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Transformation of organic matter in a Barents Sea sediment profile: coupled geochemical and microbiological processes

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Summary

Process-based, mechanistic investigations of organic matter transformation and diagenesis directly beneath the sediment-water interface in Arctic continental shelves are vital as these regions are at greatest risk of future change. This is in part due to disruptions in benthic-pelagic coupling associated with ocean current change and sea ice retreat. Here we focus on a high-resolution, multi-disciplinary set of measurements that illustrate how microbial processes involved in the degradation of organic matter are directly coupled with inorganic and organic geochemical sediment properties (measured and modeled) as well as the extent/depth of bioturbation. We find direct links between aerobic processes, reactive organic carbon and highest abundances of bacteria and archaea in the uppermost layer (0-4.5 cm depth) followed by dominance of microbes involved in nitrate/nitrite and

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11 iron/manganese reduction across the oxic-anoxic redox boundary (~4.5-10.5 cm depth).
12 Sulfate reducers dominate in the deeper (~10.5-33 cm) anoxic sediments which is consistent
13 with the modeled reactive transport framework. Importantly, organic matter reactivity as
14 tracked by organic geochemical parameters (*n*-alkanes, *n*-alkanoic acids, *n*-alkanols and
15 sterols) changes most dramatically at and directly below the sediment-water interface
16 together with sedimentology and biological activity but remained relatively unchanged
17 across deeper changes in sedimentology.

18

19 Main Text

20

21 Introduction

22

23 Organic matter (OM) processing and transformation at the seafloor, ultimately drives the
24 sequestration of organic carbon and the biogeochemical modifications that occur prior to
25 long-term burial [1]. Across this important marine transition zone biological, geological and
26 physical processes take place at variable rates, including deposition of organic and inorganic
27 material, partial degradation of OM by microbes, sediment mixing by benthic fauna and,
28 dissolution and precipitation of mineral phases. Interactions between these coupled
29 processes are typically poorly characterised, but it is increasingly recognised that it is the
30 combined biogeochemical properties of sediments adjacent to OM that determine its
31 degradation and preservation trajectories [1], with alterations to the fate of deposited OM
32 particularly prevalent in high-latitude oceans. Arctic seafloor sediments are, sensitive to
33 changes in pelagic to benthic coupling as a result of alterations in the distribution of water
34 masses and sea-ice extent linked to climate changes [2], with process-based coupled
35 sedimentary organic-inorganic-microbial studies useful to capture the detail in the key
36 diagenetic processes and interactions which occur during OM transformation. It is also
37 important to distinguish external parameter changes that have impacts on organic carbon
38 reactivity from those that do not.

39

40 The OM at and below the Arctic shelf seafloor sustains a key ecological niche, including high
41 microbial diversity [3] and a rich benthic ecosystem [4]. Processing of organic carbon at the
42 seafloor is closely linked to water column productivity [5] and to delivery of algal biomass
43 from melting sea ice [6]. Over longer timescales marine organic carbon burial is the principal
44 mechanism of millennial scale carbon sequestration [7, 8] which, subject to processing and
45 transformation, becomes part of the geological record [9].

46

47 OM deposited at the seafloor undergoes intensive diagenetic transformation, with up to
48 ~99% degraded at the sediment-water interface (SWI), escaping long-term burial [10]. At
49 the SWI, the extent of transformation of OM results from the complex interactions between
50 OM composition and its stability to processing (e.g. redox conditions, microbial community
51 structure, mineralogy) [11, 12]. Consequently, such interactions result in distinct OM
52 reactivity changes during burial and differences in the rates of early diagenesis between
53 autochthonous (typically more reactive) and allochthonous sources (typically less reactive)
54 [13]. OM which 'survives' the uppermost sediment layer is subject to further microbial
55 activity where polymer hydrolysis, iron and manganese reduction, denitrification, nitrate
56 dissimilation, sulfate reduction and methanogenesis take place. Microbes indicative of these
57 processes inhabit often clearly stratified communities [14-16]. As OM is gradually broken
58 down, only the least reactive OM is left behind [17]. Redox processes, whereby sediments
59 transition from oxic to anoxic conditions, are an additional control on OM reactivity as
60 anaerobes inhabiting oxygen-free environments are limited in their ability to hydrolyze
61 more structurally complex compounds [10]. Simultaneously, bioturbating animals which
62 burrow into and physically mix sediments help control the thickness of the oxic layer,
63 regulating the amount and quality of organic carbon accumulated [18].

64

65 We selected the Barents Sea seafloor as our study location because it is characterised by a
66 mix of marine and terrestrial organic matter input, a clearly defined sequence of microbially
67 controlled redox zones, a variable input of inorganic material from land, and a strong
68 seasonality that affects chemical, physical and biological processes in a predictable manner.
69 The Barents Sea is also known to be vulnerable to climate change, with the existing extent of
70 sea ice loss expected to intensify in Arctic regions over the coming decades [19-21]. As well
71 as having a clear impact on wider Earth system processes [22, 23], sea ice loss driven by
72 atmospheric and oceanic warming is modifying the timing and abundance of biological
73 productivity within the Barents Sea by altering water column stratification [24], including the
74 relative balance of Arctic and Atlantic water masses [25], potentially altering the type of OM
75 delivered to the seafloor.

76

77 Although previous studies have combined microbiological and geochemical measurements
78 in Arctic continental shelf settings, they tend to focus on surface sediment transects [26],
79 down-core at low-resolution in deeper sediments [15, 16, 27, 28], or were limited by
80 sequencing libraries and study location [14], and so unable to show so clearly the depth-

81 successional redox transition close to the SWI. By using these techniques in tandem, it is
82 possible to fully explore the microbiological and geochemical basis underpinning diagenetic
83 models [29] highlighting the complexity of these processes and enabling quantification.
84

85 The main objective of this study is to improve our understanding of the interactions that
86 regulate and mediate OM processing at and below the SWI, by combining downcore
87 organic, inorganic and microbial measurements from the north western Barents Sea. We aim
88 to link biological and mineralogical mediated geochemical changes, by providing insight
89 into the reactivity of OM as a function of down-core trends in the context of microbial
90 abundances and activities related to redox processes. Overall, we expected that the
91 uppermost sediments would show evidence of a rapid decrease in the reactivity of OM
92 associated with the oxic layer, aerobic microbial activity, and biological sediment mixing (the
93 bioturbated layer). Beneath, we used our set of multi-disciplinary measurements to assess
94 the extent to which highly reactive carbon inputs are mineralised before cessation of aerobic
95 processes, and whether reactive carbon survives the transition to anoxia. We include
96 inorganic geochemical and grain size measurements to assess how changes in
97 sedimentation over the later Holocene affect trends in organic geochemical parameters.
98

99 **Methods**

100 **i) Study sites and sampling**

101 Two sediment cores from the same location (B15) were obtained during the JR16006 cruise
102 (2017) of the RRS James Clark Ross in the Barents Sea [30] and included multicore sampling
103 from station B15 E144 (78.25169 °N; 30.00909 °E) for depth resolved organic geochemistry
104 [31], microbial abundances and community compositions, and B15 E146 (78.25152 °N;
105 30.00849 °E) for inorganic geochemistry, to 33 cm depth (Supplements: Table S1). Station
106 B15 is located to the east of Svalbard's Edge Island and south of the island of Kongsoya
107 (Supplements: SI Fig. 1) and was sea-ice-covered during sampling [32]. The sediments were
108 taken from 315 m water depth in a glacial trough. Cores were sectioned at 0.5 cm intervals
109 to 2 cm depth and at 1 cm intervals to the base of the core. Sections were stored and flash
110 frozen in combusted foil (organic geochemistry (flash frozen -80 °C, stored -20 °C)), plastic
111 bags (inorganic geochemistry (-20 °C)), and plastic vials (microbiology (-80 °C)).
112
113
114

115 **ii) Bulk organic geochemistry**

116
117 Total organic carbon (TOC) was analysed on freeze-dried acidified sediments (HCl; 4M; 4 h),
118 dried overnight (60 °C) and analysed with a CS230 Carbon/Sulfur Determinator (Leco
119 Corporation, Michigan, USA) using porous crucibles. The TOC content is expressed as the
120 weight percentage of dried sediment (wt.%). Nitrogen measurements were made using a
121 Vario MAX CNS analyser (Elementar, Langensfeld, Germany). TOC:N ratios were not
122 corrected for the molar weight of C and N. Stable nitrogen isotope measurements ($\delta^{15}\text{N}$)
123 were performed using an ECS 4010 Elemental Analyser (Costech Analytical Technologies
124 Inc., Valencia, CA) coupled to a Delta V Advantage (Thermo Finnigan, Hemel Hempstead, UK)
125 isotope ratio mass spectrometer and are reported in (δ) notation in per mille (‰) relative to
126 atmospheric N_2 (AIR). Sample precision was <0.2‰.

127

128 **iii) Grain size analysis**

129

130 Bulk sediment samples were disaggregated in an ultrasonic bath (15 minutes) and analysed
131 on a Mastersizer 2000E laser diffractometer for particles of a diameter range 0.1-1000 μm at
132 the University of Leeds. Results were categorised into 6 size fractions and are presented as
133 cumulative volume percentages.

134

135 **iv) Molecular organic geochemistry**

136

137 Lipids were extracted and analysed in a similar method to Holtvoeth *et al.* [33]. Briefly,
138 freeze-dried sediment (3-4 g) spiked with internal extraction standard (5 α -androstane) was
139 sonicated in dichloromethane: methanol (9:1 v/v) three times (15 mins each), with the
140 resulting total lipid extract (TLE) concentrated, left overnight in the presence of activated
141 copper to remove sulfur and passed through an anhydrous sodium sulfate column to
142 remove water. Transmethylation was performed by adding acetyl chloride in methanol (1:30
143 v/v) at 45 °C, left overnight and followed by a clean-up step with potassium carbonate to
144 neutralise excess acids. Prior to analysis, derivatisation of compounds containing hydroxyl
145 groups was performed using N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1%
146 trimethylchlorosilane (TMS) at 65 °C for 1 h.

147

148 Samples were injected (1 μl) into an Agilent 7890B Gas Chromatograph (GC) coupled to a
149 5977B MSD Mass Spectrometer (MS) operated in full scan mode (70 eV; source temp 230 °C;

150 helium flow rate 1 mL/min). A 60 m J&W Scientific HP-1ms fused silica capillary column was
151 used for GC separation (0.25 mm x 0.25 μ m) with an oven temperature of 6 °C/min to 170
152 °C; hold of 1 min; followed by a slower ramp of 2.5 °C/min to 315 °C and a hold of 22 min.
153 Compounds were identified from their respective mass spectra and retention times, with
154 quantities calculated relative to the peak area of the internal standard 5 α -androstane and an
155 assumption of a 1:1 response.

156
157 For *n*-alkanoic acids parameters include total FAMES (fatty acid methyl esters), ratio of the
158 C₁₅ anteiso/C₁₆ FAME, terrigenous to aquatic fatty acid ratio (TAR_{FA}) [34] and total carbon
159 preference index (CPI_T) [35]. For sterols parameters include cholesterol/brassicasterol,
160 cholesterol/ β -sitosterol, stigmasterol/stigmastanol and β -sitosterol/stigmastanol. For *n*-
161 alkanes parameters were carbon preference index (CPI) [36] and odd over even
162 predominance for *n*-C₁₇₋₂₁ & *n*-C₂₁₋₂₅ (OEP₁₇₋₂₁ & ₂₁₋₂₅) [37]. Terrestrial to aquatic ratio (TAR)
163 and Aut/All (autochthonous/allochthonous) ratio was selected for *n*-alkanols [38]. Error
164 displayed is the standard deviation of a sample analysed in triplicate.

165 166 **v) Inorganic geochemistry**

167
168 X-ray fluorescence (XRF) was performed on freeze dried and gently grinded sediment
169 samples (700 mg) from B15 E146, mixed with di-lithiumtetraborate (4200 mg, Li₂B₄O₇,
170 Spectromelt A10), preoxidized at 500 °C with 1.0 g NH₄NO₃ (p.a.) and fused to homogenous
171 glass beads. Samples were analysed using a PW-2400 WD-XRF Scanner (Philips,
172 Netherlands) calibrated with geostandards at the University of Oldenburg with Fe, P and Mn
173 used in this study. Analytical precision and accuracy was <5%.

174 175 **vi) Microbiology**

176
177 Genomic DNA was extracted using the DNeasy® PowerSoil® kit (QIAGEN, Hilden,
178 Germany). Concentration and viability were tested using Qubit™ (Thermo Fisher Scientific,
179 Waltham, Massachusetts, USA) and polymerase chain reaction (PCR) respectively, prior to
180 sequencing. High throughput DNA sequencing was performed by the NUomics sequencing
181 service at Northumbria University (UK). 16S rRNA gene libraries were prepared following
182 protocol [39], in which each fragment was composed by an Illumina adapter, followed by an
183 index sequence (only for forward primer), a 10-nt pad to avoid formation of hairpin
184 structures, linkers and the V4 region specific either forward or the reverse primer. Primers

185 used were 4515F (GTGYCAGCMGCCGCGGTAA) and 806R (GGACTACHVGGGTWTCTAAT) as
186 per the Earth Microbiome Project protocol [40]. Sequencing was performed on the MiSeq
187 Personal Sequencer (Illumina, San Diego, CA, USA) using the V2 500 reagent kit.
188 Demultiplexed paired end FASTQ files were analysed using QIIME2 [41] using a pipeline
189 (<https://github.com/peterleary/markergene>). Amplicon sequence variants were generated in
190 QIIME2 using DADA2 [42] and taxonomy was classified using the SILVA 132 reference
191 database [43]. Taxonomic abundance data is expressed as percentage abundance (%)
192 enumerated from fractional abundances in sample libraries.

193
194 Quantitative PCR (qPCR) was used to determine the abundance of archaeal and bacterial
195 16S rRNA genes using the following primer pairs: Parch519F (CAGCCGCCGCGGTAA) and
196 ARC915R (GTGCTCCCCCGCCAATTCCT) [44] for archaea and Bact1369F
197 (CGGTGAATACGTTTCY-CGG) and Prok1492R (GGWTACCTTGTTACGACTT) [45] for bacteria
198 using primer concentrations and qPCR cycling conditions described in [46] and a LightCycler
199 96 instrument (Roche Life Science, Penzberg, Germany). Assays contained a standard curve
200 ranging from 10^2 to 10^8 amplicons μl^{-1} using cloned sequences. rRNA numbers were
201 quantified via comparison to standard curves using the Lightcycler 96 detection software.
202 No-template controls were below the threshold in all experiments. Measurements of 16S
203 rRNA for bacteria and archaea are presented as copies of genes per gram/wet weight
204 sediment.

205 206 **vii) Complementary measurements and datasets**

207
208 To provide constraint on the long-term sedimentation rates at the study site (and provide a
209 temporal framework to interpret the results) radiocarbon measurements (^{14}C -AMS) were
210 carried out on mixed foraminifera picked from samples at 27.5 cm depth, near the base of
211 the core. Sediment was dried, disaggregated, filtered and sieved ($>125\ \mu\text{m}$). Light
212 microscopy was used to pick and sort benthic and planktonic foraminifera tests for the Mini
213 Carbonate Dating System (MICADAS) (Ionplus, Dietikon, Switzerland) at the University of
214 Bristol. Measurements of ^{14}C were performed on both samples without graphitisation, but
215 with an acidification step, followed by analysis in the presence of a gas-ion source [47].
216 Bayesian calibration was carried out in MATLAB [48]. Acknowledging the challenges that
217 would be encountered by developing a sediment mass accumulation rate (MAR) on the
218 basis of a single point and its likely difference compared with a recent radionuclide

219 approach [49], instead here we calculate percentage yr^{-1} TOC loss based on the youngest
220 basal age to provide an estimation and comparison of reactivity between oxic and anoxic
221 parts of the core.

222
223 We sourced empirical data on macrofaunal particle reworking from Solan *et al.* [50] based
224 on sediment profile imaging of introduced optically distinct particle tracers (luminophores)
225 to the surface of sediment cores after 12 days incubation [51]. Specifically, values for the
226 mean mixed depth ($f\text{-SPL}_{\text{mean}}$, time dependent indication of short term faunal mixing, [52])
227 and the maximum mixed depth ($f\text{-SPL}_{\text{max}}$, maximum vertical extent of faunal mixing [52]) are
228 presented alongside organic geochemical (Fig. 2) and microbial parameters (Fig. 3).

229
230 Porewater analysis of oxygen (O_2) was completed on sediment cores from the same station
231 (B15) in 2019 using a portable O_2 probe, with data sourced from Freitas *et al.* [29] and
232 presented against changes in microbial parameters (Fig. 3).

233
234 Modeled estimations of the relative contribution of metabolic pathways (aerobic respiration
235 ($\text{O}_2 - \text{M}$), denitrification ($\text{NO}_3 - \text{M}$), iron reduction ($\text{Fe}(\text{OH})_3 - \text{M}$), sulfate reduction ($\text{SO}_4 - \text{M}$)
236 and manganese reduction ($\text{MnO}_2 - \text{M}$) to based on reactive transport modelling are from
237 Freitas *et al.* [29] and are also presented against changes in microbial parameters (Fig. 3). We
238 additionally include model-derived oxygen concentration depth profiles (SI Fig. 2 & 3) [29].

239

240 **viii) Statistical analysis**

241

242 Data was explored for correlations between bulk variables, organic geochemistry,
243 geomicrobiology, porewater oxygen and modeled metabolic pathway processes, with
244 statistically significant relationships (using Pearson's correlation) listed in Fig. S2-S6.
245 Modeled datasets were resampled in Matlab (ver. R2019a) to the same depth intervals using
246 spline interpolation. Principal components analysis (PCA) was conducted due to short DCA
247 gradient lengths (<2) in Canoco v4.51 [53] on \log_{10} transformed and centred data, with
248 samples highlighted in blue for proximity to the maximal extent of faunal reworking (Fig. 4).
249 Microbial taxa (defined by presence, absence and abundance), geochemical concentrations
250 and modeled percentage contribution of metabolic pathways to OM heterotrophic
251 degradation were included in the PCA table to create dissimilarity distances and eigenvalues
252 of the samples, with the two largest PCs plotted and superimposed over samples.

253

254 Results

255
256 An age-estimation was carried out at 27.5 cm depth with a mixed planktonic foraminifera
257 ^{14}C -AMS age of 4075 ± 180 (1σ) ^{14}C year, calibrated to a median age of 4121 cal. yr BP
258 (3632 to 4612 cal. yr BP, 95% confidence interval, Fig. 1). At the same depth, a paired mixed
259 benthic foraminifera measurement gave a ^{14}C -AMS age of 5079 ± 91 (1σ) ^{14}C , calibrated to a
260 median age of 5433 cal. yr BP (5245 to 5630 cal. yr BP, 95% confidence interval). Differences
261 in the shape of planktonic compared with benthic foraminifera make them susceptible to
262 bioturbation and sedimentation at different rates, providing ^{14}C evidence of key processes
263 taking place in this system.

264
265 TOC content declined from a maximum of 1.78 wt.% at ~2.5 cm to minima of 1.33 wt.% at
266 ~10.5 cm and 1.28 wt.% at ~32.5 cm (Fig. 1). Total N followed a similar trend, declining
267 rapidly from 0.23 wt.% at the top of the core to 0.17 wt.% by ~10.5 cm and 0.15 wt.% at the
268 base (Fig. 1). The ratio of TOC:N fluctuated throughout the core but gradually increased as a
269 function of burial depth trend from a minimum of 7.5 at the top of the core to a maximum
270 of 9.2 close to the base. The nitrogen isotope ratio ($\delta^{15}\text{N}$) declined from a maximum of
271 7.1‰ at the top of the core to a minimum of 5.8‰ at the base.

272
273 Profiles of total Fe and P concentrations displayed similar trends but with different
274 magnitudes and were stable (5.1-5.6% and 0.16-0.17%, respectively) from the SWI to ~9.5
275 cm, below this depth, Fe and P increases to a maximum of 8.4% Fe and 0.3% P at a clear
276 peak by ~14.5 cm. Below this peak Fe and P sharply declined to minimum values by ~16.5
277 cm with Fe ranging from 4.3% to 5.0% and P ranging from 0.11% to 0.13% to the bottom of
278 the core. Total Mn was highest in the upper part of the core, peaking at ~4.5 cm at 1.02%
279 and again at 8.5 cm to 0.96%, followed by a decline to low concentrations by ~10.5 cm
280 which remained low to the base of the core.

281
282 Grain size was dominated by clay and silt from the top of the core (cumulative <63 μm
283 fraction ~78%) to ~0.75 cm where coarser particles >63 μm (mainly fine sands) accounted
284 for ~82% of the fraction until ~2.5 cm where finer particulates again dominated (<63 μm
285 fraction >89%) (Fig. 1). Finer silts then decreased to < 16% (<63 μm fraction) by 5.5 cm, with
286 a marked increase at ~14.5 cm to ~53 % coincident with Fe and P peaks. By ~19.5 cm finer

287 silts returned to previous levels <16% (<63 μm fraction), before a gradual rise from ~24 cm,
288 peaking at ~90% from ~30.5 cm to the base of the core.

289

290 Organic geochemical ratios of key compounds displayed clear changes in the uppermost
291 ~9.5 cm of the core, with the most pronounced changes coincident with maximum
292 bioturbation in the top ~4.5 cm (4.3 cm is greatest of three maximum bioturbation
293 replicates [50]) (Fig. 2). Some compounds had especially pronounced changes in the
294 uppermost sample coincident with mean bioturbation at 0.5 cm (0.5 cm is the average of
295 three mean bioturbation replicates [50]). Total FAMEs declined rapidly from >1400 $\mu\text{g g}^{-1}$
296 TOC at 0.5 cm to ~200 $\mu\text{g g}^{-1}$ TOC at ~2 cm, with subsequent values ranging narrowly
297 between ~200 and 500 $\mu\text{g g}^{-1}$ TOC to the base (Fig. 2). The ratio of C_{15} anteiso: C_{16} FAME, an
298 indicator of microbial activity, was high in samples just below the sediment surface, within
299 maximum bioturbation (0-4.3 cm) from ~0.75-2.5 cm with values 0.15-0.19 and also at ~5.5
300 cm with a value of 0.18, followed by a general declining trend to ~25.5 cm (0.06). TAR_{FA}
301 increased from a minimum of ~0.1 at the top of the core to a maximum of ~1.2 at ~1.75 cm
302 within the zone of maximum bioturbation. The CPI_{T} ratio for *n*-alkanoic acids was high in the
303 uppermost sample (~13.5) coincident with mean bioturbation, declining to fluctuations
304 between ~5 and 9.4 to the base.

305

306 The ratio of cholesterol/brassicasterol was low at the top of the core (<1.3), increasing to ~3
307 (2.5 cm) within the zone of bioturbation, before decreasing to <1.8 by ~3.5 cm, with a
308 further peak to ~2.4 at ~9.5 cm. Similarly, cholesterol/ β -sitosterol also peaked at ~2.5 cm
309 depth (to >4), prior to a general decrease to the base of the core (<1.3). In contrast,
310 stigmasterol/stigmastanol declined from a maximum of 1.0 at the top of the core to 0.2 at
311 ~9.5 cm, followed by fluctuations between 0.1 and 0.4 to the base. Similarly, the ratio of
312 sterols β -sitosterol/stigmastanol declined rapidly from a peak of 4.2 at the top of the core to
313 ~1.2 by ~9.5 cm, remaining stable to the base of the core (1.4 to 0.9). The CPI ratio for *n*-
314 alkanes declined from a maximum of 2.5 at the top of the core to 1.7 at a depth of ~9.5 cm
315 below the seafloor. With further increase in burial depth to ~17.5 cm, there was a
316 subsequent smaller increase in CPI with values for deeper horizons below this ranging from
317 1.9 to 1.7. The OEP for *n*-alkanes from C_{21} - C_{25} ranged from a maximum of 1.6 at the top of
318 the core to a minimum of 1.1 by ~3.5 cm, with values below this fluctuating between 1.1 and
319 1.2. OEP for *n*-alkanes C_{21-25} were especially prominent in the uppermost sample (~1.6)
320 coincident with mean bioturbation, with all values below this <1.3. The TAR index for *n*-
321 alkanes increased from a maximum of ~1 at the top of the core to >4 at ~9.5 cm, prior to

322 fluctuations between ~2 and ~3.3 to the base. The autochthonous/allochthonous ratio for
323 *n*-alkanols also showed a decline in the uppermost layer from a maximum of 0.9 at the top
324 of the core to a minimum of 0.4 by ~9.5 cm.

325
326 16S rRNA gene counts representative of bacterial and archaeal cell numbers fluctuated but
327 were present in abundance from the SWI down to ~11.5 cm, below which abundances were
328 orders of magnitude lower (Fig. 3). For bacterial 16S rRNA genes above 11.5 cm the mean
329 was 3.32×10^7 copies g^{-1} wet sediment, declining markedly to 9.23×10^5 copies g^{-1} wet
330 sediment below 11.5 cm, while for archaea the mean above 11.5 cm was 7.28×10^7 copies g^{-1}
331 wet sediment declining to 2.31×10^6 copies g^{-1} wet sediment (Fig. 3). The greatest peaks in
332 bacterial and archaeal 16S rRNA genes were within the uppermost ~4.5 cm coincident with
333 most intense bioturbation. The progressive decline in these numbers could either be
334 attributable to the balance between depositional inputs at the surface and subsequent
335 death and cell lysis with sedimentation, or may relate to in-situ growth. Based on 16S rRNA
336 gene sequence analysis these depth related declines in absolute abundances were
337 accompanied by distinctive successional changes in the relative abundances of some
338 dominant archaeal and bacterial taxa indicative of a depth related transition from aerobic to
339 anaerobic microbial processes, linked to bioturbation depth. For instance, 16S rRNA gene
340 sequences related to the BD7-8 marine group [54] declined sharply from a maximum of
341 2.36% of sequences in the amplicon library at the top of the core to 0% by ~5.5 cm, with
342 only minor occurrences in amplicon libraries from depths below this (Fig. 3). Group BD7-8 is
343 considered cosmopolitan in marine benthic habitats and are putative aerobic and nitrate
344 reducing mixotrophs [55, 56]. Declines in group BD7-8 were coincident with both decreases
345 in measured ($R=0.97$, $p < 0.01$) and modeled ($R = 0.94$, $p < 0.01$) O_2 concentration depth-
346 profiles (Supplements; Figure S2) and the zone of bioturbation (Fig. 3). Highlighting links
347 between organic matter quality and aerobic processes, there were positive correlations
348 between CPI for *n*-alkanes and both measured ($R = 0.81$, $p < 0.05$) and modeled ($R= 0.92$, p
349 < 0.01) O_2 concentration depth-profiles (Supplements, Figure S2). Similar positive
350 correlations between modeled relative oxygen contribution, $\delta^{15}N$ ($R = 0.89$, $p < 0.01$), %N (R
351 $= 0.93$, $p < 0.01$) and %TOC ($R = 0.86$, $p < 0.01$) were found, with similar but slightly weaker
352 correlations between model-derived O_2 concentration depth-profiles and $\delta^{15}N$ ($R = 0.83$, p
353 < 0.01), %N ($R = 0.88$, $p < 0.01$) and %TOC ($R = 0.84$, $p < 0.01$) (Supplements; Figure S3).
354 Corroborative of the presence and depth related consumption of molecular oxygen in the
355 upper few cm (above ~9.5 cm) of the sediment, sequences related to aerobic ammonia

356 oxidizers from the family *Nitrosopumilaceae* [57] followed a general declining trend from
357 the top of the core to the base, although their abundance varied (Fig. 3). *Nitrosopumilaceae*
358 was negatively correlated with TOC:N ratio ($R = 0.62$, $P < 0.01$) and positively correlated with
359 $\delta^{15}\text{N}$ ($R = 0.91$, $p < 0.01$) (Supplements; Figure S4).

360

361 In contrast to these depth related declines, sequences related to the putatively iron reducing
362 *Shewanellaceae* family [58] which variably increased their abundance in amplicon libraries
363 were persistent up to ~ 10.5 cm (Fig. 3). Similarly, sequences related to the
364 *Desulfuromonadales* family (also putatively capable of iron reduction [59]) generally
365 increased their relative abundances up to ~ 10.5 cm but with an additional peak at ~ 15.5 cm.
366 Likewise, sequences related to the family *Methylomirabilaceae* (capable of methane
367 oxidation coupled to nitrite reduction [60]) increased in abundance at the top of the core
368 peaking at 14.1% of the amplicon library at 10.5 cm. In a similar region of the core,
369 sequences of the *Brocadiales* group (involved in anammox by ammonia oxidation linked to
370 nitrate/nitrite reduction [61]) were at highest sustained abundance between 5.5 and 10.5 cm
371 (Fig. 3). All four of these groups had varying associations with modeled relative
372 denitrification contribution. The strongest relationship was with *Brocadiales* ($R = 0.74$, $p <$
373 0.01), followed by *Methylomirabilaceae* ($R = 0.57$, $p < 0.01$), *Shewanellaceae* ($R = 0.53$, p
374 < 0.01) and *Desulfuromonadales* ($R = 0.45$, $p < 0.01$) (Supplements; Figure S5). In contrast to
375 all of the other taxa detailed above, sequences related to the sulfate reducing
376 *Desulfobacteraceae* [62]) were largely absent above ~ 10.5 cm (Fig. 3). The presence of
377 *Desulfobacteraceae* continued below this oxic-anoxic transition to the base of the core and
378 was closely correlated with modeled relative sulfate reduction contribution ($R = 0.88$, $p <$
379 0.01) (Supplements; Fig. S6).

380

381 The PCA ordination biplot provides insight into co-associations between geochemical,
382 geomicrobial, modeled relative metabolic pathways and bioturbation datasets (Fig. 4). For
383 example, the assemblage to the right part of the biplot is closest in ordination space to the
384 uppermost core samples in the oxic and bioturbated zone which includes modeled and
385 measured O_2 , Arctic marine cosmopolitan aerobic marine group BD7-8, measurements of
386 bacterial and archaeal 16S rRNA gene abundance and Mn. All organic geochemical variables
387 (sterols, *n*-alkanes, *n*-alkanols and *n*-alkanoic acids) and $\delta^{15}\text{N}$ appear to co-vary and are
388 grouped at the lower right part of the biplot. In contrast, *Desulfobacteraceae*, $\text{SO}_4 - \text{M}$,
389 $\text{Fe}(\text{OH})_3 - \text{M}$, TOC:N and TOC are present towards the lower left part of the biplot. To the top
390 left of the biplot, $\text{NO}_3 - \text{M}$ and $\text{MnO}_2 - \text{M}$ are grouped, with *Brocadiales*, Fe, P,

391 *Methylomirabilaceae*, *Desulfuromonadales*, *Nitrosopumilaceae* and *Shewanellaceae* grouped
392 towards the top of the right quadrant. PCA axis 1 decreased from a maximum of ~2 at the
393 top of the core clearly to a minimum of ~ -0.5 by ~7.5 cm, highlighting changes initially in
394 indicators sensitive to the oxic interface (e.g. organic geochemistry, BD7-8, 16S
395 archaea/bacteria), below which variance fluctuated (Supplements; Fig. S7). PCA axis 2
396 featured an initial peak in the oxic zone (~1.2 at 1.25 cm), a decrease (-0.2 by 4.5 cm), and
397 then a peak to ~2 by 6.5 cm coincident with fluctuations in multiple sequenced microbial
398 indicators, below which variance fluctuated to the base.

399

400 Discussion

401

402 We examine evidence for changes in OM reactivity with depth below the seafloor across the
403 redox succession and assess the influence of changes in sedimentology on the reactivity of
404 OM, to provide new insight on the coupling between geochemical and microbiological
405 processes in Arctic shelf sea carbon cycling.

406

407 There are clear changes in bulk parameters (~10 cm) as well as biomarker distributions (~4.5
408 cm) in the uppermost part of the core (Fig. 1 & 2), with coincident declines in aerobic
409 microbiological proxies (Fig. 3). Changes closest to the SWI are consistent with extensive
410 transformations of OM in the aerobic and bioturbated sediment layer [10, 63, 64]. Below the
411 aerobic zone, the most reactive OM has been largely consumed with clear deeper
412 succession of microbes indicative of a transition to anoxia. This is evidenced by microbes
413 capable of iron, manganese and nitrite dependent methane oxidation (~4.5 - 10.5 cm),
414 transitioning at greater depth to sulfate reduction in these deeper sediments (~10.5-33 cm)
415 where OM is less reactive (Fig. 3). Despite bioturbation levels being consistent with regional
416 [65] and local [50] studies (i.e. maximal depth of faunal mixing ~4.3 cm), these results
417 provide clear evidence of distinct successional redox zones transitioning with depth and
418 associated stratification of microbial community composition [15] coupled to the diagenesis
419 of reactive carbon, but at a reduced capacity.

420

421 i) Organic matter transformation and diagenesis below the SWI

422

423 As well as the decrease in bulk TOC and N in the uppermost ~10 cm, changes inferred by
424 molecular organic geochemical parameters indicate a rapid decrease in the reactivity of OM

425 (Fig. 2). The most pronounced changes (top ~4.5 cm) are coincident with the extent of
426 bioturbation [50]. A marked decrease in the ratio of β -sitosterol/stigmastanol can be
427 explained by the mechanism of hydrogenation [66] and decreases in the ratio of
428 stigmasterol/stigmastanol by reduction reactions [67]. Such reactions are also observed in
429 the transformation and diagenesis of all sterols [68]. Although some sterols, such as β -
430 sitosterol and stigmasterol, can be of a terrestrial plant origin [69], in this location in
431 sediments with a mixed but mainly marine signature [31] sterols could also have a marine
432 origin [70]. The CPI index for *n*-alkanes also shows a marked decline in the uppermost
433 sediments, which reflects OM diagenesis as the more abundant odd chain lengths degrade
434 [71]. This is mirrored by declines from the uppermost sample in *n*-alkanoic acid CPI_{T} index
435 (where the more abundant even compounds degrade) [35] and pronounced decreases in
436 the concentration of these compounds. Although changes in the mixing or delivery of
437 terrestrial OM can result in changes in CPI [72], the low values in these sediments suggest a
438 mixed, but primarily marine signature.

439
440 Coincident with CPI decreases, OEP for *n*-alkanes in the range C_{17} - C_{21} and C_{21} - C_{25} also decline,
441 with marked changes between the sample at the SWI (~ 0.5 cm) and deeper sediment layers
442 [37]. With decreases in OEP, OM rapidly becomes degraded and less bioavailable, a process
443 which is most pronounced close to the SWI. Similarly, for the more labile *n*-alkanols,
444 changes in the ratio of autochthonous to allochthonous-derived compounds [38] in the
445 uppermost layer indicate active processing of compounds in the organic rich layer. A reverse
446 trend in the *n*-alkanol TAR ratio probably can be explained to ~4.5 cm by dilution by more
447 abundant short chain compounds close to the SWI, which are also less resistant to
448 degradation than longer chain compounds [73]. However, increases to the TAR *n*-alkanol
449 values to ~5 at ~9.5 cm could point to past deposition of OM, which appears to be reflected
450 by increases in CPI_{T} for *n*-alkanoic acids and the ratio of cholesterol/brassicasterol. The pulse
451 in TAR for *n*-alkanoic acids at ~1.75 cm suggests delivery of terrestrial material is unlikely to
452 have been consistent and likely varied over time. Overall, the changes close to the SWI
453 reflect the early diagenesis of lipid biomarkers observed in the oxic layer of ocean sediments
454 [13] and are coincident with observed bioturbation zone [50], while also highlight an
455 underlying terrestrial influence [29, 74].

456
457 Loss of TOC with depth (Fig. 1) is markedly more pronounced in the oxic layer compared
458 with the anoxic sediments (indicated by the relative abundance of *Desulfobacteraceae*, in
459 sequence libraries Fig. 3). For instance, TOC declines from a peak of ~1.8% close to the top

460 of the core at ~2.5 cm to ~1.3% by 10.5 cm at the base of the oxic zone, prior to the
461 transitional zone indicated by *Desulfobacteraceae* (Fig. 3). Based on extrapolating the age
462 estimation, this corresponds to a loss, given dating approximations of 3.8×10^{-4} % TOC per
463 year. In marked contrast, in the established zone of anoxia from ~13.5 cm to the base, TOC
464 declines from ~1.5 to ~1.3 over a longer time period corresponding to a loss of 8.4×10^{-5} %
465 TOC per year. Although this estimation does not resolve changes in sedimentation rate and
466 is based only on a basal age, the difference in relative TOC loss with depth corroborates
467 changes in molecular proxies (*n*-alkanes, *n*-alkanols, sterols) which provides evidence that
468 OM reactivity is greatest in the uppermost layer. Future changes in the relative position of
469 the oxic/anoxic interface could lead to changes in carbon cycling driven by reactivity at the
470 seafloor.

471
472 Both organic geochemistry (CPI *n*-alkanes, TOC, N, $\delta^{15}\text{N}$) and measured/modeled porewater
473 O_2 in the uppermost layers are statistically correlated with declines in the proportion of the
474 BD7-8 marine group (Fig. 3; Supplements Fig. S2 & 3), attributed to bacterial diversity in oxic
475 marine sedimentary environments [54] and previously detected in surface sediments of the
476 South Atlantic Ocean [75] and the western Arctic Ocean [76]. Although more variable, 16S
477 rRNA data show that bacteria and archaea are also only present in abundance in the
478 uppermost 0-9.5 cm mixed layer (Fig. 3). Bacterial and archaeal richness and abundance is
479 known to decrease exponentially with depth [77, 78] and links between organic degradation
480 and microbial activity are particularly pronounced close to the SWI [79]. Similarly, the
481 highest consistent levels of *Nitrosopumilaceae* (capable of ammonia oxidation to nitrite [80])
482 are in the uppermost sediments, correlating with lower TOC:N ratios and higher $\delta^{15}\text{N}$
483 indicative of microbial activity (Supplements Fig. S4). Here, ammonia oxidising archaea
484 utilise ammonia likely generated through OM mineralisation in the sediments below which
485 diffuse up to the bioturbated, oxic zone. The ratio of C_{15} anteiso/ C_{16} FAMES is corroborated
486 by extensive microbial activity just below the sediment-surface interface (Fig. 2), with this
487 compound often linked to bacterial activity as they are major constituents of bacterial
488 membrane lipids [81] and have been detected in aquatic environments [82] including ocean
489 sediments [83]. Peaks in the ratio of cholesterol/brassicasterol and cholesterol/ β -sitosterol
490 within the zone of bioturbation at ~2.5 cm have a similar explanation as cholesterol is a key
491 component of bacterial membrane lipids [84]. Decreases in bulk $\delta^{15}\text{N}$ (Fig. 1) are probably
492 explained by preferential degradation of compounds such as proteins rich in ^{15}N , deposited

493 at the SWI and subsequently degraded [64, 85], potentially sourced from under ice algal
494 blooms.

495

496 **ii) Stratification of microbes and geochemistry across the oxic to anoxic interface**

497

498 Further changes linked to the processing of OM take place below the aerobic, bioturbated
499 zone. In the aerobic to anaerobic transition zone peaks in the relative abundance of
500 bacterial taxa *Desulfuromonadales* and *Shewanellaceae* from ~6.5 cm downwards indicate
501 that Fe³⁺ and Mn⁴⁺ reduction is taking place (Fig. 3) [86]. These taxa can utilise (reduce
502 through dissolution) metals such as Fe³⁺ and Mn⁴⁺ oxides as terminal electron acceptors.
503 *Shewanella spp.* are adapted to chemically stratified redox transitions [58]. Sediment Mn
504 concentrations also increase coincident with the two major peaks in *Desulfuromonadales* in
505 the oxic zone, suggesting that taxa capable of metal reduction are important close to the
506 redox transition (Fig. 3). Seasonal or decadal oscillations in the delivery of OM causing the
507 position of the redox boundary to fluctuate could be a process here, potentially explaining
508 the position of Mn at the upper part of the redox boundary based on kinetics of oxidation
509 and reduction [87]. The oxic to anoxic redox transition is most clearly illustrated by the
510 marked increase of *Desulfobacteraceae* from ~10.5 cm downwards which are known sulfate
511 reducers [88] and correlates with modeled sulfate reduction (Fig. 3; Supplements Fig. S6).
512 Sulfate reducing taxa are known to persist below the oxic layer, typically also below the
513 oxidants NO₃⁻, Fe³⁺ and Mn⁴⁺, where they are involved in the remineralisation of organic
514 carbon [89].

515

516 Coincident with the increase in sulfate-reducing taxa at and below the oxic-anoxic transition,
517 the abundance of methane oxidizing taxa evidenced by bacteria in the group
518 *Methylomirabilaceae* peaked markedly (Fig. 3). Based on amplicon library relative
519 abundance (15%) the *Methylomirabilis* are an important group in this sequence. This family
520 have been shown to participate in anaerobic methane oxidation linked to nitrate/nitrite
521 reduction (via the generation of molecular oxygen utilised by methane monooxygenase
522 (MMO)) [90]. *Methylomirabilis* have been previously detected in ocean sediments [91], sub-
523 Arctic lake sediments [92] and are abundant in methane rich environments such as paddy
524 fields [93]. On balance, the coincidence of this group with sequences related to the
525 *Brocardiales*, which are implicated in anammox (ammonia oxidation linked to nitrate/nitrite
526 reduction [61]), may suggest involvement in ammonia oxidation. Genomic studies have
527 suggested the potential for the oxidation of ammonia by *Methylomirabilis* by use of their

528 oxygen dependent MMO [90] rather than by the annamox pathway involving hydrazine
529 production [61]. Increases in TOC:N ratio in the anoxic sediments and transition zone (Fig.
530 3) are probably explained in this system by microbial activity utilising more N, where this is
531 limited and more labile than C, producing OM with TOC:N ratios ~10 which gradually dilutes
532 the lower TOC:N ratio of phytoplankton derived matter, characteristic of the uppermost
533 layer. Additionally, if *Methylomirabilis* is acting as an ammonia oxidiser it likely produces N₂
534 as an inert gas, likely resulting in the gradual loss of solid phase N down the core evidenced
535 by increases in TOC:N ratios in the anoxic sediments. Many of these bacterial taxa have the
536 potential to be involved in multiple processes at this key transition, but denitrification (Fig.
537 3) also appears to be particularly important at this key transition with associations between
538 *Methylomirabilis*, *Brocardiales*, *Desulfuromonadales* and *Shewanellaceae* and modeled
539 denitrification [29] (Supplements; Fig. S5).

540

541 **iii) How does the reactivity of OM delivered to and preserved within sediments**
542 **change across differences in sedimentology?**

543

544 Fine particulates (silty clays) are abundant close to the SWI (Fig. 1), together with biomarkers
545 which infer more reactive OM such as high CPI and OEP_(17-21 & 21-25) for *n*-alkanes, high ratios
546 of stigmaterol/stigmastanol and β -sitosterol/stigmastanol, plus high total alkanolic acids
547 (Fig. 2). Close to the SWI the weaker bonds of more reactive organic components may
548 continue to be attached and the fine particulate (clay-like) minerals may help, in part
549 entrain, enmesh or adsorb organics in a mineral matrix [94]. The coarser fraction
550 immediately beneath from ~0.75 until 2.5 cm could be associated with bioturbation sorting
551 and be a particle capture layer [95], immediately below the most intensive reworking zone.
552 Finer particles from ~2.5 to 5.5 cm remain within the maximum bioturbation zone, with
553 these size classes potentially supporting capture of microbially influenced biomarkers (e.g.
554 pulses of C₁₅ anteiso:16:0 FAMES and cholesterol:brassicasterol ratios, Fig. 2) when evidence
555 of microbial activity (e.g. 16s RNA archaea, Fig. 3) is high.

556

557 The transition to finer particulates peaking at ~14.5 cm, which is accompanied by increases
558 in Fe and P (Fig. 1) could be a sediment deposition event similar to scenarios across the
559 Barents Sea. Although the specific underlying mechanism driving this potential deposition
560 cannot be disentangled from this evidence, possibilities include regional transport from land
561 [96], cross-shelf transport [97] or accumulations linked to seasonal redox oscillations [87].

562 We might expect organic biomarker evidence of either source (e.g. terrestrial input) or
563 reactivity changes to be coeval with this change in sedimentology, but there is little
564 evidence of response at similar magnitudes to OM transformations at the SWI. Slight
565 fluctuations in *n*-alkane CPI at ~17.5 cm and OEP₁₇₋₂₁ at ~15.5 cm (Fig. 2) could indicate
566 slightly more reactive organics is being preserved in finer particulates, but the response is
567 minor and offset slightly from changes in grain size. Since the change in sedimentology
568 does not have a clear link with reactivity of OM evidenced by bulk parameters (TOC, N,
569 TOC:N ratio) or biomarker distributions (*n*-alkanes, *n*-alkanols or sterol ratios) then this
570 suggests the change in sedimentology was either not accompanied by significant organic
571 material, or processes at the SWI have removed any noticeable geochemical signatures.
572 Previous studies suggest the material released from ice sheets and glaciers are sources of
573 quickly processed highly reactive OM [98, 99]. Potential reactive material, which may have
574 been brought into the system during past disturbances or reworking may have been
575 subsequently degraded, and does not continue to exert a major impact on OM cycling
576 (evidenced by extractable lipid fractions), except by potentially supporting in part, microbial
577 taxa capable of using metals for respiration (*Shewanellaceae* and *Desulfuromonadales*, Fig. 3).
578 The Mn and Fe changes in sedimentology (Mn peak is shallower) may be offset due to
579 different kinetics of oxidation and reduction between oxides of these compounds [87] and
580 these microbes may also be sensitive to porewater diffusion of metals.

581

582 **iv) The role of coupled microbial and geochemical studies for understanding carbon**
583 **cycling in Arctic shelf systems**

584

585 Clear separation between indicators of OM reactivity, microbial communities at the redox
586 interface and indicators of sulfate reduction processes in the PCA biplot (Fig. 4), which vary
587 across the redox profile (Supplements; Figure S7), highlights the coupled relationships
588 between a multiplicity of complementary but competing processes which stratify according
589 to depth. This clear separation supports close relationships between geochemical variables
590 (e.g. CPI *n*-alkanes, $\delta^{15}\text{N}$, %N, %TOC) and O₂, beneath which across the oxic to anoxic
591 transition microbes involved in multiple processes stratify (denitrification, nitrite production
592 and iron/manganese reduction etc.), prior to evidence of sulfate reduction below the
593 transition to depth (Supplements; Fig. S2 - 6).

594

595 This detailed geochemistry and microbiology study provides a coupled framework with
596 wider sedimentary processes including porewater geochemistry (from reactive transport

597 modelling and measured O₂ [29]) and bioturbation [50], consistent with expectations for a
598 continental shelf system [100]. The extent of successional redox associated processes
599 controlling the cycling of carbon in sediments at and below the SWI is coupled closely to
600 the environmental setting (Barents Sea continental shelf) and is likely to be sensitive to
601 future changes, especially those driven by atmospheric and oceanic warming. The trends in
602 OM transformations and redox succession observed at B15 are likely to be typical of shelf
603 environments with similar water depth, sediment type, overlying water masses and levels of
604 primary production and carbon export. Specifically, although this study focuses on one
605 station (B15) it is possible to suggest, broadly that this station may be representative of
606 wider regional processes. In terms of surface sediment particle size in the Barents Sea, this
607 station is consistent with locations in a southerly direction south (to ~ 75 °N) [101] and so
608 profiles may be similar across a wider part of the continental shelf. If upscaled, this study
609 would demonstrate there is a key pool of reactive OM dependent on microbial control,
610 making up part of the more reactive carbon burial component which could be lost from this
611 key store if the redox interface was shallower. This scenario is possible as changes in OM
612 supply are likely to adjust with future changes in ocean stratification and sea-ice retreat [25].

613
614 Future studies should follow a similar approach to assess how the depth and extent of redox
615 sensitive successional processes might be affected by geographical position across Arctic
616 continental shelves (e.g. Chukchi Sea, Bering Sea, East Siberian Sea, Laptev Sea).
617 Comparisons of profiles will be particularly insightful to help understand how changes to the
618 Arctic including sea ice losses and associated changes in water column vertical mixing [25,
619 102] are influencing ocean primary productivity in the Arctic [5], which is tightly coupled to
620 carbon fluxes reaching the seafloor [9]. Such studies will assess the stability and
621 bioavailability of carbon sequestered as organic carbon burial is the principal mechanism for
622 long-term carbon sequestration [7, 8], which ultimately becomes part of the permanent
623 geological record [9].

624 625 **Conclusions**

626
627 Our study demonstrates mechanistic links between microbial processing and changes in
628 organic and inorganic parameters across the oxic to anoxic interface are distinct, but
629 interactive and tightly coupled to biological mixing and the reactivity of OM. Specifically we
630 found:

- 631 i) Distinct links between aerobic processes, reactive carbon and highest abundances
632 of bacteria and archaea in the uppermost layer (0-4.5 cm), coincident with the
633 extent of biological mixing and changes in the reactivity of OM (indicated by *n*-
634 alkanes, *n*-alkanols, *n*-alkanoic acids and sterols).
- 635 ii) A dominance of microbes involved in nitrate/nitrite and iron/manganese
636 reduction across the oxic-anoxic redox boundary (~4.5-10.5 cm), with convincing
637 denitrification relationships confirming this key intermediate zone.
- 638 iii) Sulfate reducers dominate in deeper anoxic sediments which is consistent with
639 OM transformations and biological reworking, but that deeper changes in
640 sedimentology have only minor effects on the reactivity of organic carbon
641 (compared with at the SWI), probably due to past processing.

642

643 Future research should compare coupled geochemistry-microbial profiles between ice-
644 covered and ice-free zones of the Arctic to elucidate linkages between ice cover and
645 microbial processing of OM at the seafloor. This is especially pertinent and should be
646 coupled with estimates of carbon burial in different locations across the Barents Sea, given
647 the trend for increasing oceanographic changes in this region [25].

648

649

650 Additional Information

651

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660

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665

666 Data Accessibility

667 Data used in this study is available in the supplements.

668

669 **Competing Interests**

670 *We have no competing interests*

671

672 **Authors' Contributions**

673 M.A.S. wrote the manuscript initial draft, conducted fieldwork/sampling, compiled datasets
674 and carried out bulk and organic geochemical analyses. J.C.F. provided inorganic XRF data,
675 conducted fieldwork/sampling, contributed ideas on sedimentology and to the initial
676 manuscript. L.L.A. carried out microbiological analyses. F.S.F. advised on suitable organic
677 geochemical techniques and provided insight into OM reactivity. N.D.G. designed
678 microbiological approach and contributed key ideas on redox stratification to initial
679 manuscript. K.T. carried out quantitative 16S rRNA analyses and co-designed microbiological
680 approach. K.R.H project managed ¹⁴C radiocarbon analyses. R.G.H carried out $\delta^{15}\text{N}$ analyses
681 with M.A.S. and advised on geochemical sampling strategy. S.F.H. & A.T. carried out
682 fieldwork & porewater nutrient analysis which underpins model comparison. P.L. carried out
683 bioinformatics and constructed sequencing pipeline. S.P. carried out ¹⁴C analyses on
684 foraminifera. A.F. carried out grain size analysis. C.M. conducted fieldwork/sampling, advised
685 on sedimentology and project managed inorganic geochemical aspects. G.D.A. contributed
686 early ideas, revised the initial manuscript and project managed organic geochemical aspects.
687 All authors commented on the manuscript and approved the final submission.
688

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Figure and table captions

Figures

Figure 1: Bulk organic, inorganic and grain size data against depth (cm) to highlight changes taking place below the sediment-water interface with age estimation at 27.5 cm depth for radiocarbon (^{14}C -AMS) on planktonic and benthic foraminifera. Bulk organic parameters include: total organic carbon (TOC), total nitrogen (N), TOC:N ratio and nitrogen stable isotopes ($\delta^{15}\text{N}$). Bulk inorganic parameters include iron (Fe), phosphorus (P) and Manganese (Mn). Grain size is plotted on a % cumulative basis, categorised in six size fractions (<2 μm , 2-63 μm , 63-128 μm , 128-250 μm , 250-500 μm , 500 - 2000 μm).

Figure 2: Organic geochemical parameters plotted against depth (cm) with $f\text{-SPL}_{\text{mean}}$ (0.5 cm, average of three replicates) and $f\text{-SPL}_{\text{Lmax}}$ (4.3 cm, greatest of three replicates) bioturbation depths indicated, together with bioturbation activity (insert provides detail 0-4.5 cm) [50]. For *n*-alkanoic acids parameters include total FAMES (fatty acid methyl esters), ratio of the C_{15} anteiso/ C_{16} FAME, terrigenous to aquatic fatty acid ratio (TAR_{FA}) [34] and total carbon preference index (CPI_{T}) [35]. For sterols parameters include cholesterol/brassicasterol, cholesterol/ β -sitosterol, stigmasterol/stigmastanol and β -sitosterol/stigmastanol. For *n*-alkanes parameters include carbon preference index (CPI) [36] and odd over even predominance for *n*- C_{17-21} & *n*- C_{21-25} (OEP_{17-21} & OEP_{21-25}) [37]. For *n*-alkanols parameters include terrestrial to aquatic ratio (TAR) and Aut/All (autochthonous/allochthonous) ratio [38].

Figure 3: Microbial parameters plotted against depth (cm) with mean and maximum bioturbation depths indicated, bioturbation activity (insert provides detail 0-4.5 cm) [50], coincident pore-water oxygen transition [29] and modeled relative contribution of metabolic pathway to OM heterotrophic degradation [29]. Microbial parameters include 16s RNA bacteria, 16s RNA archaea, *Nitrosopumilaceae*, *Shewanellaceae*, *Desulfuromonadales*, *Methylomirabilaceae*, and *Desulfobacteraceae*. Modeled data include relative aerobic respiration, denitrification, iron reduction, sulfate reduction and manganese reduction [29].

Figure 4: Principal components analysis (PCA) of bulk organic, inorganic, organic geochemical, geomicrobiological and modeled processes [29] based on \log^{10} transformed and centred datasets. Samples within the uppermost oxic and bioturbated layer [50] to ~4.5 cm depth are indicated by blue circles with deeper layers indicated by red circles.

Supplements

Supplementary Table S1 – Summary of analyses and purpose for cores from B15.

Supplementary Figures S1 – S7 – Map of study location in the Barents Sea, correlations between key geochemical, modeled and measured datasets. PCA axis 1 & 2 scores plotted against depth.

Supplementary information datasets – Datasets utilised within this study.







