Does Arctic warming reduce preservation of organic matter in Barents Sea sediments?

Johan.C. Faust[1]*, Mark A. Stevenson[2], Geoffrey D. Abbott[2], Jochen Knies[3,4], Allyson Tessin[5], Isobel Mannion[1], Ailbe Ford[1], Robert Hilton[6], Jeffrey Peakall[1] and Christian März[1]

[1]*School of Earth and Environment, University of Leeds, UK*
[2]*School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne, UK*
[3]*Geological Survey of Norway, Trondheim, Norway*
[4]*CAGE – Centre for Arctic Gas Hydrate, Environment and Climate, Department of Geology, UiT the Arctic University of Norway, Tromsø, Norway*
[5]*Department of Geology, Kent State University, Kent, OH, USA*
[6]*Department of Geography, Durham University, UK*

Keywords: Barents Sea, Geochemical sediment composition, Organic carbon bound to reactive iron, Carbon cycle, Arctic Ocean, Marine Surface Sediments

Summary

Over the last few decades, the Barents Sea experienced substantial warming, an expansion of relatively warm Atlantic water and a reduction in sea ice cover. This environmental change forces the entire Barents Sea ecosystem to adapt and restructure and therefore changes in pelagic-benthic coupling, organic matter sedimentation and long-term carbon sequestration are expected. Here we combine new and existing organic and inorganic geochemical surface sediment data from the western Barents Sea and show a clear link between the modern ecosystem structure, sea ice cover and the organic carbon and $CaCO_3$ contents in Barents Sea surface sediments. Furthermore, we discuss the sources of total and reactive iron phases and evaluate the spatial distribution of organic carbon bound to reactive iron. Consistent with a recent global estimate we find that on average 21.0±8.3 per cent of the total organic carbon is associated to reactive iron ($fOC\text{-}Fe_R$) in Barents Sea surface sediments. The spatial distribution of $fOC\text{-}Fe_R$, however, seems to be unrelated to sea ice cover, Atlantic water inflow or proximity to land. Future Arctic warming might, therefore, neither increase nor decrease the burial rates of iron-associated organic carbon. However, our results also imply that ongoing sea ice reduction and the associated alteration of vertical carbon fluxes might cause accompanied shifts in the Barents Sea surface sedimentary organic carbon content, which might result in overall reduced carbon sequestration in the future.

*Author for correspondence (J.Faust@Leeds.ac.uk).
†Present address: School of Earth and Environment (SEE), The University of Leeds, LS2 9JT Leeds, United Kingdom

Introduction

One of the most apparent signs of current global climate change is Arctic sea ice loss. Over the past four decades, summer sea ice extent has drastically decreased by over 30% [1, 2] and the ongoing transformation of the Arctic Ocean from an "icy land" into an open ocean forces the entire Arctic ecosystem to adapt and restructure [3]. As the Arctic Barents Sea shelf area (Fig. 1) is a transition zone between the temperate North Atlantic and the cold Arctic Ocean, it is climatically divided into two distinct regions. The northern area experiences a cold and harsh Arctic climate and sustains an ice-associated ecosystem, while the southern part has an Atlantic climate with a rich open water ecosystem and lucrative fisheries [4, 5]. During recent decades, enhanced inflow of Atlantic water and atmospheric heat transport have dramatically warmed the Arctic, and in particular the Barents Sea [6]. Sea ice loss and "Atlantification" of the northern Barents Sea are the consequences [6-8]. Higher water temperatures and sea ice reduction modifies the Arctic marine ecosystem structure and, therefore, changes the Arctic carbon cycle, i.e., atmospheric CO_2 uptake, pelagic-benthic coupling, organic matter sedimentation and long term sequestration [3, 9-13]. An increase in the annual net primary production in the Arctic and the Barents Sea has already been observed since the late 1990s and might rise in the future, due to further summer sea ice reduction and longer phytoplankton growing seasons [10, 14]. However, these environmental changes are complex and so far only a few studies link ongoing changes in the Arctic Ocean to organic carbon burial, sedimentary biogeochemical cycles and the marine ecosystems [11, 15, 16]. Thus, there is substantial uncertainty regarding current and future productivity and carbon burial estimates in the Arctic and the Barents Sea.

The sequestration of organic matter in marine sediments is a fundamental mechanism for the removal of carbon from the atmosphere and its storage over geological time periods [17]. Examining climatically induced biogeochemical changes in Arctic marine sediments, is therefore, important for a better understanding of the global carbon cycle. However, the processes that control organic carbon preservation in marine sediments, including sedimentation rate [18, 19], presence and absence of oxygen [20-22], selective preservation of biochemically unreactive compounds [23, 24], and protection of organic matter through interactions with a mineral matrix [25-27] are complex and still not fully understood. A possible connection between iron and organic carbon in marine sediments was already identified in 1970 [28], but only recently has the importance of this relationship for organic matter preservation in marine sediments been recognised [29]. Due to their high sorption capacity, iron oxides, in particular freshly precipitated and poorly crystalline iron (oxyhydr)oxides, like ferrihydrite, have a strong influence on organic carbon stabilization. During burial at the seafloor, organic carbon adsorbed to these oxides is preserved against microbial degradation and can therefore bypass the shallower oxic degradation regimes into, and possibly beyond, the zone of dissimilatory metal oxide reduction

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[29]. Therefore, reactive iron phases may serve as an efficient shuttle to enhance organic carbon burial and preservation in marine sediments. Lalonde et al. [29] investigated surface sediment samples from several marine environments including the Southern Ocean, Mexican and Indian Margins, St. Lawrence estuary and gulf, and the Black Sea. They proposed that on average 21.5% of the total organic carbon in marine surface sediments is associated with reactive iron globally. Hence, Lalonde et al. [29] stated that "reactive iron phases serve as an extremely efficient 'rusty sink' for organic carbon and are a key factor in the long-term storage of organic carbon and the global cycles of carbon, oxygen and sulphur". However, since this pioneering publication only a few studies investigated the role of reactive iron on the preservation of organic carbon in natural marine sediments [30-37]. And except for one study from the East Siberian Arctic Shelf [30], the type and amount of organic carbon bound to iron oxides has not been examined in Arctic marine sediments. Moreover, there is still a general lack of knowledge about reactive iron sources in relation to total iron content, the general sediment composition, and the environmental setting. Making these mechanistic links is, however, necessary to evaluate the role of organic carbon bound to iron phases and its role in the global carbon cycle, especially in a fast-changing environment such as the Arctic Ocean.

To better understand how ongoing "Atlantification" of the Barents Sea will change the organic and inorganic sediment composition in the future, we combined new and existing surface sediment (0-1 cm) data of organic carbon, total iron, calcium carbonate and grain size distribution of the seasonally ice-covered north and permanently ice-free south western Barents Sea. Furthermore, to better constrain the controls on, and efficiency of, carbon burial in the Arctic shelf seas we analysed the fraction of organic carbon bound to dithionite-extractable iron phases ($fOC\text{-}Fe_R$).

Study Area

The Barents Sea is located between 70-81°N off the northern Norwegian coast and is bordered by the shelf edge towards the Norwegian Sea in the west, the Norwegian archipelago Svalbard in the northwest and the islands of Franz Josef Land and Novaya Zemlya (Russia) in the northeast and east. It is the largest pan-Arctic shelf sea covering an area of 1.6 million square km with an average water depth of 230 m [38]. There are several extensive overviews and reviews about the modern climate setting and ecosystem of the Barents Sea and we refer to these references for a detailed description of the physical and ecological conditions [4, 10, 39-42]. In brief, the present ecological setting as in all Arctic seas is characterized by very pronounced seasonal fluctuations in insolation and, hence, primary production. However, despite the relatively short duration of the growing season in the Arctic, the Barents Sea is a high productivity shelf area where 40% of the total primary production of the Arctic Ocean takes place [43]. Water column primary productivity is generally inversely related to sea ice cover, i.e., lower rates occur in the north-east (30-70 g C $m^{-2}y^{-1}$) and higher and less variable rates in the Atlantic water-

influenced south-west (100-150 g C $m^{-2}y^{-1}$) [39, 44]. The general oceanic circulation pattern of the western Barents Sea is dominated by the relatively warm northward flowing North Atlantic Current (temperature 2-8°C, salinity >35‰) which enters the Barents Sea from the southwest and the southward flowing cold Arctic currents (Spitsbergen and Persey; temperature <0°C, salinity <35‰) entering the Barents Sea from the northeast. The relatively sharp boundary between these water masses forms the oceanographic Polar Front (Fig. 1) [45] which is mainly determined by the bathymetry and is, therefore, relatively stable from year to year [46]. The northern Barents Sea is seasonally ice covered with maximum and minimum ice coverage in March-April and August-September, respectively. The heat content of the Atlantic water keeps the southern Barents Sea permanently ice-free. River runoff into the Barents Sea is very limited. Only one larger river, the Petchora River, enters directly into the south-eastern Barents Sea in Russia. Rivers on the Kola Peninsula, on Svalbard and in Norway are small and often drain into fjords. Thus, sediment discharge through river inflow is low and the main processes responsible for Barents Sea surface sediment distribution are re-deposition by winnowing from shallow banks into troughs and depressions, and deposition from sea ice. Hence, sedimentation rates are generally low, 0.04-2.1 mm/y since the last glacial period, but can be much higher proximal to glacier outlets e.g. close to Svalbard (Fig. 2; supplementary Tab. S1).

Material and Methods

Surface sediments: sampling and preparation

In July 2017, surface sediment samples were collected by using a multi-corer at 15 stations (supplementary Tab. S2) along a general south-north gradient in the western Barents Sea (Fig. 1). The first 1 cm of an undisturbed short sediment core at each station was sampled on-board the Royal Research Vessel James Clark Ross immediately after core recovery. At seven stations (B3, B13-B18) samples were taken in 0.5 cm intervals and all samples were stored in plastic bags at -20°C. Prior to any sediment analysis, except for grain size measurements, all samples were freeze-dried and homogenized by gentle grinding using an agate mortar and pestle.

Bulk elemental composition and grain size analysis

Element composition of Barents Sea surface sediments was determined by wavelength dispersive X-ray fluorescence (XRF). A sample split of 700 mg was mixed with 4200 mg di-lithiumtetraborate ($Li_2B_4O_7$, Spectromelt A10), preoxidized at 500°C with 1.0 g NH_4NO_3 (p.a.) and fused to homogenous glass beads. The glass beads were analysed for 31 elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, As, Ba, Co, Cr, Cu, Ni, Pb, Rb, Sr, V, Y, Zn, Zr) using a Philips PW-2400 WD-XRF spectrometer calibrated with 53 geostandards at the University of Oldenburg. Analytical precision and accuracy were better than 5% as checked by in-house and international reference materials. Results are provided in the supplementary table S3.

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Grain size distribution was determined using a Mastersizer 2000E laser diffractometer at Leeds University, UK. Samples taken in 0.5 cm intervals (stations B3, B13-B18) were mixed prior to grain size analysis. Sediment samples were disaggregated in an ultrasonic bath for at least 15 min and grain size distribution of all samples were analysed on bulk and on decarbonated samples, which were treated with 10% (vol.) HCl before analysis. Grain size analysis was carried out on material within a particle diameter range of 0.1 to 1000 μm and results are presented as cumulative volume percentages (supplementary Tab. S4 and S5).

Organic carbon and reactive iron extraction and analysis (OC-Fe)

To quantify the amount of organic carbon bound to iron oxides in Barents Sea surface sediment samples we applied a citrate–dithionite iron reduction method which simultaneously dissolves all reactive iron (oxyhydr)oxides and the organic carbon associated with these phases (OC-Fe). A detailed description of the method can be found in Salvadó et al. [30]. Briefly, 0.25 g of each sample was transferred into 30 ml centrifuge tubes. 15 ml of a solution containing 0.27M trisodium citrate ($Na_3C_6H_5O_7 \cdot H_2O$) and 0.11M sodium bicarbonate ($NaHCO_3$) was added, well mixed and heated up to 80°C in water bath. 0.1M sodium dithionite ($Na_2S_2O_4$) was added to the mixture, maintained at 80°C and shaken every five minutes. After 15 min, the mixture was centrifuged for 10 min at 4000 rpm and the supernatant was decanted and 200 μl of HCl were added to prevent Fe precipitation. The sediment samples were rinsed three times with artificial seawater and then freeze-dried. To quantify the organic carbon loss during the experiment, which was unrelated to iron oxides dissolution, a control experiment was conducted. For the control experiment, a 0.25 g aliquot of each sample was treated the same way as for the reduction experiment but the complexing and reducing agents (sodium citrate and sodium dithionate) were replaced with sodium chloride to reach a solution of the same ionic strength. All samples were weighed after the experiment to account for mass loss during the experiment. Dissolved iron in the supernatant and rinse water of the control and reduction experiment was analysed using a Thermo Scientific iCE3000 Atomic Absorption Spectrometer (AAS) at Leeds University, UK. Results are shown in the supplementary table S6 and the relative error of the Fe analysis was ±2.6%.

Organic carbon (OC) content of the bulk sediment before and after the reduction and control experiments was analysed on decarbonated samples using 10% (vol.) HCl, rinsed three times and dried overnight at 50°C. OC content was determined with a LECO SC-144DR combustion analyser at Leeds University, UK (supplementary Tab. S6). The certified reference material LECO 502-062 and blanks were included in every batch, and results are given in weight percentage. The relative error of the OC analysis was ±1.7%.

Sedimentary nitrogen and carbon isotope analysis

Freeze dried sediments (~0.1 g) were acidified using 4 mol HCl (hydrochloric acid) to remove carbonates for 4 h, dried overnight at 60°C and analysed on a CS230 Carbon/Sulfur Determinator (Leco Corporation, Michigan, USA) using porous crucibles to derive total organic carbon content (TOC). Precision/reproducibility was ±<0.1%. Total carbon (TC) and nitrogen were determined on a VarioMAX CNS Analyser (Elementar, Langenselbold, Hesse, Germany) in at least duplicate (precision/reproducibility ±<0.1%). Total inorganic carbon (TIC) was calculated as the difference between the TC and TOC (TC-TOC). The calcium carbonate ($CaCO_3$) content was estimated by multiplying TIC by 8.333. Bulk $\delta^{13}C_{org}$ was analysed at Elemtex Laboratories (Cornwall, UK) using IRMS on samples acidified three times using 4 mol HCL with drying at 60 °C between each acidification (precision/reproducibility to ±0.2‰).

Results and discussion

Sources, spatial distribution and burial of organic carbon

Compared to organic carbon cycling processes in the water column, there is generally a lack of knowledge about the fate of sedimentary organic matter at and in the Arctic Barents Sea seafloor [47-50]. The link between vertical carbon export and accumulation to primary productivity patterns and terrestrial sources is still not well understood. Therefore, uncertainty remains about the origin of the sedimentary organic carbon, especially in the northern Barents Sea. Based on C_{org}/N_{tot} ratios, $\delta^{13}C_{org}$ signatures and pigment analysis, several studies argue that the main source of sedimentary organic matter (OM) in Barents sea surface sediments is marine and derives from productivity in the water column and ice-associated algae production [16, 47, 51-54]. However, by accounting for the sedimentary inorganic nitrogen content, Knies et al. [55] showed that high amounts of terrigenous OM (≥50 rel. %) can be present in the seasonally sea ice covered and coastal regions of the northern Barents Sea, while high contributions of marine OM (>60 rel. %) occur in the ice-free southwestern Barents Sea. Our $\delta^{13}C_{org}$ values from the northern station B13-B17 vary between -21.35‰ to -23.08‰ and C_{org}/N_{tot} values range in all stations between 6 and 8.5 (supplementary Tab. S3), which indicates that these locations are strongly influenced by marine OM.

The total organic carbon (OC) content of the Barents Sea surface sediments from this study, as well as available OC data from the literature (Fig. 3) [47, 50, 56] show very similar trends. The OC content is higher in northern Barents Sea surface sediments and in coastal areas, whereas the ice-free southern areas show much lower OC contents (Fig. 3). Previous investigation of carbon burial rates in the northern Barents Sea show that carbon preservation in these sediments is considerably higher compared to other Arctic shelf areas [47]. A compilation of published linear sedimentation rates (Fig. 2; supplementary Tab. S1; adapted and extended from Pathirana et al. [50]) shows that sedimentation rates vary between 4 and 210 cm/kyr^{-1} (average 64 cm/kyr^{-1}) for

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the entire western Barents Sea. They are lowest close to the western continental shelf edge, probably due to higher current velocities, and sedimentation rates in the seasonally ice covered northern Barents Sea (north of the median winter sea ice extent) are on average slightly higher (78.9 cm/kyr) than in the permanently ice-free southern regions (53.8 cm/kyr, south of the median winter sea ice extent, Fig. 2). This might be related to lower bottom current speed and higher sediment input from Svalbard and sea ice. The OC spatial distribution pattern could be related to different sedimentation rates and thus different oxygen exposure times as OC remineralization via oxygen reduction in marine sediments is the most effective process for OM degradation. However, investigations of sediment mixing and oxygen penetration depth of Barents Sea surface sediment show that at least the first centimetre is homogenised through physical and/or biological mixing [52, 57] and that the oxygen penetration depth in most locations of the Barents Sea is >1 cm [49, 58]. Hence, we assume that the overall OC decomposition is comparable between the northern and southern Barents Sea and that the spatial distribution of OC between the northern and southern Barents Sea is related to other controlling factors. Hence, we used the average sedimentation rates to estimate the average carbon burial rates north and south of the median winter sea ice extent (supplementary Tab. S7). In the seasonally sea ice covered northern area organic carbon burial rates are (6.3 gC/m^2yr^1) more than twice as high as in the ice-free southern region (2.4 gC/m^2yr^1). Even though these numbers present only an approximation derived from surface sedimentary OC, they are in relatively good agreement with carbon accumulation rate of 5.5 gC/m^2yr^1 published previously for the northern Barents Sea area [47]. Based on these findings, we suggest that carbon sequestration in the ice-free southern Barents Sea sediments is lower compared to the ice-covered northern region.

Inverse relationship between total organic carbon content and calcium carbonate

In pelagic sediments, variations in biogenic carbonate content are mainly controlled by dissolution, dilution, and/or productivity changes. Hence, due to the strong relationship of $CaCO_3$ to marine productivity and, thus, water temperature, salinity, nutrient supply and degree of ice coverage, $CaCO_3$ is often applied as a proxy to reconstruct climate and environmental changes. Carbonate content in surface sediments from the eastern central Arctic Ocean, north of the Barents Sea, were found to be mainly of biogenic origin [59] and $CaCO_3$ contents in southern Barents Sea surface sediments show a good correspondence with planktonic foraminifera abundances [60]. In agreement with these findings, our results show a strong relationship between $CaCO_3$ and Ca ($r = 0.99$) and both parameters are anti-correlated to terrigenous elements like Si, Fe, K, Ti and Al ($r \leq -0.49$; supplementary Fig S1). This suggests that the carbonate content in Barents Sea sediments largely reflects the calcareous shell fragments from either planktonic or benthic organisms and, that terrigenous $CaCO_3$ sources have only a very minor effect on the composition of Barents Sea surface sediments.

The variable carbonate content is also reflected in the grain size distribution in Barents Sea surface sediments (Fig. 4). In the southern Barents Sea, bulk grain size distribution at stations B1 to B11 is much more heterogeneous with higher contributions of coarse-grained material (35% >63 μm) compared to the clay and silt fraction dominated northern stations B13 to B18 (87% <63 μm). The decarbonated grain size analyses, however, show that the siliciclastic fraction is dominated by the silt fraction (average 81%) and very homogeneously distributed in Barents Sea surface sediments (Fig. 4). This shows that the bulk grain size measurements of Barents Sea sediments are strongly modulated by their carbonate content.

Since $CaCO_3$ in Barents Sea surface sediments is assumed to be mainly of marine origin, higher $CaCO_3$ content indicates higher primary productivity, which could be expected to result in higher organic matter fluxes towards the seafloor. But the $CaCO_3$ content in Barents Sea surface sediments shows an opposite pattern to the OC distribution, i.e., low OC content in the south-western part coincides with high $CaCO_3$ content, and vice versa in the north-eastern part (Fig. 3) [56]. A possible reason could be OC dilution through higher $CaCO_3$ contents in the south-western area of the Barents Sea. However, a calculation of OC contents on a $CaCO_3$ basis (see supplementary Fig. S2) does not indicate a strong dilution effect of OC through inorganic carbon. Moreover, in the very productive Storfjord trough south of Svalbard (Station B7, B9-B11), both OC and $CaCO_3$ show relatively high concentrations. Steinsund et al. [60] attributed differences in the $CaCO_3$ content to carbonate dissolution in the north-eastern Barents Sea caused by dense, cold, saline and CO_2-rich bottom water produced by sea ice formation. However, while this may explain the lower carbonate content north of the polar front, it cannot explain the described regional differences in the OC content, since OC is not susceptible to dissolution by CO_2-rich waters. Moreover, dense cold bottom water currents produced by sea ice brine formation also occur in areas where $CaCO_3$ concentrations are high, for example in the Storfjord trough (Station B7, B9-B11) [61-63]. Hebbeln et al. [64] showed that the carbonate content in the surface sediments of the Polar North Atlantic reflect the influx of temperate Atlantic waters into the Nordic Seas, where the highest carbonate content follows the main axis of the Norwegian Current and decreases with lower water temperature northwards and to the west. Moreover, sea ice cover reconstruction based on a sediment core from the south-western Barents Sea showed that seasonal sea ice cover during the early Holocene was accompanied by lower carbonate content and a clear increase in the total sedimentary organic carbon concentrations [65]. These findings indicate that low carbonate content in the north-east Barents Sea is likely related to cold Arctic [39] water masses, with lower carbonate production, while higher $CaCO_3$ content in the south-western Barents Sea sediments are probably related to the warmer Atlantic water inflow (Fig. 3). Hence, we suggest that the opposite distribution pattern of OC and $CaCO_3$ in the seasonally sea ice-covered north-western Barents Sea and the ice-free southern area (Fig. 3) could be related to differences in primary productivity and vertical OM flux rates. Wassmann et al. [66 and references therein] showed that the main phytoplankton bloom development occurs in May/June in the southern Barents

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Sea and is relatively predictable. The spring bloom in the northern Barents Sea, however, depends on the sea ice conditions which are highly variable, and the bloom develops more rapidly than in the southern Barents Sea. It follows that while predators are well-adapted to the spring bloom in the southern Barents Sea, the rapid and unpredictable development of the spring bloom in the marginal ice zone typically decouples phytoplankton development from zooplankton grazing [39]. Thus, despite the ice cover, OC pelagic-benthic fluxes are probably higher in the northern Barents Sea due to lower OM consumption in the water column. Additionally, the export of ice algae (diatoms) might substantially contribute to high OM export fluxes in the marginal ice zone [67]. Beyond OM export quantity, high pelagic consumption and recycling also reduces the quality of vertically exported OM, while low to moderate pelagic consumption allows OM of higher quality to reach the seafloor [68]. In accordance with investigations of the pelagic-benthic coupling and related OM fluxes from the water column to the seabed in the Arctic and Northeast Atlantic [9, 66] we suggest that the increased sedimentary OC contents in the northern Barents Sea (Fig. 3) are related to higher rates of OC delivery to the seafloor. This trend in OM export appears to be matched by similar trends in the benthic macro- and megafauna. A clear and consistent south-north distribution pattern of benthic organisms with generally more taxa, higher biomass and higher abundance in the northern Barents Sea implies increased OM fluxes, which support the benthic ecosystem [40]. If we use the environmental setting of the southern ice free Barents Sea as an analogue for a future ice free northern Barents Sea, these findings imply that with ongoing climate change, the northern Barents Sea may transform from a cold and stratified Arctic to a southern Barents Sea-like warm and well-mixed Atlantic-dominated climate regime [6]. This change may lead to a shift from the current "sea ice algae–benthos" ecosystem to a "phytoplankton–zooplankton" dominated ecosystem [9]. Since our findings indicate a link between marine productivity and the geochemical composition of Barents Sea surface sediments, ongoing sea ice reduction and the associated alteration of pelagic primary productivity are expected to cause accompanied shifts in the Barents Sea surface sediment composition. Compared to the modern situation, the northern Barents Sea surface sediments might contain higher contents of $CaCO_3$ and less OC, which could result in reduced OC burial rates in the future.

Preservation of organic matter promoted by iron in Barents Sea surface sediments

To evaluate the preservation of OC in the seasonally ice covered northern Barents Sea and the ice-free southern area, we determined the amount of organic carbon associated with reactive iron phases by applying a citrate–dithionite iron reduction method [29]. In the following, we will discuss the sources of total and reactive iron in Barents Sea surface sediments. Thereafter, we evaluate the spatial distribution pattern of OC bound to iron and show that the fraction of total organic carbon bound to reactive iron phases is not related to sea ice cover.

In accordance with the previously published spatial distribution pattern of iron in surface sediments from the southern Barents Sea, our results show that the bulk iron contents in Barents Sea surface sediments are highest to the eastern side of the Svalbard archipelago (stations B14-B18) (Fig. 5 and 6 B; Knies et al. [56]). Values decrease towards the south with intermediate concentrations south of Svalbard (station B9-B13), and lowest values in the south-western Barents Sea (stations B1-B6). Higher iron contents in northern Barents Sea sediments are probably related to bedrock erosion by glaciers on Svalbard [69-71], deposition from sea ice [72, 73] and erosion of Barents Sea Mesozoic bedrock [71, 74]. Our results show that the reactive iron (Fe_R) abundance is strongly related to the sedimentary bulk iron content ($r = 0.94$, $n=22$, supplementary Fig. S3). Thus, the Fe_R contents and the relative contributions of dithionite-extractable reactive iron oxides show a south-north gradient as well (Fig. 6 C and D). The reactive iron fraction of the total iron content (fFe_R) in samples from the south-western stations B1-B13 is on average 16.2%, whereas fFe_R contents in samples north of the Polar Front (B14-18) are on average 27.9%. Thus, as sediment samples from seasonally sea ice covered stations contain the highest OC content and show highest fFe_R contribution (Fig. 6 A and D) we would expect them to have a high potential to bind OC to iron oxides as well. Indeed, we find that the amount of OC bound to iron ($OC\text{-}Fe_R$) is on average about three times higher in the northern Barents Sea compared to the south-western area (Fig. 5 E). The strong relationship between Fe_R and $OC\text{-}Fe_R$ is in accordance with Ma et al. [34] who investigated literature data of $OC\text{-}Fe_R$ and suggest that $OC\text{-}Fe_R$ contents in marine surface sediments are highly dependent on OC and Fe_R availability. Moreover, our data show no clear spatial relation between sea ice cover and $OC\text{-}Fe_R$ content. Stations B6, B7 and B11 were affected by winter sea ice at least for the past 40 years (Fig. 1) [2]. But compared to B11, $OC\text{-}Fe_R$ concentrations at B6 and B7 are very low. B13 is not affected by sea ice but $OC\text{-}Fe_R$ concentrations are high (Fig. 6 E). This implies that sea ice cover has no direct impact on the preservation of OC through Fe_R sorption.

In contrast to $OC\text{-}Fe_R$, the spatial distribution of the OC fraction of the total sedimentary OC pool bound to Fe_R ($fOC\text{-}Fe_R$) (Fig. 6 F) shows no relationship to either TOC or Fe_R contents and, therefore, does not show a spatial south-north gradient. Also, an association to sea ice cover, proximity to land, grain size distribution or sediment composition were not identified either. In fact, the fraction of OC bound to Fe_R in the southern Barents Sea is very similar to that in the northern Barents Sea region (Fig. 6F), even though sample locations are very different in terms of their environmental settings, sediment sources, OC and Fe_R contents (see discussion above). Thus, a relatively high fraction of OC can be bound to Fe_R even if absolute Fe_R contents are relatively low. This suggests that the amount of OC bound to reactive iron is not dependent on the total amount of Fe_R available, but that other factors such as the organic matter type and composition as well as redox processes play an important role. This assumption is in accordance with findings from the Eurasian Arctic Shelf. Salvadó et al. [30] showed that the composition of the OC associated with the Fe phases changes with the OM source (i.e.,

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marine versus terrigenous), and that in Arctic shelf areas dominated by marine OM, fOC-Fe_R can be lower than in areas dominated by remobilized terrigenous OC, e.g. from thawing permafrost. Also Zhao et al. [31] found that in estuarine sediments in southern China, Fe_R was largely associated with terrigenous OC. Moreover, the association between OC and Fe_R is formed mainly through co-precipitation/chelation and/or adsorption [29, 33, 75]. Coprecipitation has a higher sorption capacity of OC and occurs when upward diffusing pore water Fe^{2+} is oxidized at the redox interface in the presence of dissolved OC. Thus, it has been proposed that Fe redox processes are "ultimately the overarching determinant" of fOC-Fe_R in marine sediments [34]. Even though most observations suggest that the oxygen penetration depth in the Barents Sea is >1 cm [49, 58] and that the first centimetre of Barents Sea surface sediments is affected and homogenised through physical and/or biological mixing [52, 57], the redox interface might still reach into the first centimetre, e.g. due to high Fe^{2+} upward fluxes or seasonal changes of the oxygen penetration depth through primary productivity variability. At seven stations (B3, B13-B18) we analysed the OC bound to iron in 0.5 cm depth intervals. The results show no significant differences between the TOC, Fe and Fe_R contents in the 0-0.5 cm and 0.5-1 cm sections (supplementary Fig. S4), confirming that the first centimetre is well mixed. Compared to the 0.5-1 cm section, fFe_R, OC-Fe_R and fOC-Fe_R contents are in general slightly higher in the first half centimetre. This implies that the effect of redox processes (Fe^{2+} upward fluxes) on the fOC-Fe_R content in the first centimetre of Barents Sea sediments is minor.

Besides the investigation of natural samples, recent experimental laboratory studies on the composition of Fe_R-associated organic matter revealed that varying OC_F:Fe_R molar ratios are related to the binding mechanism of OC with Fe_R phases: adsorption results in lower OC_F:Fe_R ratios (≤1), while co-precipitation yields ratios between 6 and 10 [76]. In turn, the impact of adsorption and co-precipitation on organic matter loadings ultimately depends on the organic matter composition and redox processes [33, 75]. In Barents Sea surface sediments, OC_F:Fe_R molar ratios vary between 0.9 and 3.8 (average = 1.8) and are in the range for sediments overlain by oxic bottom waters [29] (supplementary Tab. S6 and Fig. S5). The majority of OC_F:Fe_R values show only small variations between about 1-2; only stations B1, B2 and B11 show relatively high values of 2.9, 3.3 and 3.8, respectively. This might indicate that besides the large differences in the biogeochemical characteristics of the Barents Sea shelf regimes, the composition of OC bound to Fe_R is relatively similar, maybe due to generally low contributions of terrigenous OM at all investigated locations [77]. However, OC_F:Fe_R values of stations B3 and B14-B18 show average values of 1.6 and 1.9 for the upper and lower half centimetre, respectively (supplementary Tab. S6). This indicates that the effect of coprecipitation is either very small or that factors other than the binding mechanisms of OC to Fe oxides, such as mineralogy or Fe-oxide reactivity influence the OC_F:Fe_R ratio. Moreover, competitive sorption by arsenic (As) or phosphorus species onto Fe oxide surfaces, can influence the OC_F:Fe_R ratio. For example, As contents in our Barents Sea samples are strongly related to Fe_R contents (r = 0.9, n = 15) but show a weak correlation with fOC-Fe_R (r = 0.5, n = 15), hence it is likely that surface

sorption sites on Fe oxides can be "blocked" by As and thus are unavailable for OC binding. To further evaluate differences in the OC_F:Fe_R ratios in natural sediments from the Barents Sea and globally, we need to develop a better understanding of the composition and type of the organic matter bound to iron oxides and the timing of when this bonding occurs.

Implications and Conclusion

Strong regional differences in the surface sediment composition between the northern, seasonally sea ice-covered and the southern, ice-free region of the western Barents Sea reveal that $CaCO_3$ content shows an opposite pattern to the OC distribution, i.e., low OC content in the south-western part coincide with high $CaCO_3$ content, and vice versa in the north-eastern part. We propose that this is likely related to the modern ecosystem structure with higher primary productivity but lower vertical organic carbon flux rates in the southern than in the northern Barents Sea. Low $CaCO_3$ content in the north-east Barents Sea might be related to cold Arctic water masses, with lower carbonate production, while higher $CaCO_3$ content in the south-western Barents Sea sediments is probably related to the warmer Atlantic water inflow.

Arctic warming will result in higher water temperatures, increased river run-off and reduced sea ice cover. Thus, the northern Barents Sea may transform from a cold and stratified Arctic to a southern Barents Sea-like warm and well-mixed Atlantic-dominated climate regime. This enormous environmental change will certainly induce substantial marine ecosystem changes. More extensive open water conditions and enhanced nutrient inputs through rivers are expected to enhance primary productivity. However, less sea ice cover in the northern Barents Sea may also lead to a shift of the typical "sea-ice algae–benthos" ecosystem to a "phytoplankton–zooplankton" dominated ecosystem. The proposed link between marine productivity and the geochemical composition of Barents Sea surface sediments implies that ongoing "Atlantification" of the Barents Sea will affect the Barents Sea surface sediment composition and that compared to the modern situation the northern Barents Sea surface sediments might contain higher contents of $CaCO_3$ and less OC in the future. Thus, a rise in primary productivity may lead to higher atmospheric CO_2 uptake but higher carbon turnover rates/remineralisation in the water column may decrease vertical OC fluxes in the northern Barents Sea.

To better constrain the controls on, and efficiency of, carbon burial in the Arctic shelf seas, we analysed the fraction of organic carbon bound to dithionite-extractable iron phases (fOC-Fe_R). Consistent with the global estimate by Lalonde et al. [29] 21% of the total organic carbon is on average associated to iron in Barents Sea surface sediments. We found that a relatively high fraction of OC can be bound to reactive iron even if absolute reactive iron contents are relatively low. Moreover, our findings indicate that the amount of OC bound to reactive iron is not dependent on the total amount of reactive iron available, but that the organic matter type

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and composition seem to be important factors in natural sediments. Furthermore, the spatial distribution of the organic carbon bound to iron seems to be unrelated to sea ice cover, Atlantic water inflow proximity to land, grain size distribution or sediment composition. Future Arctic warming might therefore neither enhance nor decrease carbon burial through the adsorption to iron oxides.

Additional Information

Acknowledgments

We thank the crew of the RRS James Clark Ross for their professional support during our expedition. Further, we would like to express our gratitude to Andy Connelly, Andrew Hobson, Fiona Keay, Gareth Keevil, Carola Lehners, Corinna Mori and Bernhard Schnetger for their help with the laboratory work at the University of Leeds and at the ICBM Oldenburg. We are grateful for the comments of two anonymous reviewers, which helped to improve the manuscript.

Funding Statement

This work resulted from the ChAOS project (NE/P006493/1), part of the Changing Arctic Ocean programme, jointly funded by the UKRI Natural Environment Research Council (NERC) and the German Federal Ministry of Education and Research (BMBF). JK was funded by the Research Council of Norway (grant 223259).

Data Accessibility

The datasets supporting this article have been uploaded as part of the supplementary material.

Competing Interests

We declare we have no competing interests.

Author contributions

J.C.F. was the lead author and wrote the manuscript. J.C.F, M.A.S., A.T. and C.M. conducted fieldwork/sampling together and compiled datasets. J.C.F, M.A.S., A.F., I.M., G.D.A., R.H. and J.P. carried all the required analytical work and J.K. provided organic and inorganic elemental data. All authors contributed early ideas, revised the initial manuscript and provided a lively discussion.

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Figure captions

Figure 1: Map of the western Barents Sea and sampling locations (red dots). The northern Barents Sea is seasonally ice-covered and winter maximum and median sea ice coverage over the past forty years [2] are shown as white area and blue line, respectively. The boundary between the relatively warm northward flowing North Atlantic Current and the southward flowing cold Arctic currents forms the oceanographic Polar Front (yellow line).

Figure 2: Published linear sedimentation rates (LSR) in the Barents Sea. Data and references are provided in supplementary table S1.

Figure 3: Spatial distribution of $CaCO_3$ (left) and total organic carbon (right) in Barents Sea surface sediments. For further legend details see Fig. 1.

Figure 4: Grain size distribution in Barents Sea surface sediments in a) decarbonated and b) bulk sediment samples.

Figure 5: Spatial distribution of iron in Barents Sea surface sediments. Data from this study and Knies et al. [56].

Figure 6: Distribution of A) TOC, B) bulk Fe, C) reactive ion, D) reactive iron fraction of total iron (fFe_R), E) organic carbon bound to reactive iron ($OC\text{-}Fe_R$) and F) the organic carbon fraction of total organic carbon bound to reactive iron ($fOC\text{-}Fe_R$) in Barents Sea surface sediments (0-1 cm). Circles mark stations which are seasonally sea ice covered and crosses are stations which are ice free during winter. Station locations (B1-B18) and ice coverage is shown in Fig. 1.

Supplementary material

Supporting information associated with this article (figure S1 to S5 and table S1 to S7) can be found in the online version.

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