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

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Process-based, mechanistic investigations of organic matter transformation and diagenesis directly beneath the sediment–water interface (SWI) 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 modelled) 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 iron/manganese reduction across the oxic-anoxic redox boundary (approx. 4.5–10.5 cm depth). Sulfate reducers dominate in the deeper (approx. 10.5–33 cm) anoxic sediments which is consistent with the modelled reactive transport framework. Importantly, organic matter reactivity as tracked by organic geochemical parameters (*n*-alkanes, *n*-alkanoic acids, *n*-alkanols and sterols) changes most dramatically at and directly below the SWI together with sedimentology and biological activity but remained relatively unchanged across deeper changes in sedimentology.

This article is part of the theme issue ‘The changing Arctic Ocean: consequences for biological communities, biogeochemical processes and ecosystem functioning’.

1. Introduction

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

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

OM deposited at the seafloor undergoes intensive diagenetic transformation, with up to approximately 99% degraded at the sediment–water interface (SWI), escaping long-term burial [10]. At the SWI, the extent of transformation of OM results from the complex interactions between OM composition and its stability to processing (e.g. redox conditions, microbial community structure, mineralogy [11,12]). Consequently, such interactions result in distinct OM reactivity changes during burial and differences in the rates of early diagenesis between autochthonous (typically more reactive) and allochthonous sources (typically less reactive [13]). OM which ‘survives’ the uppermost sediment layer is subject to further microbial activity where polymer hydrolysis, iron and manganese reduction, denitrification, nitrate dissimilation, sulfate reduction and methanogenesis take place. Microbes indicative of these processes inhabit often clearly stratified communities [14–16]. As OM is gradually broken down, only the least reactive OM is left behind [17]. Redox processes, whereby sediments transition from oxic to anoxic conditions, are an additional control on OM reactivity as anaerobes inhabiting oxygen-free

environments are limited in their ability to hydrolyse more structurally complex compounds [10]. Simultaneously, bioturbating animals which burrow into and physically mix sediments help control the thickness of the oxic layer, regulating the amount and quality of organic carbon accumulated [18].

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

Although previous studies have combined microbiological and geochemical measurements in Arctic continental shelf settings, they tend to focus on surface sediment transects [26], down-core at low-resolution in deeper sediments [15,16,27,28], or were limited by sequencing libraries and study location [14], and so unable to show so clearly the depth-successional redox transition close to the SWI. By using these techniques in tandem, it is possible to fully explore the microbiological and geochemical basis underpinning diagenetic models [29] highlighting the complexity of these processes and enabling quantification.

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

2. Methods

(a) Study sites and sampling

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

(b) Bulk organic geochemistry

Total organic carbon (TOC) was analysed on freeze-dried acidified sediments (HCl; 4 M; 4 h), dried overnight (60°C) and analysed with a CS230 Carbon/Sulfur Determinator (Leco

Corporation, Michigan, USA) using porous crucibles. The TOC content is expressed as the weight percentage of dried sediment (wt. %). Nitrogen measurements were made using a Vario MAX CNS analyser (Elementar, Langensfeld, Germany). TOC:N ratios were not corrected for the molar weight of C and N. Stable nitrogen isotope measurements ($\delta^{15}\text{N}$) were performed using an ECS 4010 Elemental Analyser (Costech Analytical Technologies Inc., Valencia, CA) coupled to a Delta V Advantage (Thermo Finnigan, Hemel Hempstead, UK) isotope ratio mass spectrometer and are reported in (δ) notation in per mille (‰) relative to atmospheric N_2 (AIR). Sample precision was less than 0.2‰.

(c) Grain size analysis

Bulk sediment samples were disaggregated in an ultrasonic bath (15 min) and analysed on a Mastersizer 2000E (Malvern Panalytical, Malvern, UK) laser diffractometer for particles of a diameter range 0.1–1000 μm at the University of Leeds. Results were categorized into six size fractions and are presented as cumulative volume percentages.

(d) Molecular organic geochemistry

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

Samples were injected (1 μl) into a 7890B gas chromatograph (GC) coupled to a 5977B MSD mass spectrometer (MS) (Agilent, Santa Clara, CA, USA) operated in full scan mode (70 eV; source temp 230°C; helium flow rate 1 ml min^{-1}). A 60 m HP1 ms fused silica capillary column (J&W Scientific, Folsom, CA, USA) was used for GC separation (0.25 mm $\times$ 0.25 μm) with an oven temperature of 6°C/min to 170°C; hold of 1 min, followed by a slower ramp of 2.5°C/min to 315°C and a hold of 22 min. Compounds were identified from their respective mass spectra and retention times, with quantities calculated relative to the peak area of the internal standard 5 α -androstane and an assumption of a 1:1 response.

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 were carbon preference index (CPI) [36] and odd over even predominance for *n*- C_{17-21} and *n*- C_{21-25} (OEP_{17-21} and $21-25$ [37]). Terrestrial to aquatic ratio (TAR) and Aut/All (autochthonous/allochthonous) ratio was selected for *n*-alkanols [38]. Error displayed is the standard deviation of a sample analysed in triplicate.

(e) Inorganic geochemistry

X-ray fluorescence (XRF) was performed on freeze dried and gently grinded sediment samples (700 mg) from B15 E146, mixed with di-lithiumtetraborate (4200 mg, $\text{Li}_2\text{B}_4\text{O}_7$, Spectromelt A10), pre-oxidized at 500°C with 1.0 g NH_4NO_3 (p.a.) and fused to homogenous glass beads. Samples were analysed using a PW-2400 WD-XRF Scanner (Philips, The Netherlands) calibrated with geostandards at the University of Oldenburg with Fe, P and Mn used in this study. Analytical precision and accuracy was less than 5%.

(f) Microbiology

Genomic DNA was extracted using the DNeasy® PowerSoil® kit (QIAGEN, Hilden, Germany). Concentration and viability were tested using Qubit™ (Thermo Fisher Scientific, Waltham, Massachusetts, USA) and polymerase chain reaction (PCR), respectively, prior to sequencing. High-throughput DNA sequencing was performed by the NUomics sequencing service at Northumbria University (UK). 16S rRNA gene libraries were prepared following protocol [39], in which each fragment was composed by an Illumina adapter, followed by an index sequence (only for forward primer), a 10-nt pad to avoid formation of hairpin structures, linkers and the V4 region specific either forward or the reverse primer. Primers used were 4515F (GTGYCAGCMGCCGCGGTAA) and 806R (GGACTACHVGGGTWTCTAAT) as per the Earth Microbiome Project protocol [40]. Sequencing was performed on the MiSeq Personal Sequencer (Illumina, San Diego, CA, USA) using the V2 500 reagent kit. Demultiplexed paired end FASTQ files were analysed using QIIME2 [41] using a pipeline (<https://github.com/peterleary/markergene>). Amplicon sequence variants were generated in QIIME2 using DADA2 [42] and taxonomy was classified using the SILVA 132 reference database [43]. Taxonomic abundance data is expressed as percentage abundance (%) enumerated from fractional abundances in sample libraries.

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

(g) Complementary measurements and datasets

To provide constraint on the long-term sedimentation rates at the study site (and provide a temporal framework to interpret the results) radiocarbon measurements (^{14}C -AMS) were carried out on mixed foraminifera picked from samples at 27.5 cm depth, near the base of the core. Sediment was dried, disaggregated, filtered and sieved (greater than $125\ \mu\text{m}$). Light microscopy was used to pick and sort benthic and planktonic foraminifera tests for the Mini Carbonate Dating System (MICADAS) (Ionplus, Dietikon, Switzerland) at the University of Bristol. Measurements of ^{14}C were performed on both samples without graphitization, but with an acidification step, followed by analysis in the presence of a gas-ion source [47]. Bayesian calibration was carried out in MATLAB [48]. Acknowledging the challenges that would be encountered by developing a sediment mass accumulation rate (MAR) on the basis of a single point and its likely difference compared with a recent radionucleotide approach [49]; instead here we calculate percentage yr^{-1} TOC loss based on the youngest basal age to provide an estimation and comparison of reactivity between oxic and anoxic parts of the core.

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

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

Modelled estimations of the relative contribution of metabolic pathways (aerobic respiration ($\text{O}_2 - \text{M}$), denitrification ($\text{NO}_3 - \text{M}$), iron reduction ($\text{Fe}(\text{OH})_3 - \text{M}$), sulfate reduction ($\text{SO}_4 - \text{M}$) and manganese reduction ($\text{MnO}_2 - \text{M}$) to based on reactive transport modelling are from Freitas *et al.* [29] and are also presented against changes in microbial parameters (figure 3). We additionally include model-derived oxygen concentration depth profiles (electronic supplementary material, figures S2 and S3; [29]).

(h) Statistical analysis

Data were explored for correlations between bulk variables, organic geochemistry, geomicrobiology, porewater oxygen and modelled metabolic pathway processes, with statistically significant relationships (using Pearson's correlation) listed in electronic supplementary material, figure S2–S6. Modelled datasets were resampled in Matlab (v. R2019a) to the same depth intervals using spline interpolation. Principal components analysis (PCA) was conducted due to short DCA gradient lengths (less than 2) in Canoco v. 4.51 [53] on $\log_{10}$ transformed and centred data, with samples highlighted in blue for proximity to the maximal extent of faunal reworking (figure 4). Microbial taxa (defined by presence, absence and abundance), geochemical concentrations and modelled percentage contribution of metabolic pathways to OM heterotrophic degradation were included in the PCA table to create dissimilarity distances and eigenvalues of the samples, with the two largest PCs plotted and superimposed over samples.

3. Results

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

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

Profiles of total Fe and P concentrations displayed similar trends but with different magnitudes and were stable (5.1–5.6% and 0.16–0.17%, respectively) from the SWI to approximately 9.5 cm, below this depth, Fe and P increases to a maximum of 8.4% Fe and 0.3% P at a clear peak by approximately 14.5 cm (figure 1). Below this peak Fe and P sharply declined to minimum values by approximately 16.5 cm with Fe ranging from 4.3% to 5.0% and P ranging from 0.11% to 0.13% to the bottom of the core. Total Mn was highest in the upper part of the core, peaking at approximately 4.5 cm at 1.02% and again at 8.5 cm to 0.96%, followed by a decline to low concentrations by approximately 10.5 cm which remained low to the base of the core.

Grain size was dominated by clay and silt from the top of the core (cumulative less than $63\text{ }\mu\text{m}$ fraction approximately 78%) to approximately 0.75 cm where coarser particles greater than $63\text{ }\mu\text{m}$ (mainly fine sands) accounted for approximately 82% of the fraction until approximately 2.5 cm where finer particulates again dominated (less than $63\text{ }\mu\text{m}$ fraction greater than 89%) (figure 1). Finer silts then decreased to less than 16% (less than $63\text{ }\mu\text{m}$ fraction) by 5.5 cm, with a marked increase at approximately 14.5 cm to approximately 53% coincident with Fe and P peaks. By approximately 19.5 cm finer silts returned to previous levels less than 16% (less than $63\text{ }\mu\text{m}$

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, categorized in six size fractions (less than 2 μm , 2–63 μm , 63–128 μm , 128–250 μm , 250–500 μm and 500–2000 μm).

fraction), before a gradual rise from approximately 24 cm, peaking at approximately 90% from approximately 30.5 cm to the base of the core.

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

The ratio of cholesterol/brassicasterol was low at the top of the core (less than 1.3), increasing to approximately 3 (2.5 cm) within the zone of bioturbation, before decreasing to less than 1.8 by approximately 3.5 cm, with a further peak to approximately 2.4 at approximately 9.5 cm (figure 1). Similarly, cholesterol/ β -sitosterol also peaked at approximately 2.5 cm depth (to greater than 4), prior to a general decrease to the base of the core (less than 1.3). By contrast, stigmasterol/stigmastanol declined from a maximum of 1.0 at the top of the core to 0.2 at approximately 9.5 cm, followed by fluctuations between 0.1 and 0.4 to the base. Similarly, the ratio of sterols β -sitosterol/stigmastanol declined rapidly from a peak of 4.2 at the top of the core to approximately 1.2 by approximately 9.5 cm, remaining stable to the base of the core (1.4 to 0.9). The CPI ratio for *n*-alkanes declined from a maximum of 2.5 at the top of the core to 1.7 at a depth of approximately 9.5 cm below the seafloor. With further increase in burial depth to approximately 17.5 cm, there was a subsequent smaller increase in CPI with values for deeper horizons below this ranging from 1.9 to 1.7. The OEP for *n*-alkanes from C_{21} to C_{25} ranged from a maximum of 1.6 at the top of the core to a minimum of 1.1 by approximately 3.5 cm, with values below this fluctuating between 1.1 and 1.2. OEP for *n*-alkanes C_{21-25} were especially prominent in the uppermost sample (approx. 1.6) coincident with mean bioturbation, with all values below this less than 1.3. The TAR index for *n*-alkanes increased from a maximum of approximately 1 at the top of the core to greater than 4 at approximately 9.5 cm, prior to fluctuations between approximately 2 and approximately 3.3 to the base. The autochthonous/allochthonous ratio for *n*-alkanols also showed a decline in the uppermost layer from a maximum of 0.9 at the top of the core to a minimum of 0.4 by approximately 9.5 cm.

The 16S rRNA gene counts representative of bacterial and archaeal cell numbers fluctuated but were present in abundance from the SWI down to approximately 11.5 cm, below which abundances were orders of magnitude lower (figure 3). For bacterial 16S rRNA genes above 11.5 cm, the mean was 3.32×10^7 copies g^{-1} wet sediment, declining markedly to 9.23×10^5 copies g^{-1} wet sediment below 11.5 cm, while for archaea the mean above 11.5 cm was 7.28×10^7 copies g^{-1} wet sediment declining to 2.31×10^6 copies g^{-1} wet sediment (figure 3). The greatest peaks in bacterial and archaeal 16S rRNA genes were within the uppermost approximately 4.5 cm coincident with most intense bioturbation. The progressive decline in these numbers could either be attributable to the balance between depositional inputs at the surface and subsequent death and cell lysis with sedimentation, or may relate to *in situ* growth. Based on 16S rRNA gene sequence analysis, these depth-related declines in absolute abundances were accompanied by distinctive successional changes in the relative abundances of some dominant archaeal and bacterial taxa indicative of a depth-related transition from aerobic to anaerobic

Figure 2. Organic geochemical parameters plotted against depth (cm) with f^{SPIL}_{L-mean} (0.5 cm, average of three replicates) and f^{SPIL}_{L-max} (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 C₁₅ anteiso/C₁₆ 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, stigmastanol/stigmastanol and β-sitosterol/stigmastanol. For n -alkanes, parameters include carbon preference index (CPI) [36] and odd over even predominance for n -C_{27–21} and n -C_{21–25} (OEP_{17–21} and 21–25) [37]. For n -alkanols, parameters include terrestrial to aquatic ratio (TAR) and Aut/All (autochthonous/allochthonous) ratio [38].

microbial processes, linked to bioturbation depth. For instance, 16S rRNA gene sequences related to the BD7–8 marine group [54] declined sharply from a maximum of 2.36% of sequences in the amplicon library at the top of the core to 0% by approximately 5.5 cm, with only minor occurrences in amplicon libraries from depths below this (figure 3). Group BD7–8 is considered cosmopolitan in marine benthic habitats and are putative aerobic and nitrate reducing mixotrophs [55,56]. Declines in group BD7–8 were coincident with both decreases in measured ($R = 0.97$, $p < 0.01$) and modelled ($R = 0.94$, $p < 0.01$) O₂ concentration depth profiles (electronic supplementary material, figure S2) and the zone of bioturbation (figure 3). Highlighting links between organic matter quality and aerobic processes, there were positive correlations between CPI for *n*-alkanes and both measured ($R = 0.81$, $p < 0.05$) and modelled ($R = 0.92$, $p < 0.01$) O₂ concentration depth profiles (electronic supplementary material figure S2). Similar positive correlations between modelled relative oxygen contribution, $\delta^{15}\text{N}$ ($R = 0.89$, $p < 0.01$), %N ($R = 0.93$, $p < 0.01$) and %TOC ($R = 0.86$, $p < 0.01$) were found, with similar but slightly weaker correlations between model-derived O₂ concentration depth profiles and $\delta^{15}\text{N}$ ($R = 0.83$, $p < 0.01$), %N ($R = 0.88$, $p < 0.01$) and %TOC ($R = 0.84$, $p < 0.01$) (electronic supplementary material, figure S3). Corroborative of the presence and depth-related consumption of molecular oxygen in the upper few cm (above approximately 9.5 cm) of the sediment, sequences related to aerobic ammonia oxidizers from the family Nitrosopumilaceae [57] followed a general declining trend from the top of the core to the base, although their abundance varied (figure 3). Nitrosopumilaceae was negatively correlated with TOC:N ratio ($R = 0.62$, $p < 0.01$) and positively correlated with $\delta^{15}\text{N}$ ($R = 0.91$, $p < 0.01$) (electronic supplementary material, figure S4).

In contrast with these depth-related declines, sequences related to the putatively iron reducing Shewanellaceae family [58] which variably increased their abundance in amplicon libraries were persistent up to approximately 10.5 cm (figure 3). Similarly, sequences related to the Desulfuromonadales family (also putatively capable of iron reduction [59]) generally increased their relative abundances up to approximately 10.5 cm but with an additional peak at approximately 15.5 cm. Likewise, sequences related to the family Methyloirabillaceae (capable of methane oxidation coupled to nitrite reduction [60]) increased in abundance at the top of the core peaking at 14.1% of the amplicon library at 10.5 cm. In a similar region of the core, sequences of the Brocadiales group (involved in anammox by ammonia oxidation linked to nitrate/nitrite reduction [61]) were at highest sustained abundance between 5.5 and 10.5 cm (figure 3). All four of these groups had varying associations with modelled relative denitrification contribution. The strongest relationship was with Brocadiales ($R = 0.74$, $p < 0.01$), followed by Methyloirabillaceae ($R = 0.57$, $p < 0.01$), Shewanellaceae ($R = 0.53$, $p < 0.01$) and Desulfuromonadales ($R = 0.45$, $p < 0.01$) (electronic supplementary material, figure S5). In contrast with all of the other taxa detailed above, sequences related to the sulfate-reducing Desulfobacteraceae [62]) were largely absent above approximately 10.5 cm (figure 3). The presence of Desulfobacteraceae continued below this oxic-anoxic transition to the base of the core and was closely correlated with modelled relative sulfate reduction contribution ($R = 0.88$, $p < 0.01$) (electronic supplementary material, figure S6).

The PCA ordination biplot provides insight into co-associations between geochemical, geomicrobial, modelled relative metabolic pathways and bioturbation datasets (figure 4). For example, the assemblage to the right part of the biplot is closest in ordination space to the uppermost core samples in the oxic and bioturbated zone which includes modelled and measured O₂, Arctic marine cosmopolitan aerobic marine group BD7–8, measurements of bacterial and archaeal 16S rRNA gene abundance and Mn. All organic geochemical variables (sterols, *n*-alkanes, *n*-alkanols and *n*-alkanoic acids) and $\delta^{15}\text{N}$ appear to covary and are grouped at the lower right part of the biplot. By contrast, Desulfobacteraceae, SO₄ – M, Fe(OH)₃ – M, TOC:N and TOC are present towards the lower left part of the biplot. To the top left of the biplot, NO₃ – M and MnO₂ – M are grouped, with Brocadiales, Fe, P, Methyloirabillaceae, Desulfuromonadales, Nitrosopumilaceae and Shewanellaceae grouped towards the top of the right quadrant. PCA axis 1 decreased from a maximum of approximately 2 at the top of the core clearly to a minimum of approximately –0.5 by approximately 7.5 cm, highlighting changes initially in indicators

Figure 3. Microbial parameters plotted against depth (cm) with $f\text{-SPI}_{L\text{mean}}$ (0.5 cm, average of three replicates) and $f\text{-SPI}_{L\text{max}}$ (4.3 cm, greatest of three replicates) bioturbation depths indicated, together with 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].

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

sensitive to the oxic interface (e.g. organic geochemistry, BD7–8, 16S archaea/bacteria), below which variance fluctuated (electronic supplementary material, figure S7). PCA axis 2 featured an initial peak in the oxic zone (approx. 1.2 at 1.25 cm), a decrease (−0.2 by 4.5 cm) and then a peak to approximately 2 by 6.5 cm coincident with fluctuations in multiple sequenced microbial indicators, below which variance fluctuated to the base.

4. Discussion

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

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

(a) Organic matter transformation and diagenesis below the sediment–water interface

As well as the decrease in bulk TOC and N in the uppermost approximately 10 cm, changes inferred by molecular organic geochemical parameters indicate a rapid decrease in the reactivity of OM (figure 2). The most pronounced changes (top approximately 4.5 cm) are coincident with the extent of bioturbation [50]. A marked decrease in the ratio of β -sitosterol/stigmastanol can be explained by the mechanism of hydrogenation [66] and decreases in the ratio of stigmastanol/stigmastanol by reduction reactions [67]. Such reactions are also observed in the transformation and diagenesis of all sterols [68]. Although some sterols, such as β -sitosterol and stigmastanol, can be of a terrestrial plant origin [69], in this location in sediments with a mixed but mainly marine signature [31], sterols could also have a marine origin [70]. The CPI index for *n*-alkanes also shows a marked decline in the uppermost sediments, which reflects OM diagenesis as the more abundant odd chain lengths degrade [71]. This is mirrored by declines from the uppermost sample in *n*-alkanoic acid CPI_T index (where the more abundant even compounds degrade; [35]) and pronounced decreases in the concentration of these compounds. Although changes in the mixing or delivery of terrestrial OM can result in changes in CPI [72], the low values in these sediments suggest a mixed, but primarily marine signature.

Coincident with CPI decreases, OEP for *n*-alkanes in the range C₁₇–C₂₁ and C₂₁–C₂₅ also decline, with marked changes between the sample at the SWI (approx. 0.5 cm) and deeper sediment layers (figure 2) [37]. With decreases in OEP, OM rapidly becomes degraded and less bioavailable, a process which is most pronounced close to the SWI. Similarly, for the more labile *n*-alkanols, changes in the ratio of autochthonous to allochthonous-derived compounds [38] in the uppermost layer indicate active processing of compounds in the organic rich layer. A reverse trend in the *n*-alkanol TAR ratio probably can be explained to approximately 4.5 cm by dilution by more abundant short chain compounds close to the SWI, which are also less resistant to degradation than longer chain compounds [73]. However, increases to the TAR *n*-alkanol values to approximately 5 at approximately 9.5 cm could point to past deposition of OM, which appears to be reflected by increases in CPI_T for *n*-alkanoic acids and the ratio of cholesterol/brassicasterol. The pulse in TAR for *n*-alkanoic acids at approximately 1.75 cm suggests delivery of terrestrial material is unlikely to have been consistent and likely varied over time. Overall, the changes close to the SWI reflect the early diagenesis of lipid biomarkers observed in the oxic layer of ocean sediments [13] and are coincident with observed bioturbation zone [50], while also highlight an underlying terrestrial influence [29,74].

Loss of TOC with depth (figure 1) is markedly more pronounced in the oxic layer compared with the anoxic sediments (indicated by the relative abundance of Desulfobacteraceae, in sequence libraries figure 3). For instance, TOC declines from a peak of approximately 1.8% close to the top of the core at approximately 2.5 cm to approximately 1.3% by 10.5 cm at the base of the oxic zone, prior to the transitional zone indicated by Desulfobacteraceae (figure 3). Based on extrapolating the age estimation, this corresponds to a loss, given dating approximations of $3.8 \times 10^{-4}\%$ TOC per year. In marked contrast, in the established zone of anoxia from approximately 13.5 cm to the base, TOC declines from approximately 1.5 to approximately 1.3 over a longer time period corresponding to a loss of $8.4 \times 10^{-5}\%$ TOC per year. Although this estimation does not resolve changes in sedimentation rate and is based only on a basal age, the difference in relative TOC loss with depth corroborates changes in molecular proxies (*n*-alkanes, *n*-alkanols, sterols) which provides evidence that OM reactivity is greatest in the uppermost layer. Future changes in the relative position of the oxic–anoxic interface could lead to changes in carbon cycling driven by reactivity at the seafloor.

Both organic geochemistry (CPI *n*-alkanes, TOC, N, $\delta^{15}\text{N}$) and measured/modelled porewater O₂ in the uppermost layers are statistically correlated with declines in the proportion of the BD7–8 marine group (figure 3; electronic supplementary material, figure S2 and S3), attributed to bacterial diversity in oxic marine sedimentary environments [54] and previously detected in surface sediments of the South Atlantic Ocean [75] and the western Arctic Ocean [76]. Although more variable, 16S rRNA data show that bacteria and archaea are also only present in abundance

in the uppermost 0–9.5 cm mixed layer (figure 3). Bacterial and archaeal richness and abundance is known to decrease exponentially with depth [77,78] and links between organic degradation and microbial activity are particularly pronounced close to the SWI [79]. Similarly, the highest consistent levels of Nitrosopumilaceae (capable of ammonia oxidation to nitrite [80]) are in the uppermost sediments, correlating with lower TOC:N ratios and higher $\delta^{15}\text{N}$ indicative of microbial activity (electronic supplementary material, figure S4). Here, ammonia oxidizing archaea use ammonia likely generated through OM mineralization in the sediments below which diffuse up to the bioturbated, oxic zone. The ratio of C_{15} anteiso/ C_{16} FAMES is corroborated by extensive microbial activity just below the sediment–surface interface (figure 2), with this compound often linked to bacterial activity as they are major constituents of bacterial membrane lipids [81] and have been detected in aquatic environments [82] including ocean sediments [83]. Peaks in the ratio of cholesterol/brassicasterol and cholesterol/ β -sitosterol within the zone of bioturbation at approximately 2.5 cm have a similar explanation as cholesterol is a key component of bacterial membrane lipids [84]. Decreases in bulk $\delta^{15}\text{N}$ (figure 1) are probably explained by preferential degradation of compounds such as proteins rich in ^{15}N , deposited at the SWI and subsequently degraded [64,85], potentially sourced from under ice algal blooms.

(b) Stratification of microbes and geochemistry across the oxic to anoxic interface

Further changes linked to the processing of OM take place below the aerobic, bioturbated zone. In the aerobic to anaerobic transition zone peaks in the relative abundance of bacterial taxa, Desulfuromonadales and Shewanellaceae from approximately 6.5 cm downwards indicate that Fe^{3+} and Mn^{4+} reduction is taking place (figure 3; [86]). These taxa can use (reduce through dissolution) metals such as Fe^{3+} and Mn^{4+} oxides as terminal electron acceptors. *Shewanella* spp. are adapted to chemically stratified redox transitions [58]. Sediment Mn concentrations also increase coincident with the two major peaks in Desulfuromonadales in the oxic zone, suggesting that taxa capable of metal reduction are important close to the redox transition (figure 3). Seasonal or decadal oscillations in the delivery of OM causing the position of the redox boundary to fluctuate could be a process here, potentially explaining the position of Mn at the upper part of the redox boundary based on kinetics of oxidation and reduction [87]. The oxic to anoxic redox transition is most clearly illustrated by the marked increase of Desulfobacteraceae from approximately 10.5 cm downwards which are known sulfate reducers [88] and correlates with modelled sulfate reduction (figure 3; electronic supplementary material, figure S6). Sulfate-reducing taxa are known to persist below the oxic layer, typically also below the oxidants NO_3^- , Fe^{3+} and Mn^{4+} , where they are involved in the remineralization of organic carbon [89].

Coincident with the increase in sulfate-reducing taxa at and below the oxic-anoxic transition, the abundance of methane oxidizing taxa evidenced by bacteria in the group Methyloirabilaceae peaked markedly (figure 3). Based on amplicon library relative abundance (15%), the *Methyloirabilis* are an important group in this sequence. This family has been shown to participate in anaerobic methane oxidation linked to nitrate/nitrite reduction (via the generation of molecular oxygen used by methane monooxygenase (MMO)) [90]. *Methyloirabilis* have been previously detected in ocean sediments [91], sub-Arctic lake sediments [92] and are abundant in methane rich environments such as paddy fields [93]. On balance, the coincidence of this group with sequences related to the *Brocardiales*, which are implicated in anammox (ammonia oxidation linked to nitrate/nitrite reduction [61]), may suggest involvement in ammonia oxidation. Genomic studies have suggested the potential for the oxidation of ammonia by *Methyloirabilis* by use of their oxygen-dependent MMO [90] rather than by the anammox pathway involving hydrazine production [61]. Increases in TOC:N ratio in the anoxic sediments and transition zone (figure 3) are probably explained in this system by microbial activity using more N, where this is limited and more labile than C, producing OM with TOC:N ratios approximately 10 which gradually dilutes the lower TOC:N ratio of phytoplankton derived matter, characteristic of the uppermost layer. Additionally, if *Methyloirabilis* is acting as an ammonia oxidizer it likely produces N_2 as an inert gas, likely resulting in the gradual loss of solid phase N down the core

evidenced by increases in TOC:N ratios in the anoxic sediments. Many of these bacterial taxa have the potential to be involved in multiple processes at this key transition, but denitrification (figure 3) also appears to be particularly important at this key transition with associations between *Methyloirabilis*, *Brocardiales*, *Desulfuromonadales* and *Shewanellaceae* and modelled denitrification ([29]; electronic supplementary material, figure S5).

(c) How does the reactivity of organic matter delivered to and preserved within sediments change across differences in sedimentology?

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

The transition to finer particulates peaking at approximately 14.5 cm, which is accompanied by increases in Fe and P (figure 1) could be a sediment deposition event similar to scenarios across the Barents Sea. Although the specific underlying mechanism driving this potential deposition cannot be disentangled from this evidence, possibilities include regional transport from land [96], cross-shelf transport [97] or accumulations linked to seasonal redox oscillations [87]. We might expect organic biomarker evidence of either source (e.g. terrestrial input) or reactivity changes to be coeval with this change in sedimentology, but there is little evidence of response at similar magnitudes to OM transformations at the SWI. Slight fluctuations in *n*-alkane CPI at approximately 17.5 cm and OEP_{17–21} at approximately 15.5 cm (figure 2) could indicate slightly more reactive organics is being preserved in finer particulates, but the response is minor and offset slightly from changes in grain size. Since the change in sedimentology does not have a clear link with reactivity of OM evidenced by bulk parameters (TOC, N, TOC:N ratio) or biomarker distributions (*n*-alkanes, *n*-alkanols or sterol ratios) then this suggests the change in sedimentology was either not accompanied by significant organic material, or processes at the SWI have removed any noticeable geochemical signatures. Previous studies suggest the material released from ice sheets and glaciers are sources of quickly processed highly reactive OM [98,99]. Potential reactive material, which may have been brought into the system during past disturbances or reworking may have been subsequently degraded and does not continue to exert a major impact on OM cycling (evidenced by extractable lipid fractions), except by potentially supporting in part, microbial taxa capable of using metals for respiration (*Shewanellaceae* and *Desulfuromonadales*, figure 3). The Mn and Fe changes in sedimentology (Mn peak is shallower) may be offset due to different kinetics of oxidation and reduction between oxides of these compounds [87] and these microbes may also be sensitive to porewater diffusion of metals.

(d) The role of coupled microbial and geochemical studies for understanding carbon cycling in Arctic shelf systems

Clear separation between indicators of OM reactivity, microbial communities at the redox interface and indicators of sulfate reduction processes in the PCA biplot (figure 4), which vary across the redox profile (electronic supplementary material, figure S7), highlights the coupled relationships between a multiplicity of complementary but competing processes which stratify

according to depth. This clear separation supports close relationships between geochemical variables (e.g. CPI *n*-alkanes, $\delta^{15}\text{N}$, %N, %TOC) and O_2 , beneath which across the oxic to anoxic transition microbes involved in multiple processes stratify (denitrification, nitrite production and iron/manganese reduction etc.), prior to evidence of sulfate reduction below the transition to depth (electronic supplementary material, figure S2–S6).

This detailed geochemistry and microbiology study provides a coupled framework with wider sedimentary processes including porewater geochemistry (from reactive transport modelling and measured O_2 [29]) and bioturbation [50], consistent with expectations for a continental shelf system [100]. The extent of successional redox associated processes controlling the cycling of carbon in sediments at and below the SWI is coupled closely to the environmental setting (Barents Sea continental shelf) and is likely to be sensitive to future changes, especially those driven by atmospheric and oceanic warming. The trends in OM transformations and redox succession observed at B15 are likely to be typical of shelf environments with similar water depth, sediment type, overlying water masses and levels of primary production and carbon export. Specifically, although this study focuses on one station (B15) it is possible to suggest, broadly that this station may be representative of wider regional processes. In terms of surface sediment particle size in the Barents Sea, this station is consistent with locations in a southerly direction south (to approx. 75°N [101]) and so profiles may be similar across a wider part of the continental shelf. If upscaled, this study would demonstrate there is a key pool of reactive OM dependent on microbial control, making up part of the more reactive carbon burial component which could be lost from this key store if the redox interface was shallower. This scenario is possible as changes in OM supply are likely to adjust with future changes in ocean stratification and sea ice retreat [25].

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

5. Conclusions

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

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

Future research should compare coupled geochemistry microbial profiles between ice-covered and ice-free zones of the Arctic to elucidate linkages between ice cover and microbial processing of OM at the seafloor. This is especially pertinent and should be coupled with estimates of carbon

burial in different locations across the Barents Sea, given the trend for increasing oceanographic changes in this region [25].

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

Authors' contributions. M.A.S. wrote the manuscript initial draft, conducted fieldwork/sampling, compiled datasets and carried out bulk and organic geochemical analyses. J.C.F. provided inorganic XRF data, conducted fieldwork/sampling, contributed ideas on sedimentology and to the initial manuscript. L.L.A. carried out microbiological analyses. F.S.F. advised on suitable organic geochemical techniques and provided insight into OM reactivity. N.D.G. designed microbiological approach and contributed key ideas on redox stratification to initial manuscript. K.T. carried out quantitative 16S rRNA analyses and co-designed microbiological approach. K.R.H. project managed ^{14}C radiocarbon analyses. R.G.H. carried out $\delta^{15}\text{N}$ analyses with M.A.S. and advised on geochemical sampling strategy. S.F.H. and A.T. carried out fieldwork and porewater nutrient analysis which underpins model comparison. P.L. carried out bioinformatics and constructed sequencing pipeline. S.P. carried out ^{14}C analyses on foraminifera. A.F. carried out grain size analysis. C.M. conducted fieldwork/sampling, advised on sedimentology and project managed inorganic geochemical aspects. G.D.A. contributed early ideas, revised the initial manuscript and project managed organic geochemical aspects. All authors commented on the manuscript and approved the final submission.

Competing interests. We declare we have no competing interests.

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