichols, P.D., Sullivan, C.W., 1993. Fatty acid, sterol and  
186 hydrocarbon composition of Antarctic sea ice diatom communities during  
187 the spring bloom in McMurdo Sound. *5*, 271–273.

188 Rampen, S.W., Abbas, B.A., Schouten, S, Sinninghe Damsté, J.S.D., 2010. A  
189 comprehensive study of sterols in marine diatoms (Bacillariophyta):  
190 Implications for their use as tracers for diatom productivity. *Limnology*  
191 *and Oceanography* *55*, 91–105.

192 Volkman, J.K., 1986. A review of sterol markers for marine and terrigenous  
193 organic matter. *Organic Geochemistry* *9*, 83–99.

194 Volkman, J.K., Barrett, S.M., Blackburn, S.I., Mansour, M.P., Sikes, E.L., Gelin,  
195 F., 1998. Microalgal biomarkers: a review of recent research  
196 developments. *Organic Geochemistry* *29*, 1163–1179.

197

## 198 **Figure legends**

199 Figure 1. Partial GC – MS chromatograms showing the presence of various  
200 sterols in Arctic and Antarctic sea ice diatoms: (a) floating sea ice aggregates  
201 from Resolute Passage (Canadian Arctic) in 2012 (sample RP-1); (b) floating sea  
202 ice aggregates from Nansen Basin (North Svalbard) in 2012; (c) Individual cells  
203 of *B. adeliensis* picked from a landfast sea ice core from Ryder Bay (Antarctic  
204 Peninsula) in 2014. Sterols are numbered as follows: (1) 22E-dehydrocholesterol;  
205 (2) cholesterol; (3) epi-brassicasterol; (4) 24-methylenecholesterol; (5) 24-  
206 methylcholesterol; (6) 24-ethylcholesterol.

207

208

209 Table 1. Percentages of sterols in sea ice algal samples. Resolute Passage (RP);  
 210 Nansen Basin (NB).

211

Sterol	Sample					
	RP-1	RP-2	RP-3	RP-4	NB	<i>B. adeliensis</i>
22E-dehydrocholesterol	10	9	11	10	19	7
cholesterol	4	4	5	4	17	40
epi-brassicasterol	30	29	29	32	24	tr
24-methylenecholesterol*	28	26	26	26	15	nd
24-methylcholesterol	tr	tr	tr	tr	tr	tr
24-ethylcholesterol	29	32	29	28	25	53

\*includes small amounts of 24-methylcholesterol

tr: trace amounts

nd: not detected

212

213 Figure 1.

